Development of an SPR based thin-film sensing system

Hassaan Majeed

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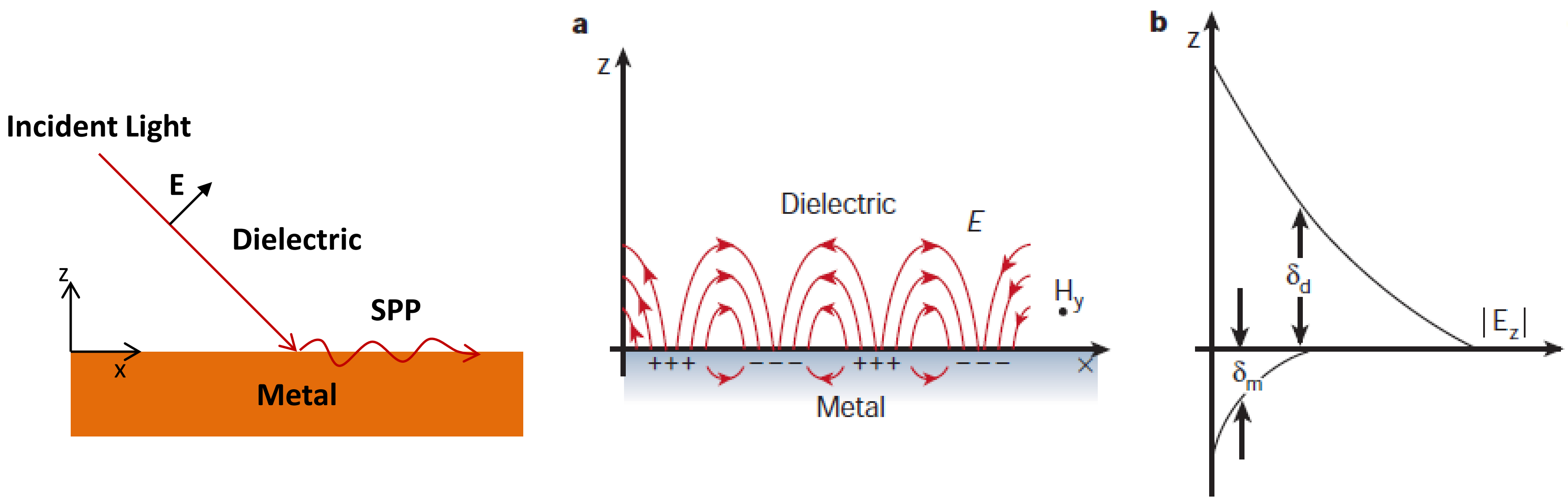
Breakdown

- Introduction
- Theory
- Experiment design and setup
- Experimental procedures and results
- Future goals and work

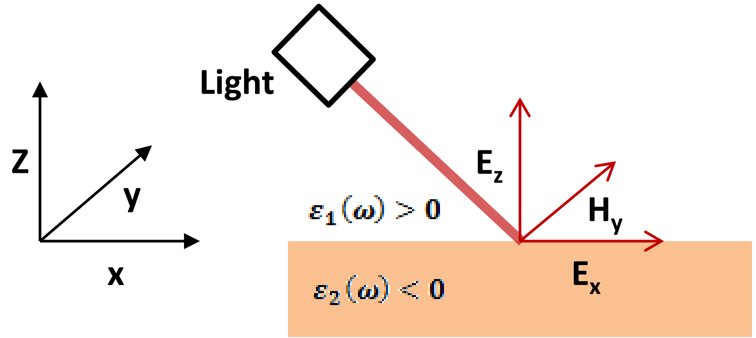
Surface Plasmon Resonance (SPR)

- Corresponds to propagating surface modes (SPPs) being excited at a metal/dielectric interface by coupling of TM polarized incident light and electron oscillations (plasmons)
- Electric field confined in sub-wavelength volumes leading to local field enhancement



W. L. Barnes, A. Dereux, and T. W. Ebbesen, "Surface plasmon subwavelength optics," *Nature,* vol. 424, pp. 824-830, 2003.

Theory: Derivation



Maxwell's Equations + Boundary Conditions

if $|\varepsilon_2| > |\varepsilon_1|$

$$k_{1z} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2}}$$

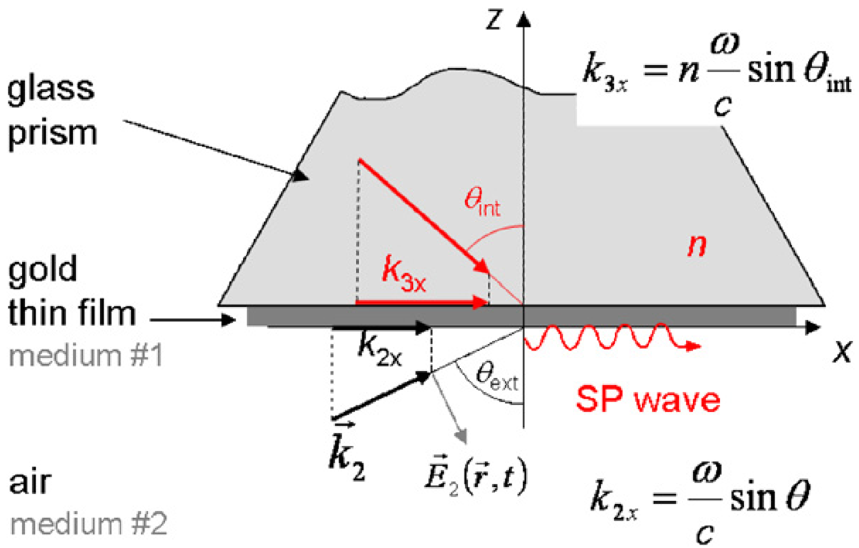
$$k_{2z} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_2}{\varepsilon_1 + \varepsilon_2}}$$

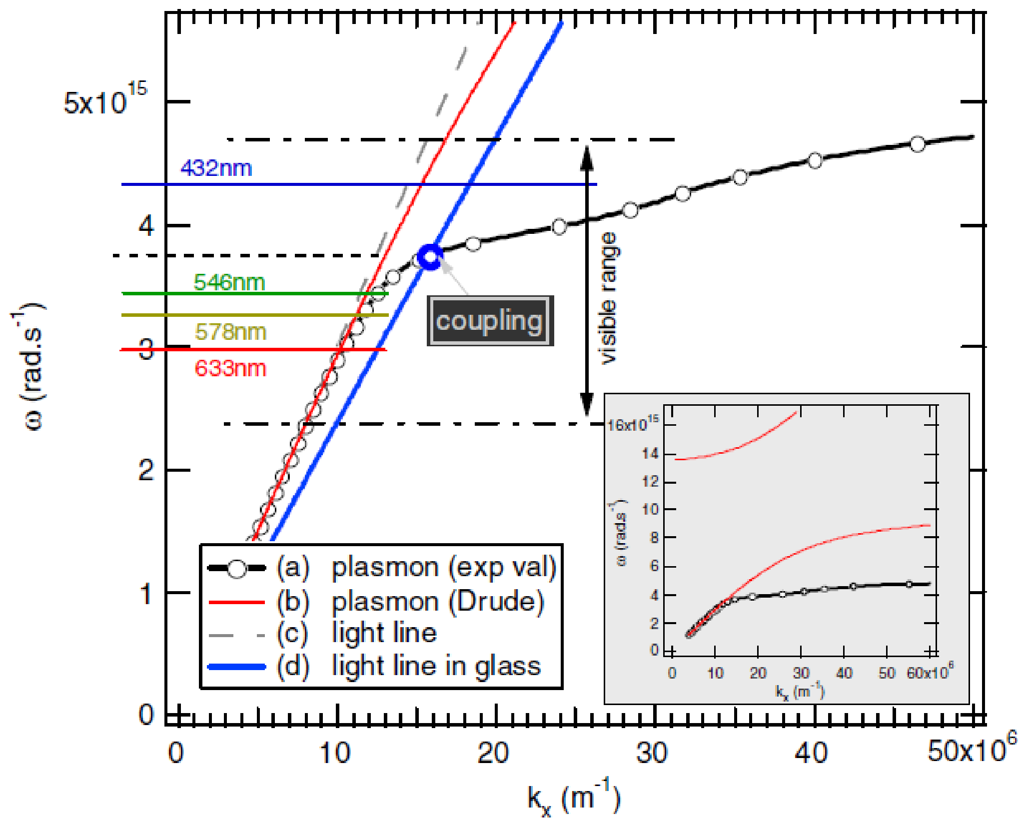
→ **Imaginary**

$$k_x = \frac{\omega}{c}\sqrt{\frac{\varepsilon_2 \varepsilon_1}{\varepsilon_1 + \varepsilon_2}}$$

