Presented at the COMSOL Conference 2009 Boston

Periodic Near-field Enhancement on Metal-Dielectric Interfacial Gratings at Optimized Azimuthal Orientation

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- ***IDEA:***
  Application of plasmon-wavelength-scaled gratings in SPR based bio-sensing
  - Preparation of gratings by laser-based interference lithography
  - PFM AFM and TM AFM investigation:
  - Novel SPR phenomenon in conical mount: **RGC SPR**
  - Application of RGC SPR as a novel bio-sensing method
    - protein detection

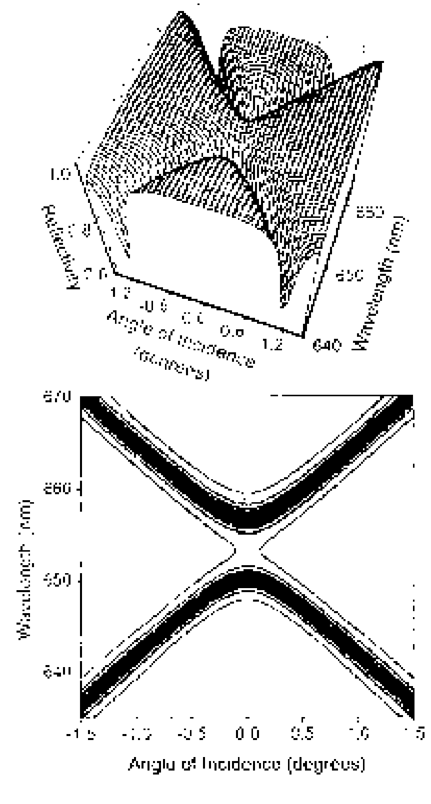
- Purpose of **Comsol calculations**:
  - Determination of the near-field distribution accompanying RGC SPR
  - Investigation of the effect of azimuthal orientation on the near-field distribution
  - Study of the effect of labeling noble metal nano- and colloidal-particles

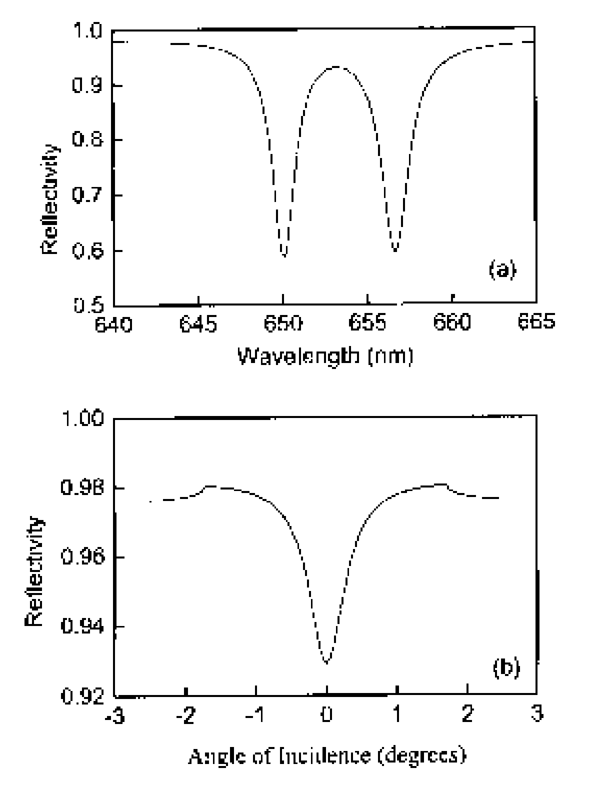
Plasmons in presence of periodic surface structures

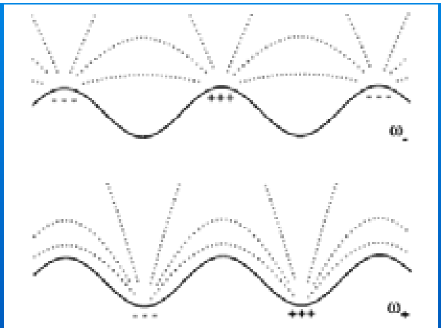
- Photonic energy-gaps: propagation forbidden, back-reflection
- Periodic EM-field and surface charge distribution
  - W. L. Barnes, T. W. Preist, S. C. Kitson and J. R. Sambles: *Phys. Rev. B,* **54**/**9,** 6227-6244 (1996).

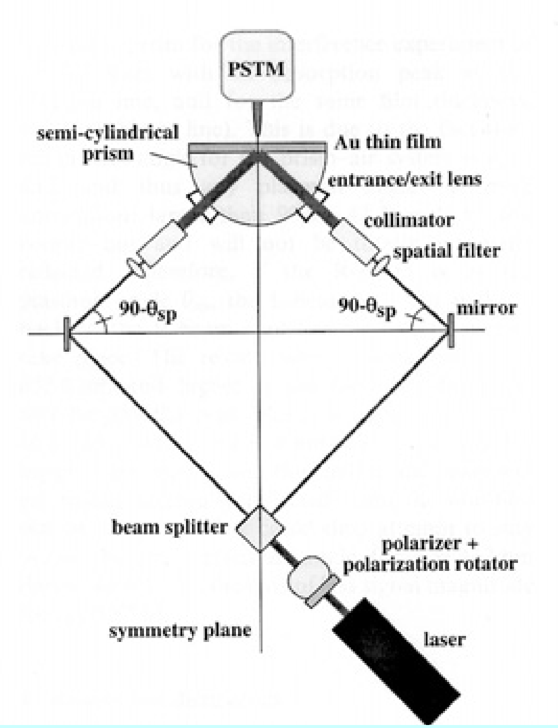
$$2K_{Bragg} = \frac{2\pi}{\lambda_g},$$

$$\lambda_{optical} = 2 \cdot \lambda_g : \quad two\ modes$$









- Near-field investigation: PSTM

◈ **Angle dependence of EM-field distribution on plasmon-wavelength-scaled structures ???**

LSPR on nano-objects

- Localized surface plasmons (LSPs) are charge density oscillations confined around metallic nano-objects

- Oscillation frequency is determined by
  - electrons density, effective mass
  - shape and size of the charge distribution

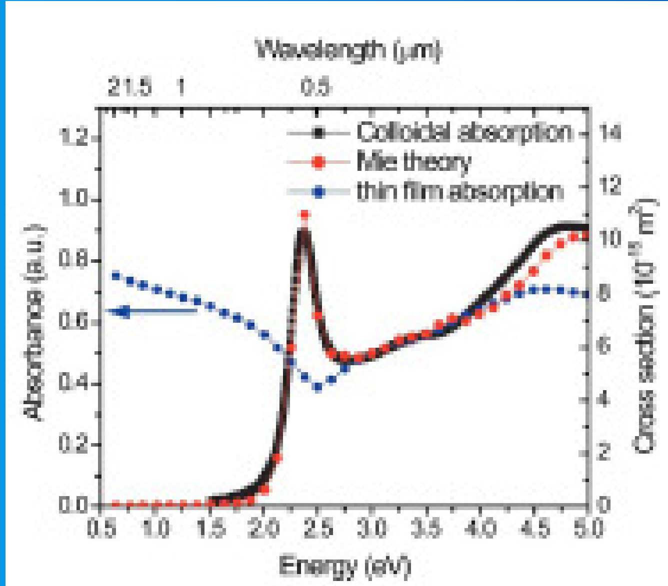
- At resonance: strong light scattering and absorption

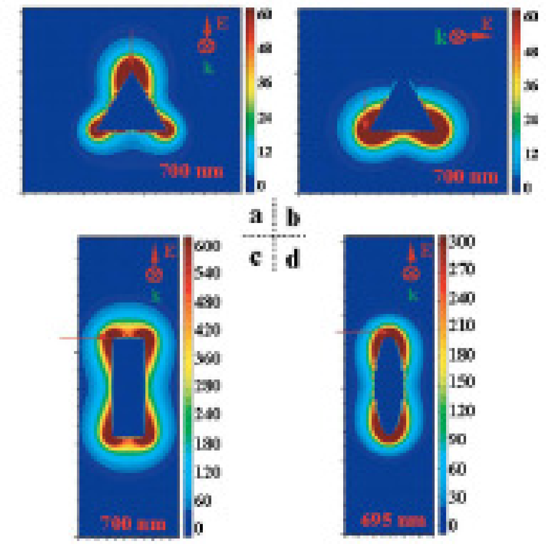
- Poynting vector: field lines indicate enhanced local electromagnetic field in case of resonance

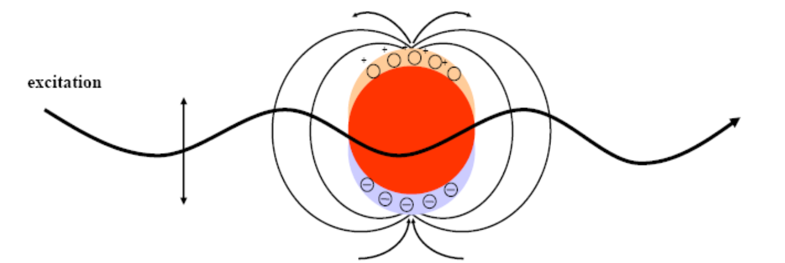
- They are EM radiations - not diffraction limited!

