Surface Plasmon Resonance (SPR) Theory: Tutorial

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1 Introduction

In the surface plasmon resonance (SPR) measurement we can detect the change of the film thickness (refractive index change) in the sub-nonometer scale using a low-cost home-made appratus (He-Ne laser, rotating stage, photo-diode detector, prism, maching oil, and 50 nm gold film on a glass plate, See Appendix). In this sense SPR is widely used, in particular, as the immunoassay to detect label-free antigen-antibody reaction.

When light is irradiated to the optical prism |thin metallic film (usually 50 nm gold film is used)| sample system, the reflectivity of the light becomes almost zero at the angle of incidence where the surface plasma wave of gold surface can couple to the part of the incident light. [1] This angle is called SPR angle and is very sensitive to the film thickness (refractivity) of the sample. In the usual automated SPR measurement-analysis routine one can get the SPR angle shift and the the change of the film thickness (and/or refractivity), thereby the measurement may be one of the "black-box". However I think it is important to know the principle for the people to do something new by an detailed analysis of the measurements.

From the name "plasmon" one may misunderstand that the quantum mechanical understanding is required for SPR principles, but the phenomena can be understood from the classical optics (or electromagnetic theory) which explain the light reflection, transmission, and absorption for the multi-layer medium. In the famous book by Raether the principle of SPR was written completely, but at least for me it is not easy to understand because the book may be for specialist. [2]

This note is written for my self-study of SPR principle in order to analyze the SPR curves, [3] . ,later was publish in "Review of Polarography, 48, No3. 2002, 209 ", and posted the revised version at http://www.scl.kyoto-u.ac.jp/ masahiro/sprtheory.html. (I am very happy that many people give me contacts and some comments.)

In this note on SPR theory I also describe the basics of the light reflection, transmission, absorption at the surface of dielectrics or metal, then it is my pleasure that

[1]Plasma oscillation is the phenomena that free electrons in the metal oscillate cooperatively from their equilibrium position where the positive charge of metal (atomic nucleus or jellium that the positive charges are averaged) bind the ensemble of the free electrons . "Plasmon" means the quasi-particle representation of plasma frequency. The surface plasmon is the plasma oscillation that localize at the surface or interface.

[2]There are a lot of review or papers which describe the SPR principle, but almost all of them did not describe the formulation and start from the equation of the SPR resonance condition. I want to formulate the equation from scratch.

[3]Tell me, and I forget. Teach me, and I may remember. Involve me , and I learn. Benjamin Franklin

those who are doing the photon-in/photon-out electrochemistry with the interface spectroscopy with evanescent wave, ellipsometry, nonlinear spectroscopy, have an interest in this note.

The SPR(surface plasmon resonance)[1] is the century-old technique from the finding of the Wood's anomaly for the reflected light from the diffraction gratings[2]. After Otto's demonstration[3] for the surface plasmon excitation by light with attenuated-total-reflection(ATR) coupler[4], the SPR method applied to the organic films[5] or the detection of antigen-antibody reaction[6]. The SPR theory is also well established[7], and the recent advance in the measurements can be reported in the reviews[8, 9, 10].

In the SPR method the dielectric constant change in the sub-nm region from the surface can be measured and the method can be easily applied to the adsorption phenomena **in the electrochemical environment**[11, 12], where the capacitance can be measured simultaneously and get the complementary information of the change in the dielectric properties on the electrode surface.

In this note "Theoretical Electromagnetics(Japanese, Kinokuniya, 1973)" by S. Sunagawa, "Principles of Optics (7th expanded edition) (Cambridge Univ. Press, 1999)" by M. Born and E. Wolf[13], and "Optics(4th edition) (Addison Wesley, 2002)" by E. Hecht[14] are used for reference.

2 Maxwell Equation

The Maxwell equations are described [4]

$$\mathrm{div}\mathbf{D} = \rho \tag{1}$$

$$\mathrm{div}\mathbf{B} = 0 \tag{2}$$

$$\mathrm{rot}\mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{3}$$

$$\mathrm{rot}\mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \tag{4}$$

Here we use MKSA-SI unit. The electric field $\mathbf{E}$ (Vm^{-1}) and magnetic field $\mathbf{H}$ (Am^{-1}) are related to the electric displacement (or dielectric flux density or electric flux density) $\mathbf{D}$ (Cm^{-2}) and magnetic-flux density (or magnetic induction) $\mathbf{B}$ (T:tesla = $\mathrm{NA}^{-1}\mathrm{m}^{-1}$)

$$\mathbf{D} = \epsilon\epsilon_0\mathbf{E} \tag{5}$$

$$\mathbf{B} = \mu\mu_0\mathbf{H} \tag{6}$$

[4] The Maxwell equations have the beautiful mathematical form. We learned the physical meaning of the equations in high school physics course and are mathematically extended to the 3-dimensional case (or 4 dimension when time is included.) by vector analysis. $\mathrm{div}\mathbf{V} \equiv \nabla \cdot \mathbf{V}$ means the difference between the input of the vector field $\mathbf{V}(\mathbf{r})$ to the infinitesimal volume $d\mathbf{r}$ and the output from there, and is called as divergence. In the vector analysis the meaning of "rot" is hard to understand, but S. Naganuma gave us a method to understand the meaning of rotation in his book (Intuitive method for phycal mathematics(Japanese)) [The rotational velocity of the infinitesimal water wheel in water flow field $\mathbf{u}$. (The water flow of the right side of the wheel in the upper direction u_y is faster than the left side ($\partial u_y/\partial x > 0$), the wheel rotates in the anticlockwise direction. In the same the water flow of the upper side of the wheel in the right direction u_x is slower than the lower side ($\partial u_x/\partial y < 0$) the wheel rotates in the anticlockwise direction. $(\mathrm{rot}\mathbf{u})_z = \partial u_y/\partial x - \partial u_x/\partial y$)] The Maxwell equations say, roughly speaking, Eq.(1): The number of the electric flux line coming(entering) from the positive (negative) charge is proportion to the amount of the charge. Eq.(2): magnet has always S and N pole. Eq.(3): When a magnet approachs the coil, the inductive current is passed to reduce the magnetic field from the magnet. Eq.(4): A current generates the rotating magnetic field in the direction of the right-handed screw.

Here ϵ and ϵ_0 are the dielectric constant (with no dimension) and electric permittivity of free space [8.854187817 $\times 10^{-12}$ Fm^{-1} $(= \mathrm{CV}^{-1}\mathrm{m}^{-1})$], respectively. μ and μ_0 are magnetic permeability (with no dimension) and magnetic permeability of free space ($4\pi \times 10^{-7}$ NA^{-2}), respectively. We will assume the Ohm's law for the relation between the current $\mathbf{J}$ and the electric field $\mathbf{E}$

$$\mathbf{J} = \sigma \mathbf{E} \tag{7}$$

2.1 Energy Conservation and Poynting Vector

The equation of motion of point charges is [5]

$$m_i \ddot{\mathbf{r}}_i = \int d\mathbf{r} \left\{ e_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \mathbf{E} + e_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \dot{\mathbf{r}}_i \times \mathbf{B} \right\}$$

If we apply $(\sum_i \mathbf{v}_i \cdot)$ from the left, and the velocity is defined as $\mathbf{v}_i = \dot{\mathbf{r}}_i$

$$\begin{aligned}
\sum_i m_i \mathbf{v}_i \cdot \dot{\mathbf{v}}_i &= \sum_i \int d\mathbf{r} \left\{ e_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \mathbf{v}_i \cdot \mathbf{E} + e_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \underbrace{\mathbf{v}_i \cdot [\mathbf{v}_i \times \mathbf{B}]}_{=0} \right\} \\
&= \sum_i \int d\mathbf{r} e_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \mathbf{v}_i \cdot \mathbf{E} \qquad (8)
\end{aligned}$$

From the definition of the current and the Eq.(4).

$$\begin{aligned}
\mathbf{J} &= \sum_i e_i \dot{\mathbf{r}}_i(t) \delta(\mathbf{r} - \mathbf{r}_i(t)) \qquad (9) \\
&= \mathrm{rot}\mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} \qquad (10)
\end{aligned}$$

Then

$$\begin{aligned}
\sum_i \frac{d}{dt} \left(\frac{1}{2} m_i \mathbf{v}_i^2 \right) &= \int d\mathbf{r} \left(\mathrm{rot}\mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} \right) \cdot \mathbf{E} \qquad (11) \\
\frac{1}{2} \frac{\partial}{\partial t} (\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H}) &= \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t} + \mathbf{H} \cdot \frac{\partial \mathbf{B}}{\partial t} \\
&= \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t} - \mathbf{H} \cdot \mathrm{rot}\mathbf{E} \\
\frac{d}{dt} \left(\sum_i \frac{1}{2} m_i \mathbf{v}_i^2 \right) &= \int d\mathbf{r} \left[-\frac{1}{2} \frac{\partial}{\partial t} (\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H}) \right. \\
&\qquad \left. \underbrace{-\mathbf{H} \cdot \mathrm{rot}\mathbf{E} + \mathbf{E} \cdot \mathrm{rot}\mathbf{H}}_{= -\mathrm{div}(\mathbf{E} \times \mathbf{H})} \right]
\end{aligned}$$

$$\frac{d}{dt} \left[\underbrace{\sum_i \frac{1}{2} m_i \mathbf{v}_i^2}_{\text{kinetic energy}} + \underbrace{\frac{1}{2} \int d\mathbf{r} (\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H})}_{\text{total energy of electromagnetic field}} \right] = -\int dS \underbrace{[\mathbf{E} \times \mathbf{H}]}_{\text{Poynting vector}} \cdot \mathbf{n} \tag{12}$$

From above equations the Poynting vector $\mathbf{S}[= \mathbf{E} \times \mathbf{H}]$ means the energy flux going out from the system.

[5] The point charge, which is given by delta function, feel the Lorentz force from the electromagnetic field.

2.2 Wave Equations

From Eqs.(3) and (6)

$$\mathrm{rot}\mathbf{E} = -\mu\mu_0 \frac{\partial \mathbf{H}}{\partial t} \tag{13}$$

From Eqs.(4), (5), and (7)

$$\mathrm{rot}\mathbf{H} = \sigma\mathbf{E} + \epsilon\epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \tag{14}$$

If we apply $\nabla\times$ to Eq.(13) and $\partial/\partial t$ to Eq.(14) and using the relation

$$\begin{aligned}
\nabla\times\nabla\times\mathbf{E} &= \mathrm{rot}\begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ E_x & E_y & E_z \end{vmatrix} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ \frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z} & \frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} & \frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} \end{vmatrix} \\
&= \mathbf{i}\left[\frac{\partial^2 E_y}{\partial x\partial y} - \frac{\partial^2 E_x}{\partial y^2} - \frac{\partial^2 E_z}{\partial z^2} + \frac{\partial^2 E_z}{\partial x \partial z}\right] + \mathbf{j}[..] + \mathbf{k}[..] \\
&= \mathbf{i}\frac{\partial}{\partial x}\left(\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z}\right) + \mathbf{j}\frac{\partial}{\partial y}\mathrm{div}\mathbf{E} + \mathbf{k}\frac{\partial}{\partial z}\mathrm{div}\mathbf{E} \\
&\quad -\mathbf{i}\nabla^2 E_x - \mathbf{j}\nabla^2 E_y - \mathbf{k}\nabla^2 E_z \\
&= \mathrm{grad}(\mathrm{div}\mathbf{E}) - \nabla^2\mathbf{E}
\end{aligned} \tag{15}$$

If we assume $\rho = 0$, $\mathrm{div}\mathbf{E} = 0$ then

$$\nabla^2\mathbf{E} = \sigma\mu\mu_0 \frac{\partial \mathbf{E}}{\partial t} + \mu\mu_0\epsilon\epsilon_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} \tag{16}$$

In the same way we can get

$$\nabla^2\mathbf{H} = \sigma\mu\mu_0 \frac{\partial \mathbf{H}}{\partial t} + \mu\mu_0\epsilon\epsilon_0 \frac{\partial^2 \mathbf{H}}{\partial t^2} \tag{17}$$

In the case that the electric field has a plane wave form

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \tag{18}$$

where $\mathbf{E}_0$ is the polarization vector and the wavevector $\mathbf{k}$ is in the direction of the wave propagation and the magnitude is given from Eq.(16)

$$k^2 = i\sigma\mu\mu_0\omega + \mu\mu_0\epsilon\epsilon_0\omega^2 \tag{19}$$

In vacuum, $\epsilon = 1, \mu = 1, \sigma = 0$ and $c/\nu = \lambda, c/\omega = \lambda/(2\pi), k = 2\pi/\lambda = \omega/c$ then

$$c = 1/\sqrt{\mu_0\epsilon_0} \tag{20}$$

The complex optical index $\tilde{n}$ may be given by

$$k = \frac{2\pi}{\lambda} = \frac{\omega}{v} = \frac{\tilde{n}\omega}{c} \tag{21}$$

$$\tilde{n}^2 = k^2c^2/\omega^2 = \mu\epsilon + i\frac{\sigma\mu}{\epsilon_0\omega} \tag{22}$$

$$\tilde{n} = n + i\kappa, \quad k = \tilde{n}\omega/c = (n + i\kappa)\omega/c \tag{23}$$

where n and κ are the real and imaginary part of the complex optical index, respectively.

$$\begin{aligned}
E(z,t) &= E_0 e^{i(kz-\omega t)} = E_0 e^{-\kappa\omega z/c} e^{i(n\omega z/c-\omega t)} && (24)\\
I(z) &\propto E^* E = |E_0|^2 e^{-2\kappa\omega z/c} = I_0 e^{-\alpha z} \qquad (\text{Lambert's Law}) &&\\
\alpha &= 2\kappa\omega/c && (25)\\
\tilde{n}^2 &= \tilde{\epsilon} = \epsilon_1 + i\epsilon_2 \qquad [\mu = 1, \sigma = 0 \text{ in Eq.(22)}] && (26)\\
\epsilon_1 &= n^2 - \kappa^2, \quad \epsilon_2 = 2n\kappa && (27)
\end{aligned}$$

Here α is the absorption coefficient, $\tilde{\epsilon}$ is the complex dielectric constant, ϵ_1 and ϵ_2 are the real and imaginary part of the complex dielectric constant, respectively.

If we take divergence of the plane-wave electric filed,

$$\begin{aligned}
\text{div}\mathbf{E} &= \left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{i}\frac{\partial}{\partial y} + \mathbf{i}\frac{\partial}{\partial z}\right) \cdot (E_{0x}\mathbf{i} + E_{0y}\mathbf{j} + E_{0z}\mathbf{k}) e^{i(k_x x + k_y y + k_z z - \omega t)} && (28)\\
&= i(k_x E_{0x} + k_y E_{0y} + k_z E_{0z}) = i\mathbf{k}\cdot\mathbf{E}_0 && (29)\\
&= \frac{\rho}{\epsilon_0 \epsilon} = 0 && (30)
\end{aligned}$$

Then we can find that the electric field is transverse wave, i.e. $\mathbf{k} \perp \mathbf{E}_0$.

