Surface Plasmom Resonance

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What is SPR?

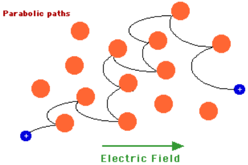
At optical frequencies metals electron gas can sustain surface and volume charge oscillations with distinct resonance frequencies. We call these as plasmom polaritons or plasmoms.

Interaction of metal nano-structures with light.

Metal

Drude Model : Crude Model which assumes free electrons roaming in between atoms.
Why Drude Model :
Interaction of em waves with metal is mostly governed by free conduction electrons. Simple

Drude Model



Electrons moving in sea of atoms
When Electric Field is applied electrons start moving in the opposite direction of the field

$$damping = \frac{momentum}{\text{time between successive collisions}}$$

Applying Newton's Law

$$m\frac{d^2r}{dt^2} = eE - \frac{m}{t}\frac{dr}{dt}$$

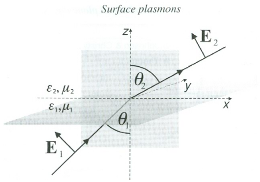
now using p = er, $P = np = ner = \epsilon_o \chi_e E$ and $\epsilon(\omega) = 1 + \chi_e$ we get:

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

$$\text{where } \omega_p = \frac{ne^2}{m_e}$$

Qualitative relation of dielectric coefficient.

Interface of Metal and any other substance



First check which type of light can excite interface.

P-polarized Light (TM waves)

Assuming no reflected light because otherwise we dont have maximum coupling between electrons and em waves and applying boundary conditions and Maxwell relations we get

$$k_x^2 = \frac{\omega^2}{c^2}\frac{\epsilon_1(\omega)\epsilon_2(\omega)}{\epsilon_1(\omega)+\epsilon_2(\omega)}$$

$$k_{1z}^2 = \frac{\omega^2}{c^2}\frac{\epsilon_1^2(\omega)}{\epsilon_1(\omega)+\epsilon_2(\omega)} \quad k_{2z}^2 = \frac{\omega^2}{c^2}\frac{\epsilon_2^2(\omega)}{\epsilon_1(\omega)+\epsilon_2(\omega)}$$

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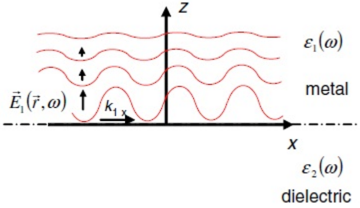
for gold at 633 nm $\epsilon \approx -11$ and for gold air interface $\epsilon_{air} = 1$

So we have real k_x and imaginary k_{1z} and k_{2z}

Thus evanescent wave is produced in z axis in both media and a propagating surface wave is produced at the interface.



S-polarized Light (TE waves)

Assuming we have no reflection and then solving boundary conditions we get $\epsilon_1 = \epsilon_2$

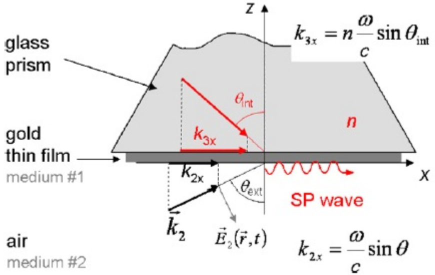
Thus our assumption is wrong.

So we must have strong reflected light in this case.