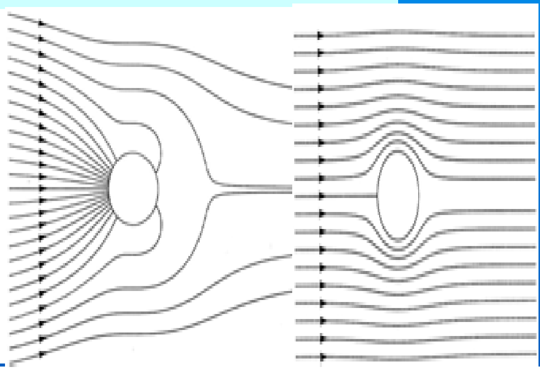
- Manifest themselves in LSPR spectra
  size, shape, surrounding medium dependent

- Shape effect: e.g. nano-rods,
  Mie theory: split absorption bands
  - S. A. Maier, H. A. Atwater: Journ. of Appl. Phys. 98 (2005) 011101





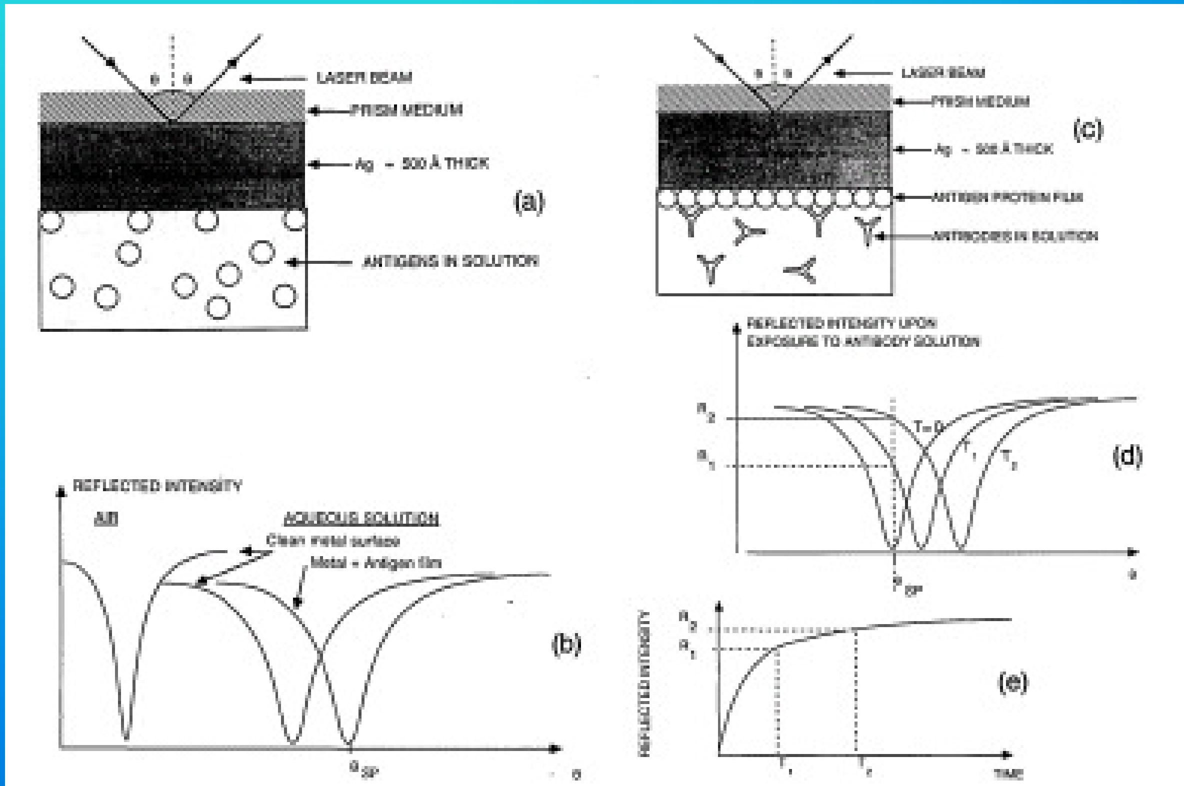


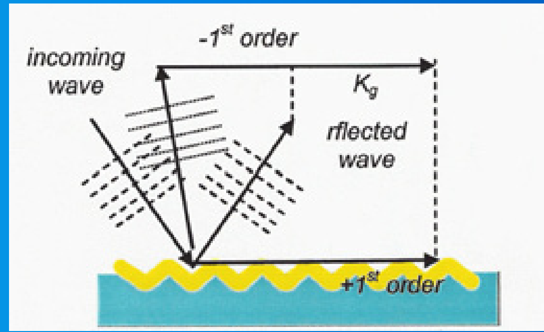


Effect of noble metal particles on angle dependent SPR???

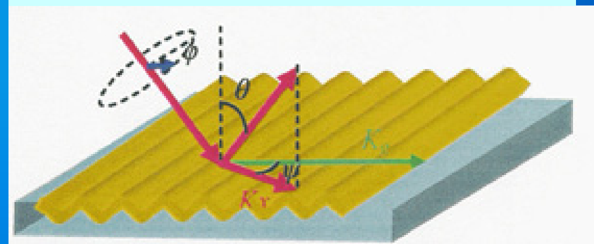
SPR-based bio-sensing

- Classical SPR bio-sensor: angle dependent measurement antigen over-layer, binding of antibodies on antigen-protein film
  - J. Homola, S.S. Yee, G. Gaulitz, Sensors and Actuators B 54 (1999) 3.
    E. Fontana, R. H. Pantell, S. Strober: Appl. Opt. 29/3 (1990) 4694.





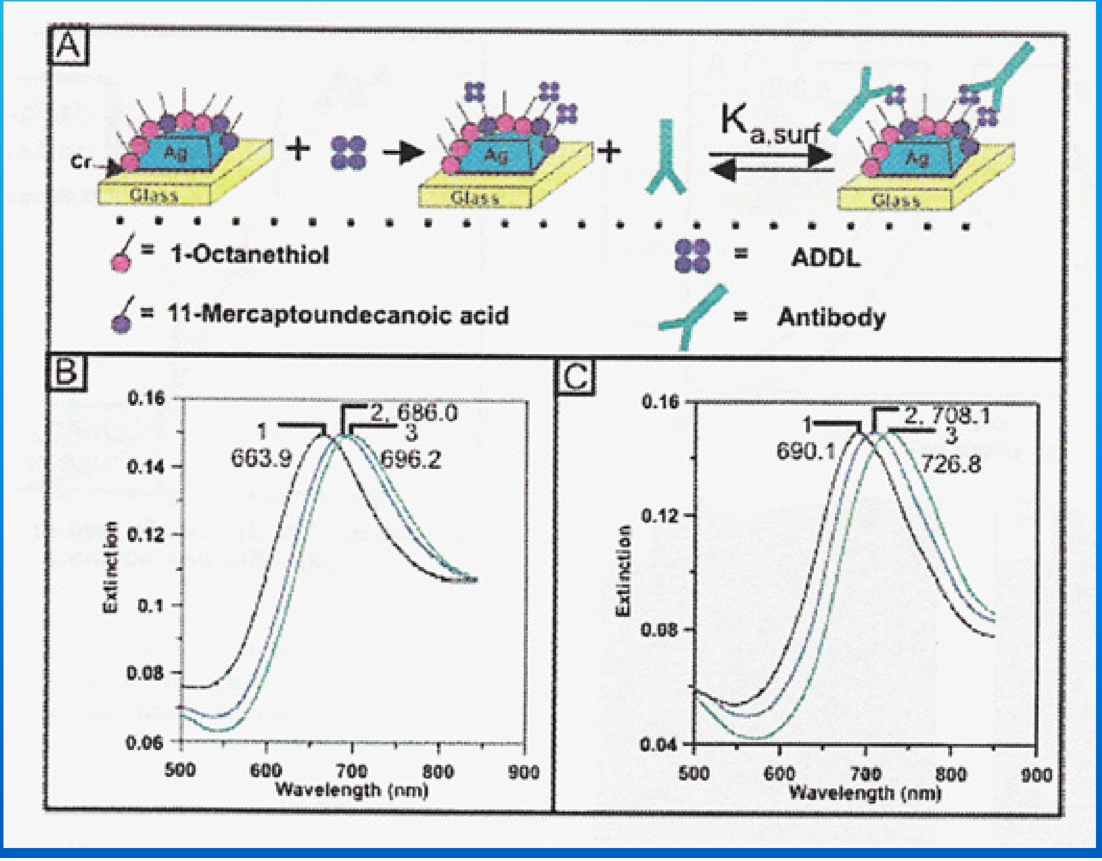
◆SPR detection in Conical mount???



- SPR bio-sensing based on diffraction gratings: immuno-sensing
  - D. C. Cullen, C. R. Lowe: Sensors and Actuators B 1/1-6 (1990) 576.
- Periodic binding on thiol treated + biotin covered surface parts
  - C. E. Jordan, B. L. Frey, S. Kornguth, R. M. Corn: Langmuir 10 (1994) 3642

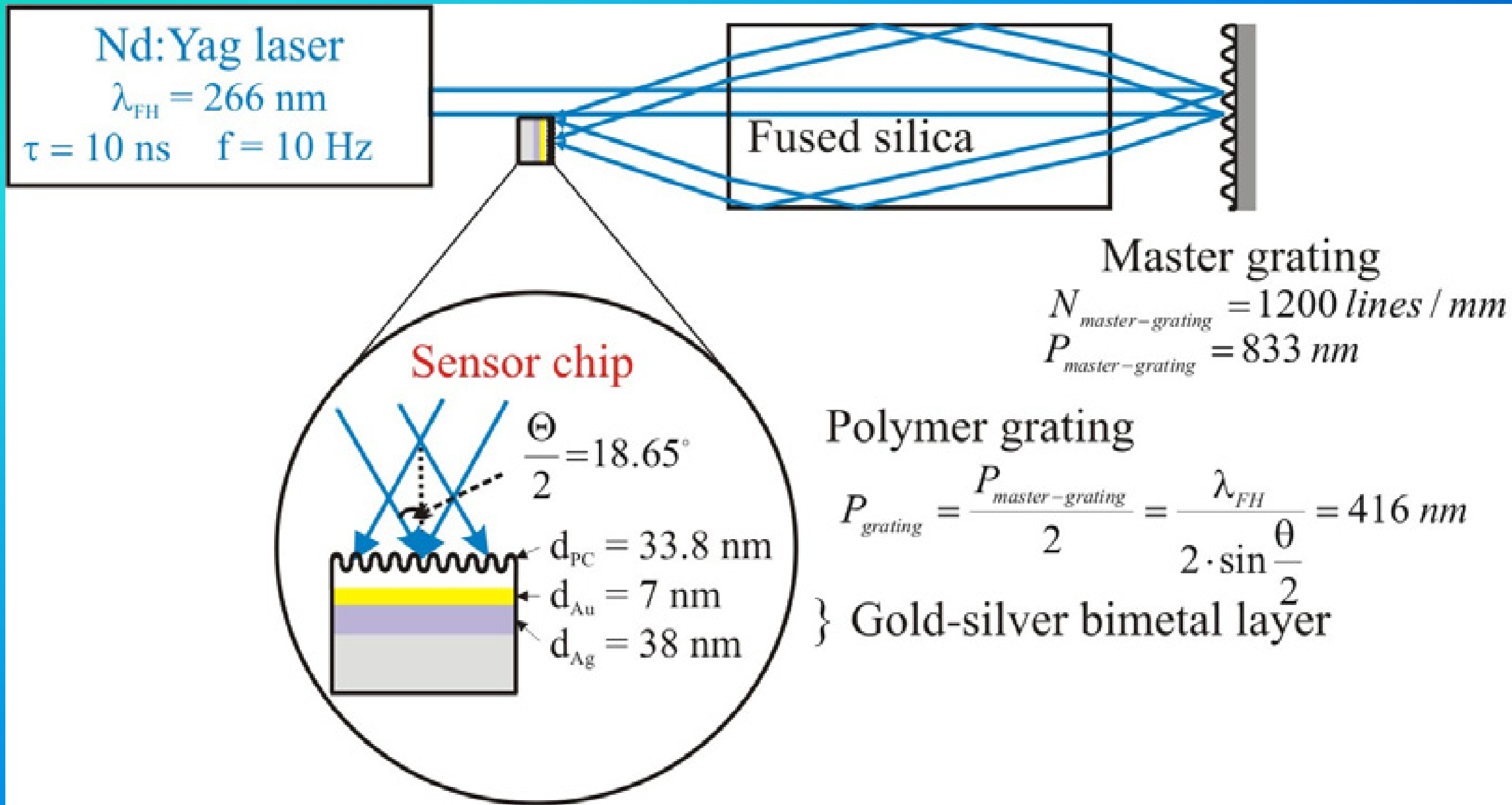
LSPR bio-sensor

- Localized plasmons around sub-wavelength objects
- Wavelength dependent investigations
  - Specific binding on functionalized nano-particles
    - C. R. Yonzon, E. Jeoung, S. Zou, G. Z. Schatz, M. Mrksich, R.P.V. Duyne: J. Am. Chem. Soc. 126 (2004) 12669.
    - A. J. Haes, W. P. Hall, L. Chang, W. L. Klein, R.P.V. Duyne: Nano Lett. 4/6 (2004) 1029.
  - Molecule-plasmon coupling on two-dimensional hole-patterns on Ag films
    - J. Dintinger, S. Klein, F. Bustos, W. L. Barbes, T. W. Ebbesen: Phys. Rev. B 71 (2005) 035424.