→ **Real**

Theory: Dispersion Relation





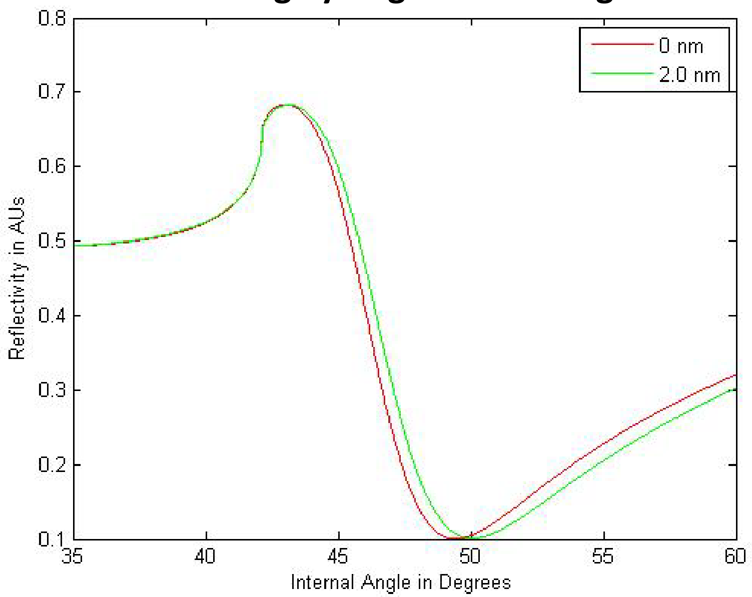
O. Pluchery, R. Vayron, and K.-M. Van, "Laboratory experiments for exploring the surface plasmon resonance," *European Journal of Physics,* vol. 32, pp. 585-599, 2011.

Theory: Dispersion Relation

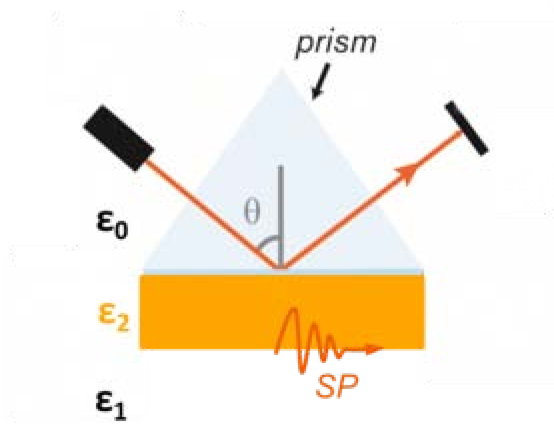
Resonance Condition

$$n \sin \theta_{int} = \sqrt{\frac{\varepsilon_2 \varepsilon_1}{\varepsilon_1 + \varepsilon_2}}$$

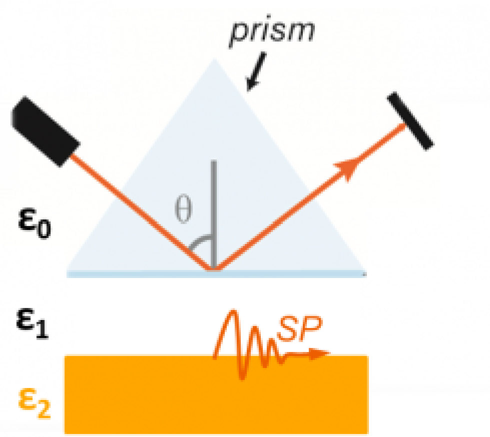
Sensing by Angular Scanning



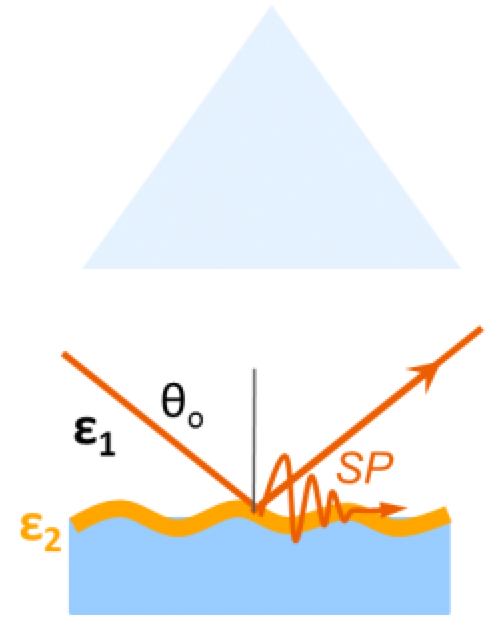
Theory: Excitation Configurations



Kretschaumm



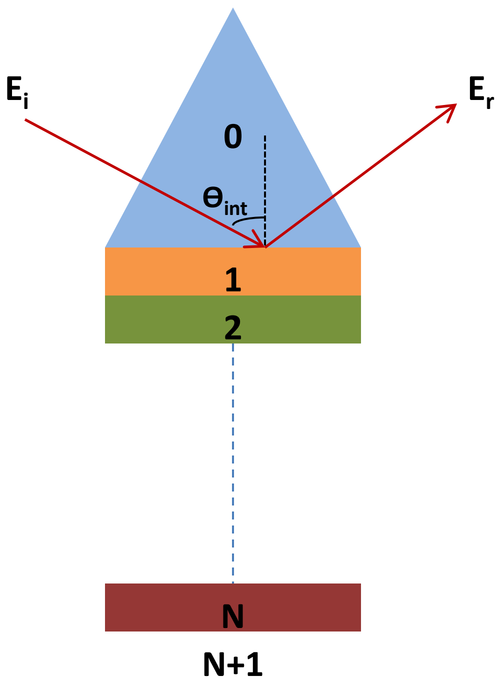
Otto



Grating

http://www.bionavis.com/technology/spr/

Theory: Multilayer Reflection Model



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

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

$$\vdots$$

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

$$\vdots$$

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

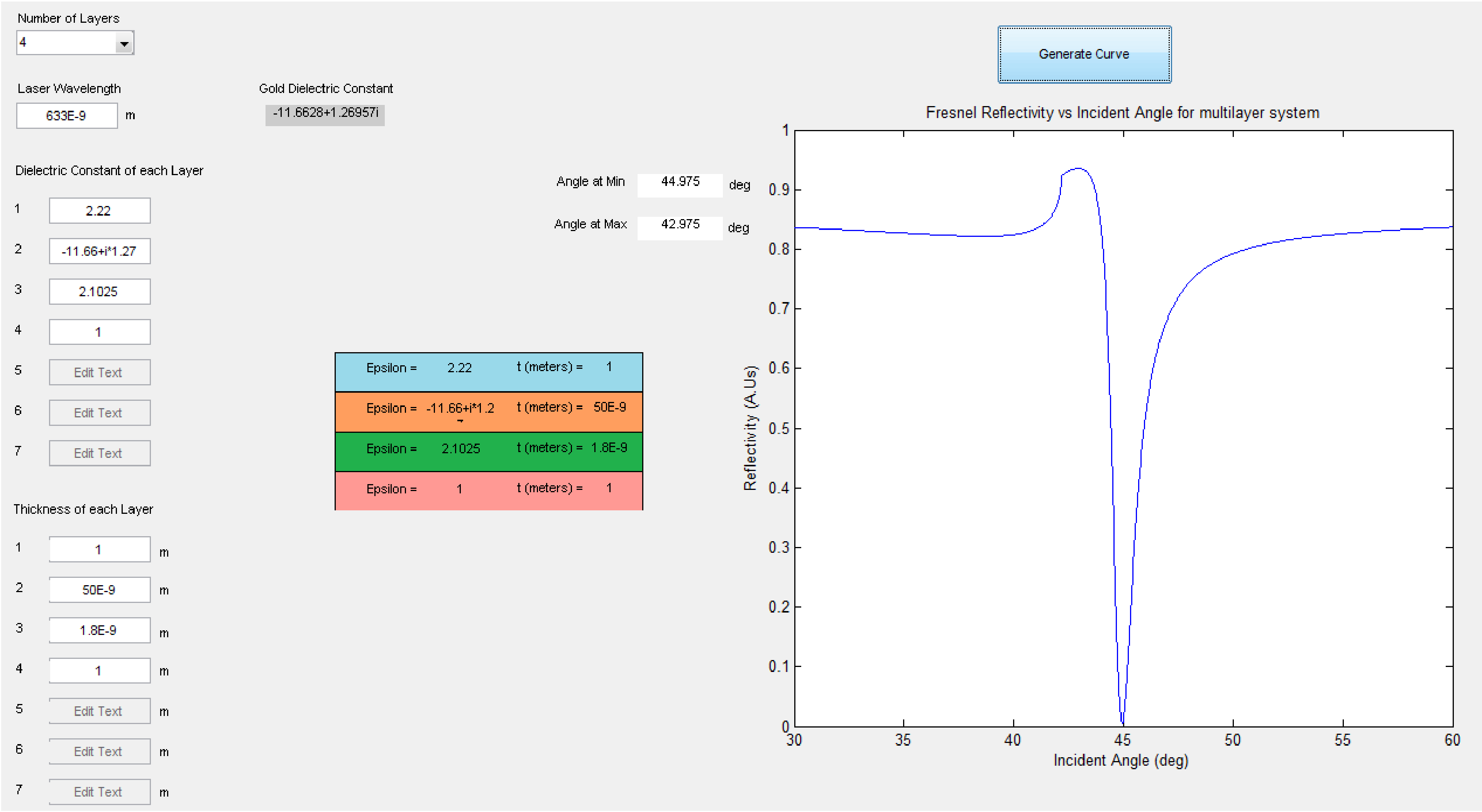
$$\hat{r}_s = \frac{\hat{n}_{s-1} - \hat{n}_s}{\hat{n}_{s-1} + \hat{n}_s} \qquad (s = 0, 1, 2, \ldots, N+1),$$