Therefore we do not have resonance condition for s-polarized light

Excitation of SPR

We must be able to excite metal so that SPR can occur.
Ways of exciting



Dispersion relation

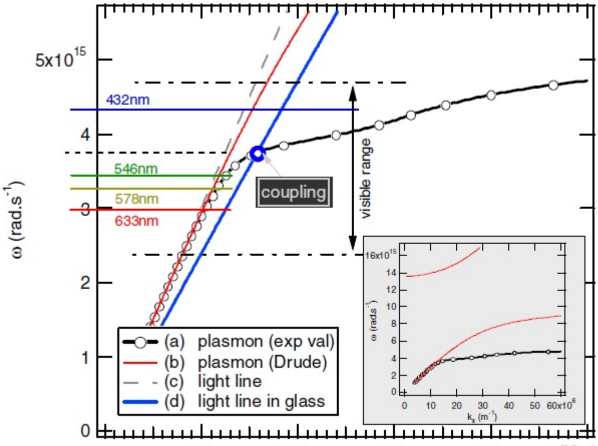
Air

$\omega = \frac{k_x c}{sin(\theta_{int})}$

for $\theta_{int} = 90^o$ we have minimum slope for dispersion **Glass**

$\omega = \frac{k_x c}{nsin(\theta_{int})}$

So we have a tilt in line by $\frac{1}{n}$



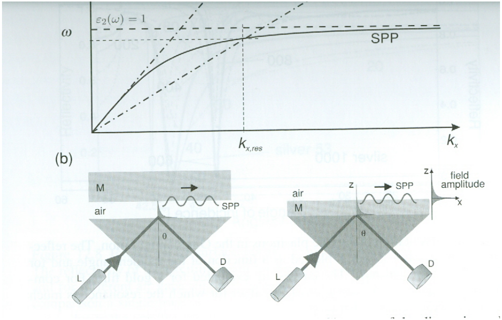
Coupling excitation wave with SP wave

Substituting k_x of wave in glass in that of metal we get

$$(nsin(\theta_{int}))^2 = \frac{\epsilon_1(\omega)\epsilon_2(\omega)}{\epsilon_1(\omega) + \epsilon_2(\omega)}$$

This is the condition for exciting SPR.
When this condition is fulfilled, incident light is converted in exciting of SPR and reflected beam is damped.
For gold/air interface we have $\epsilon_2 = 1$
General relationship to determine refractive index of adsorbed layer

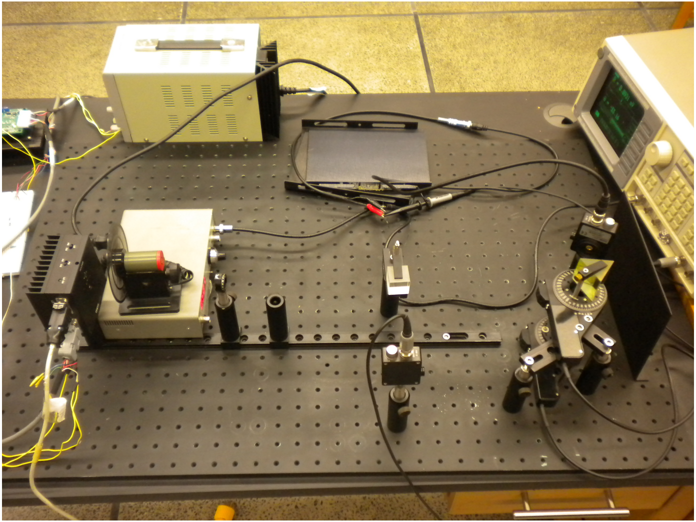
Configurations of exciting SPR



Thickness of film

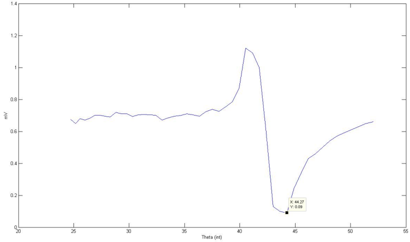
Optimum 50nm
Too thick then not enough momentum transfer
Too thin then not enough constructive interference to support SPR