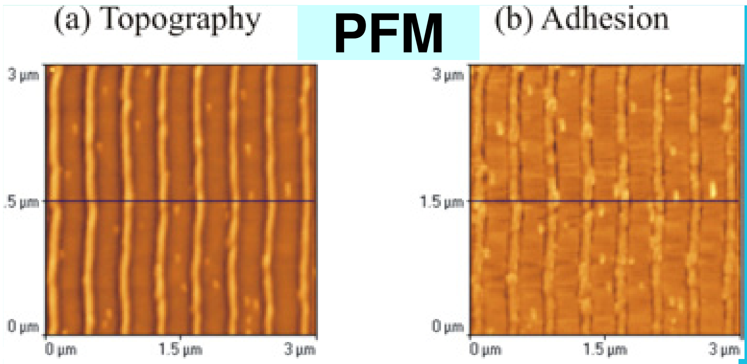


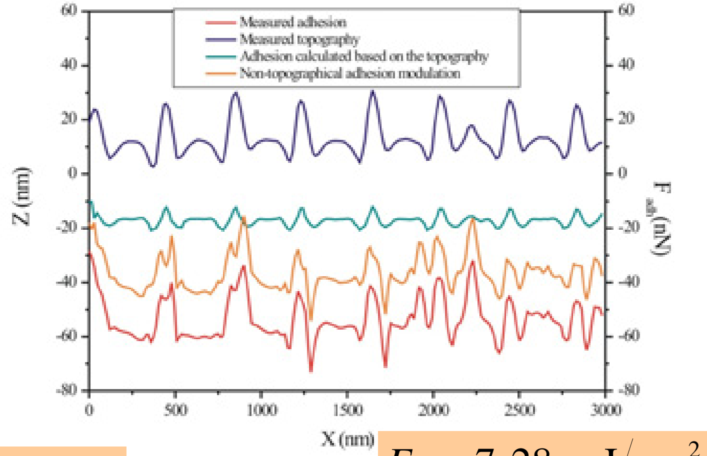
◆Effect of labeling noble metal particles on SPR curves ???

Sub-micrometer grating preparation at the interface of bimetal-polymer layers

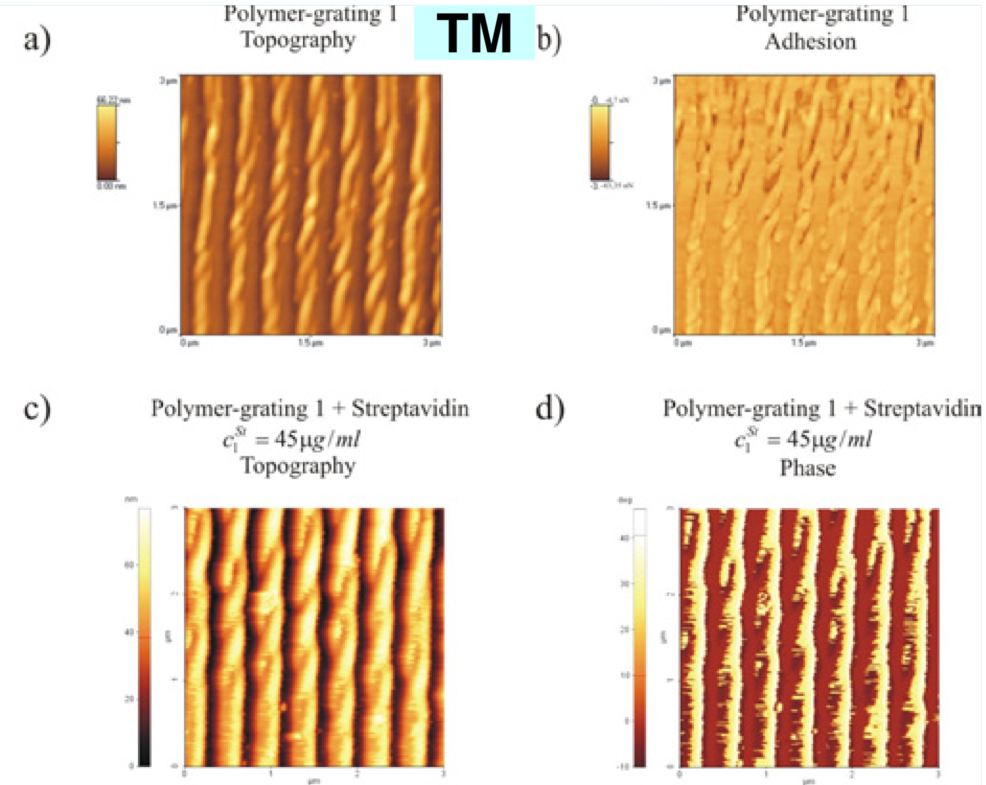


- **Sensor-chip**: **PC + Au-Ag multi-layer** on NBK7 substrate
- **Structure preparation:** two-beam interference lithography
- **Plasmonic structure:**
  sub-micrometer grating at metal-dielectric interface
  - H. M. Phillips, D. L. Callahan, R. Sauerbrey, G. Szabó, Z. Bor, Appl. Phys. A 54 (1992) 158.





$N = 500$ $F_{av} = 7.28\ \mathrm{mJ/cm^2}$



Protein detection

- TM AFM phase signal
  - Topography
  - Visco-elasticity
  - Charge distribution

Adhesion modulation ⇔ ***Topographical origin?***

Correction of the topography taking the tip radius into account: $R_{tip}^{PFM} = 25\,\mathrm{nm}$

Determination of the adhesion modulation originating from surface curvature

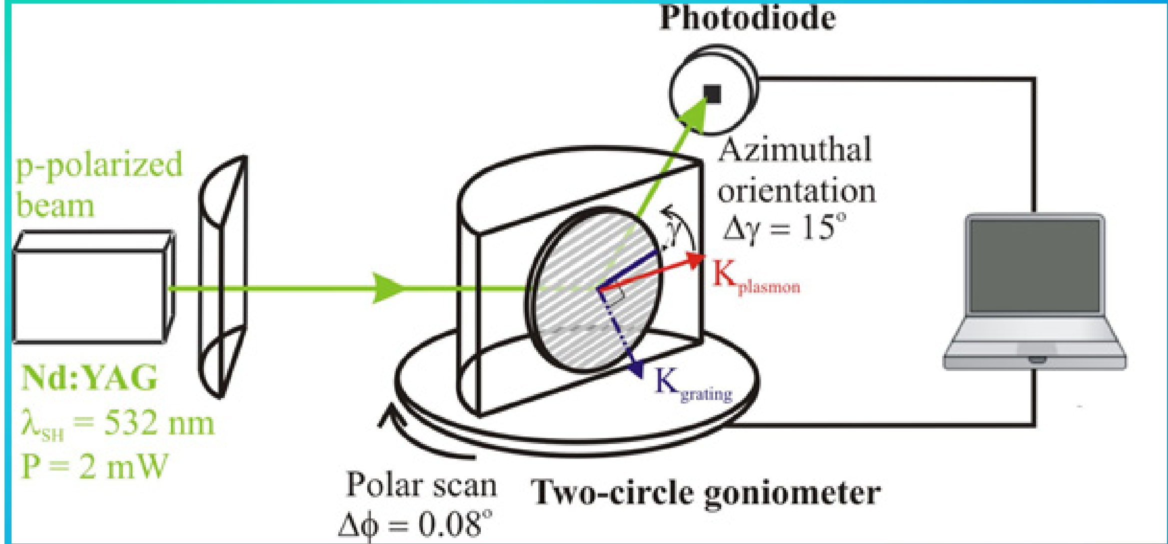
Derjaguin-Müller-Toporov (DMT) approximation:

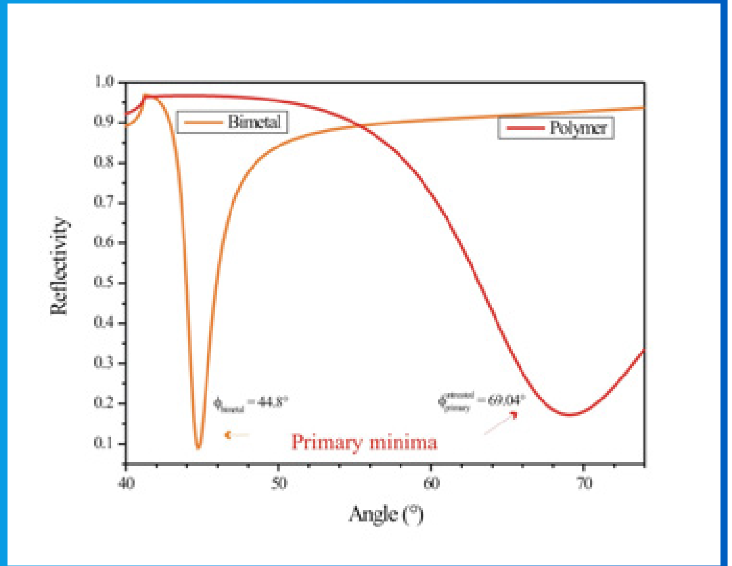
$$F_{adhesion}(R_{surface}^{corrected}) = F_{adhesion}(R_{surface} = \infty) \cdot \frac{R_{tip}^{PFM} \cdot R_{surface}^{corrected}}{R_{tip}^{PFM} + R_{surface}^{corrected}} \qquad F_{adhesion}(R_{surface} = \infty) = 17\,\mathrm{nN}$$