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

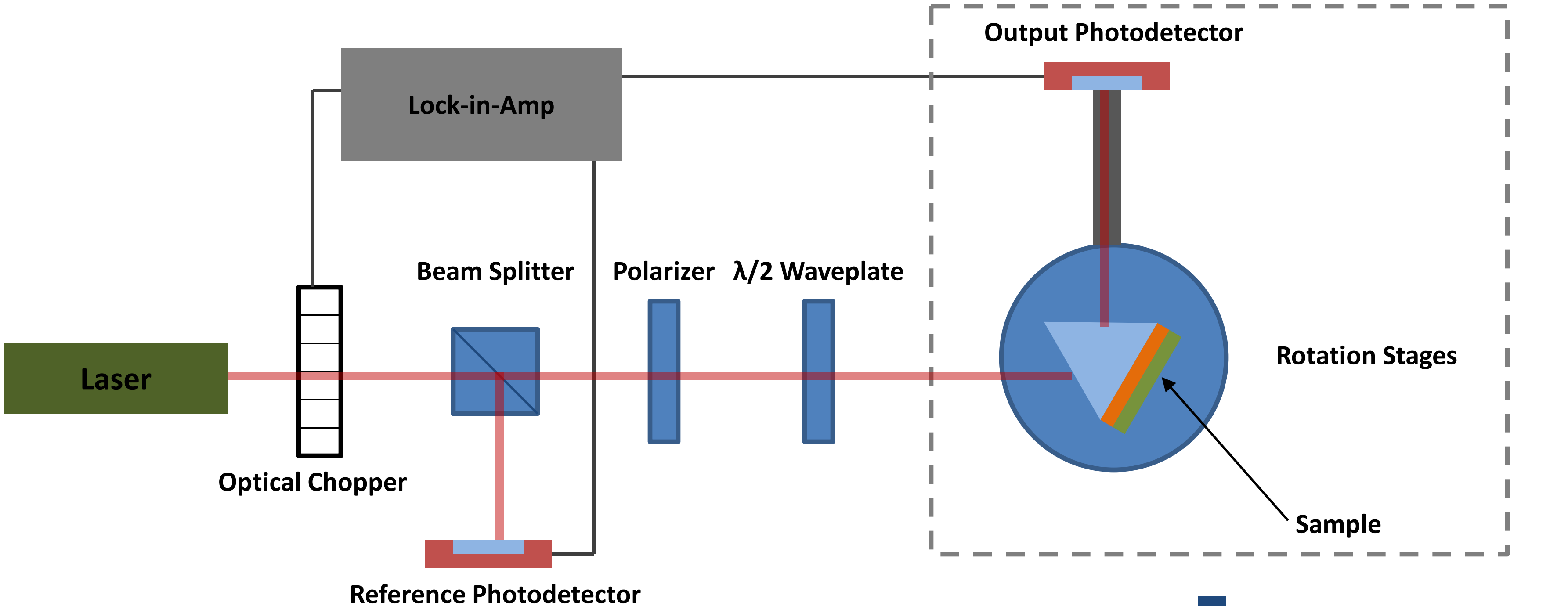
$$\hat{n}_0 \equiv n_0, \qquad \hat{n}_{N+1} \equiv \hat{n} = n + ik.$$

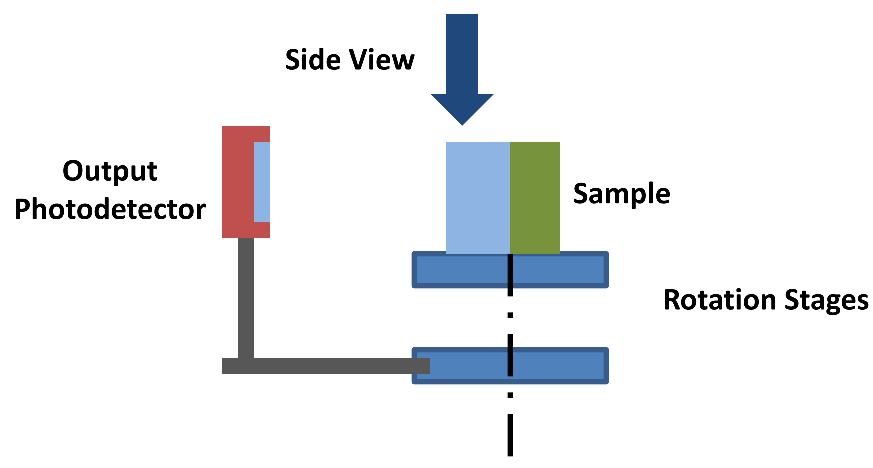
Ivan Ohlidal, “Immersion spectroscopic reflectometry of multilayersystems”, *J. Opt. Soc. Am. A,* vol. 5, no. 4, 1988, pp. 459-464