Experimentation

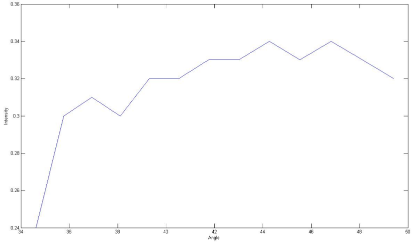


Results of Experiment

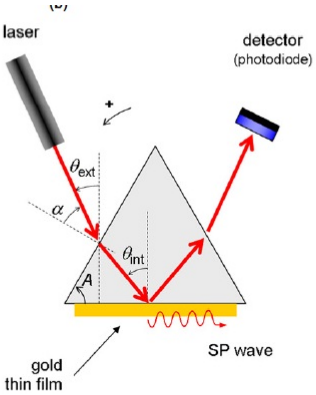
P-polarized light



S-polarized light



Interpretation

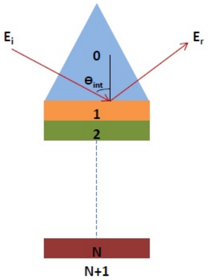


Two interpretations of dip in curve:
1- Destructive interference between light reflected from prism and light emitted by SPR due to radiation.
2- Light totally converted into SPR which carries away energy at the interface.

Problems with Experiment

Film thickness not known precisely.
Refractive index of prism is not accurately known.
Zeroing of prism position is difficult and errors due to that.

Complete theoretical modeling of SPR for multi-layers



$$\hat{R} = \sqrt{R}\exp(i\delta) = \frac{\hat{r}_1 + \hat{\bar{r}}_2 \exp(i\hat{x}_1)}{1 + \hat{r}_1\hat{\bar{r}}_2 \exp(i\hat{x}_1)},$$

$$\hat{\bar{r}}_2 = \frac{\hat{r}_2 + \hat{\bar{r}}_3 \exp(i\hat{x}_2)}{1 + \hat{r}_2\hat{\bar{r}}_3 \exp(i\hat{x}_2)},$$

$$\vdots$$

$$\hat{\bar{r}}_k = \frac{\hat{r}_k + \hat{\bar{r}}_{k+1} \exp(i\hat{x}_k)}{1 + \hat{r}_k\hat{\bar{r}}_{k+1} \exp(i\hat{x}_k)},$$

$$\vdots$$

$$\hat{\bar{r}}_N = \frac{\hat{r}_N + \hat{r}_{N+1} \exp(i\hat{x}_N)}{1 + \hat{r}_N\hat{r}_{N+1} \exp(i\hat{x}_N)},$$

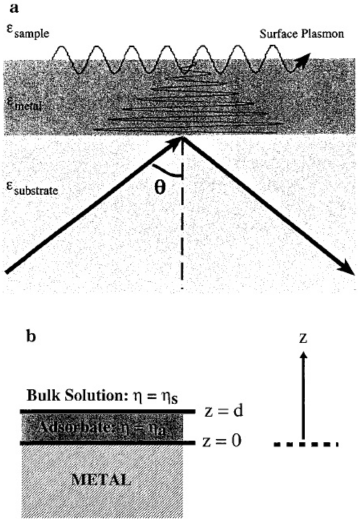
$$\hat{r}_s = \frac{\hat{n}_{s-1} - \hat{n}_s}{\hat{n}_{s-1} + \hat{n}_s} \qquad (s = 0, 1, 2, \ldots, N+1),$$

$$\hat{x}_j = \frac{4\pi}{\lambda}\hat{n}_j d_j, \qquad \hat{n}_s = n_s + ik_s \qquad (j = 1, \ldots, N),$$

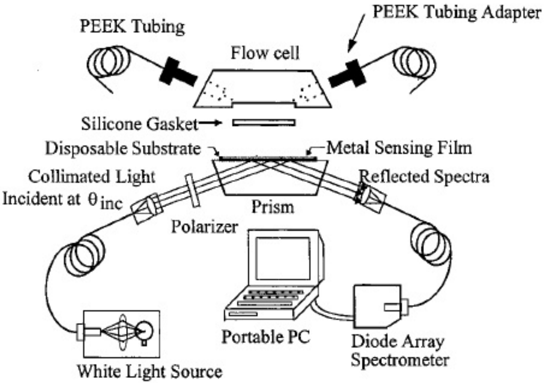
$$\hat{n}_0 \equiv n_0, \qquad \hat{n}_{N+1} \equiv \hat{n} = n + ik.$$

Towards Bio-sensing

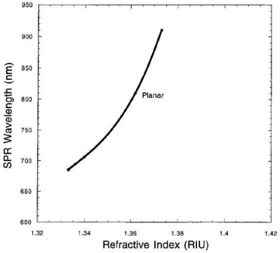
Difficult to model all systems using fresnel equations.
So we must have an alternative way of real time sensing.