Reason: Phase- and chemical changes caused by UV illumination

- B. V. Derjaguin, V. M. Muller, Yu. P. Toporov: Colloid Interf. Sci. 53. 378 (1978).
- M. Csete, G. Kurdi, J. Kokavecz, V. Megyesi, K. Osvay, Z. Schay, Zs. Bor, O. Marti: Mat. Sci. and Engin. C **26** (2006) 1056

Rotated grating geometry, RGC SPR



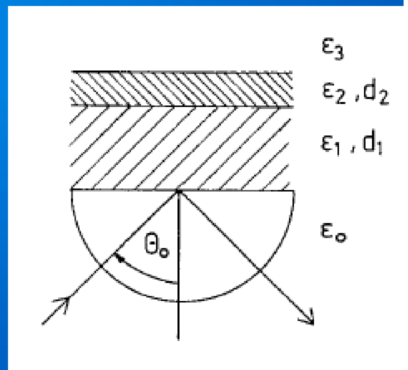


➤**Modified Kretschmann arrangement**: dual-angle dependent SPR

- **Half-cylinder**: polar angle conversion is not necessary
- **Grating**: the laser light illuminates the sensor chip from backward
- **Azimuthal orientation**: grating-coupling might be optimized
  - M. Csete, A. Kőházi-Kis, V. Megyesi, K. Osvay, Zs. Bor, M. Pietralla, O. Marti: Org. Electronics **8/2-3** (2007) 148-160

$$k'_{z2}\, d_2 << 1$$

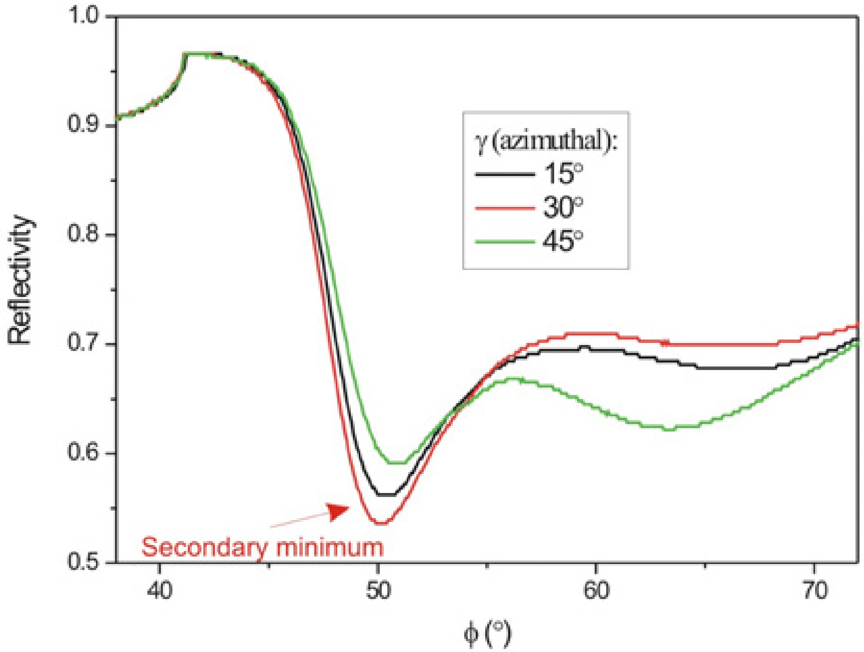
$$\Delta k_x(d_2) = \frac{\omega}{c}\frac{\varepsilon_2 - 1}{\varepsilon_2}\left(\frac{|\varepsilon'_1|}{|\varepsilon'_1| - 1}\right)^2 \frac{|\varepsilon'_1| + \varepsilon_2}{|\varepsilon'_1| + 1}\frac{1}{\sqrt{|\varepsilon'_1|}}\frac{2\pi d_2}{\lambda}$$



➤**Flat metal-dielectric interfacial layer**

- Resonance minima corresponding to reflectivity decrease caused by the plasmon excitation at metal-polymer interface: TMM calculation
- Surface roughness: broadening of the resonance minima

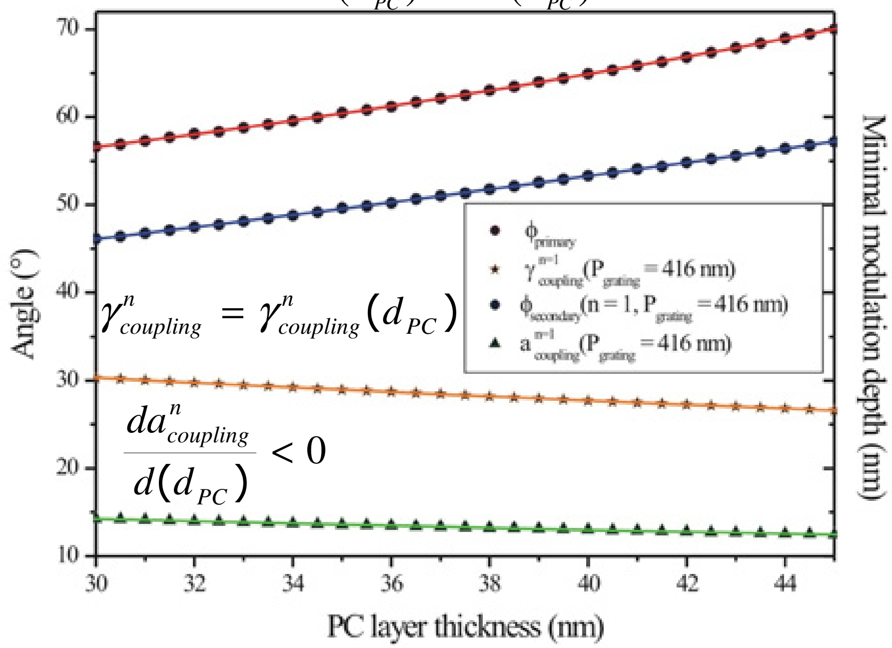
Plasmons at periodically structured metal-dielectric interfaces



Conditions of Rotated Grating Coupling Phenomenon:

- Appropriate **period**,
- appropriately large **modulation amplitude**,
- right **azimuthal orientation**

$$\frac{d\varphi_{secondary}}{d(d_{PC})} \approx \frac{d\varphi_{primary}}{d(d_{PC})}$$

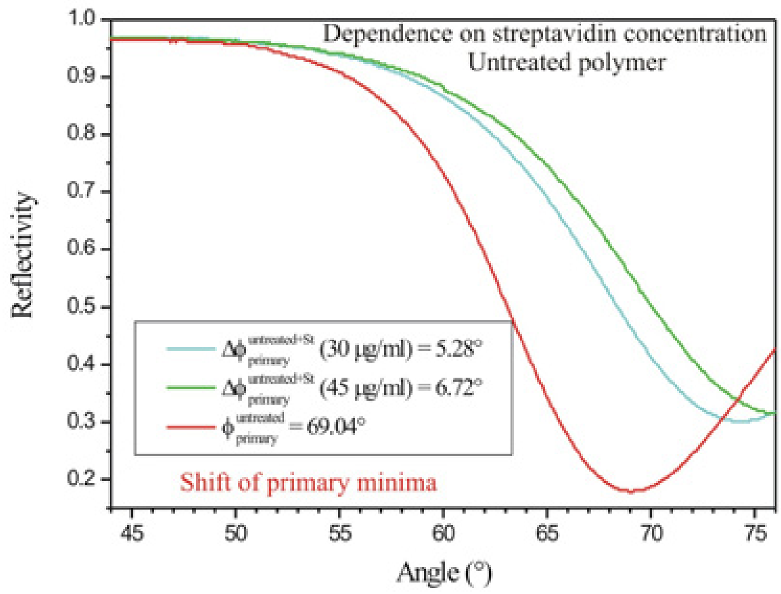


- The optimal azimuthal orientation has to be compensated
- Larger modulation depth is necessary on thin films

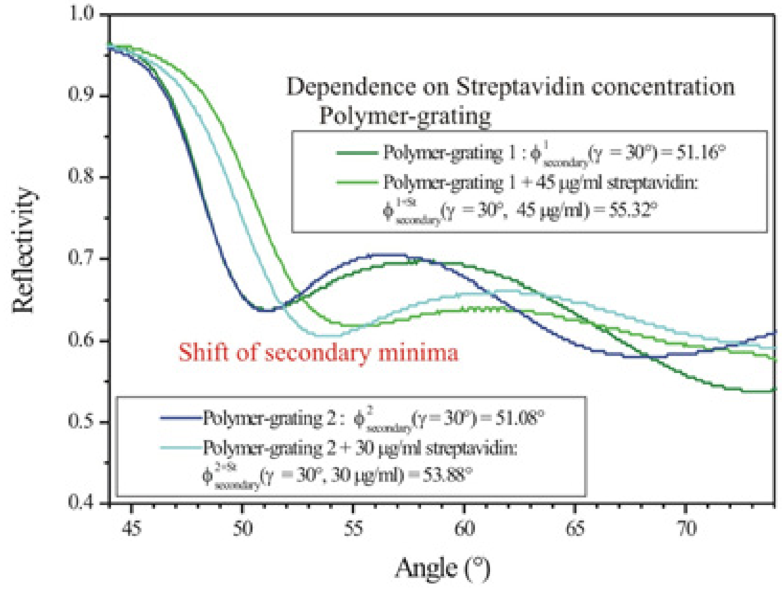
M. Csete, A. Kőházi-Kis, V. Megyesi, K. Osvay, Zs. Bor, M. Pietralla, O. Marti: Org. Electronics **8/2-3** (2007) 148-160

Protein detection on untreated multi-layers and by RGC-SPR

$$S_{primary} = \frac{\Delta \varphi^{untreated}_{primary}}{\Delta c} = 0.096 \frac{\circ}{\mu g / ml}$$



$$S_{secondary} = \frac{\Delta \varphi^{grating}_{secondary}}{\Delta c} = 0.091 \frac{\circ}{\mu g / ml}$$



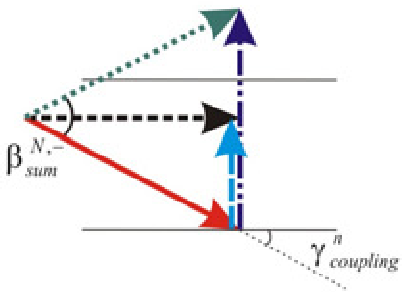
- The shift of secondary minima depends on the streptavidin concentration: adherence from denser solvent results in higher angle shift
- Sensitivity commensurable with that measurable on untreated films: cannot be explained by the slope of: $\varphi_{secondary}(d_{PC})$
- **Importance of adhesion selective adherence of bio-molecules:** **coexistence of periodic adhesion and plasmon-field modulation may result in sensitivity enhancement**