Theory: Multilayer Reflection Model



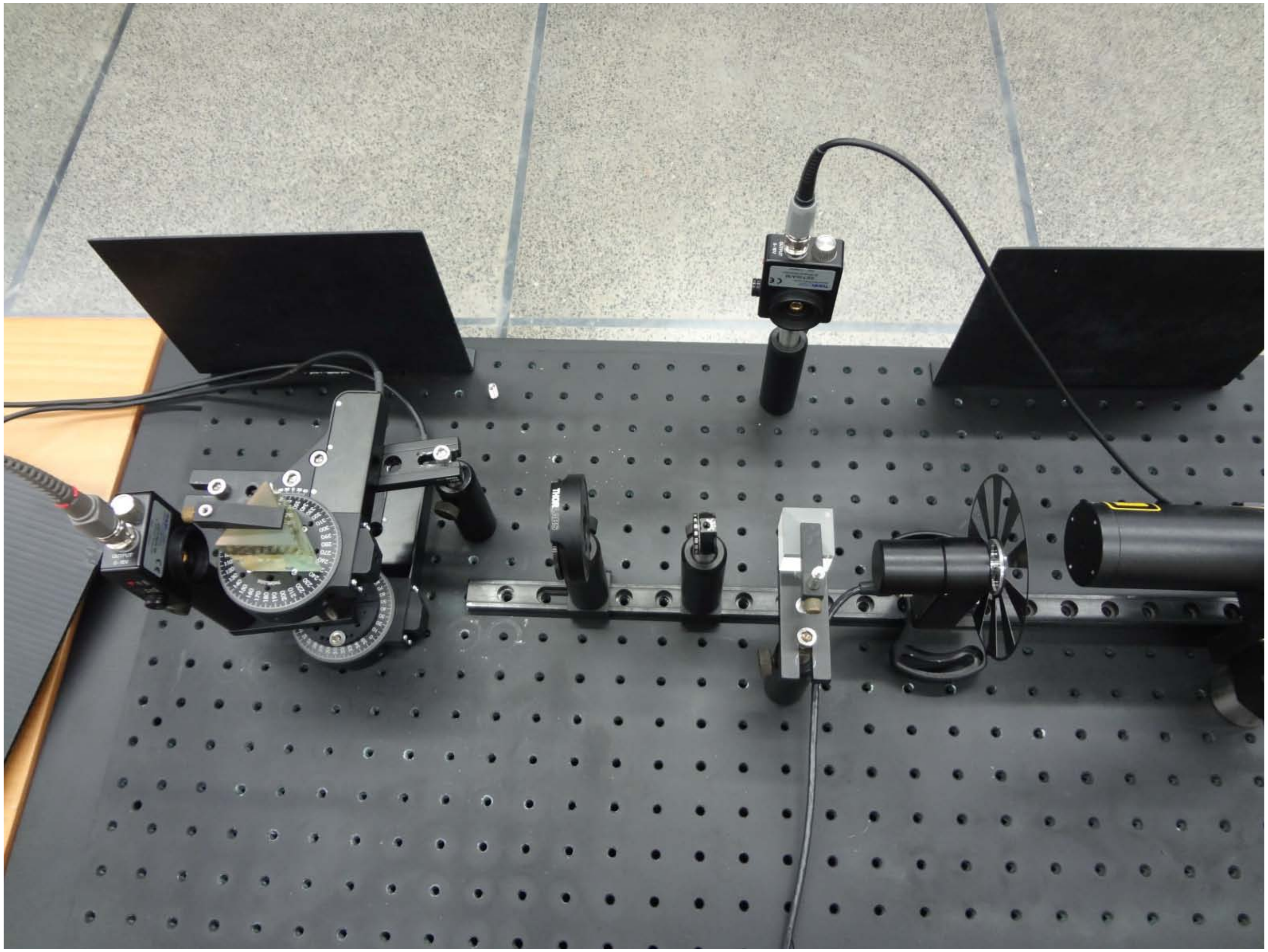
Experimental Setup



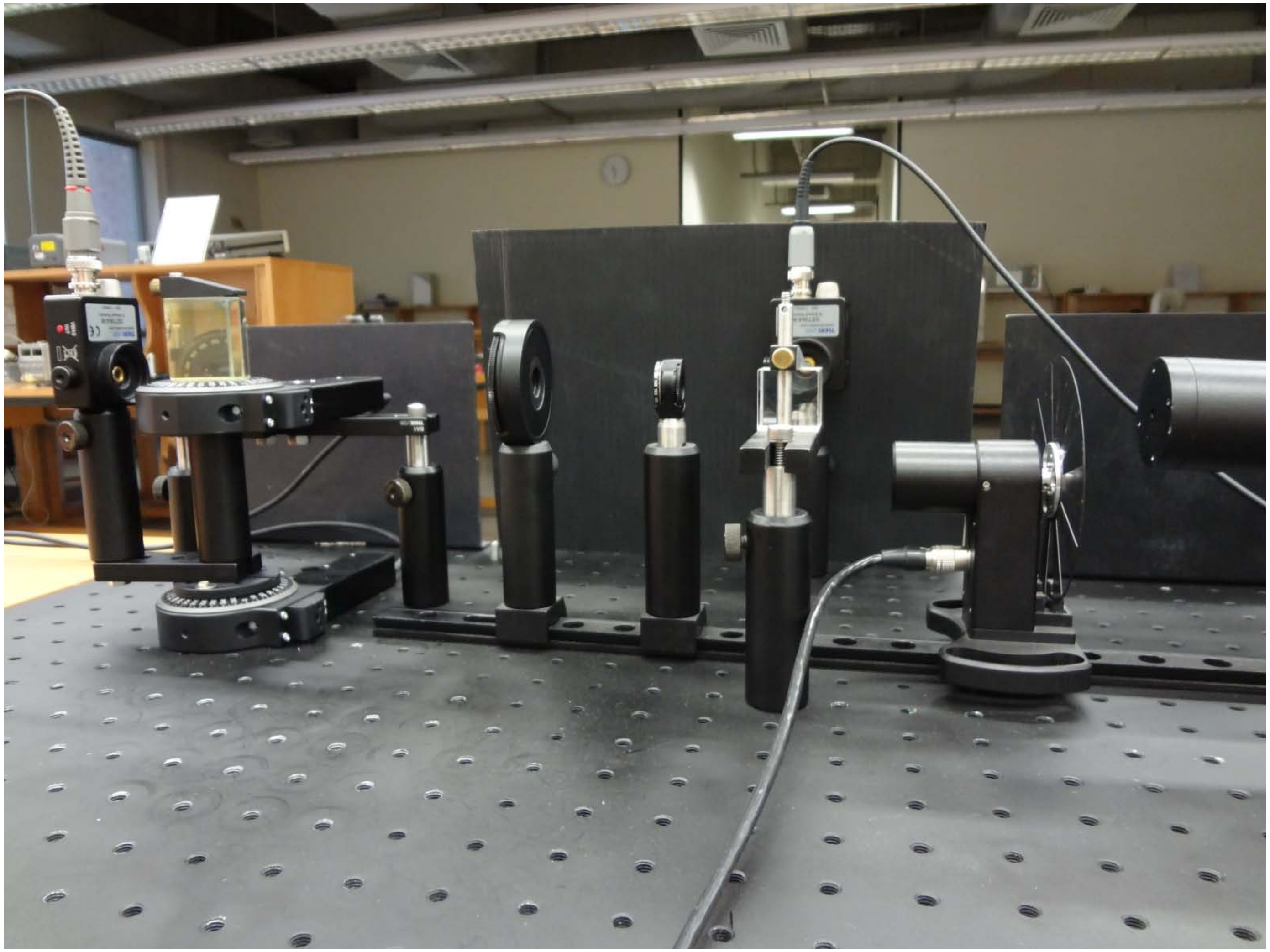


Lower stage runs at twice the angular velocity of the upper stage

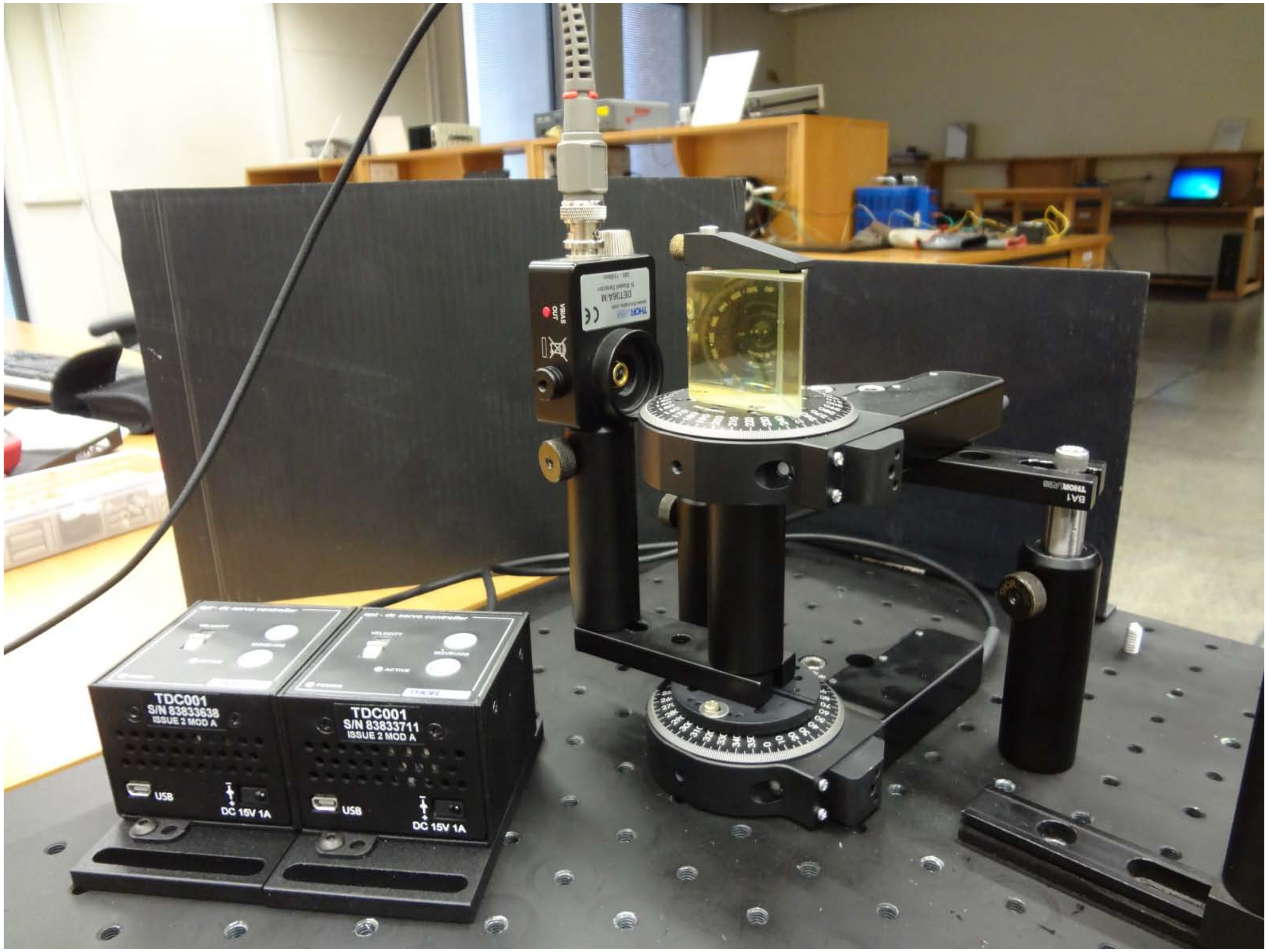
Experimental Setup



Experimental Setup

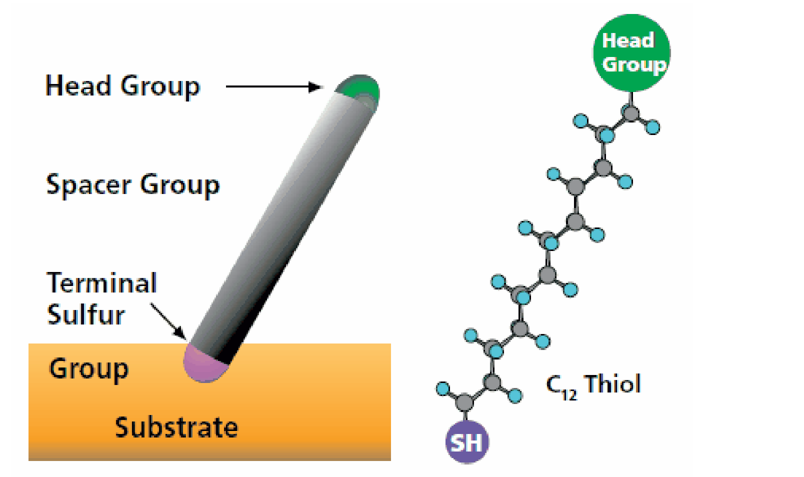


Experimental Setup

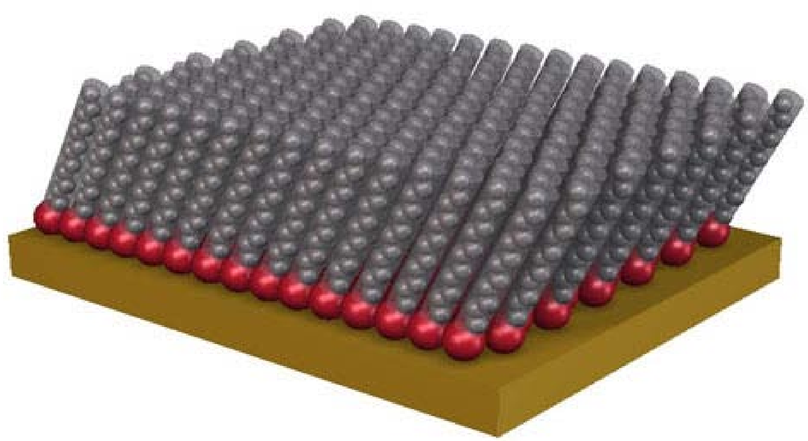


Experimental Procedures and Results: SAM Detection

- Self-Assembled Monolayers are highly ordered organic thin films formed on Gold substrates
- The cystalline-like structure is formed by the action of intermolecular forces, hence the term “Self-Assembled”
- Assembly is carried out by dipping the gold substrate in a solution of chemical containing the thiol S-H functional group (typically alkanethiols $CH_3(CH_2)_nSH$ are used)