If the magnetic-flux density $\mathbf{B}$ is written as

$$\mathbf{B} = \frac{\mathbf{k}\times\mathbf{E}_0}{\omega} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}, \tag{31}$$

then the magnetic-flux density satisfies Eq.(3), because

$$\begin{aligned}
\text{rot}\mathbf{E} &= \mathbf{i}\left(\frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z}\right) + .. && (32)\\
&= \mathbf{i}(ik_y E_z - ik_z E_y) + .. && (33)\\
&= i\mathbf{k}\times\mathbf{E} && (34)\\
-\frac{\partial \mathbf{B}}{\partial t} &= -\frac{\mathbf{k}\times\mathbf{E}_0}{\omega}(-i\omega) e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} && (35)\\
&= i\mathbf{k}\times\mathbf{E} && (36)
\end{aligned}$$

In vacuum

$$\frac{|\mathbf{E}_0|}{|\mathbf{H}_0|} = \frac{\mu_0\omega}{k} = \frac{\mu_0\omega}{\sqrt{\epsilon_0\mu_0}\omega} = \sqrt{\frac{\mu_0}{\epsilon_0}} = 376.7\ \Omega \tag{37}$$

2.3 Boundary Conditions at a Interface Between Different Media

Now we think a interface which is at the boundary medium 1 and 2 as shown in Fig.1. From Gauss law, we can get the following for the Gauss box which include the interface inside the box,

$$\int_V d\mathbf{r} \underbrace{\nabla\cdot\mathbf{D}}_{\rho} = \int_S \mathbf{D}\cdot d\mathbf{S} \tag{38}$$

In the limit that the Gauss box is very thin ($\delta h \to 0$)

$$\int_V d\mathbf{r}\rho = Q_{\text{box}} = \mathbf{n}\cdot[\mathbf{D}_1 - \mathbf{D}_2]S \tag{39}$$

where vector $\mathbf{n}$ means the surface normal unit vector pointing from media 2 to 1.

$$\mathbf{n}\cdot[\mathbf{D}_1 - \mathbf{D}_2] = Q_{\text{box}}/S = \sigma_{12} \tag{40}$$

where σ_{12} means the interface charge density. From $\nabla \cdot \mathbf{B} = 0$

$$\mathbf{n} \cdot [\mathbf{B}_1 - \mathbf{B}_2] = 0 \tag{41}$$

As shown in Fig. 2 for a general vector field $\mathbf{V}(\mathbf{r})$, Stokes theorem gives

$$\begin{aligned}
\oint \mathbf{V} \cdot d\mathbf{r} &= \text{(I)} + \text{(II)} + \text{(III)} + \text{(IV)} \\
&= V_x(x_0, y_0)dx + V_y(x_0 + dx, y_0)dy + V_x(x_0, y_0 + dy)(-dx) + V_y(x_0, y_0)(-dy) \\
&= V_x(x_0, y_0)dx + [V_y(x_0, y_0) + \frac{\partial V_y}{\partial x} dx]dy \\
&\quad -[V_x(x_0, y_0) + \frac{\partial V_x}{\partial y} dy]dx - V_y(x_0, y_0)dy \\
&= \left(\frac{\partial V_y}{\partial x} - \frac{\partial V_x}{\partial y} \right) dxdy = (\text{rot}\mathbf{V})_z dxdy
\end{aligned}$$

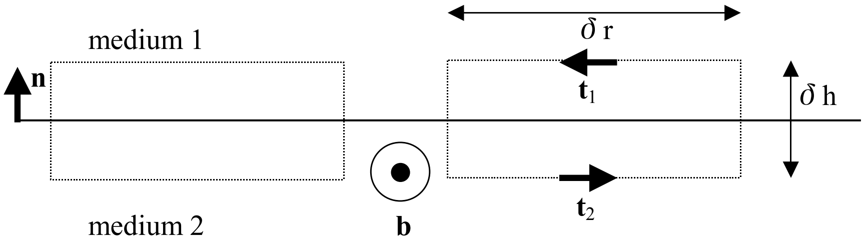


Figure 1: Gauss and Stokes box

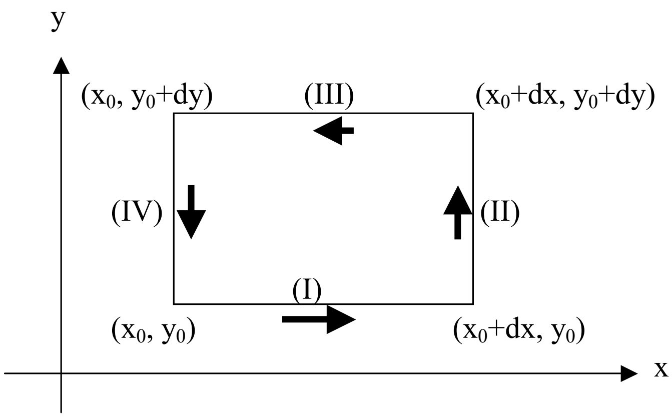


Figure 2: Stokes theorem

From Eq.(3) and Stokes theorem we can get

$$\begin{aligned}
\oint_C \mathbf{E} \cdot d\mathbf{r} &= \int_S \text{rot}\mathbf{E} \cdot d\mathbf{S} && (42) \\
&= -\int_S \frac{\partial \mathbf{B}}{\partial t} \cdot \mathbf{b} dS && (43) \\
\delta r[\mathbf{E}_1 \cdot \mathbf{t}_1 + \mathbf{E}_2 \cdot \mathbf{t}_2] &= -\frac{\partial \mathbf{B}}{\partial t} \cdot \mathbf{b} \delta r \delta h \longrightarrow 0 && (44) \\
\mathbf{t} &= \mathbf{t}_1 = -\mathbf{t}_2 && (45) \\
\mathbf{t} \cdot [\mathbf{E}_1 - \mathbf{E}_2] &= 0 && (46)
\end{aligned}$$

Here $\mathbf{b}$ is the unit vector defined by $\mathbf{b} = \mathbf{n} \times \mathbf{t}$. From Eq.(4)

$$\oint_C \mathbf{H} \cdot d\mathbf{r} = \int_S \mathrm{rot}\mathbf{H} \cdot d\mathbf{S} \tag{47}$$

$$= \int_S \left(\mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \right) \cdot \mathbf{b} dS \tag{48}$$

$$\delta r [\mathbf{H}_1 \cdot \mathbf{t}_1 + \mathbf{H}_2 \cdot \mathbf{t}_2] = \left(\mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \right) \cdot \mathbf{b} \delta r \delta h \longrightarrow \mathbf{J} \cdot \mathbf{b} \delta r \delta h \tag{49}$$

$$\mathbf{t} \cdot [\mathbf{H}_1 - \mathbf{H}_2] = \mathbf{J}_s \quad [\equiv \text{surface current density}(\mathrm{Am}^{-1})] \tag{50}$$

3 Reflection and Transmission

Now we define the incident plane wave as

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}, \quad \omega = \omega(k), \quad \mathbf{B} = \frac{\mathbf{k} \times \mathbf{E}_0}{\omega} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \tag{51}$$

reflected wave as

$$\mathbf{E}' = \mathbf{R}_0 e^{i(\mathbf{k}' \cdot \mathbf{r} - \omega' t)}, \quad \omega' = \omega'(k'), \quad \mathbf{B}' = \frac{\mathbf{k}' \times \mathbf{R}_0}{\omega'} e^{i(\mathbf{k}' \cdot \mathbf{r} - \omega' t)} \tag{52}$$

transmitted wave as

$$\mathbf{E}'' = \mathbf{T}_0 e^{i(\mathbf{k}'' \cdot \mathbf{r} - \omega'' t)}, \quad \omega'' = \omega''(k''), \quad \mathbf{B}'' = \frac{\mathbf{k}'' \times \mathbf{T}_0}{\omega''} e^{i(\mathbf{k}'' \cdot \mathbf{r} - \omega'' t)} \tag{53}$$

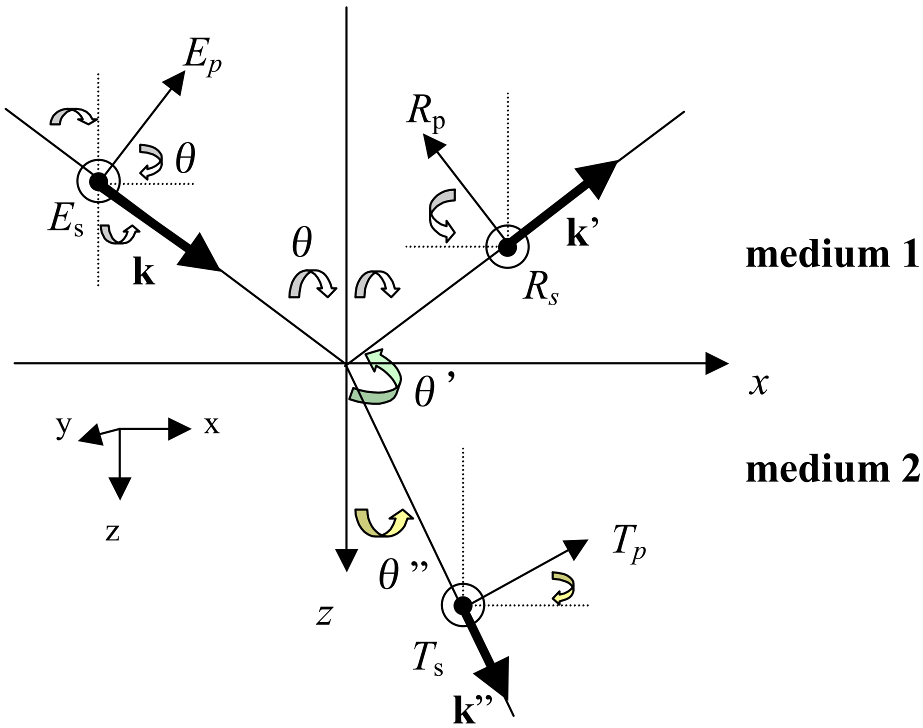


Figure 3: Reflection and Transmission of Light

From Fig.3

$$\begin{aligned}
\mathbf{k} &= (k\sin\theta, 0, k\cos\theta) && (54)\\
\mathbf{k}' &= (k'\sin\theta', 0, k'\cos\theta'), \qquad e^{i(\pi-\theta')} = -\cos\theta' + i\sin\theta' && (55)\\
\mathbf{k}'' &= (k''\sin\theta'', 0, k''\cos\theta'') && (56)
\end{aligned}$$

The p-wave has the components of x and z, but s-wave has only the y component. [6]

3.1 Condition I: $\mathbf{t}\cdot[\mathbf{E}_1 - \mathbf{E}_2] = 0$

From Eq.(46) the tangential component of the electric field become

$$\begin{aligned}
E_x + E'_x &= E''_x \quad \text{at } z = 0 && (57)\\
E_p\cos\theta e^{i(k\sin\theta x - \omega t)} + R_p\cos\theta' e^{i(k'\sin\theta' x - \omega' t)} &= T_p\cos\theta'' e^{i(k''\sin\theta'' x - \omega'' t)} && (58)
\end{aligned}$$

For any x at $z = 0$ this condition should be satisfied, then

$$\begin{aligned}
\omega &= \omega' = \omega'' && (59)\\
k\sin\theta &= k'\sin\theta' = k''\sin\theta'' && (60)
\end{aligned}$$

The magnitude of the wavevector is given by Eq.(21)

$$\sin\theta = \sin\theta' = \sin(\pi - \theta'), \quad \text{because} \;\; k = k' \tag{61}$$

The incident angle equals to the reflection angle, and

$$k\sin\theta = \tilde{n}_1\frac{\omega}{c}\sin\theta = k''\sin\theta'' = \tilde{n}_2\frac{\omega''}{c}\sin\theta'' \tag{62}$$

Then we can get **Snell's law** because $\omega = \omega''$

$$\tilde{n}_1\sin\theta = \tilde{n}_2\sin\theta'' \tag{63}$$

The Eq.(58) becomes

$$(E_p - R_p)\cos\theta = T_p\cos\theta'' \tag{64}$$

From Fig.3 we can get

$$\mathbf{E}_0 = \begin{pmatrix} E_p\cos\theta \\ E_s \\ -E_p\sin\theta \end{pmatrix}, \mathbf{R}_0 = \begin{pmatrix} -R_p\cos\theta \\ R_s \\ -R_p\sin\theta \end{pmatrix}, \mathbf{T}_0 = \begin{pmatrix} T_p\cos\theta'' \\ T_s \\ -T_p\sin\theta'' \end{pmatrix} \tag{65}$$

For y-direction we can get the condition

$$\begin{aligned}
E_y + E'_y &= E''_y \quad \text{at } z = 0 && (66)\\
(E_s + R_s)e^{i(k\sin\theta x - \omega t)} &= T_s e^{i(k''\sin\theta'' x - \omega t)} && (67)\\
(E_s + R_s) &= T_s && (68)
\end{aligned}$$

[6] Light (electromagnetic) wave is the transverse wave and has the two polarization components. (If you look at the the digital watch(almost linear polarized light!?) through the polarized sunglasses, you can see the bright and dark light at every 90 degree if you rotate the watch.) **s-wave** (s polarized light) is the component parallel to the reflection plane, and **p-wave** (p polarized light) is the component perpendicular to the paper plane. Because the electric component is perpendicular to the paper plane, s-wave is called as **TE** (transverse electric) wave. Because the magnetic component is perpendicular to the paper plane, p-wave is called as **TM** wave.