M. Csete, Á. Sipos, A. Kőházi-Kis, A. Szalai, G. Szekeres, A. Mathesz, T. Csákó, K. Osvay, Zs. Bor, B. Penke, M. A. Deli, Sz. Veszelka, A. Schmatulla, O. Marti: *Appl. Surf. Sci.,* **254/4,** 1194-1205 (2007): therapy against **amyloid-beta aggregation**

Comparison of grating-coupling with grating scattering
Bragg-scattering analogy

$N = 1$, $n = 1$

Coupling



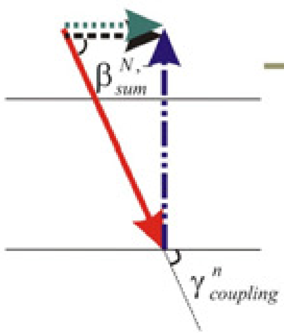
$n < 2K_{plasmon} / K_{grating}$

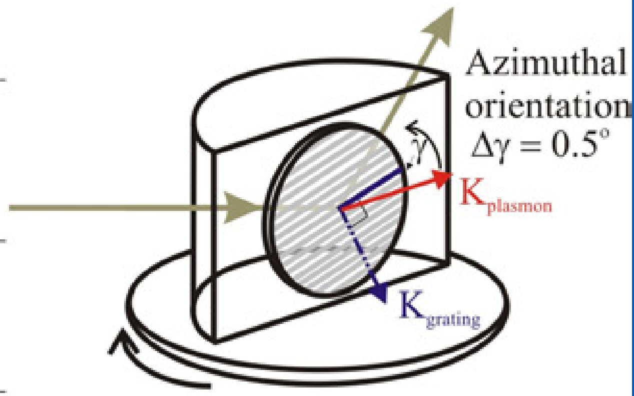
$K_{grating} = 2\pi / \Lambda_{grating}$

- - - - $K_{coupled\ plasmon}$
- —— $K_{plasmon}$
- – ·· $K_{grating}$
- – – $K_{grating}/2$
- ······ K_{sum}
- —— direction of grating grooves

$N = 1$, $n = 2$

Scattering





Polar scan $\Delta\phi = 0.08^{\circ}$

$$K_{coupled\ plasmon}^{n} = K_{plasmon} \cos\gamma_{coupling}^{n}$$

$$\sin\gamma_{coupling}^{n} = n \cdot K_{grating} / 2K_{plasmon}$$

$$\sin\theta = n \cdot K_{grating} / 2K_{wave}$$

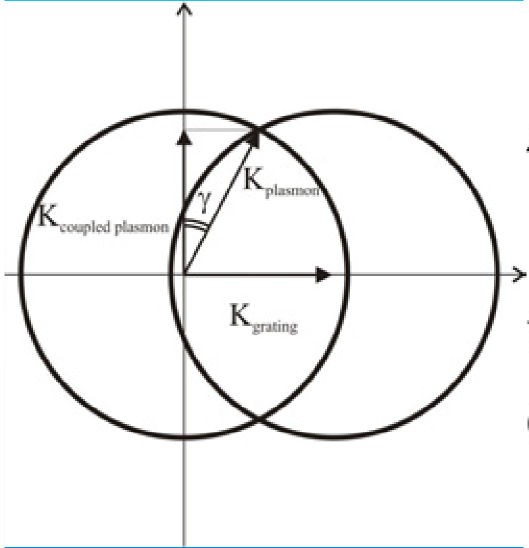
Bragg

$$K_{sum}^{N} = \sqrt{K_{plasmon}^{2} + N^{2} K_{grating}^{2} \pm 2 \cdot N \cdot K_{plasmon} \cdot K_{grating} \cdot \sin\gamma_{coupling}^{n}}$$

$$\sin\beta_{sum}^{N} = \frac{K_{grating} \cos\gamma_{coupling}^{n}}{K_{sum}^{N}}$$

- n=1 order coupling ⬄ Bragg scattering
  half wave vector
- n=2 order coupling ⬄ N = 1 order scattering
  entire wave vector

RGC SPR



Criteria of grating-coupling:

Primary resonance position : $\varphi_{primary}$

$$K_{plasmon} = K_{photon}^{projected} = K_{photon} \sin\varphi_{primary}, \quad (1)$$

where $K_{photon} = \frac{2\pi}{\lambda_{SH}} \cdot n_{glass}$

Structure period is appropriately large: $K_{grating} < 2 \cdot K_{plasmon}, \quad (2)$

where $K_{grating} = \frac{2\pi}{P_{grating}}$

Angle between the grating grooves and the plasmon propagation direction:

$$\gamma_{coupling}^{n} = \arcsin\left(n \cdot \frac{K_{grating}}{2 \cdot K_{plasmon}} \right), \quad (3)$$

where "*n*" indicates the order of the coupling.

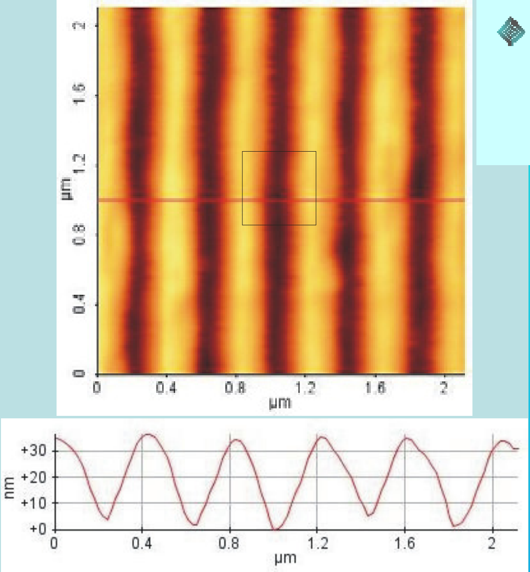
Coupled plasmon wave-vector: $K_{coupled\ plasmon}^{n} = K_{plasmon} \cos\gamma_{coupling}^{n}. \quad (4)$

Secondary resonance position: $\varphi_{secondary}^{n} = \arcsin\left(\frac{K_{coupled\ plasmon}^{n}}{K_{photon}} \right). \quad (5)$

Minimal modulation amplitude:

$$a_{coupling}^{n} = \frac{1}{\sin^2\gamma_{coupling}^{n}} \frac{\sin\varphi_{primary} - \sin\varphi_{secondary}^{n}}{\sin^2\varphi_{primary}} \cdot \frac{\sqrt{\varepsilon_{1,PC}}}{4K_{photon}}. \quad (6)$$

RF module of COMSOL to determine the near-field distribution



Sinusoidal grating

- N = 900 pulses
  F = 10.5 mJ/cm²

Media

- Cauchy formulas
  - NBK7
  - Poly-carbonate
- Combined Drude-Lorentz model
  - Silver
  - Gold
    - M. A. Ordal, L. L. Long, R. J. Bell, S. E. Bell, R. R. Bell, R. W. Alexander, Jr., and C. A. Ward: *Appl. Opt.,* **22**/**7,** 1099-1119 (1983).

Harmonic wave propagation in 3D

- Floquet: periodic nature
- Port boundary: illumination by p-polarized light

Specification of **H** field

$$H_{x\_TM} \cdot \exp(-j(k_x \cdot x + k_y \cdot y))$$

$$H_{y\_TM} \cdot \exp(-j(k_x \cdot x + k_y \cdot y))$$

$$H_{z\_TM} \cdot \exp(-j(k_x \cdot x + k_y \cdot y))$$

Components of **H** vector

$$H_{x\_TM} = H_0 \cdot \cos\gamma$$

$$H_{y\_TM} = H_0 \cdot \sin\gamma$$

$$H_{z\_TM} = 0$$

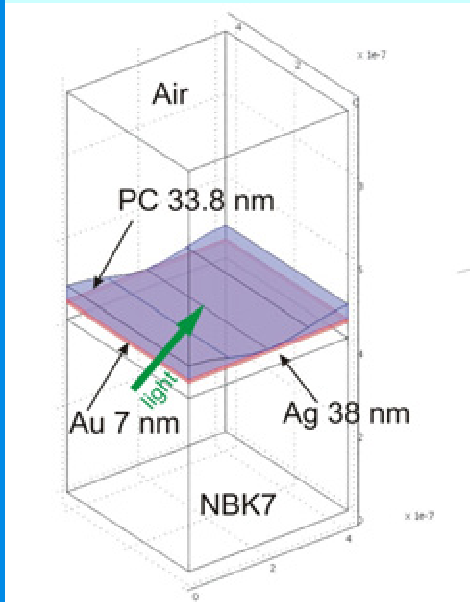
Components of the **k** vector of oblique incident beam

$$k_x = k_0 \cdot \sin\varphi \cdot \sin\gamma$$

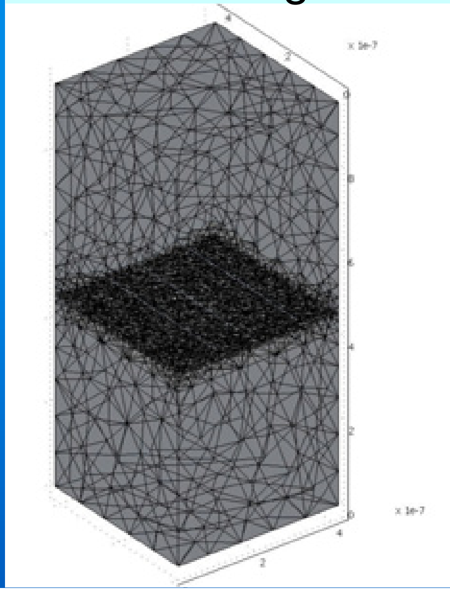
$$k_y = k_0 \cdot \sin\varphi \cdot \cos\gamma$$