- Sulfur covalently bonds to gold



Maxi Boeckl, Dr. Daniel Graham, *Material Matters* ***2006****, 1.2, 3*



www.sigmaaldrich.com

SAM Detection: Substrate Preparation

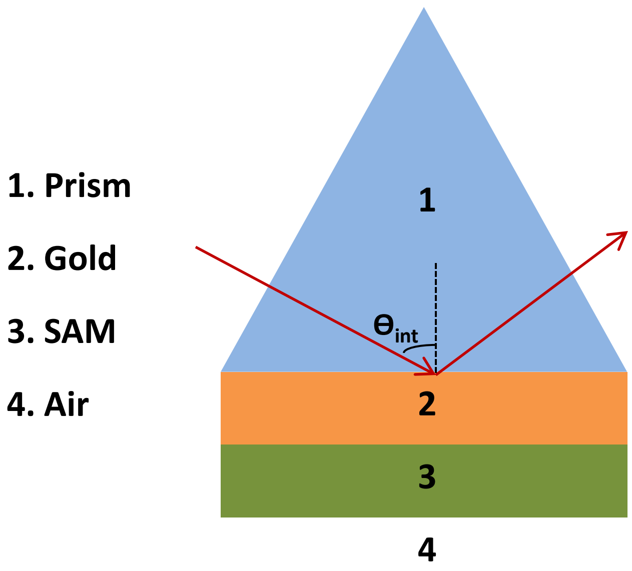
- Gold thin film sputter coated onto locally purchased equilateral prism
- Thin film thickness estimated at 50 nm based on current (20 mA) and time of sputtering (360 sec)
- Substrate Cleaning:
  - Heated at 320 deg C for 30 min
  - Rinsed with DI Water

SAM Detection: Self Assembly Procedure

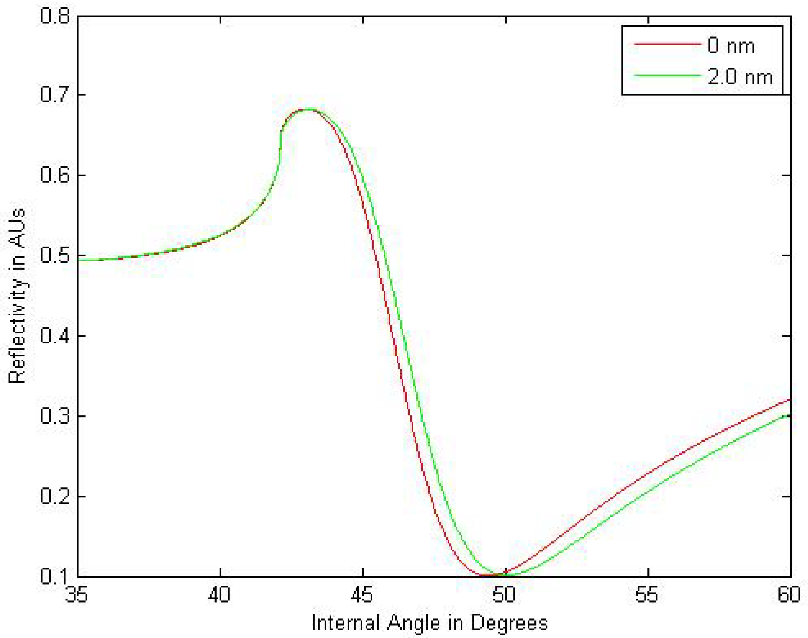
- 180 ul of dodecanethiol ($CH_3(CH_2)_{11}SH$) mixed in 150 ml of ethanol to make a 5 mM solution
- Stirred for 5-10 min to ensure dissolution
- Prism immersed in the solution and left for 36 hours
- Prism retrieved from the solution
- Rinsed with ethanol.