3.2 Condition II: $\mathbf{n} \cdot (\mathbf{B}_1 - \mathbf{B}_2) = 0$

For the boundary condition in Eq.(41)

$$\begin{aligned}
\mathbf{k} \times \mathbf{E}_0 &= \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ k\sin\theta & 0 & k\cos\theta \\ E_p\cos\theta & E_s & -E_p\sin\theta \end{vmatrix} \\
&= k[-\mathbf{i}E_s\cos\theta + \mathbf{j}(E_p\cos^2\theta + E_p\sin^2\theta) + \mathbf{k}E_s\sin\theta] && (69) \\
\omega\mathbf{B} = \mathbf{k} \times \mathbf{E}_0 &= \begin{pmatrix} -kE_s\cos\theta \\ kE_p \\ kE_s\sin\theta \end{pmatrix} && (70)
\end{aligned}$$

$$\begin{aligned}
\mathbf{k}' \times \mathbf{R}_0 &= \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ k\sin\theta & 0 & -k\cos\theta \\ -R_p\cos\theta & R_s & -R_p\sin\theta \end{vmatrix} \\
&= k[\mathbf{i}R_s\cos\theta + \mathbf{j}(R_p\cos^2\theta + R_p\sin^2\theta) + \mathbf{k}R_s\sin\theta] && (71) \\
\omega\mathbf{B}' = \mathbf{k}' \times \mathbf{R}_0 &= \begin{pmatrix} kR_s\cos\theta \\ kR_p \\ kR_s\sin\theta \end{pmatrix} && (72)
\end{aligned}$$

$$\begin{aligned}
\mathbf{k}'' \times \mathbf{T}_0 &= \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ k''\sin\theta'' & 0 & k''\cos\theta'' \\ T_p\cos\theta'' & T_s & -T_p\sin\theta'' \end{vmatrix} \\
&= k''[-\mathbf{i}T_s\cos\theta'' + \mathbf{j}(T_p\cos^2\theta + T_p\sin^2\theta'') + \mathbf{k}T_s\sin\theta''] && (73) \\
\omega\mathbf{B}'' = \mathbf{k}'' \times \mathbf{T}_0 &= \begin{pmatrix} -k''T_s\cos\theta'' \\ k''T_p \\ k''T_s\sin\theta'' \end{pmatrix} && (74)
\end{aligned}$$

The boundary condition $B_z + B'_z = B''_z$ becomes

$$\begin{aligned}
\frac{k\sin\theta}{\omega}(E_s + R_s)e^{i(k\sin\theta x - \omega t)} &= \frac{k''\sin\theta''}{\omega}T_s e^{i(k''\sin\theta'' x - \omega t)} && (75) \\
\tilde{n_1}(E_s + R_s)\sin\theta &= \tilde{n_2}T_s\sin\theta'' && (76) \\
E_s + R_s &= T_s && (77)
\end{aligned}$$

We used Snell's law in the last equation. This equation is the same as Eq.(68).

3.3 Condition III: $\mathbf{n} \cdot (\mathbf{D}_1 - \mathbf{D}_2)$

For the boundary condition in Eq.(40)

$$\begin{aligned}
\tilde{\epsilon_1}\epsilon_0(E_z + E'_z) &= \tilde{\epsilon_2}\epsilon_0 E''_z + \sigma_{12} && (78) \\
\tilde{\epsilon_1}\epsilon_0(-E_p\sin\theta - R_p\sin\theta)e^{i(k\sin\theta x - \omega t)} &= \tilde{\epsilon_2}\epsilon_0(-T_p\sin\theta'')e^{i(k''\sin\theta'' x - \omega t)} + \sigma_{12}(\mathbf{r}, t) \\
\sigma_{12}(\mathbf{r}, t) &= \delta(z)\int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} d\omega\sigma_{12}(k, \omega)e^{i(kx - \omega t)} && (79)
\end{aligned}$$

In Eq.(79) we used the Fourier transformed charge density $\sigma_{12}(k, \omega)$. If we apply $(1/2\pi)^2 \int\int dxdte^{-i(k'x - \omega' t)}$, then we use $(1/4\pi^2)\int\int dxdte^{i(k\sin\theta x - k'x)}e^{-i(\omega - \omega')t} = \delta(k\sin\theta -$

$k')\delta(\omega-\omega')$ and the above equations are held at $z=0$

$$\tilde{\epsilon_1}\epsilon_0(-E_p\sin\theta - R_p\sin\theta)\delta(k\sin\theta-k')\delta(\omega-\omega') = -\tilde{\epsilon_2}\epsilon_0 T_p\sin\theta''\delta(k''\sin\theta''-k')$$
$$\delta(\omega-\omega') + \int\int dk'''d\omega'''\sigma_{12}(k''',\omega''')\delta(k'''-k')\delta(\omega'''-\omega) \quad (80)$$

$$\begin{aligned}
\tilde{n_1}^2(E_p+R_p)\sin\theta &= \tilde{n_2}^2 T_p\sin\theta'' + \frac{\sigma_{12}(k\sin\theta,\omega)}{\epsilon_0} && (81)\\
&\text{From Snell's law} && (82)\\
\tilde{n_1}(E_p+R_p) &= \tilde{n_2}T_p + \frac{\sigma_{12}(k\sin\theta,\omega)}{\epsilon_0\tilde{n_1}\sin\theta} && (83)
\end{aligned}$$

Here we can neglect the $\sigma_{12}(k\sin\theta,\omega)$ term [7].

3.4 Condition IV: $\mathbf{t}\cdot[\mathbf{H}_1-\mathbf{H}_2]=\mathbf{J}_s$

$$\begin{aligned}
H_x + H'_x &= H''_x + (J_s)_x && (84)\\
H_y + H'_y &= H''_y + (J_s)_y && (85)\\
B_x &= \mu\mu_0 H_x, ... && (86)\\
[J_s(\mathbf{r},t)]_x &= \int\int dk d\omega [J_s(k,\omega)]_x e^{i(kx-\omega t)}, .. && (87)\\
\left(-\frac{kE_s\cos\theta}{\mu_1\mu_0\omega} + \frac{kR_s\cos\theta}{\mu_1\mu_0\omega}\right)e^{i(k\sin\theta x-\omega t)} &= -\frac{k''T_s\cos\theta''}{\mu_2\mu_0\omega}e^{i(k''\sin\theta''-\omega t)} + [J_s(\mathbf{r},t)]_x &&\\
\frac{\tilde{n_1}\cos\theta}{\mu_1}(E_s-R_s) &= \frac{\tilde{n_2}\cos\theta''}{\mu_2}T_s + c\mu_0[J_s(k\sin\theta,\omega)]_x && (88)\\
\left(\frac{kE_p}{\mu_1\mu_0\omega} + \frac{kR_p}{\mu_1\mu_0\omega}\right)e^{i(k\sin\theta x-\omega t)} &= \frac{k''T_p}{\mu_2\mu_0\omega}e^{i(k''\sin\theta'' x-\omega t)} + [J_s(\mathbf{r},t)]_y && (89)\\
\frac{\tilde{n_1}}{\mu_1}(E_p+R_p) &= \frac{\tilde{n_2}}{\mu_2}T_p + c\mu_0[J_s(k\sin\theta,\omega)]_y && (90)
\end{aligned}$$

3.5 Reflection and Transmission Coefficients

In the end we can obtain the following equation for p-wave

$$\begin{aligned}
(E_p-R_p)\cos\theta &= T_p\cos\theta'' && (91)\\
\tilde{n_1}(E_p+R_p) &= \tilde{n_2}T_p + \frac{\sigma_{12}(k\sin\theta,\omega)}{\epsilon_0\tilde{n_1}\sin\theta} && (92)\\
\frac{\tilde{n_1}}{\mu_1}(E_p+R_p) &= \frac{\tilde{n_2}}{\mu_2}T_p + c\mu_0[J_s(k\sin\theta,\omega)]_y && (93)
\end{aligned}$$

and for s-wave

$$\begin{aligned}
E_s+R_s &= T_s && (94)\\
\frac{\tilde{n_1}\cos\theta}{\mu_1}(E_s-R_s) &= \frac{\tilde{n_2}\cos\theta''}{\mu_2}T_s + c\mu_0[J_s(k\sin\theta,\omega)]_x && (95)
\end{aligned}$$

[7] Laser light(10 mW He-Ne, focused to 20 μm, 10^{26} photons/s/m^2 $= I/(\hbar\omega)$ $I = c\epsilon_0 E_0^2/2$ (J/m^2/s = W/m^2) c=299792458 m, $E_0 = 1.5\times10^5$ V/m) Bright sunlight (average 480nm, 10^{18} photons/s/m^2 $E_0 = 18$V/m.) For electrochemical systems $\sigma_{12}(k\sin\theta=0,\omega=0)$ is the order of 10 μC/cm^2= 0.1 C/m^2 (fully dissociated 3-mercaptopropionic acid in the $\sqrt{3}\times\sqrt{3}$ structure on Au(111) surface = 0.74 C/m^2). $\sigma_{12}/\epsilon_0 = (1\sim8)\times10^{10}$ V/m. However, the surface charge at the electrode in the $\omega=0$ limit do not couple to the photon field at $\omega=\omega_{\text{photon}}$.

3.5.1 Usual Solution: No Absorption in the Media 1 and 2.

Here we assume that $\sigma_{12}(k\sin\theta,\omega)=0$, $\mathrm{Im}(\tilde{n}_{1,2})=0$ (later we will consider the case that the optical constant is complex, i.e. the medium absorb the light.), $\mu_1=\mu_2=1$, $[J_s(k\sin\theta,\omega)]_x=0$, $[J_s(k\sin\theta,\omega)]_y=0$. Then for p-wave we can get

$$
\begin{aligned}
(E_p-R_p)\cos\theta &= T_p\cos\theta'' &(96)\\
n_1(E_p+R_p) &= n_2T_p &(97)
\end{aligned}
$$

and for s-wave

$$
\begin{aligned}
E_s+R_s &= T_s &(98)\\
n_1\cos\theta(E_s+R_s) &= n_2\cos\theta''T_s &(99)
\end{aligned}
$$

If we define the **amplitude reflection coefficient** r and the **amplitude transmission coefficient** for s- and p-waves,

$$
\begin{aligned}
r_p &\equiv \frac{R_p}{E_p} &(100)\\
t_p &\equiv \frac{T_p}{E_p} &(101)\\
r_s &\equiv \frac{R_s}{E_s} &(102)\\
t_s &\equiv \frac{T_s}{E_s} &(103)
\end{aligned}
$$

$$
\begin{aligned}
(1-r_p)\cos\theta &= t_p\cos\theta'' &(104)\\
n_1(1+r_p) &= n_2t_p &(105)\\
& &(106)
\end{aligned}
$$

and for s-wave

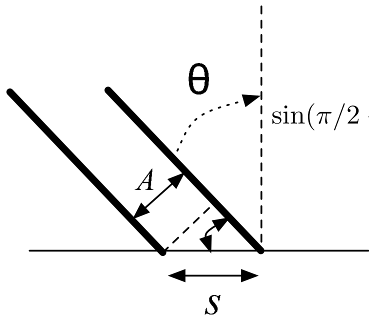
$$
\begin{aligned}
1+r_s &= t_s &(107)\\
n_1\cos\theta(1-r_s) &= n_2\cos\theta''t_s &(108)
\end{aligned}
$$

We finally get the **Fresnel**(フレネル) equations

$$
\begin{aligned}
r_p &= \frac{-n_1\cos\theta''+n_2\cos\theta}{n_1\cos\theta''+n_2\cos\theta} &(109)\\
t_p &= \frac{2n_1\cos\theta}{n_1\cos\theta''+n_2\cos\theta} &(110)\\
r_s &= \frac{n_1\cos\theta-n_2\cos\theta''}{n_1\cos\theta+n_2\cos\theta''} &(111)\\
t_s &= \frac{2n_1\cos\theta}{n_1\cos\theta+n_2\cos\theta''} &(112)
\end{aligned}
$$

The reflectance R is defined as the ratio of the reflected power (or flux) to the incident power of the light

$$
R=\frac{I'A\cos\theta'}{IA\cos\theta}=\frac{I'}{I}=\frac{n_1R^2/(2c\mu_0)}{n_1E^2/(2c\mu_0)}=r^2 \qquad (113)
$$



$$\begin{aligned}\sin(\pi/2-\theta) &= \cos\theta \\ &= \frac{A}{S} \\ A &= S\cos\theta\end{aligned}$$

Figure 4: Angle dependency of the intensity of light

The radiant flux density I (W/m^2) is given by the averaged Poynting vector $<\mathbf{E}\times\mathbf{H}>= \tilde{n}E^2/(2c\mu_0)$. In the same way **the transmittance T may be given by**

$$T=\frac{I''A\cos\theta''}{IA\cos\theta}=\frac{v_t\epsilon_t T^2\cos\theta''}{v_i\epsilon_i E^2\cos\theta}=\frac{n_2\cos\theta''}{n_1\cos\theta}t^2 \tag{114}$$

In Fig.4 and Fig.5 the r, t, R, and T are plotted for the air(1)|water(2) [air→water] and water(1)|air(2) [water→air] interface, respectively. [8] In the both cases t_s and t_p are always positive, and this means the phase shifts of transmitted wave are always zero. For the case of air(1)|water(2) [air→water] r_s is always negative and r_p is positive for $\theta < \theta_{p,air\to water}$ and become negative for $\theta > \theta_{p,air\to water}$. These means that the phase shift is π for reflected s wave and phase shift become 0 to π at $\theta_{p,air\to water}$. For the case of water(1)|air(2) [water→air] r_s is always positive and r_p is negative for $\theta < \theta_{p,water\to air}$ and become positive for $\theta > \theta_{p,water\to air}$. These means that the phase shift is 0 for reflected s wave and phase shift become π to 0 at $\theta_{p,water\to air}$. In Appnedix the plot of the phase shift of the reflected s and p waves are shown. We also shown the condition of the **black film** formation in Appendix.

3.5.2 Brewster angle

In Figs.4 and 5, we can find the point $r_p = R^p = 0$ [9] and this condition is given by

$$-n_1\cos\theta''+n_2\cos\theta=-n_1\left(\cos\theta''-\frac{\sin\theta}{\sin\theta''}\cos\theta\right)=0 \tag{115}$$

$$(\cos\theta''\sin\theta''-\cos\theta\sin\theta) = \frac{e^{i\theta''}+e^{-i\theta''}}{2}\frac{e^{i\theta''}-e^{-i\theta''}}{2i}-\frac{e^{i\theta}+e^{-i\theta}}{2}\frac{e^{i\theta}-e^{-i\theta}}{2i}$$

[8]From Fig.5 (right), intensity of the s-component of the reflected wave from the water surface is greater than the p-wave for all the reflected angles. Then the polarized sunglass should has better performance if the s-wave component is not transmitted. The s-wave has the electric field vector in the horizontal direction. Then, the polarized sunglass passes the light with the electric field vector with the vertical direction. If you try to see the light reflected from the sea surface through the polarized sun glass, the intensity of light is lowest and if you rotate the sunglass (or head if you like) 90 degree the reflected light becomes the strongest. And when you see the LCD(liquid crystal display) and the watch with liquid crystal through the polarized sunglass, the display becomes totally black if you rotate the glass to 45 degree in the clockwise direction. I think the displayed is designed we can see it even if you wear the polarized sunglass.

For the reflection from water to air interface as shown in Fig.6, total reflection of light $R = 1, T = 0$ is observed from the angle 48.66 degree.

[9]In the laser resonator silica plate is set at the Brewster angle, and the p-wave is transmitted but s-wave is reflected and decayed in the resonator.