$$k_z = k_0 \cdot \cos\varphi$$

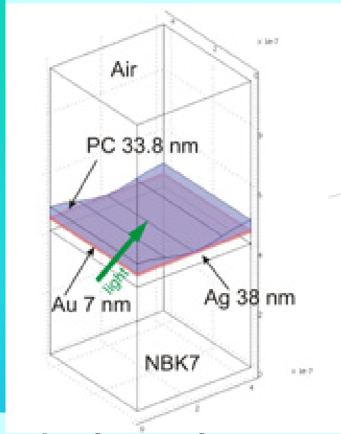
Unit cell



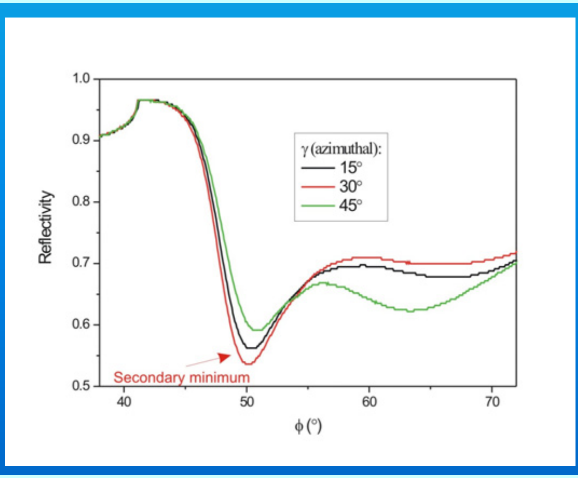
Periodic grid

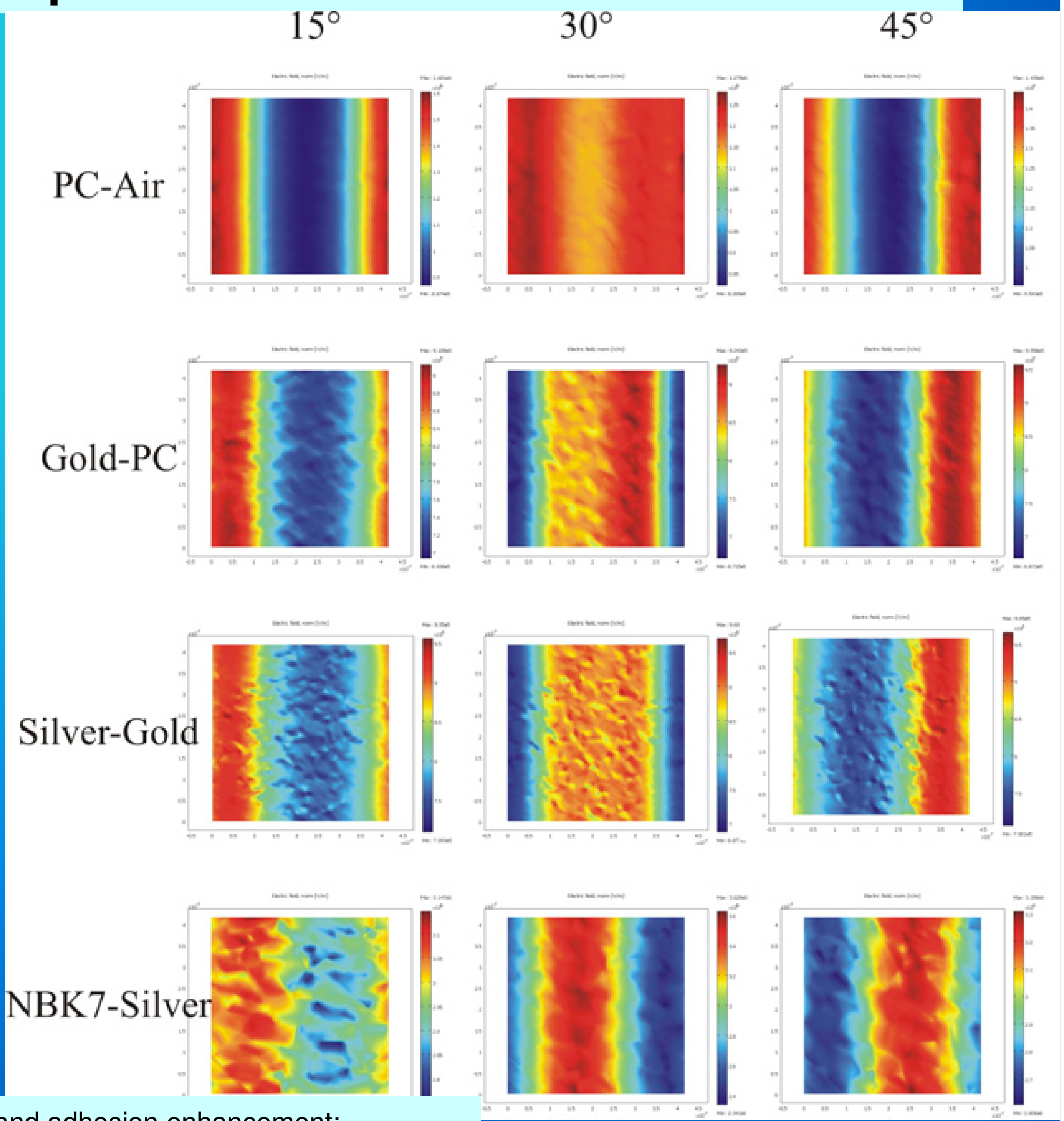


Synchronized periodic near-field enhancement:



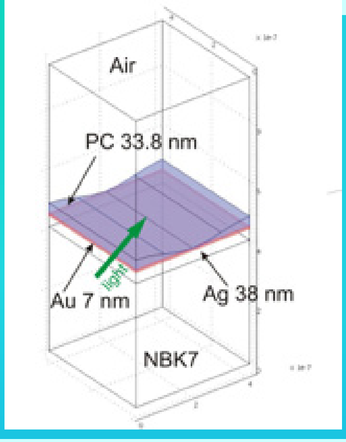
- Azimuthal angle dependence
  - Normalized electric field
  - Synchronized air- and glass-side plasmons along the valleys at optimal azimuthal orientation



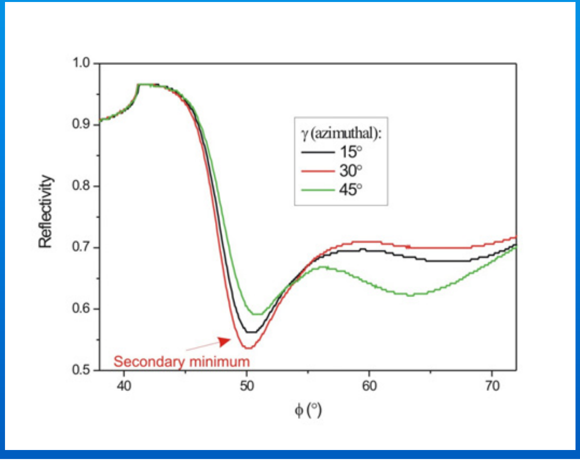


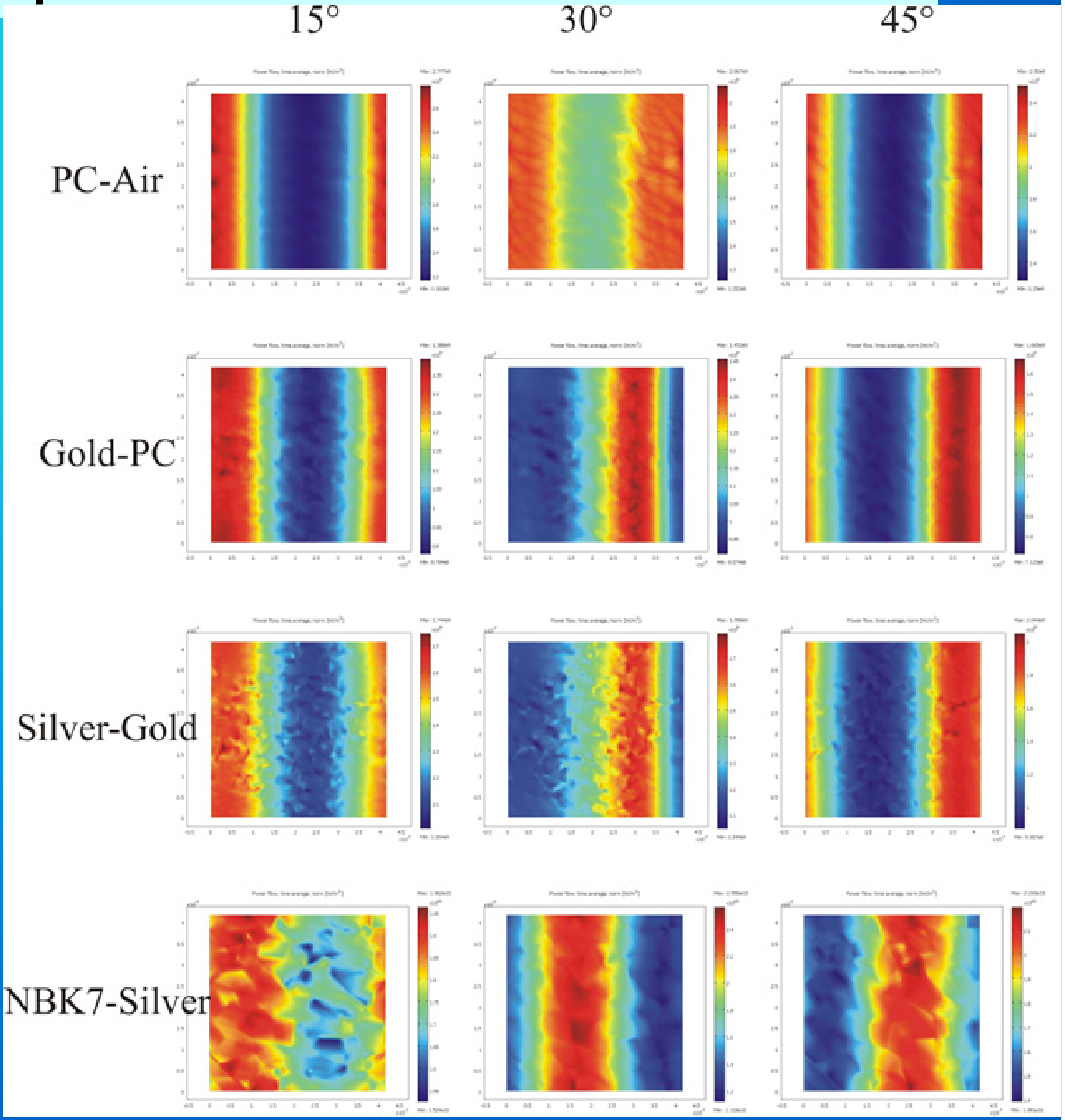
- Synchronization of periodic plasmon-field and adhesion enhancement: improve the sensitivity of bio-detection based on monitoring of RGC SPR peaks

Synchronized periodic near-field enhancement:

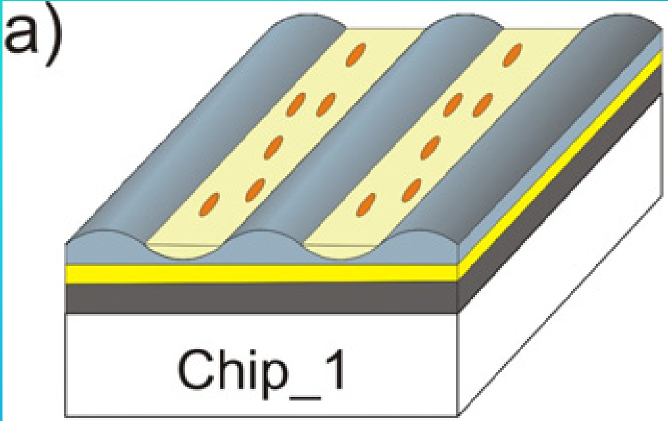


- Azimuthal angle dependence
  - Power flow, time average, normalized
  - Synchronized air- and glass-side plasmons along the valleys at optimal azimuthal orientation

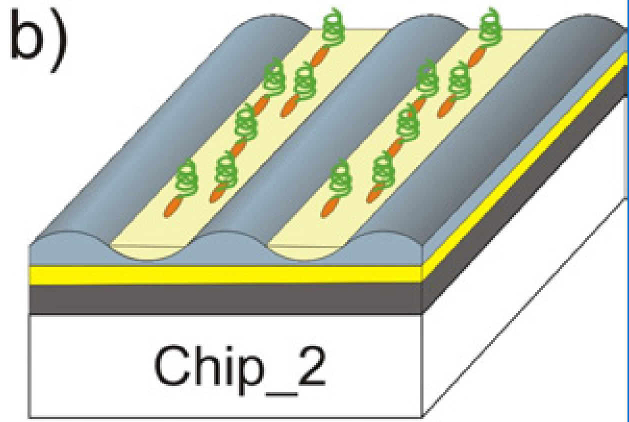




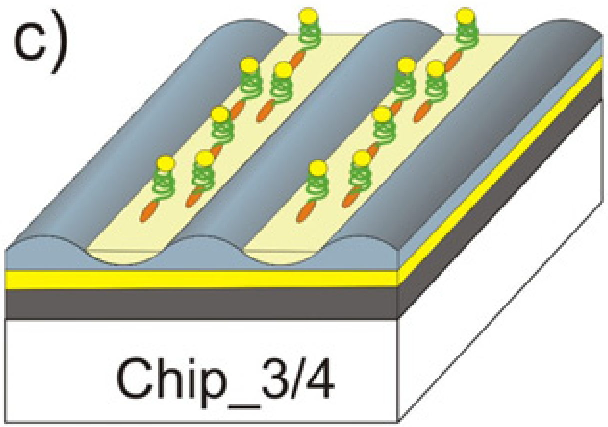
Effect of labeling nano- and colloid particles on sensitivity of RGC-SPR bio-sensing method



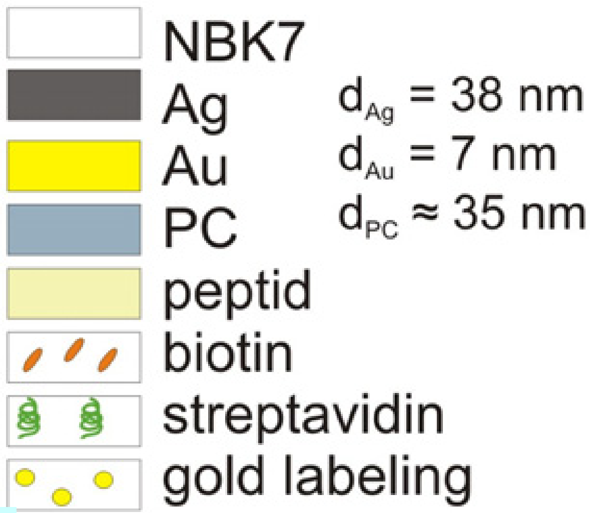
➤peptid–biotinylated-peptid mixture on **Chip_1**



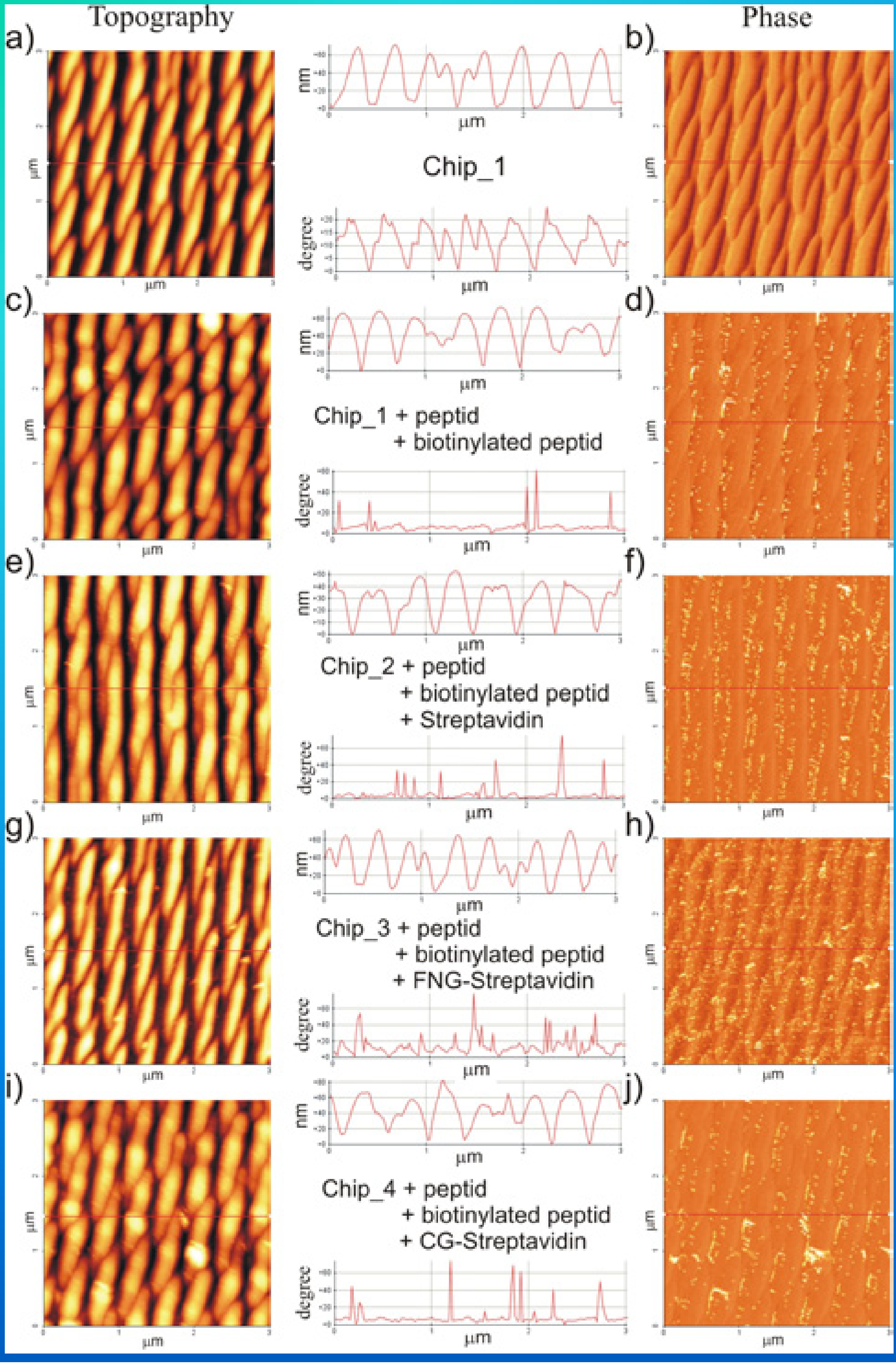
➤Streptavidin ad-layer on **Chip_2**



➤FNG-Streptavidin and CG-Streptavidin complexes on **Chip_3** and **Chip_4**



TM AFM on bio-molecule layer covered RGC SPR sensing chips



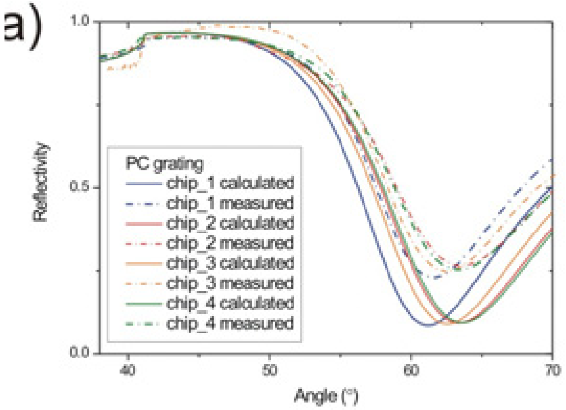
- intact grating on **Chip_1**
- peptid–biotinylated-peptid mixture covered **Chip_1**
- Streptavidin ad-layer on **Chip_2**

  $c^{St} = 4\mu g/ml$
- FNG-Streptavidin conjugate on **Chip_3**

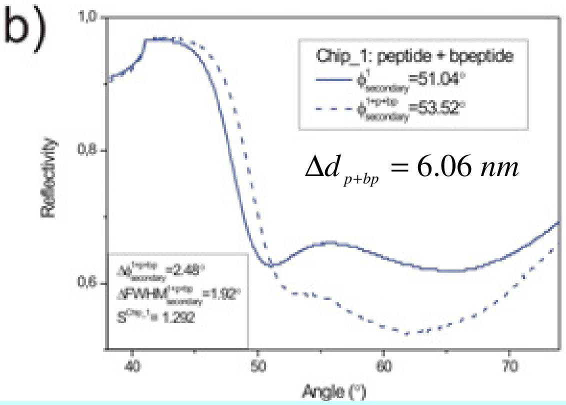
  $c^{St} = 4\mu g/ml$
- CG-Streptavidin labeled with 10 nm diameter colloidal gold particle on **Chip_4**

  $c^{St} = 4\mu g/ml$

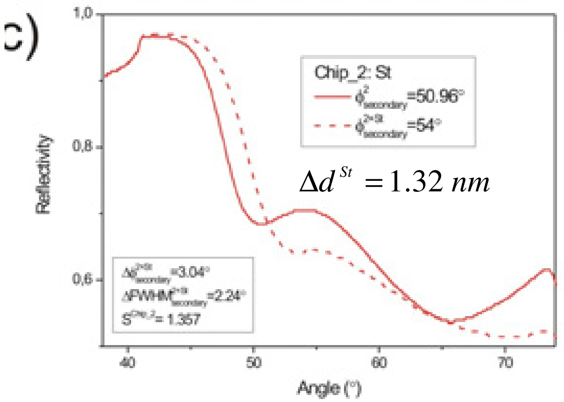
RGC SPR on labeled bio-molecule layer covered sensing chips