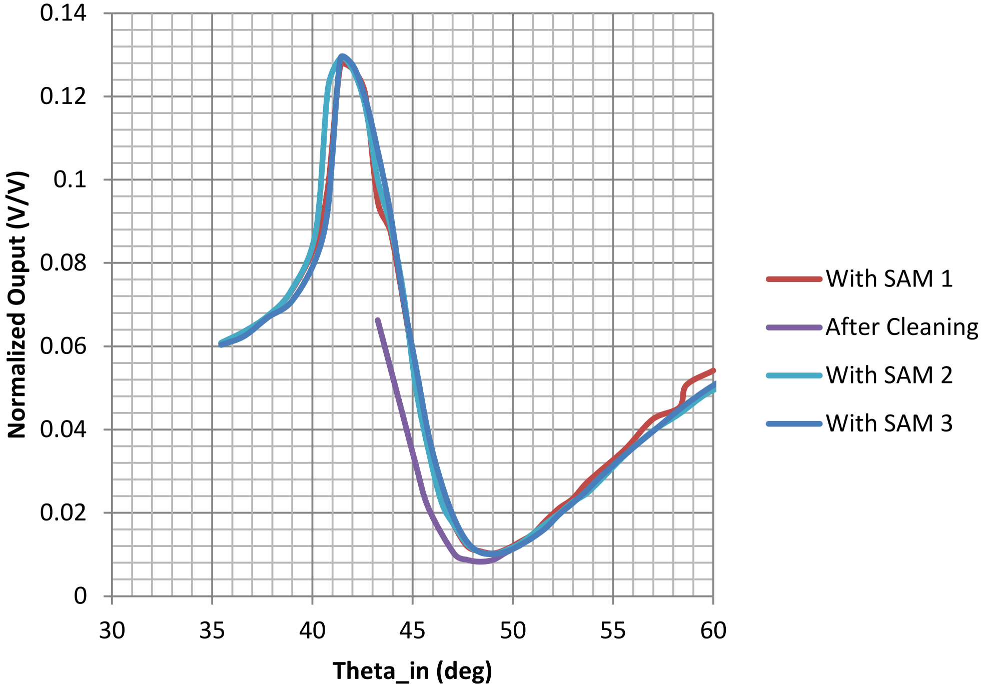
SAM Detection: Parameters

- Parameters:
  - Manual Rotation Stage: $\Delta\theta_{min} = 1$ deg
  - $\lambda = 532$ nm wavelength laser
  - $t_{gold} = 50$ nm (estimated)
  - $\varepsilon_{gold} = -4.61 + i2.44$
  - $n_{prism} = 1.49$ (based on an approximation)
  - $t_{SAM} = 2$ nm (Porter et al., *J. Am. Chem. SOC.,*1987)
  - $n_{SAM} = 1.45$ (Porter et al., *J. Am. Chem. SOC.,*1987)



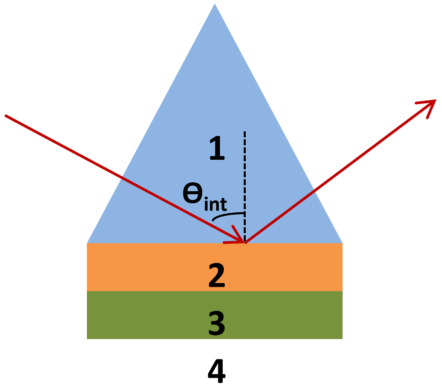
SAM Detection: Results



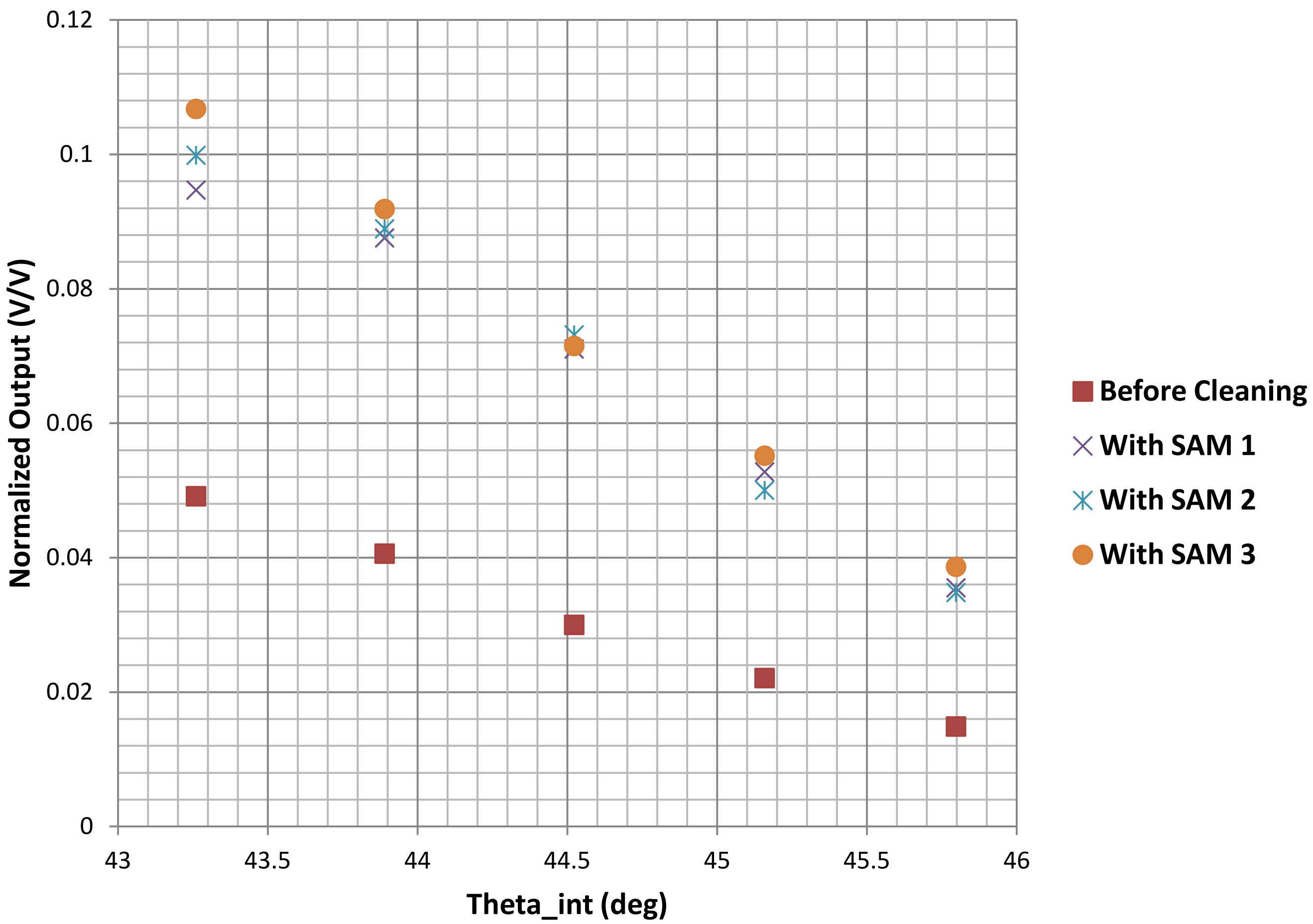


- Theoretically:
  - Before SAM formation: Resonance Angle = 49.5 deg
  - After SAM formation: Resonance Angle = 50 deg
- From the results
  - Before SAM formation: Resonance Angle = 48.5 deg
  - After SAM formation: Resonance Angle = 49 deg