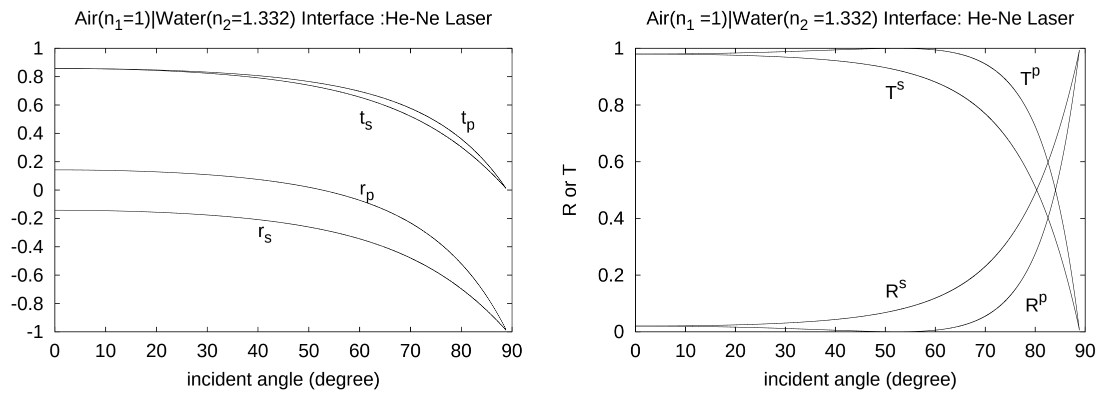


Figure 5: Reflection and transmission of He-Ne laser light at air|water interface

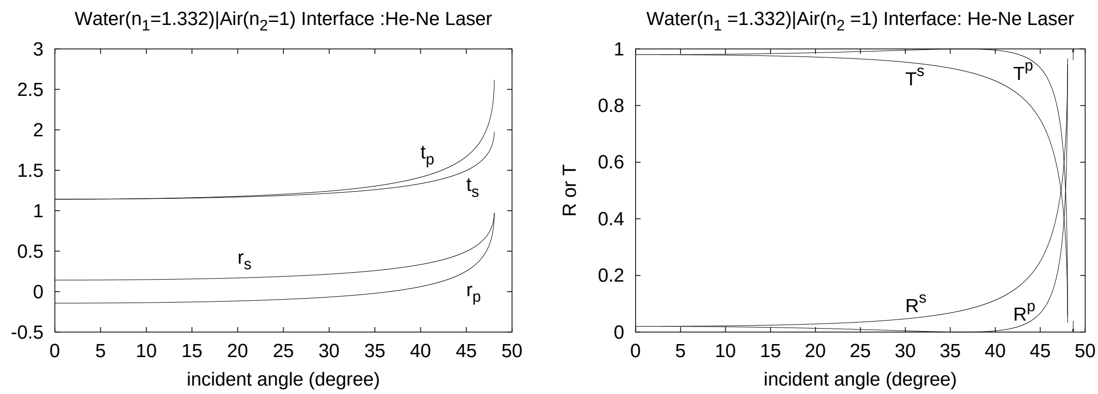


Figure 6: Reflection and transmission of He-Ne laser light at water|air interface

$$
\begin{aligned}
&= \frac{e^{2i\theta''} - e^{-2i\theta''}}{4i} - \frac{e^{2i\theta} - e^{-2i\theta}}{4i} \\
&= \frac{2i\sin(2\theta'') - 2i\sin(2\theta)}{4i} = 0
\end{aligned}
$$

Then

$$\theta'' = \frac{\pi}{2} - \theta \tag{116}$$

The angle between the reflected light and the transmitted light is orthogonal.

$$n_2 \sin\theta'' = n_2 \sin(\pi/2 - \theta) = n_2 \cos\theta = n_1 \sin\theta \tag{117}$$

$$\theta_{\text{Brewster}} = \tan^{-1}\left(\frac{n_2}{n_1}\right) \tag{118}$$

From air to water reflection, the Brewster angle is 53.10 degree, and from water to air the angle is 36.90 degree.

3.6 Total Internal Reflection

Now we will consider the case that the angle θ'' between the transmitted wave and the surface normal is 90 degree, i.e., $\sin\theta''_c = (n_1/n_2)\sin\theta_c = 1$. Here

$$\theta_c = \sin^{-1}\frac{n_2}{n_1} \tag{119}$$

and should $n_2 < n_1$. For water to air reflection $\theta_c = 48.66$ degree. In this situation the transmitted light is along the surface parallel direction. What happens if $\theta > \theta_c$?

$$\cos\theta'' = \sqrt{1-\sin^2\theta''} = i\sqrt{\sin^2\theta''-1} = i\sqrt{(n_1/n_2)^2\sin^2\theta - 1} \tag{120}$$

The transmitted wave can be written as

$$\begin{aligned}
\mathbf{E}'' &= \mathbf{T}_0 e^{i(\mathbf{k}''\cdot\mathbf{r}-\omega'' t)} && (121)\\
&= \mathbf{T}_0 e^{i(k''\sin\theta'' x + k''\cos\theta'' z - \omega'' t)} && (122)\\
&= \mathbf{T}_0 e^{i(k''\sin\theta'' x - \omega'' t)} e^{-k''\sqrt{(n_1/n_2)^2\sin^2\theta-1}z} && (123)\\
&= \mathbf{T}_0 e^{i\frac{n_2\omega\sin\theta''}{c}x} e^{-i\omega'' t} e^{-\frac{n_2\omega\sqrt{(n_1/n_2)^2\sin^2\theta-1}}{c}z} && (124)
\end{aligned}$$

The transmitted light intensity decays as $e^{-\frac{2n_2\omega\sqrt{(n_1/n_2)^2\sin^2\theta-1}}{c}z}$. The decay length is the order of wavelength because $c/\omega = \lambda/2\pi$. The Poynting vector $\mathbf{S}$ in the z direction in the medium 2,

$$\begin{aligned}
\mathbf{z}\cdot\langle\mathbf{S}\rangle &= \frac{1}{2\mu_0\mu}\mathrm{Re}(\mathbf{E}\times\mathbf{B}''^*)\cdot\mathbf{z} && (125)\\
&= \frac{1}{2\mu_0\mu\omega}\mathrm{Re}[\mathbf{E}\times(\mathbf{k}''\times\mathbf{E}'')^*]\cdot\mathbf{z} && (126)\\
&= \frac{1}{2\mu_0\mu\omega}\mathrm{Re}[\mathbf{k}''|\mathbf{E}''|^2 - \mathbf{E}''^*(\underbrace{\mathbf{k}''\cdot\mathbf{E}''}_{=0})\cdot\mathbf{z} && (127)\\
&= \frac{1}{2\mu_0\mu\omega}\mathrm{Re}(\underbrace{\mathbf{z}\cdot\mathbf{k}''}_{k''\cos\theta=\text{pure imaginary}}|\mathbf{E}''|^2) && (128)\\
&= 0 && (129)
\end{aligned}$$

Thereby the energy flux to $\hat{\mathbf{z}}$ direction in the medium 2 is zero. We call this exponential-decay wave as evanescent wave, and is used for some interface spectroscopies to detect species located at the evanescent field.

3.6.1 Phase Shift of the Total Internal Reflection Wave

For the total internal reflection the amplitudes of the incident wave and the reflected wave are the same but there is a phase shift between them.

$$\begin{aligned}
r_p &= \frac{n_2\cos\theta - n_1\cos\theta''}{n_2\cos\theta + n_1\cos\theta''} = \frac{a-ib}{a+ib} = \frac{a^2-b^2-2iab}{a^2+b^2} = e^{-i\delta_p} && (130)\\
a &= n_2\cos\theta, \quad b = n_1\sqrt{(n_1/n_2)^2\sin^2\theta-1} && (131)\\
\tan(\delta_p) &= \frac{2ab}{a^2-b^2} && (132)\\
r_s &= \frac{n_1\cos\theta - n_2\cos\theta''}{n_1\cos\theta + n_2\cos\theta''} = \frac{c-id}{c+id} = \frac{c^2-d^2-2icd}{c^2+d^2} = e^{-i\delta_s} && (133)\\
c &= n_1\cos\theta, \quad d = n_2\sqrt{(n_1/n_2)^2\sin^2\theta-1} && (134)\\
\tan(\delta_s) &= \frac{2cd}{c^2-d^2} && (135)
\end{aligned}$$

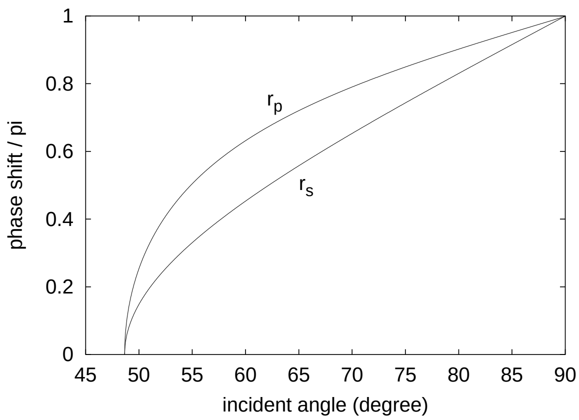


Figure 7: Phase shift of the TIR wave (He-Ne laser) from water|air interface.

3.7 Metal Surface

For the metal surface the optical index becomes complex because some part of the light is absorbed by the electronic transition of metallic electrons at Fermi level.

$$\tilde{n}_2 = n_2 + i\kappa_2, \quad k'' = \tilde{n}_2\omega/c = (n_2 + i\kappa_2)\omega/c \tag{136}$$

From the condition I,

$$n_1 \sin\theta = \tilde{n}_2 \sin\theta'' = (n_2 + i\kappa_2)\sin\theta'' \tag{137}$$

Now θ'' is complex, and we define[13]

$$\tilde{n}_2 \cos\theta'' \equiv u_2 + iv_2, \qquad \text{Here } u_2 \text{ and } v_2 \text{ are real.} \tag{138}$$

$$(u_2 + iv_2)^2 = \tilde{n}_2^2 \cos^2\theta'' = \tilde{n}_2^2 (1 - \frac{n_1^2}{\tilde{n}_2^2}\sin^2\theta) = \tilde{n}_2^2 - n_1^2 \sin^2\theta \tag{139}$$

For the real and imaginary parts of Eq.(139)

$$u_2^2 - v_2^2 = n_2^2 - \kappa_2^2 - n_1^2 \sin\theta^2 \tag{140}$$

$$2u_2v_2 = 2n_2\kappa_2 \tag{141}$$

Then we can get

$$u_2^2 = \frac{n_2^2 - \kappa_2^2 - n_1^2\sin^2\theta + \sqrt{(n_2^2 - \kappa_2^2 - n_1^2\sin^2\theta)^2 + 4n_2^2k_2^2}}{2} \tag{142}$$

$$v_2^2 = \frac{-(n_2^2 - \kappa_2^2 - n_1^2\sin^2\theta) + \sqrt{(n_2^2 - \kappa_2^2 - n_1^2\sin^2\theta)^2 + 4n_2^2k_2^2}}{2} \tag{143}$$

For p wave,

$$r_p \equiv \rho_p e^{i\phi_p} = \frac{\tilde{n}_2\cos\theta - n_1\cos\theta''}{\tilde{n}_2\cos\theta + n_1\cos\theta''} = \frac{\tilde{n}_2^2\cos\theta - n_1\tilde{n}_2\cos\theta''}{\tilde{n}_2^2\cos\theta + n_1\tilde{n}_2\cos\theta''} \tag{144}$$

$$= \frac{(n_2^2 - \kappa_2^2 + 2in_2\kappa_2)\cos\theta - n_1(u_2 + iv_2)}{(n_2^2 - \kappa_2^2 + 2in_2\kappa_2)\cos\theta + n_1(u_2 + iv_2)} \tag{145}$$

$$\rho_p^2 = \left|\frac{(n_2^2 - \kappa_2^2)\cos\theta - n_1u_2 + i(2n_2\kappa_2\cos\theta - n_1v_2)}{(n_2^2 - \kappa_2^2)\cos\theta + n_1u_2 + i(2n_2\kappa_2\cos\theta + n_1v_2)}\right|^2 \tag{146}$$

$$= \frac{[(n_2^2-\kappa_2^2)\cos\theta - n_1u_2]^2 + (2n_2\kappa_2\cos\theta - n_1v_2)^2}{[(n_2^2-\kappa_2^2)\cos\theta + n_1u_2]^2 + (2n_2\kappa_2\cos\theta + n_1v_2)^2} \quad (147)$$

$$\begin{aligned}
\tan\phi_p &= \{[(n_2^2-\kappa_2^2)\cos\theta + n_1u_2](2n_2\kappa_2\cos\theta - n_1v_2) - [(n_2^2-\kappa_2^2)\cos\theta - n_1u_2] \\
&\quad (2n_2\kappa_2\cos\theta + n_1v_2)\}/[(n_2^2-\kappa_2^2)^2\cos^2\theta - n_1^2u_2^2 + 4n_2^2\kappa_2^2\cos\theta - n_1^2v_2^2] \\
&= 2n_2\cos\theta\frac{2n_2u_2\kappa_2 - (n_2^2-k_2^2)v_2}{(n_2^2+\kappa_2^2)^2\cos^2\theta - n_1^2(u_2^2+v_2^2)} && (148) \\
t_p &= \tau_p e^{i\chi_p} = \frac{2n_1\cos\theta}{n_1\cos\theta'' + \tilde{n}_2\cos\theta} = \frac{2n_1\tilde{n}_2\cos\theta}{n_1\tilde{n}_2\cos\theta'' + \tilde{n}_2^2\cos\theta} && (149) \\
&= \frac{2n_1n_2\cos\theta + i2n_1\kappa_2\cos\theta}{n_1u_2 + (n_2^2-\kappa_2^2)\cos\theta + i(n_1v_2 + 2n_2\kappa_2\cos\theta)} && (150) \\
\tau_p^2 &= 4n_1^2\cos^2\theta = \frac{n_2^2+\kappa_2^2}{[n_1u_2 + (n_2^2-\kappa_2^2)\cos\theta]^2 + (n_1v_2 + 2n_2\kappa_2\cos\theta)^2} && (151) \\
\tan\chi_p &= 2n_1\cos\theta\frac{n_1\kappa_2u_2 + \kappa_2(n_2^2-\kappa_2^2)\cos\theta - n_1n_2v_2 - 2n_2^2\kappa_2\cos\theta}{2n_2\cos\theta[n_1^2u_2 + n_1(n_2^2-\kappa_2^2)\cos\theta + n_1\kappa_2v_2 + 2n_2\kappa_2^2\cos\theta]} && (152)
\end{aligned}$$

The t_p in the book "Born and Wolf, Principles of Optics (7th ed) p.575 Eqs.(14) and (15)"[13] may be wrong.