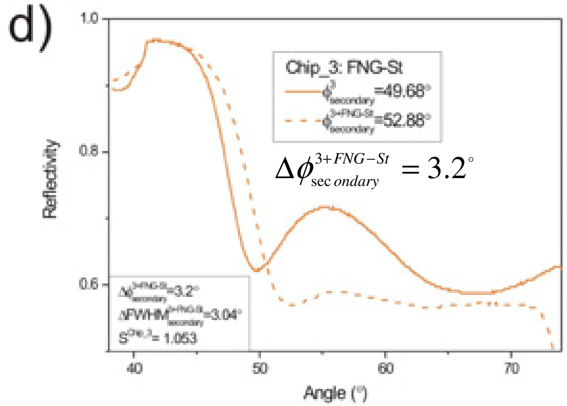
➤untreated PC films on **Chips_1-4**



➤peptid–biotinylated-peptid on **Chip_1**



➤Streptavidin ad-layer on **Chip_2**



➤FNG-Streptavidin conjugate on **Chip_3**

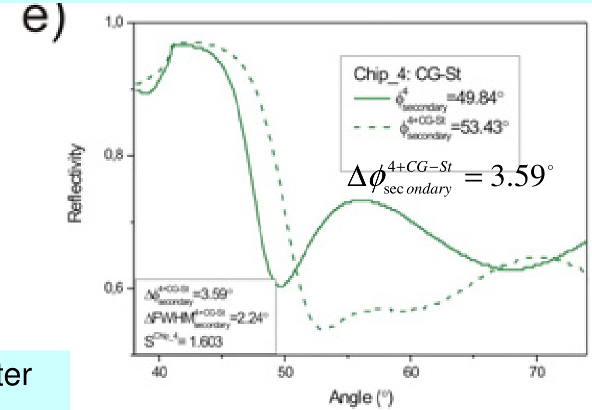
$$\frac{\Delta d_{Au}}{\Delta d_{St}} = \frac{\Delta m_{Au}}{\Delta m_{St}} \frac{\rho_{St}}{\rho_{Au}}$$

$$\Delta d_{Au} / \Delta d_{St} \big|_{FNG-St} = 0.316 \cdot \rho_{St} / \rho_{Au} = 1.64 \cdot 10^{-2}$$

$$\Delta d_{Au} / \Delta d_{St} \big|_{CG-St} = 1.148 \cdot \rho_{St} / \rho_{Au} = 5.98 \cdot 10^{-2}$$

$$\Delta d_{Au} \big|_{FNG-St} = 0.02\ nm$$

$$\Delta d_{Au} \big|_{CG-St} = 0.08\ nm$$



➤CG-Streptavidin labeled with 10 nm diameter colloidal gold particle on **Chip_4**

Idea:

➤tight binding between biotin and avidin

➤same amount of
- unlabeled
- FNG-labeled
- CG-labeled

Streptavidin

➤determined by the biotinylated portion of the peptide pre-cover

➤Larger shift, than expected based on composition of solvents

➤Differences in sensitivity

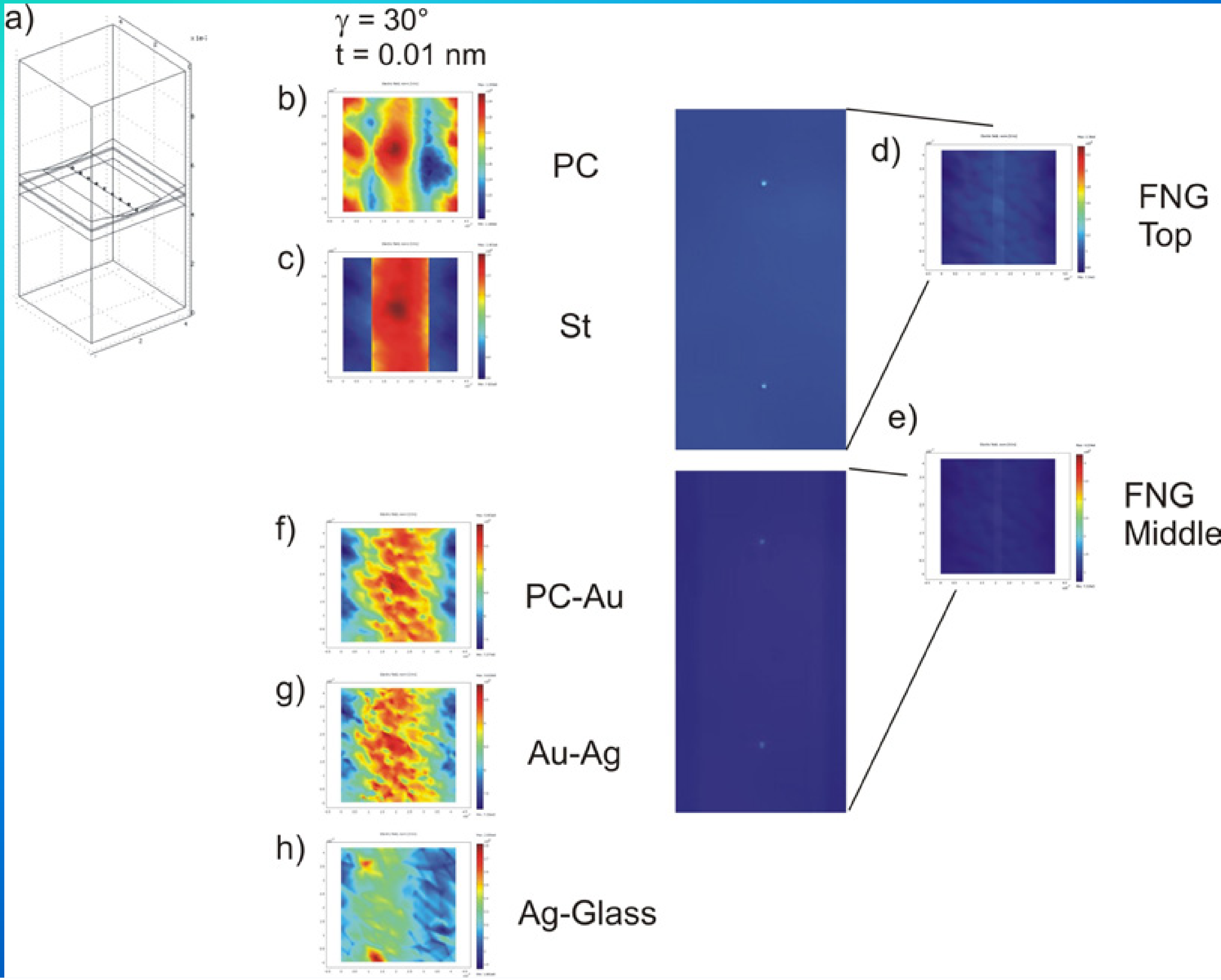
$$S_{normalized} = \frac{\Delta\varphi}{\Delta FWHM}$$

$$S_{-2} \approx S_{-3}$$

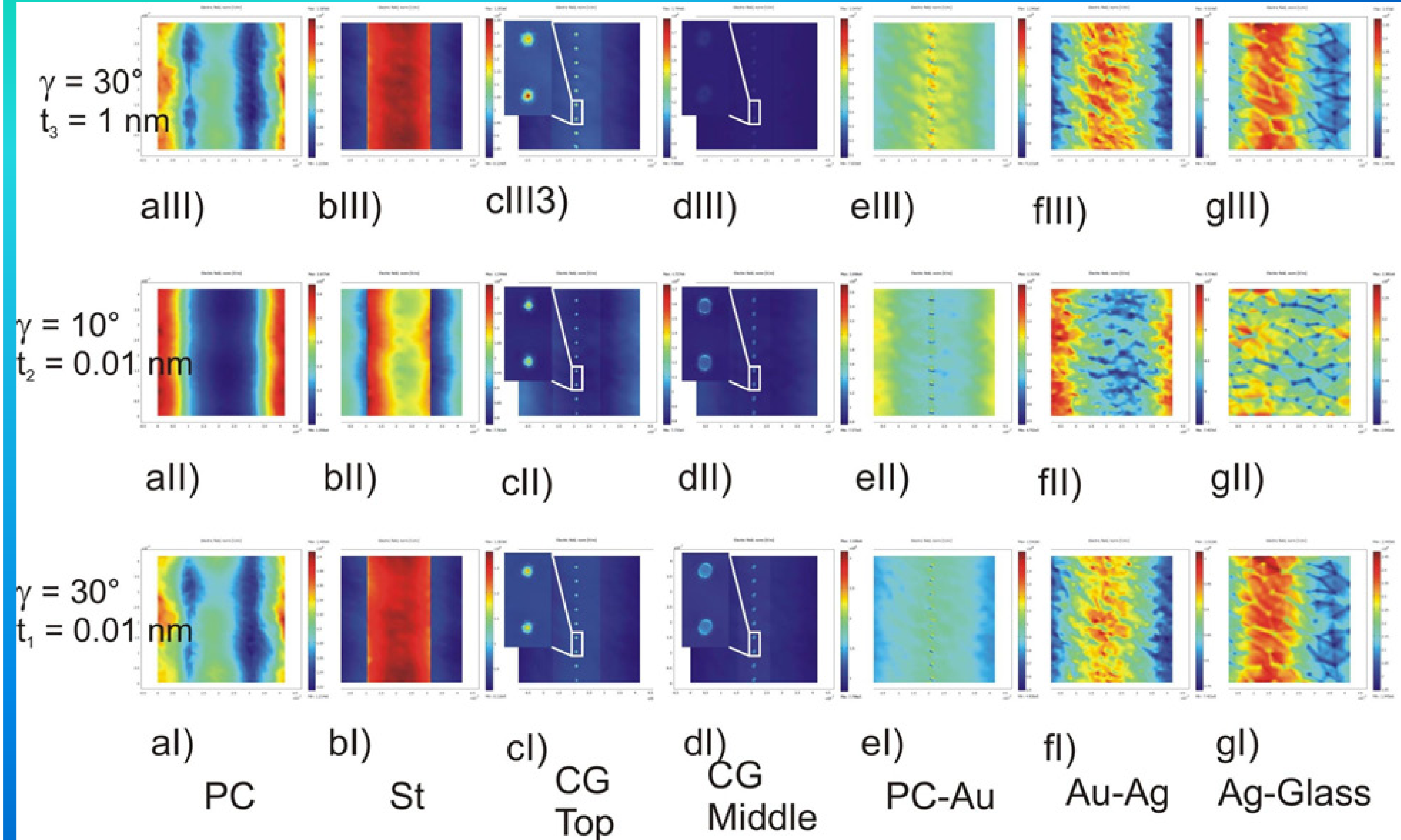
$$S_{-2} << S_{-4}$$

➤Originate from gold in form of **FNG** and **CG**

Effect of FNG-labeling particles in streptavidin molecules



EM-field confinement around colloidal labeling particles



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