1. Prism
2. Gold
3. SAM
4. Air



SAM Detection: Results

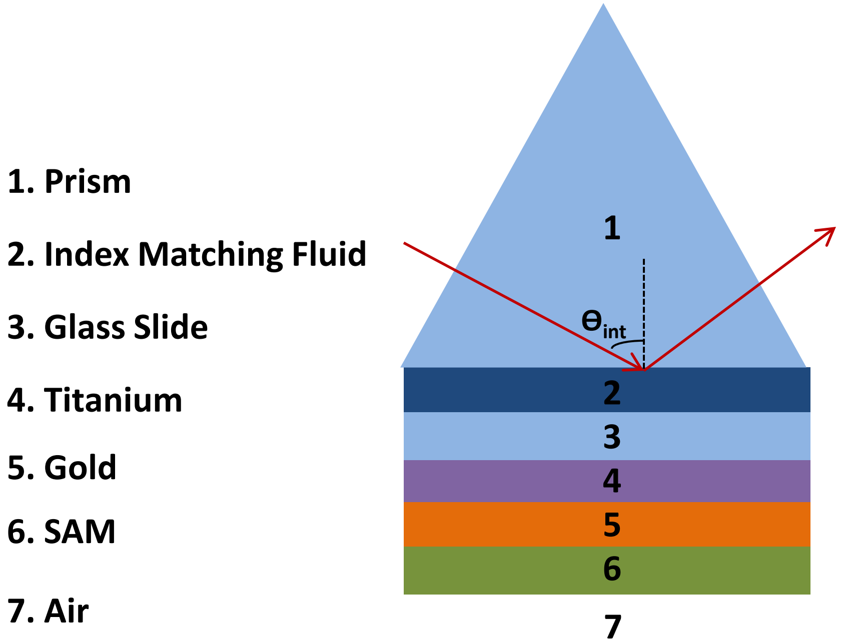


SAM Detection: Problems

- Difference between theoretical and experimental resonance conditions. Maybe due to:
  - Inaccurate determination of n_{prism}
  - Inaccurate estimation of t_{gold}
  - $\Delta\theta_{min}$ is too large
- Other desired improvements:
  - $\lambda = 633$ nm since $\varepsilon_{gold}(633nm) = -11.66 + i1.27$
  - Convenience in handling gold substrate
  - Better adhesion of gold required

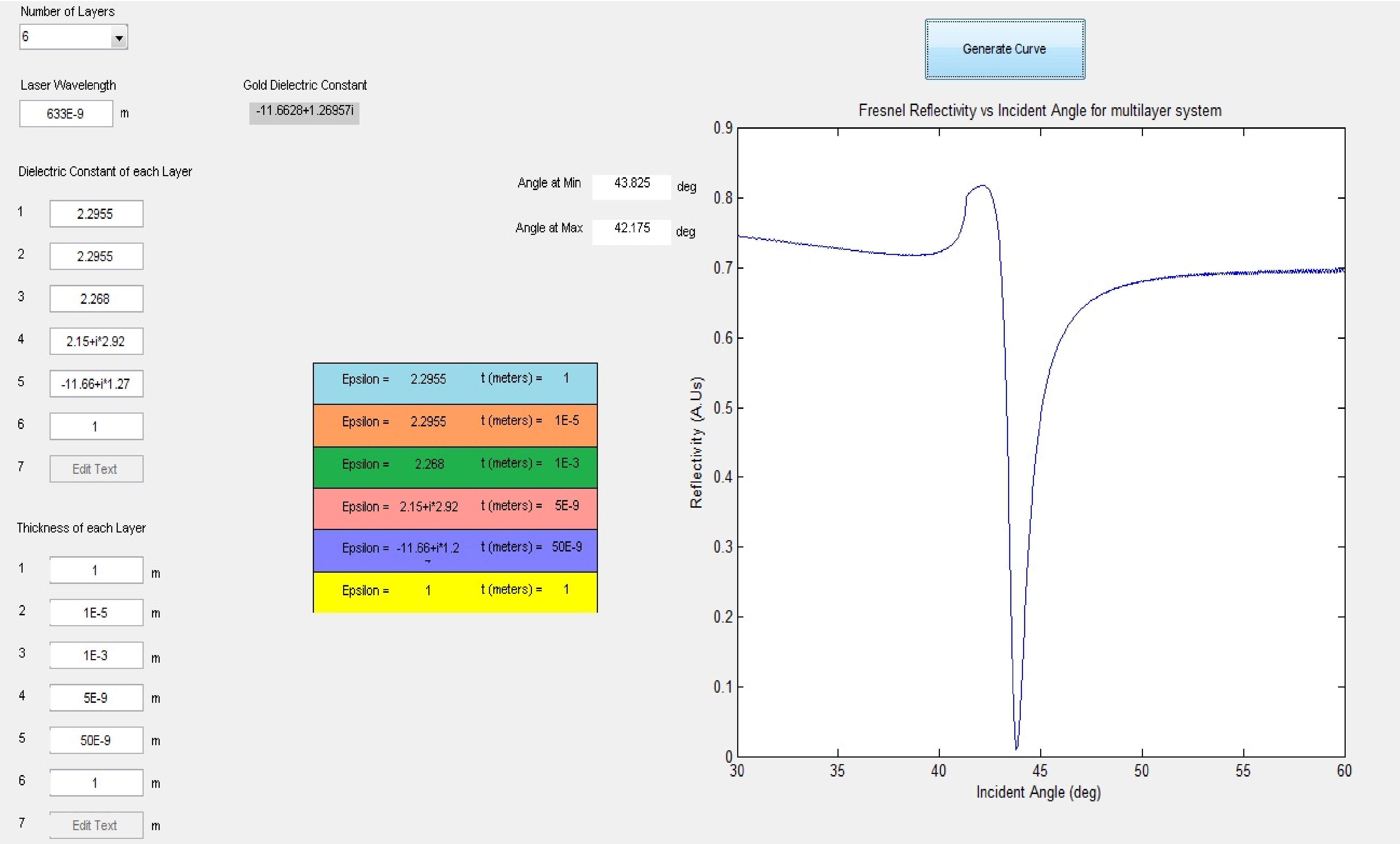
SAM Detection: Improvements in Design

- Thorlabs BK7 prism used: n_{prism}=1.51508
- λ = 633 nm
- Slides with t_{ti} = 5 nm and t_{gold} = 50 nm on n_{slide} = 1.507 glass obtained from Phasis
- Prism and slide index matched using index matching fluid from Cargille Labs n_{fluid} = 1.51508
- Motorized Stages with $\Delta\theta_{min}$ = 1 arcsec

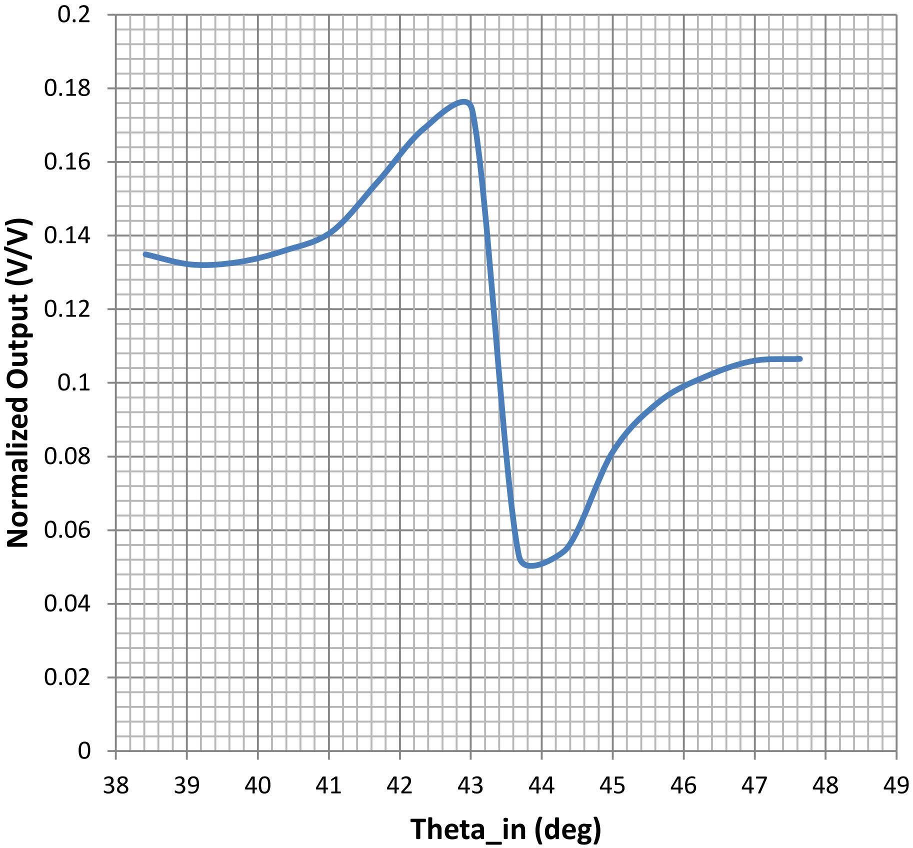


Results: Before SAM formation

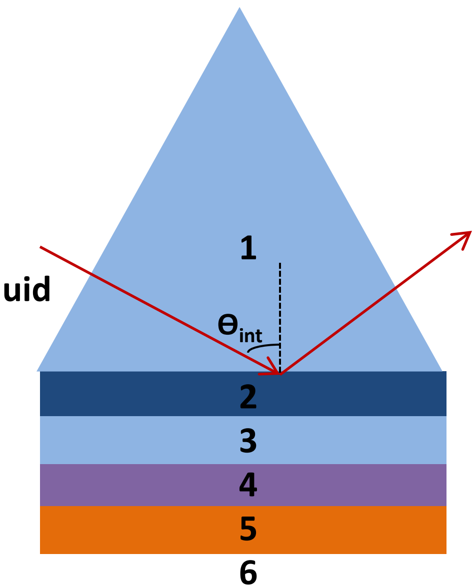
Theoretically



Results: Before SAM formation



1. Prism
2. Index Matching Fluid
3. Glass Slide
4. Titanium
5. Gold
6. Air



From Experiment:

θ_{res}= 43.8 deg

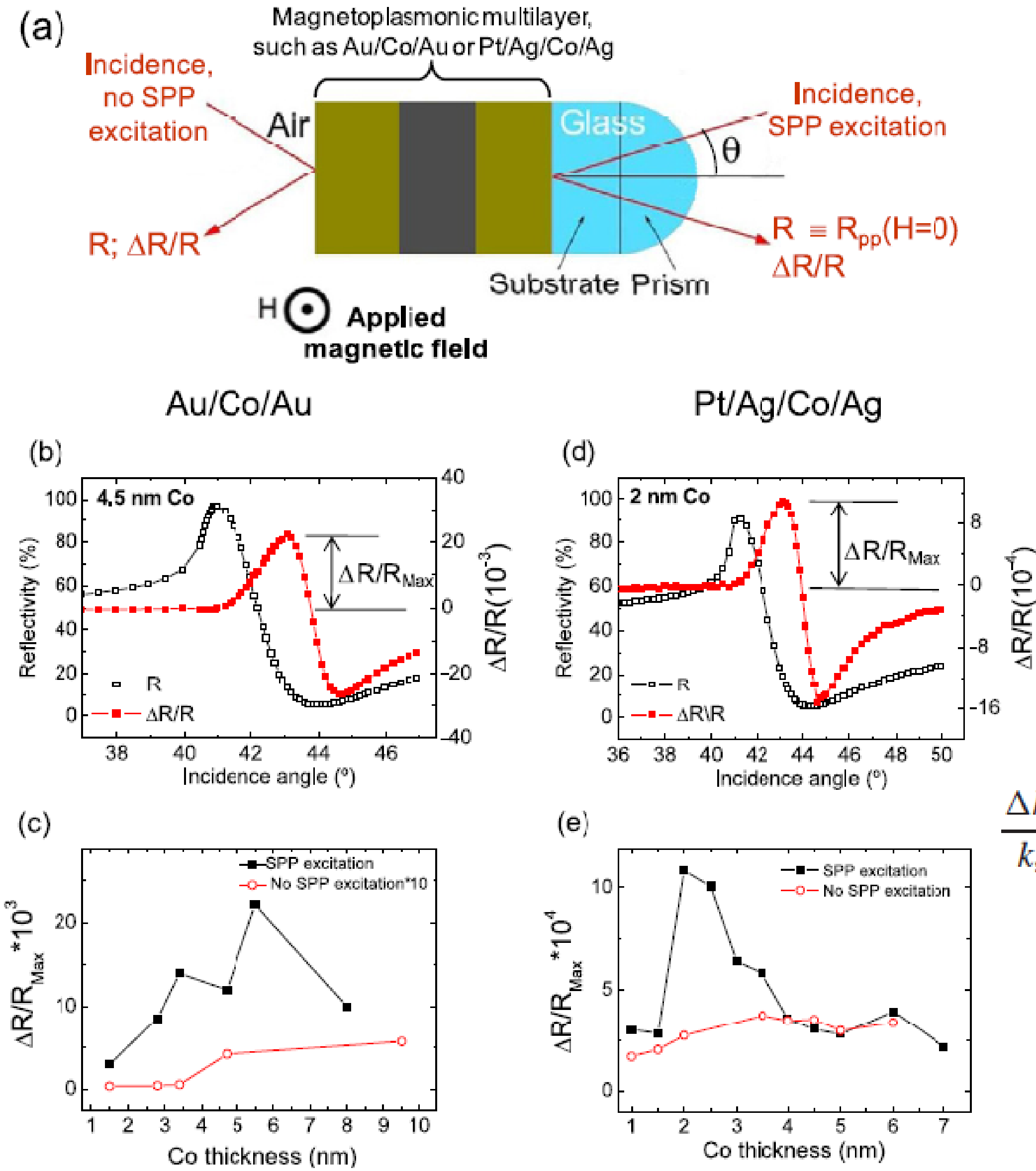
Theoretically (Fresnel Equations):

θ_{res} = 43.825 deg

Future Goals: Magnetoplasmonics

- We want to study the interaction of plasmonics and magneto-optic activity:
  - Magnetic field can be used to modulate the SPR angle as in a magneto-optically active material it influences the dielectric constant
  - SPR related field enhancement can be used to increase the magneto –optical activity of a material (enhancement of complex Kerr rotation and transverse Kerr Reflectivity)

Future Goals: Magnetoplasmonics



$$\frac{\Delta k_{sp}}{k_{sp}} \equiv \frac{k_{sp}(\pm H) - k_{sp}(0)}{k_{sp}(0)} = \frac{2i}{\varepsilon_{xx}^2 - 1}\sqrt{\frac{\varepsilon_{xx}}{1+\varepsilon_{xx}}}\frac{2\pi d}{\lambda}(\pm\varepsilon_{xz})$$

$$\left.\frac{\Delta R_{pp}}{R_{pp}}\right|_{Mag} = \frac{\partial R}{\partial \theta}\frac{\Delta\theta}{R_{pp}}.$$

G. Armelles, A. Cebollada, A. García-Martín, J. M. García-Martín, M. U. González, J. B. González-Díaz, E. Ferreiro-Vila, and J. F. Torrado, "Magnetoplasmonic nanostructures: systems supporting both plasmonic and magnetic properties," *Journal of Optics A: Pure and Applied Optics,* vol. 11, p. 114023, 2009.

Future Goals: SPR at Cryogenic Temperatures

- Both Dielectric properties and Thickness of materials change with temperature which affect the SPR properties of a thin film system.
- We intend to study the change in SPR parameters resulting from carrying out angular reflectivity scanning with the sample inside a cryostat

References

1. W. L. Barnes, A. Dereux, and T. W. Ebbesen, "Surface plasmon subwavelength optics," *Nature,* vol. 424, pp. 824-830, 2003.

2. O. Pluchery, R. Vayron, and K.-M. Van, "Laboratory experiments for exploring the surface plasmon resonance," *European Journal of Physics,* vol. 32, pp. 585-599, 2011.

3. Maxi Boeckl, Dr. Daniel Graham, "Self-Assembled Monolayers: Advantages of Pure Alkanethiols" , *Material Matters,* vol 1.2*,* 2006.

4. Ivan Ohlidal, "Immersion spectroscopic reflectometry of multilayersystems", *J. Opt. Soc. Am. A,* vol. 5, no. 4, 1988, pp. 459-464

5. G. Armelles, A. Cebollada, A. García-Martín, J. M. García-Martín, M. U. González, J. B. González-Díaz, E. Ferreiro-Vila, and J. F. Torrado, "Magnetoplasmonic nanostructures: systems supporting both plasmonic and magnetic properties," *Journal of Optics A: Pure and Applied Optics,* vol. 11, p. 114023, 2009.

6. Marc D. Porter, Thomas B. Bright, David L. Allara, and Christopher E. D. Chidseyi, "Structural Characterization of n-Alkyl Thiol Monolayers on Gold by Optical Ellipsometry, Infrared Spectroscopy, and Electrochemistry", *J. Am. Chem. SOC,* vol. 109, 1987, pp. 3559-3568

QUESTIONS?