For s wave

$$\begin{aligned}
r_s &= \rho_s e^{i\phi_s} = \frac{n_1\cos\theta - \tilde{n}_2\cos\theta''}{n_1\cos\theta + \tilde{n}_2\cos\theta''} = \frac{n_1\cos\theta - (u_2+iv_2)}{n_1\cos\theta + u_2 + iv_2} && (153) \\
\rho_s^2 &= \left|\frac{n_1\cos\theta - u_2 - iv_2}{n_1\cos\theta + u_2 + iv_2}\right|^2 = \frac{(n_1\cos\theta - u_2)^2 + v_2^2}{(n_1\cos\theta + u_2)^2 + v_2^2} && (154) \\
\tan\phi_s &= \frac{-2v_2n_1\cos\theta}{n_1^2\cos^2\theta - u_2^2 - v_2^2} && (155) \\
t_s &= \tau_s e^{i\chi_s} = \frac{2n_1\cos\theta}{n_1\cos\theta + \tilde{n}_2\cos\theta''} = \frac{2n_1\cos\theta}{n_1\cos\theta + u_2 + iv_2} && (156) \\
\tau_s^2 &= \left|\frac{2n_1\cos\theta}{n_1\cos\theta + u_2 + iv_2}\right|^2 = \frac{4n_1^2\cos^2\theta}{(n_1\cos\theta + u_2)^2 + v_2^2} && (157) \\
\tan\chi_s &= -\frac{2v_2n_1\cos\theta}{2n_1^2\cos^2\theta + 2u_2n_1\cos\theta} = -\frac{v_2}{n_1\cos\theta + u_2} && (158)
\end{aligned}$$

For He-Ne laser (632.8 nm) the reflectance at the air|gold surface ($n = 0.181, \kappa = 2.99$) is shown in Fig.7. For IR light at 3100 nm the reflectance at the air|gold surface ($n = 1.728, \kappa = 19.2$) is shown in Fig. 8.

The intensities of light in the z- and y-component per unit area on the Au surface becomes

$$\begin{aligned}
(E_p^{\perp}/E_p)^2/\cos\theta &\equiv |\mathbf{E}_{0z} + \mathbf{R}_{0z}|^2/E_p^2/\cos\theta = |-E_p\sin\theta - R_p\sin\theta|^2/E_p^2/\cos\theta \\
&= |-E_p\sin\theta - r_pE_p\sin\theta|^2/E_p^2/\cos\theta \\
&= |-E_p\sin\theta - (\rho_p\cos\phi_p + i\rho_p\sin\phi_p)E_p\sin\theta_p|^2/E_p^2/\cos\theta \\
&= \sin\theta^2(1 + 2\rho_p\cos\phi_p + \rho_p^2)/\cos\theta && (159) \\
(E_s^{\|}/E_s)^2/\cos\theta &\equiv |\mathbf{E}_{0y} + \mathbf{R}_{0y}|^2/E_s^2/\cos\theta \\
&= |E_s + R_s|^2/E_s^2/\cos\theta = |E_s + r_sE_s|^2/E_s^2\cos\theta \\
&= (1 + 2\rho_s\cos\phi_s + \rho_s^2)/\cos\theta && (160)
\end{aligned}$$

These equations give the basics of the surface sensitivity of the RAIRS(Reflection Absorption Infrared Spectroscopy) and Polarization-Modulation FTIR spectroscopy, and the

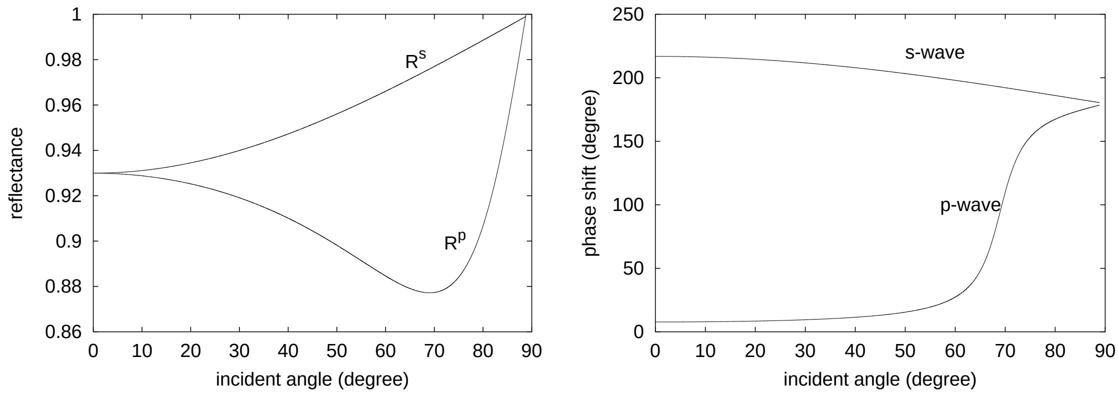


Figure 8: He-Ne laser (632.8 nm) reflection from air|Au surface

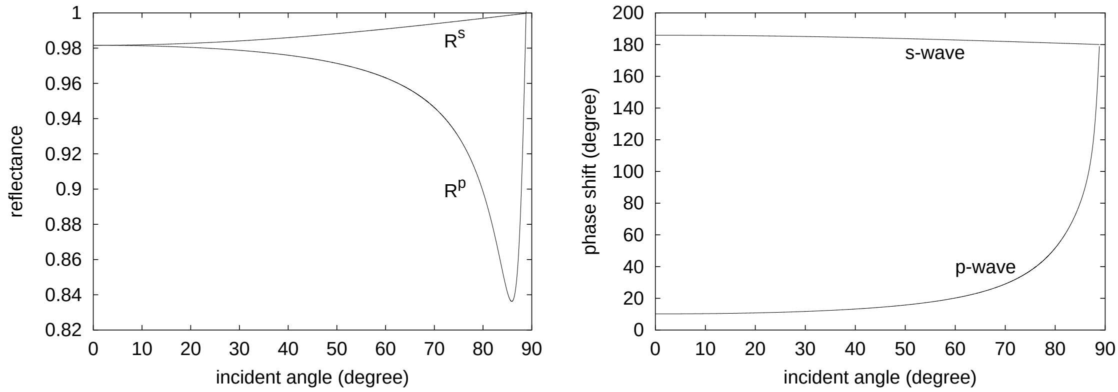


Figure 9: IR light (3100 nm) reflection from air|Au surface

angle dependence are shown in Fig.9. The 180 degree phase change of s-wave leads to destructive interference and no interaction with surface dynamic dipoles from molecular vibrations. [10] For the surface normal component of the p-wave the interference is constructive and it can excite the dynamic dipole perpendicular to the surface. The excitation is efficient for a higher angle of incidence.

4 Surface Plasmon

The electronic charges on metal boundary can perform coherent fluctuations which are called surface plasma oscillations. The fluctuations are confined at the boundary and vanishes both sides of the metal surface. This plasmon waves have p-character because the surface charge induce the discontinuity of the electric field in the surface normal z-direction, but s-waves has only E_y component (no E_z component).

Now we consider the air(medium 2)|metal(medium 1) surface where the electric fields are dumped both side of the interface.

Using a pure imaginary k_{z2} the electric and magnetic field in medium 2(air, $z > 0$)

[10] The surface parallel x-component (not shown here) of p-wave is also negligible.

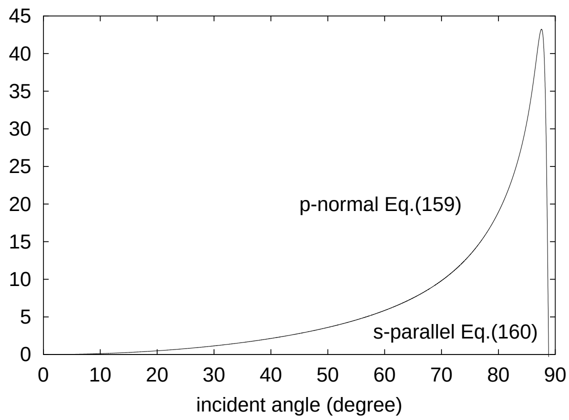


Figure 10: plots of $(E_p^{\perp}/E_p)^2/\cos\theta$ and $(E_s^{\|}/E_s)^2/\cos\theta$. The IR light is 3100 nm and the IR light is reflected from the air|Au surface. $(E_s^{\|}/E_s)^2/\cos\theta$ is negligible because the phase shift is almost 180 degree between the incident wave and the reflected wave.

can be given by

$$\mathbf{E}_2 = \begin{pmatrix} E_{x2} \\ 0 \\ E_{z2} \end{pmatrix} e^{i(k_{x2}x+k_{z2}z-\omega t)} \tag{161}$$

$$\mathbf{H}_2 = \begin{pmatrix} 0 \\ H_{y2} \\ 0 \end{pmatrix} e^{i(k_{x2}x+k_{z2}z-\omega t)} \tag{162}$$

Using a pure imaginary k_{z1} the electric and magnetic field in medium 1(metal, $z > 0$) can be given by

$$\mathbf{E}_1 = \begin{pmatrix} E_{x1} \\ 0 \\ E_{z1} \end{pmatrix} e^{i(k_{x1}x-k_{z1}z-\omega t)} \tag{163}$$

$$\mathbf{H}_1 = \begin{pmatrix} 0 \\ H_{y1} \\ 0 \end{pmatrix} e^{i(k_{x1}x-k_{z1}z-\omega t)} \tag{164}$$

From the Condition I, we can get

$$k_{x1} = k_{x2} = k_x \tag{165}$$

$$E_{x1} = E_{x2} \tag{166}$$

$$E_{z1} = E_{z2} \tag{167}$$

From condition IV,

$$H_{y1} = H_{y2} \tag{168}$$

$$\text{here we assume} \quad (J_s)_y \approx 0 \tag{169}$$

From condition III,

$$\tilde{\epsilon}_1\epsilon_0 E_{z1} = \tilde{\epsilon}_2\epsilon_0 E_{z2} \tag{170}$$

$$\text{here we assume} \quad \sigma_{12}(k_x,\omega) \ll D_{1z}, D_{2z} \tag{171}$$

From Eq.4 and $\mathbf{J} \approx 0$

$$\mathrm{rot}\mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} \tag{172}$$

$$\mathrm{rot}\mathbf{H} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ 0 & H_{yi} & 0 \end{vmatrix} = -\mathbf{i}\frac{\partial}{\partial z}H_{yi} + \mathbf{k}\frac{\partial}{\partial x}H_{yi} \tag{173}$$

From the $\mathbf{i}$ component of the above equation,

$$ik_{z1}H_{y1} = -i\omega\epsilon_0\tilde{\epsilon}_1 E_{x1} \tag{174}$$

$$-ik_{z2}H_{y2} = -i\omega\epsilon_0\tilde{\epsilon}_2 E_{x2} \tag{175}$$

$E_{x1} = E_{x2}$ then

$$\frac{k_{z1}}{\omega\epsilon_0\tilde{\epsilon}_1}H_{y1} + \frac{k_{z2}}{\omega\epsilon_0\tilde{\epsilon}_2}H_{y2} = 0 \tag{176}$$

$H_{y1} = H_{y2}$ then

$$\frac{k_{z1}}{\tilde{\epsilon}_1} + \frac{k_{z2}}{\tilde{\epsilon}_2} = 0 \tag{177}$$

From Eqs.(21) and (26)

$$k^2 = k_x^2 + k_{zi}^2 = \tilde{\epsilon}_i\left(\frac{\omega}{c}\right)^2 \tag{178}$$

$$k_x^2 = \tilde{\epsilon}_1\left(\frac{\omega}{c}\right)^2 - k_{z1}^2 \tag{179}$$

$$\begin{aligned} k_x^2 &= \tilde{\epsilon}_2\left(\frac{\omega}{c}\right)^2 - k_{z2}^2 \\ &= \tilde{\epsilon}_2\left(\frac{\omega}{c}\right)^2 - \left(-\frac{\tilde{\epsilon}_2}{\tilde{\epsilon}_1}k_{z1}\right)^2 \end{aligned} \tag{180}$$

From the last two equations Eqs.(179) and (180).

$$k_x^2 = \left(\frac{\tilde{\epsilon}_1\tilde{\epsilon}_2}{\tilde{\epsilon}_1 + \tilde{\epsilon}_2}\right)\left(\frac{\omega}{c}\right)^2 \tag{181}$$

$$k_{z1}^2 = \left(\frac{\tilde{\epsilon}_1^2}{\tilde{\epsilon}_1 + \tilde{\epsilon}_2}\right)\left(\frac{\omega}{c}\right)^2 \tag{182}$$

$$k_{z2}^2 = \left(\frac{\tilde{\epsilon}_2^2}{\tilde{\epsilon}_1 + \tilde{\epsilon}_2}\right)\left(\frac{\omega}{c}\right)^2 \tag{183}$$

If we remind that $\tilde{\epsilon}_1 = \epsilon_1' + i\epsilon_1''$, $\tilde{\epsilon}_2 = \epsilon_2$

$$\begin{aligned} k_x^2 &= \left(\frac{\omega}{c}\right)^2 \frac{(\epsilon_1' + i\epsilon_1'')\epsilon_2}{(\epsilon_1' + i\epsilon_1'') + \epsilon_2} \\ &= \left(\frac{\omega}{c}\right)^2 \epsilon_2 \frac{\epsilon_1'(\epsilon_1' + \epsilon_2) + \epsilon_1''^2 + i[\epsilon_1''(\cancel{\epsilon_1'} + \epsilon_2) - \cancel{\epsilon_1'}\ \cancel{\epsilon_1''}]}{(\epsilon_1' + \epsilon_2)^2 + \epsilon_1''^2} \end{aligned} \tag{184}$$

If we assume $\epsilon_1'' < |\epsilon_1'|$

$$\mathrm{Re}(k_x) = \frac{\omega}{c}\left(\frac{\epsilon_1'\epsilon_2}{\epsilon_1' + \epsilon_2}\right)^{1/2} \tag{185}$$

$$\mathrm{Im}(k_x) = \frac{\omega}{c}\left(\frac{\epsilon_1'\epsilon_2}{\epsilon_1' + \epsilon_2}\right)^{3/2}\frac{\epsilon_1''}{2\epsilon_1'^2} \tag{186}$$

The surface plasmon decay in x-direction can be evaluated from $\mathrm{Im}(k_x)$ because the intensity decreased as $\exp[-2\mathrm{Im}(k_x)x]$. The decay length L_{12} may be obtained as

$$L_{12} = [2\mathrm{Im}(k_x)]^{-1} = \frac{c}{\omega}\left(\frac{\epsilon_1'\epsilon_2}{\epsilon_1' + \epsilon_2}\right)^{-3/2}\frac{\epsilon_1'^2}{\epsilon_1''} \tag{187}$$

For the water|metal interface the decay lengths L_{12} are 6.4 μm for gold (16.6 μm for air|gold surface), 12.3 μm for silver, and 5.5 μm for aluminum. The decay length L_{12} is the key parameter to carry out a SPR imaging measurements [11]. In addition there is a temporal decay in ω, please refer the Raether's book for details[7].