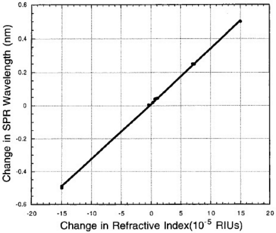


Experimental Setup



SPR response to bulk solutions





For small range of n: Linear response $\Longrightarrow R = m\Delta n$
For broad range of n: Non-linear curve
$\Longrightarrow R = m_1\Delta n + m_2\Delta n^2$

Determining adsorbate thickness

For pure bulk solution n_s

Some effective refractive index of adsorbate and bulk solution n_{eff}

$$R = m(n_{eff} - n_s)$$

n_{eff} some average of adsorbate and bulk sol.

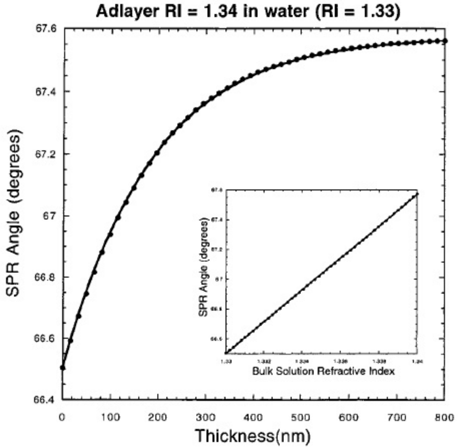
$$n_{eff} = \frac{\int_0^\infty n(z) exp(\frac{-2z}{l_d}) dz}{\int_0^\infty exp(\frac{-2z}{l_d}) dz}$$

where $n(z) = n_a$ for $0 < z < d$ and $n(z) = n_s$ for $d < n < \infty$. Thus

$$n_{eff} = n_s + (n_a - n_s)[1 - exp(-\frac{2d}{l_d})]$$

Substituting we get

$$R = m(n_a - n_s)[1 - exp(-\frac{2d}{l_d})]$$



Estimating adsorbate thickness

$$d = -(\frac{l_d}{2})(ln(1 - \frac{R}{R_{max}}))$$

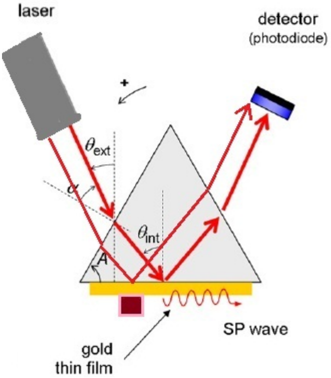
where $R_{max} = m(n_a - n_s)$

for d small compared to l_d we have

$$d = \frac{l_d}{2}\frac{R}{m(n_a - n_s)}$$

My Predictions

Refractive index measurement and microscopy using SPR At Resonance angle of Gold/Air interface dark background on which bright spots will be visible because of particles attached to it.



First look at resonance angle of Gold/Air.
Then see when those bright spots turn darkest to get their refractive index.

References

1- Laboratory experiments for exploring the surface plasmon resonance, Olivier Pluchery et al, 2011, Eur. J.
2- Quantitative Interpretation of the Response of Surface Plasmon Resonance Sensors to Adsorbed Films, Linda S. Jung et al, 1998, American Chemical Society.
3- Principles of Nano-Optics, Lukas Novotny and Bert Hetch, Cambridge University Press.