The dispersion relation k_x vs ω become close to the light line $\sqrt{\epsilon_2}\omega/c$ at small k_x, because in the limit that $\omega \to 0, \epsilon_1' >> \epsilon_2$. At large k_x the denominator of Eq.(185) becomes zero

$$\epsilon_1' + \epsilon_2 = 0 \tag{188}$$

For simple metals the dielectric constant is given by the plasma frequency ω_p[16] [12]

$$\epsilon_1' = 1 - \frac{\omega_p^2}{\omega^2} \tag{189}$$

From Eqs.(188) and (189) the surface plasma frequency ω_{sp} may be obtained as

$$\omega_{\mathrm{sp}} = \omega_p \frac{1}{\sqrt{1+\epsilon_2}} \tag{190}$$

In Fig.10 we plot the dispersion relation Eq.(185).

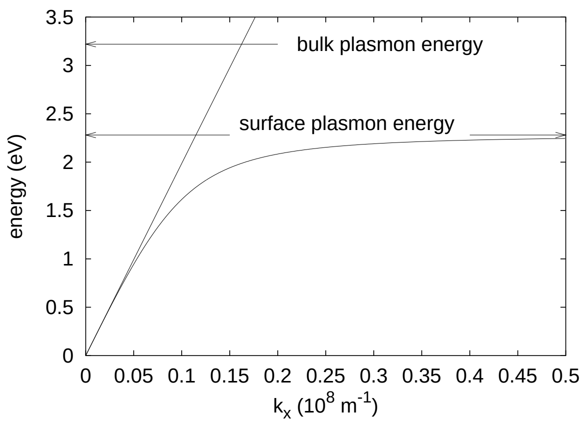


Figure 11: Surface plasmon dispersion $\omega(k_x)$ on gold surface. The vertical axis is scaled as $\hbar\omega$ (eV). The straight solid line in the figure shows the light line $k_x = \sqrt{\epsilon_2}\omega/c$. The energy of bulk plasmon is 3.22 eV, and that of surface plasmon is 2.28 eV and shown as the arrows in the figure.

In the z-direction the electric field of the surface plasmon decays as $E_z \propto e^{-|k_{zi}||z|}$. If we assume $\epsilon_1'' < |\epsilon_1'|$ again,

$$k_{z1}^2 \approx \left(\frac{\epsilon_1'^2}{\epsilon_1' + \epsilon_2}\right)\left(\frac{\omega}{c}\right)^2 \tag{191}$$

$$k_{z2}^2 \approx \left(\frac{\epsilon_2^2}{\epsilon_1' + \epsilon_2}\right)\left(\frac{\omega}{c}\right)^2 \tag{192}$$

[11] From this discussion the lateral resolution of SPR is more than micrometer size. Aluminium has small L_{12} and living cell is observed with SPR imaging. [15]

[12] If the energy loss of electron beam reflected from the metal surface is measured, the plasma frequency can be determined. Surface plasma frequency can be also measured in the same way.

$\epsilon_1' + \epsilon_2 < 0$ then k_{zi} is purely imaginary. For He-Ne laser light (632.8 nm) on the gold surface

$$1/\mathrm{Re}(k_{z1})(\mathrm{metal}) = 32 \text{ nm}, \quad 1/\mathrm{Re}(k_{z2})(\mathrm{air}) = 285 \text{ nm} \tag{193}$$

From the $\mathbf{k}$ component of $\mathrm{rot}\mathbf{H} = \partial\mathbf{D}/\partial t$ [cf. Eq.(173)]

$$\frac{\partial H_{y1}}{\partial x} = ik_{x1}H_{y1} = -i\omega\epsilon_0\tilde{\epsilon_1}E_{z1} \tag{194}$$

$$\frac{\partial H_{y2}}{\partial x} = ik_{x2}H_{y2} = -i\omega\epsilon_0\tilde{\epsilon_2}E_{z2} \tag{195}$$

From the $\mathbf{i}$ component of Eqs.(172-173) and Eq.(194)

$$H_{y1} = -\frac{\omega\epsilon_0\tilde{\epsilon_1}E_{x1}}{k_{z1}} = -\frac{\omega\epsilon_0\tilde{\epsilon_1}E_{z1}}{k_{x1}} \tag{196}$$

$$\frac{E_{z1}}{E_{x1}} = \frac{k_{x1}}{k_{z1}} \tag{197}$$

$$H_{y2} = \frac{\omega\epsilon_0\tilde{\epsilon_2}E_{x2}}{k_{z2}} = -\frac{\omega\epsilon_0\tilde{\epsilon_2}E_{z2}}{k_{x2}} \tag{198}$$

$$\frac{E_{z2}}{E_{x2}} = -\frac{k_{x2}}{k_{z2}} \tag{199}$$

$$\tag{200}$$

5 Excitation of Surface Plasmon by Light

5.1 ATR (Attenuated Total Reflection) Coupler Method

We will consider the situation that the light is reflected from a metal surface covered with a dielectric medium ($\epsilon_{pr} > 1$) , e.g. with a BK7 half cylinder glass prism (n=1.515 at 633 nm) or SF10 glass prism (n=1.723 at 643.8 nm). The x and z components of the wavevector in the prism are given by

$$k_x^{pr} = \sqrt{\epsilon_{pr}}\frac{\omega}{c}\sin\theta_{pr} = n_{pr}\frac{\omega}{c}\sin\theta_{pr} \tag{201}$$

$$k_z^{pr} = \sqrt{\epsilon_{pr}}\frac{\omega}{c}\cos\theta_{pr} = n_{pr}\frac{\omega}{c}\cos\theta_{pr} \tag{202}$$

Here pr means the prism.

The resonance condition of the light in the prism with the surface plasmon at metal(1)|air(2) interface (Kretschmann-Raether configuration) is [13]

$$k_x^{pr} = k_x^{sp} \tag{203}$$

$$\sqrt{\epsilon_{pr}}\frac{\omega}{c}\sin\theta_{pr} = \sqrt{\frac{\tilde{\epsilon}_1\tilde{\epsilon}_2}{\tilde{\epsilon}_1+\tilde{\epsilon}_2}}\left(\frac{\omega}{c}\right) \tag{204}$$

Here we use Eq.(181) for k_x^{sp}.

[13] In the ATR coupler there are two types, one is prism|metal film|sample Kretschmann-Raether type and the other is prism|thin sample(thickness is wavelength of light)|metal Otto type. In the Otto type the controll of the thin gap is difficult, and then Kretschmann-Raether type is usually used. However, the Au film thickness should be controlled around 50 nm in the Kretschmann-Raether type, otherwise the SPR resonance ($T \simeq 0$) become un-sharp. In the electrochemical environment the gold film is not stably deposited on the glass plate when the potential is applied. Then (3-mercaptopropyl)trimethoxysilane(MPS) is used for the binder between the glass and gold (see Appendix). Otto first showed that light can excite surface plasmon by the use of ATR coupler[3], but He claimed that the surface plasmon can not be excited by the Kretschmann-Raether type ATR coupler and later it was found that his claim was wrong. After that Otto never went mainstream in the SPR world!?

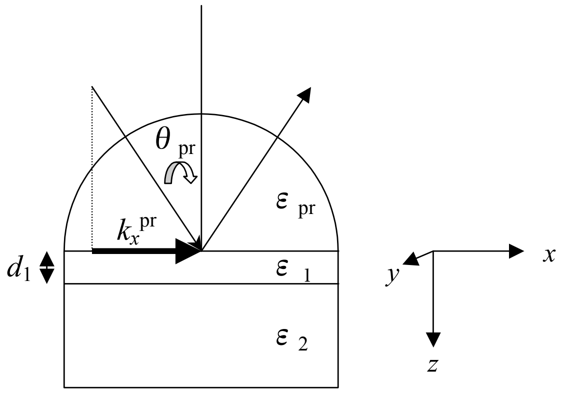


Figure 12: Schematic diagram of ATR coupler: Kretschmann-Raether type

5.1.1 Prisim|Metal|Medium Three-Layer Model

The reflectivity $R_{pr|1|2}$ may be given by Frensel's equations of the prism|metal|air three-layer system.

$$
\begin{aligned}
r_{ik}^p &= \frac{\tilde{n}_k \cos\theta_i - \tilde{n}_i \cos\theta_k}{\tilde{n}_k \cos\theta_i + \tilde{n}_i \cos\theta_k} = \frac{\tilde{n}_k \frac{k_{zi}}{k_i} - \tilde{n}_i \frac{k_{zk}}{k_k}}{\tilde{n}_k \frac{k_{zi}}{k_i} + \tilde{n}_i \frac{k_{zk}}{k_k}} = \frac{\frac{\tilde{n}_k k_{zi} c}{\tilde{n}_i \omega} - \frac{\tilde{n}_i k_{zk} c}{\tilde{n}_k \omega}}{\frac{\tilde{n}_k k_{zi} c}{\tilde{n}_i \omega} + \frac{\tilde{n}_i k_{zk} c}{\tilde{n}_k \omega}} && (205) \\
&= \frac{\frac{k_{zi}}{\tilde{n}_i^2} - \frac{k_{zk}}{\tilde{n}_k^2}}{\frac{k_{zi}}{\tilde{n}_i^2} + \frac{k_{zk}}{\tilde{n}_k^2}} = \frac{k_{zi}/\tilde{\epsilon}_i - k_{zk}/\tilde{\epsilon}_k}{k_{zi}/\tilde{\epsilon}_i + k_{zk}/\tilde{\epsilon}_k} && (206) \\
r_{ki}^p &= -r_{ik}^p && (207)
\end{aligned}
$$

For transmission

$$
\begin{aligned}
t_{ik}^p &= \frac{\tilde{n}_i}{\tilde{n}_k}(1 + r_{ik}^p) && (208) \\
t_{ki}^p &= \frac{\tilde{n}_k}{\tilde{n}_i}(1 + r_{ki}^p) = \frac{\tilde{n}_k}{\tilde{n}_i}(1 - r_{ik}^p) && (209) \\
t_{ik}^p t_{ki}^p &= (1 + r_{ik}^p)(1 - r_{ik}^p) && (210)
\end{aligned}
$$

The total reflection of the three-layer model becomes

$$
\begin{aligned}
R &= |r_{\mathrm{pr}12}^p|^2 = \left| \frac{r_{\mathrm{pr}1}^p + r_{12}^p e^{2ik_{z1}d_1}}{1 + r_{\mathrm{pr}1}^p r_{12}^p e^{2ik_{z1}d_1}} \right|^2 && (211) \\
r_{ik}^p &= \frac{\tilde{n}_k \cos\theta_i - \tilde{n}_i \cos\theta_k}{\tilde{n}_k \cos\theta_i + \tilde{n}_i \cos\theta_k} = \frac{\cos\theta_i/\tilde{n}_i - \cos\theta_k/\tilde{n}_k}{\cos\theta_i/\tilde{n}_i + \cos\theta_k/\tilde{n}_k} && (212) \\
n_{pr} \sin\theta_{pr} &= \tilde{n}_1 \sin\theta_1 = \tilde{n}_2 \sin\theta_2 \\
\tilde{n}_k \cos\theta_k &= \tilde{n}_k (1 - \sin^2\theta_k)^{1/2} = \tilde{n}_k (1 - n_{pr}^2 \sin^2\theta_{pr}/\tilde{n}_k^2)^{1/2} = (\tilde{n}_k^2 - n_{pr}^2 \sin^2\theta_{pr})^{1/2} \\
r_{ik}^p &= \frac{(\tilde{\epsilon}_i - n_{pr}^2 \sin^2\theta_{pr})^{1/2}/\tilde{\epsilon}_i - (\tilde{\epsilon}_k - n_{pr}^2 \sin^2\theta_{pr})^{1/2}/\tilde{\epsilon}_k}{(\tilde{\epsilon}_i - n_{pr}^2 \sin^2\theta_{pr})^{1/2}/\tilde{\epsilon}_i + (\tilde{\epsilon}_k - n_{pr}^2 \sin^2\theta_{pr})^{1/2}/\tilde{\epsilon}_k} && (213) \\
r_{\mathrm{pr}1}^p &= \frac{\cos\theta_{pr}/n_{pr} - (\tilde{\epsilon}_1 - n_{pr}^2 \sin^2\theta_{pr})^{1/2}/\tilde{\epsilon}_1}{\cos\theta_{pr}/n_{pr} + (\tilde{\epsilon}_1 - n_{pr}^2 \sin^2\theta_{pr})^{1/2}/\tilde{\epsilon}_1} && (214)
\end{aligned}
$$

The above equation for R can be understood by considering

$$\begin{aligned}
r^p_{\rm pr12} &= \frac{r^p_{\rm pr1} + r^p_{12} e^{2ik_{z1}d_1}}{1 + r^p_{\rm pr1} r^p_{12} e^{2ik_{z1}d_1}} \qquad (215)\\
&\approx (r^p_{\rm pr1} + r^p_{12} e^{2ik_{z1}d_1})(1 - r^p_{\rm pr1} r^p_{12} e^{2ik_{z1}d_1} + (r^p_{\rm pr1})^2 (r^p_{12})^2 e^{4ik_{z1}d_1} - ....)\\
&= r^p_{\rm pr1} + r^p_{12} e^{2ik_{z1}d_1} - (r^p_{\rm pr1})^2 r^p_{12} e^{2ik_{z1}d_1}\\
&\quad -r^p_{\rm pr1}(r^p_{12})^2 e^{4ik_{z1}d_1} + (r^p_{\rm pr1})^3 (r^p_{12})^2 e^{4ik_{z1}d_1} + ...\\
&= r^p_{\rm pr1} + (1 - r^p_{\rm pr1})^2 r^p_{12} e^{2ik_{z1}d_1} + r^p_{\rm pr1}[(r^p_{\rm pr1})^2 - 1](r^p_{12})^2 e^{4ik_{z1}d_1} + ...\\
&= r^p_{\rm pr1} + \underbrace{(1 + r^p_{\rm pr1}) r^p_{12} (1 - r^p_{\rm pr1})}_{t^p_{\rm pr1} r^p_{12} t^p_{\rm 1pr}} e^{2ik_{z1}d_1}\\
&\quad + \underbrace{(1 + r^p_{\rm pr1}) r^p_{12} (-r^p_{\rm pr1}) r^p_{12} (1 - r^p_{\rm pr1})}_{t^p_{\rm pr1} r^p_{12} r^p_{\rm 1pr} r^p_{12} t^p_{\rm 1pr}} e^{4ik_{z1}d_1}\\
&= r^p_{\rm pr1} + t^p_{\rm pr1} r^p_{12} t^p_{\rm 1pr} e^{2ik_{z1}d_1} + t^p_{\rm pr1} r^p_{12} r^p_{\rm 1pr} r^p_{12} t^p_{\rm 1pr} e^{4ik_{z1}d_1} \qquad (216)
\end{aligned}$$

phase factor $\quad k_{z1}d_1 = k_1(d_1 \cos\theta_1)$ is optical path length. (217)

$$\begin{aligned}
k_{z1}d_1 &= k_1 d_1 \cos\theta_1 = \tilde{n}_1 \frac{\omega}{c} d_1 \left(1 - \frac{n^2_{pr}}{\tilde{n}^2_1} \sin^2\theta_{pr}\right)^{1/2}\\
&= \frac{\omega}{c} d_1 (\tilde{\epsilon}_1 - n^2_{pr} \sin^2\theta_{pr})^{1/2} \qquad (218)
\end{aligned}$$

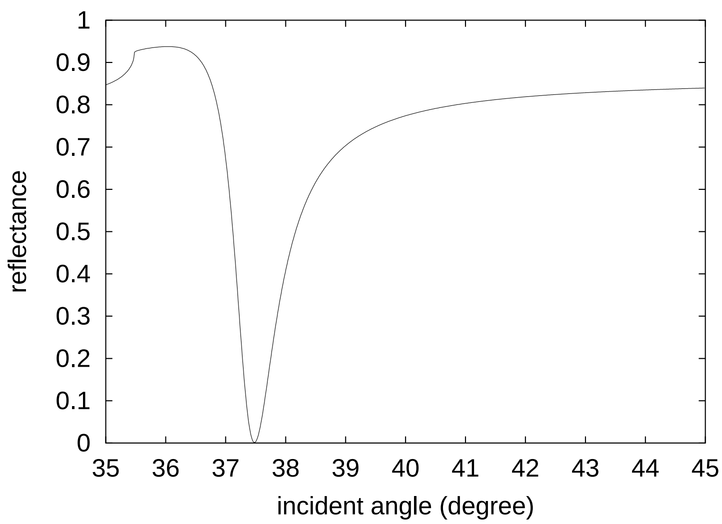


Figure 13: SPR curve for SF10($n = 1.723$)|gold(50nm, $\tilde{n}_1 = 0.1726{+}i3.4218$) |air($n = 1.0$) for He-Ne laser light (633 nm).

The FORTRAN program to get the SPR curve by Eq.(211) is

```
c234567-- spr_angle_3layer.f ---
c     complex calculation
      implicit real*8 (a-h,o-z)

      complex*16 e1,rpr1,r12,rpr12,rpr12c,alpha,ref
      complex*16 aaa,fukso,e2
```

```
      c=2.99792458d8
      hbar=6.5822d-16
      pi=acos(-1.0d0)
c     ------ air ----
      e2=dcmplx(1.0d0,0.0d0)
c     ----- SF10 633 nm
      enpr=1.723d0
c     ----- gold 633 nm
      e1n=0.1726d0
      e1k=3.4218d0
      e1r=e1n**2-e1k**2
      e1i=2.0d0*e1n*e1k
      e1=dcmplx(e1r,e1i)
c     ---- gold thickness (m)
      d1=50.0d-9
c
      ramd=633.0d-9
      omega=2.0d0*pi/ramd*c
      fukso=dcmplx(0.0d0,1.0d0)
      write (6,*) ramd,omega,hbar*omega
c     --------- angle scan ----------
      ang0=35.0d0
      ang1=45.0d0
      do i=1, 1001
       theta=(ang0+dble(i-1)/1000.0d0*(ang1-ang0))/180.0d0*pi
       rpr1=(cos(theta)/enpr -
     &       sqrt(e1-enpr**2*sin(theta)**2)/e1)
     &      / (cos(theta)/enpr +
     &      sqrt(e1-enpr**2*sin(theta)**2)/e1)

       r12=( sqrt(e1-enpr**2*sin(theta)**2)/e1 -
     &       sqrt(e2-enpr**2*sin(theta)**2)/e2 )
     &     / ( sqrt(e1-enpr**2*sin(theta)**2)/e1 +
     &         sqrt(e2-enpr**2*sin(theta)**2)/e2 )
       aaa=2.0d0*omega/c*d1*sqrt(e1-enpr**2*sin(theta)**2)
       alpha=aaa*fukso
       rpr12=(rpr1+ r12*exp(alpha))/(1.0d0+rpr1*r12*exp(alpha))
       rpr12c=conjg(rpr12)
       ref=rpr12*rpr12c
       write (6,*) theta/pi*180.0d0,dble(ref)
      enddo
      end
```

The calculated results are shown in Fig. 12. At resonance or $R = 0$ the power of the SPs is lost by internal absorption in the metal. This loss is compensated by the power of the incoming light. Both have to be equal in the steady state.

If the reflectivity R has lowest value, the intensity of the electromagnetic field reaches its maximum at the metal surface. For 600 nm light **the maximum enhancement of the electric field intensity** is ca. 200 for silver film (60 nm thickness), 30 for gold film, 40 for aluminum film, and 7 for copper film, respectively[7].

5.2 General solution of N-layer model. [F. Abelès, Ann. Phys. (Paris) 5, (1950) 596. W. N. Hansen, J. Opt. Soc. Amer. 58 (1968) 380.]

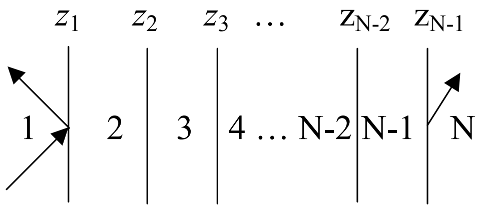


Figure 14: N-layer model for SPR measurement.

The tangential fields at the first boundary $z = z_1 = 0$ are related to those at the final boundary $z = z_{N-1}$ by

$$\begin{bmatrix} U_1 \\ V_1 \end{bmatrix} = M_2 M_3 ... M_{N-1} \begin{bmatrix} U_{N-1} \\ V_{N-1} \end{bmatrix} = M \begin{bmatrix} U_{N-1} \\ V_{N-1} \end{bmatrix} \tag{219}$$

For p-wave at boundary k,

$$U_k = H_y^T + H_y^R \tag{220}$$

$$V_k = E_x^T + E_x^R \tag{221}$$

and

$$M_k = \begin{bmatrix} \cos\beta_k & -i\sin\beta_k/q_k \\ -iq_k \sin\beta_k & \cos\beta_k \end{bmatrix} \tag{222}$$

$$\text{Here } q_k = (\mu_k/\tilde{\epsilon_k})^{1/2}\cos\theta_k \tag{223}$$

$$\mu_k \cong 1$$

$$q_k \cong (1/\tilde{\epsilon_k})^{1/2}\cos\theta_k = \frac{(\tilde{\epsilon_k} - n_1^2 \sin^2\theta_1)^{1/2}}{\tilde{\epsilon_k}} \tag{224}$$

$$\beta_k = \frac{2\pi}{\lambda_0}\tilde{n}_k \cos\theta_k (z_k - z_{k-1}) = (z_k - z_{k-1})\frac{2\pi}{\lambda_0}(\tilde{\epsilon}_k - n_1^2\sin^2\theta_1)^{1/2} \tag{225}$$

The reflection and transmission coefficient for p-wave (TM) is

$$r^p = \frac{(M_{11} + M_{12}q_N)q_1 - (M_{21} + M_{22}q_N)}{(M_{11} + M_{12}q_N)q_1 + (M_{21} + M_{22}q_N)} \tag{226}$$

$$M_{ij} = \left(\prod_{k=2}^{N-1} M_k\right)_{ij}, \quad i,j = 1,2 \tag{227}$$

$$R_p = |r_p|^2 \tag{228}$$

$$r_p = R_p^{1/2} e^{i\phi_p^r} \tag{229}$$

$$\phi_p^r = \arg(r^p) \tag{230}$$

$$t_H^p = \frac{2q_1}{(M_{11} + M_{12}q_N)q_1 + (M_{21} + M_{22}q_N)} \tag{231}$$

$$t_E^p = \frac{\mu_N n_1}{\mu_1 \tilde{n}_N} t_H^p \tag{232}$$

$$T_p = \frac{\mu_N \mathrm{Re}(\tilde{n}_N \cos\theta_N/\tilde{n}_N^2)}{\mu_1 n_1 \cos\theta_1/n_1^2}|t_H^p|^2 \tag{233}$$

$$\phi_p^t = \arg(t_E^p) \tag{234}$$

For s-wave (TE) the above equations hold except

$$q_k = \sqrt{\frac{\tilde{\epsilon_k}}{\mu_k}} \cos\theta_k \tag{235}$$

In this sense these equations are easy to calculate the multilayer optical problem.

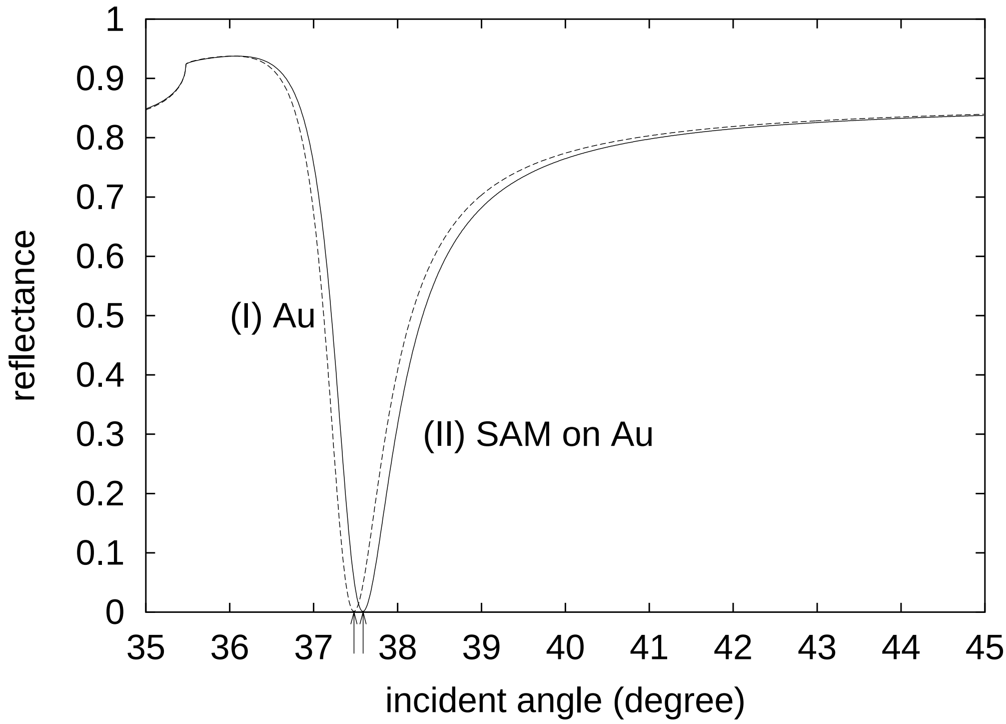


Figure 15: SPR curves for (I) the SF10 glass prism(n=1.723)|Au($n + ik$ = 0.1726+i3.4218, 50nm)|Air(n=1.0) and (II) the SF10 prism|Au(50nm)|SAM(n=1.61245, 1nm)|Air systems.

The SPR resonance calculation FORTRAN program for N-layer system is given in the following, and the results for the 4-layer system [prism|gold|Self-Assmbled-Monolayer(SAM, 1 nm thickness)|Air] is shown in Fig. 14. **The SAM film thickness of 1 nm is clearly seen as the shift of the SPR angle.**

```
c234567-- spr_angle_Nlayer.f ---
c     1 | 2 | 3 ...  N-2|N-1|N :N layer system
c     complex calculation
      implicit real*8 (a-h,o-z)

      parameter (nlay=10)
      complex*16 e(nlay) , em(nlay,2,2) ,emtot(2,2)
      complex*16 emtot1(2,2)
      dimension en(nlay), ek(nlay), d(nlay)
      complex*16 beta,q,rp,q1,qn,ref,tp,tra
      complex*16 fukso

      c=2.99792458d8
      hbar=6.5822d-16
```

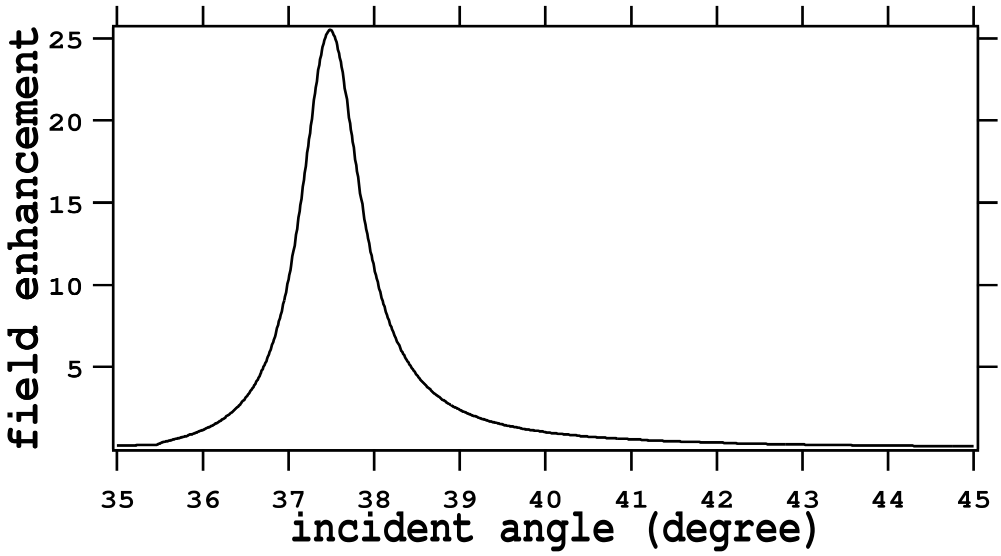


Figure 16: Field enhancement factor $|t_{\mathrm{h}}^{p}|^2$ for the the SF10 prism|Au(50nm)|SAM(n=1.61245, 1nm)|Air system.

```
      pi=acos(-1.0d0)
c     ------- N layer ----
      nlayer=4
c     ------ air ----
      en(4)=1.d0
      ek(4)=0.0d0
      er=en(4)**2-ek(4)**2
      ei=2.0d0*en(4)*ek(4)
      e(4)=dcmplx(er,ei)
c     ----- SF10 633 nm
      en(1)=1.723d0
      ek(1)=0.0d0
      er=en(1)**2-ek(1)**2
      ei=2.0d0*en(1)*ek(1)
      e(1)=dcmplx(er,ei)
c     ----- gold 633 nm
      en(2)=0.1726d0
      ek(2)=3.4218d0
      er=en(2)**2-ek(2)**2
      ei=2.0d0*en(2)*ek(2)
      e(2)=dcmplx(er,ei)
c     ---- gold thickness (m)
      d(2)=50.0d-9
c     ------ SAM -----------
      en(3)=1.61245
      ek(3)=0.0d0
      er=en(3)**2-ek(3)**2
      ei=2.0d0*en(3)*ek(3)
      e(3)=dcmplx(er,ei)
c     ----- SAM thickness ---
```

```
      d(3)=1.0d-9
c
      ramd=633.0d-9
      omega=2.0d0*pi/ramd*c
      fukso=dcmplx(0.0d0,1.0d0)
      write (6,*) ramd,omega,hbar*omega
c     --------- angle scan ----------
      ang0=35.0d0
      ang1=45.0d0
      do i=1, 1001
       theta=(ang0+dble(i-1)/1000.0d0*(ang1-ang0))/180.0d0*pi
       q1=sqrt(e(1)-en(1)**2*sin(theta)**2)/e(1)
       qn=sqrt(e(nlayer)-en(1)**2*sin(theta)**2)/e(nlayer)
       do j=2, nlayer-1
        beta=d(j)*2.0d0*pi/ramd*sqrt(e(j)-en(1)**2*sin(theta)**2)
        q=sqrt(e(j)-en(1)**2*sin(theta)**2)/e(j)
        em(j,1,1)=cos(beta)
        em(j,1,2)=-fukso*sin(beta)/q
        em(j,2,1)=-fukso*sin(beta)*q
        em(j,2,2)=cos(beta)
       enddo
        emtot(1,1)=dcmplx(1.0d0,0.0d0)
        emtot(2,2)=dcmplx(1.0d0,0.0d0)
        emtot(1,2)=dcmplx(0.0d0,0.0d0)
        emtot(2,1)=dcmplx(0.0d0,0.0d0)
       do j=2, nlayer-1
        emtot1(1,1)=em(j,1,1)
        emtot1(1,2)=em(j,1,2)
        emtot1(2,1)=em(j,2,1)
        emtot1(2,2)=em(j,2,2)
        emtot=matmul(emtot,emtot1)
       enddo

       rp=( (emtot(1,1)+emtot(1,2)*qn)*q1 -
     &      (emtot(2,1)+emtot(2,2)*qn) )
     &    / ( (emtot(1,1)+emtot(1,2)*qn)*q1 +
     &      (emtot(2,1)+emtot(2,2)*qn) )
       tp=2.0d0*q1/( (emtot(1,1)+emtot(1,2)*qn)*q1 +
     &      (emtot(2,1)+emtot(2,2)*qn) )

       rp=( (emtot(1,1)+emtot(1,2)*qn)*q1 -
     &      (emtot(2,1)+emtot(2,2)*qn) )
     &    / ( (emtot(1,1)+emtot(1,2)*qn)*q1 +
     &      (emtot(2,1)+emtot(2,2)*qn) )
       tp=2.0d0*q1/( (emtot(1,1)+emtot(1,2)*qn)*q1 +
     &      (emtot(2,1)+emtot(2,2)*qn) )

       ref=rp*conjg(rp)
       enh=tp*conjg(tp)
       tra=tp*conjg(tp)/cos(theta)*en(1)*dble(qn)
```

```
        write (6,*) theta/pi*180.0d0,dble(ref),enh
c       write (6,*) theta/pi*180.0d0,dble(ref),dble(tra)
        enddo
        end
```

6 Acknowledgement

The author would like to thank for Mr. A. Shirakami for his great contribution to the startup of the SPR study in our laboratory. The author also thank Prof. R. Corn, Prof. T. Kakiuchi and Dr. D. Hobora for helpful discussions on this subject.

7 Appendix

In Fig.16 the phase shifts of the reflected wave(He-Ne laser light) are shown in the case of Air($n = 1$) →Water($n = 1.332$)(top figure) and Water→Air(bottom figure). For the case of Water→Air the critical angle for total reflection is 48.66 degree and the phase shift is shown in Fig.6.

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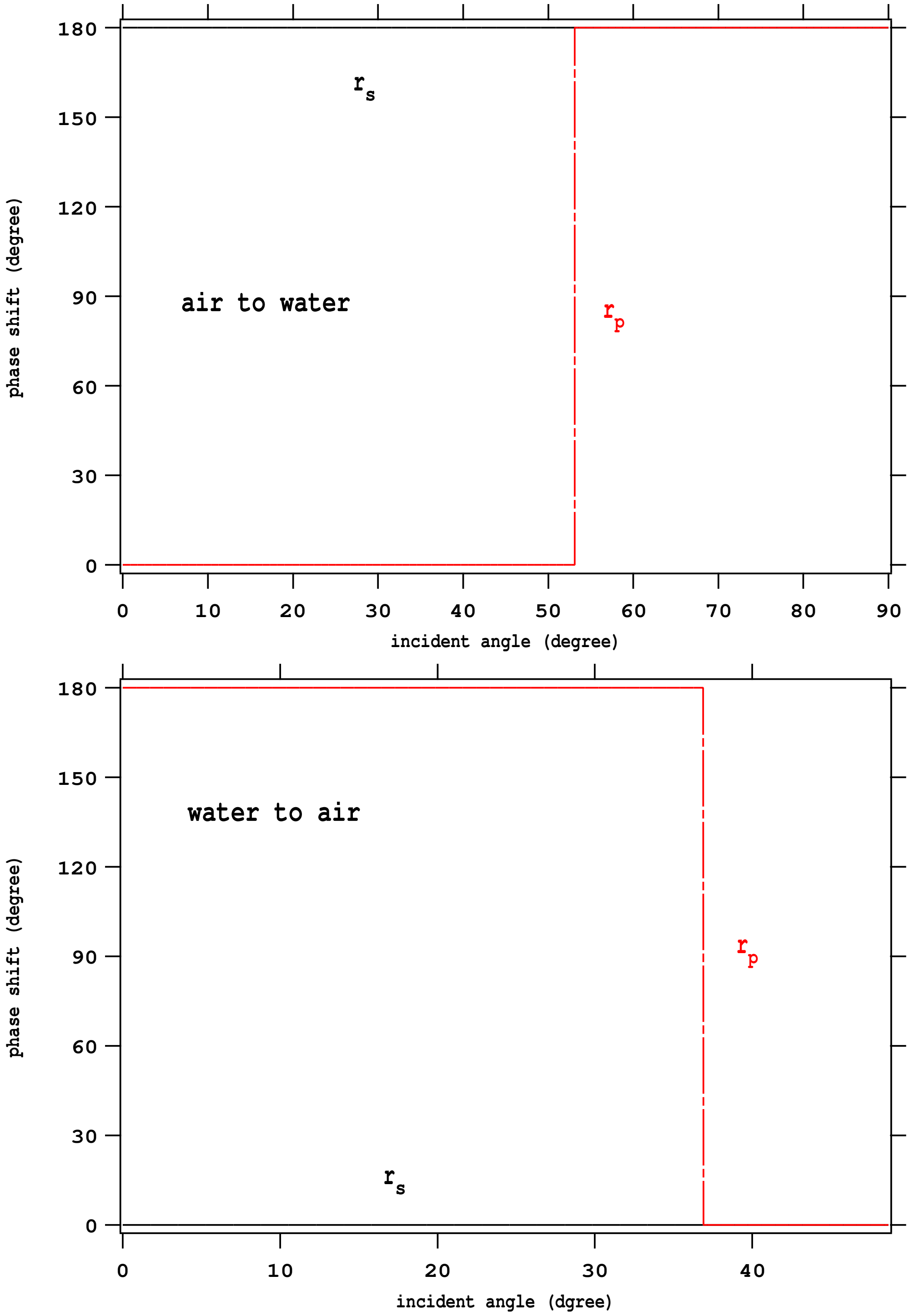

Figure 17: Phase shifts of the reflected wave(He-Ne laser light) are shown in the case of Air($n = 1$) →Water($n = 1.332$)(top figure) and Water→Air(bottom figure). For the case of Water→Air the critical angle for total reflection is 48.66 degree and the phase shift is shown in Fig.6.

In Fig.17 schematic diagram of light reflection from black film is shown. When the incident angle is small, the phase shift of s wave is π for OC and zero for OAB and the phase shift of p wave is zero for OC and π for OAB.(Please see Fig.16) If the film thickness d is much smaller than the wavelength/4, the interference between OC and wave from B become destructive.(Please note that the formulation is shown in the inset of Fig.17). Then we can see no light from thin film like lipid bilayer or soap bubble.

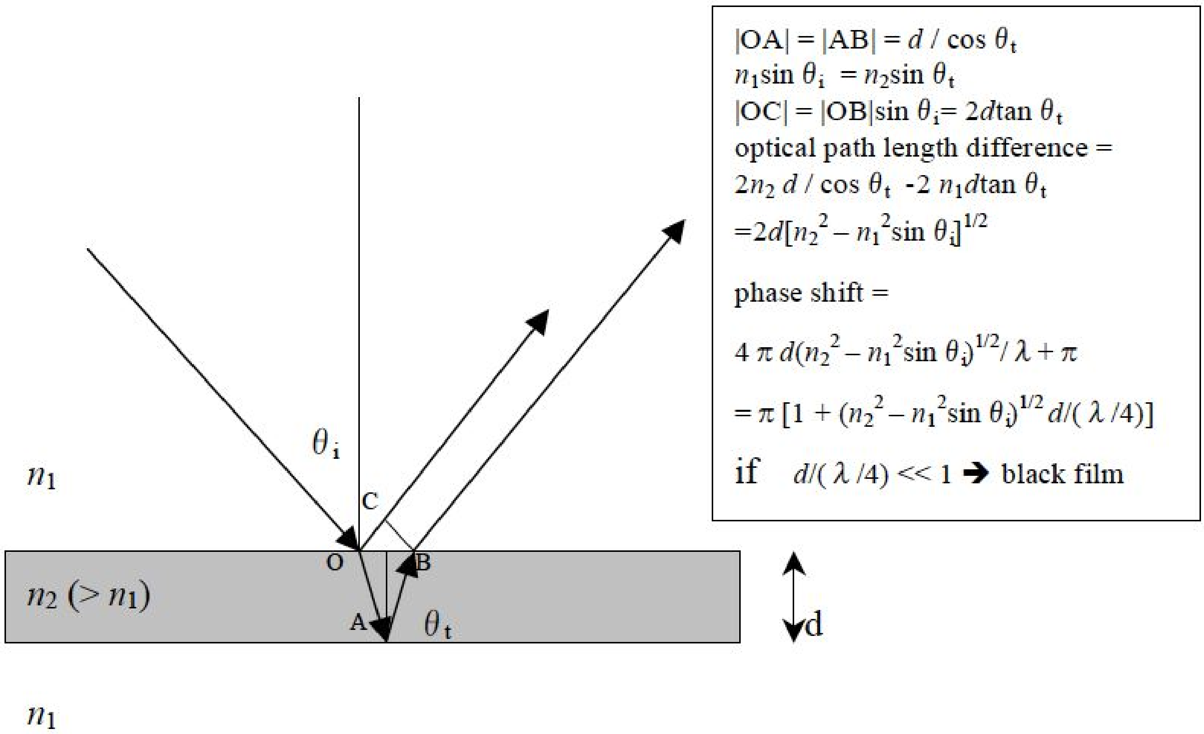

Figure 18: Schematic diagram of light reflection for black film. When the incident angle is small, the phase shift of s wave is π for OC and zero for OAB and the phase shift of p wave is zero for OC and π for OAB.(Please see Fig.16) If the film thickness d is much smaller than the wavelength/4, the interference between OC and wave from B become destructive. Please note that the formulation is shown in the inset. Then we can see no light from thin film like lipid bilayer or soap bubble.

Appendix

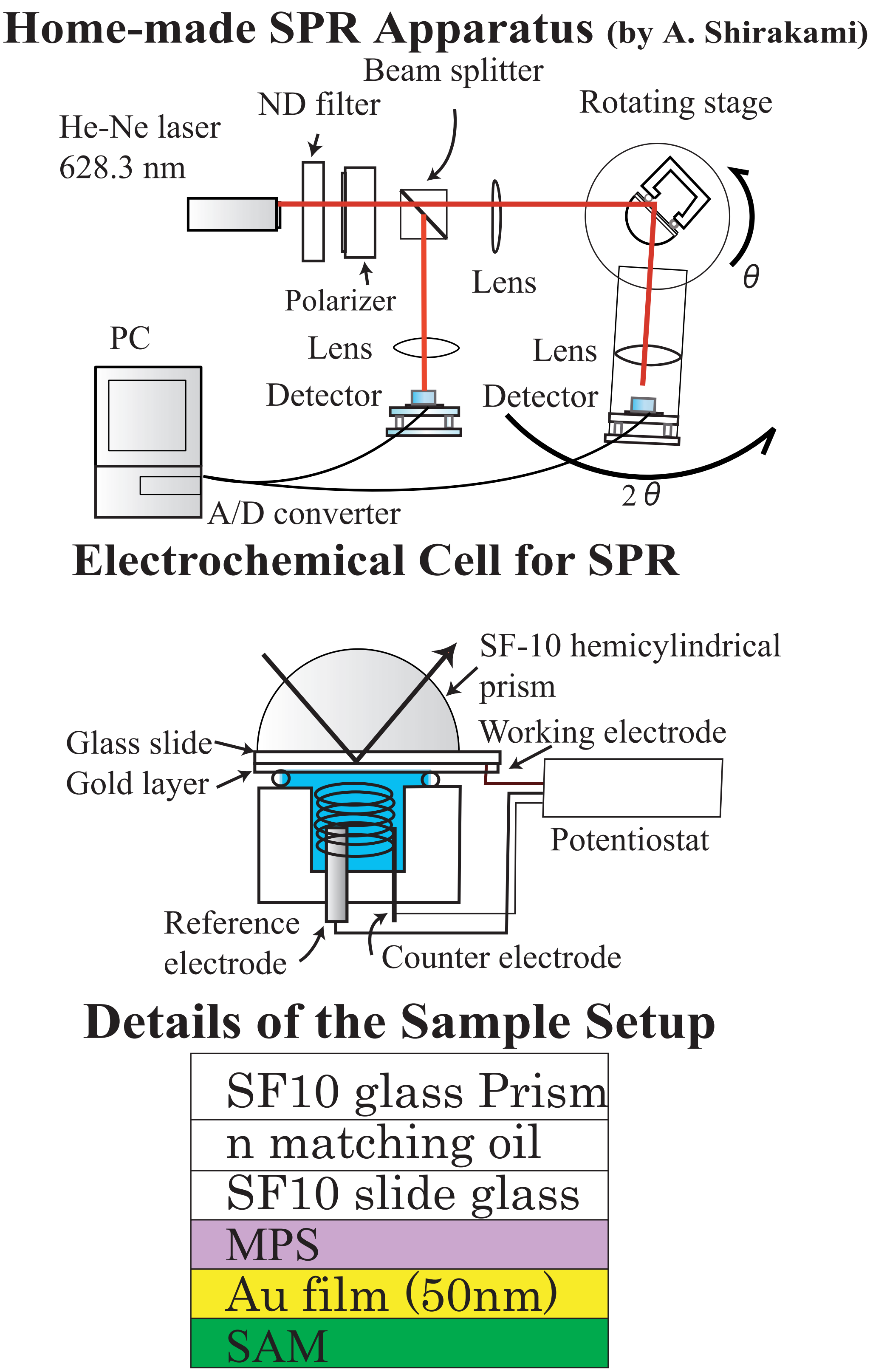

Figure 19: