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Surface plasmon resonance sensing with applications in biological objects and health control

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Directions of scientific activity

Physics of interaction processes between electromagnetic radiation and matter;

Physics of low-dimensional systems, micro- and nano-electronics;

Optoelectronics and solar power engineering;

Semiconductor materials science and sensor systems.

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Outline:

Nature of plasmonics

Plasmon excitation conditions

Theoretical description of Surface plasmon resonance

Excitation configuration and coupling of light

Type of modulation

Sensitivity and ways to its increasing

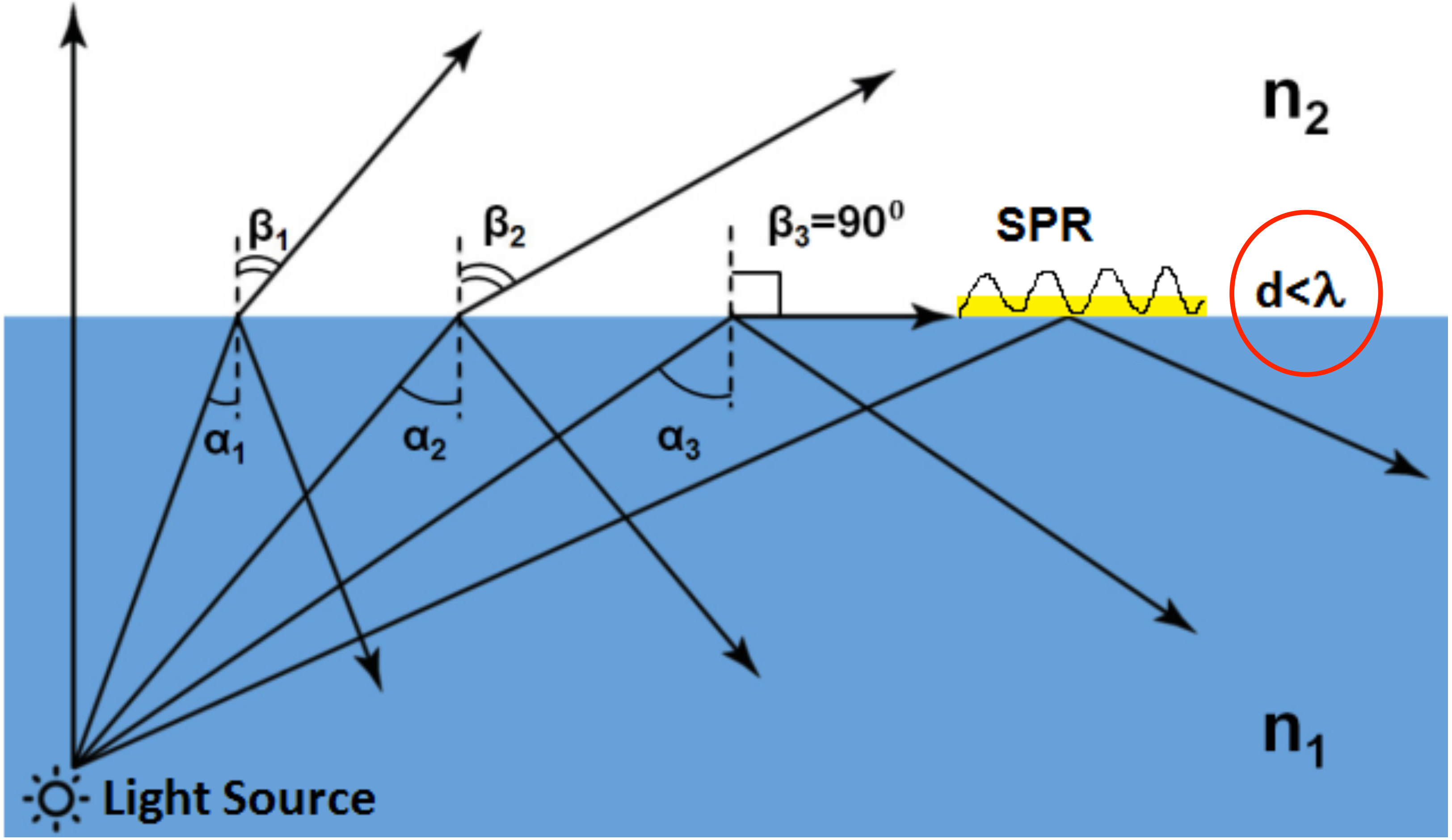
Influence of surface microgeometry on resonant peak position

Application of SPR and LSPR for biosensing

SPR in disc format

Introduction of Plasmon-6 for experimental session

Nature of Plasmonics



Snell's law: $n_1 \sin\alpha = n_2 \sin\beta$

From total internal reflection to excitation of surface plasmon

Definitions

Plasmons – quants of collective electrons oscillations in conductive materials or electron density waves

Surface plasmon resonance (SPR) – resonant excitation of plasmons in thin conductive material between two medias with different refractive indices.

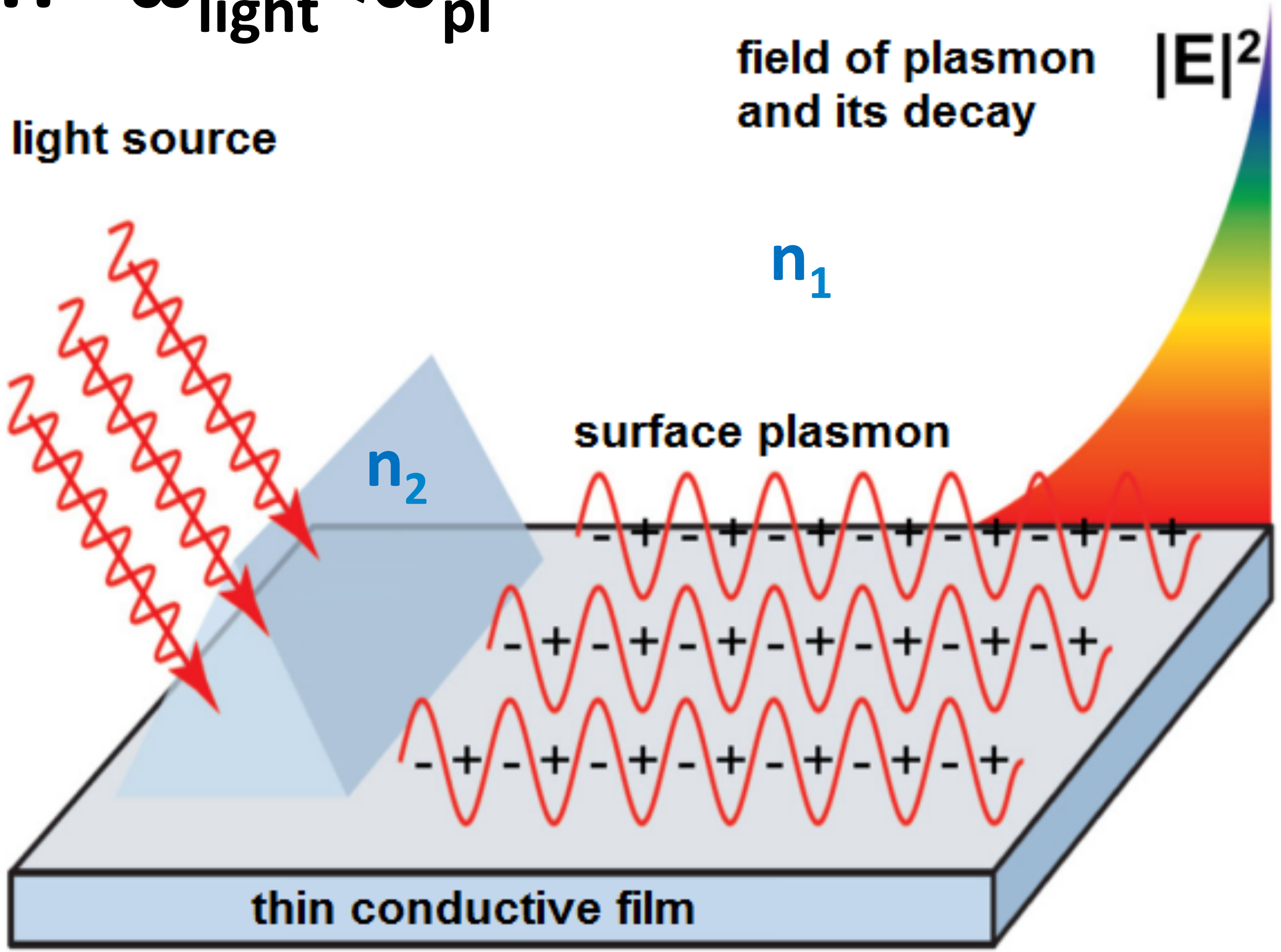
Surface plasmon polariton – electromagnetic waves that travel along a metal-dielectric or metal-air interface. The term "surface plasmon polariton" explains that the wave involves both charge motion in the metal ("surface plasmon") and electromagnetic waves in the air or dielectric ("polariton").

Localized surface plasmon resonance (LSPR) -is the result of the confinement of a surface plasmon in a nanoparticle of size comparable to or smaller than the wavelength of light used to excite the plasmon.

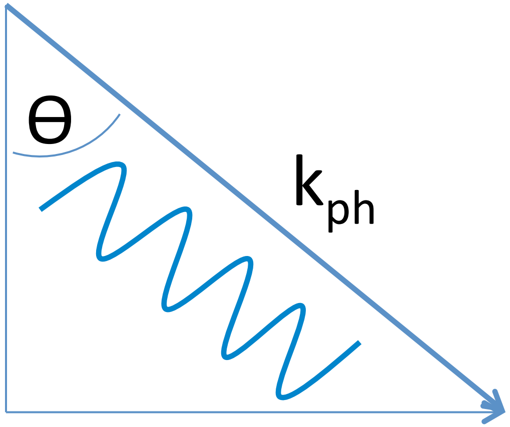
Surface magnetic resonance

Nature of Plasmonics

!!! $\omega_{light}<\omega_{pl}$

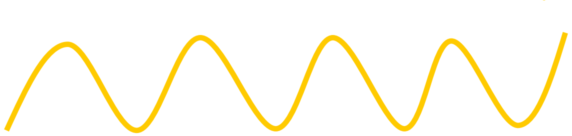


Conditions of excitation of Surface Plasmon



$k_x^{ph} = f(n_{prysm}, \lambda, \Theta)$

$k_x = f(\omega_{pl}, \varepsilon_m, \varepsilon_d)$



$$k_x^{ph} = \sqrt{\varepsilon_p}\,\frac{2\pi}{\lambda}\sin\theta \cong \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} = k_x$$

x component of incident photons wavevector should be close to the value of surface plasmon wavevector

Conditions of excitation of Surface Plasmon

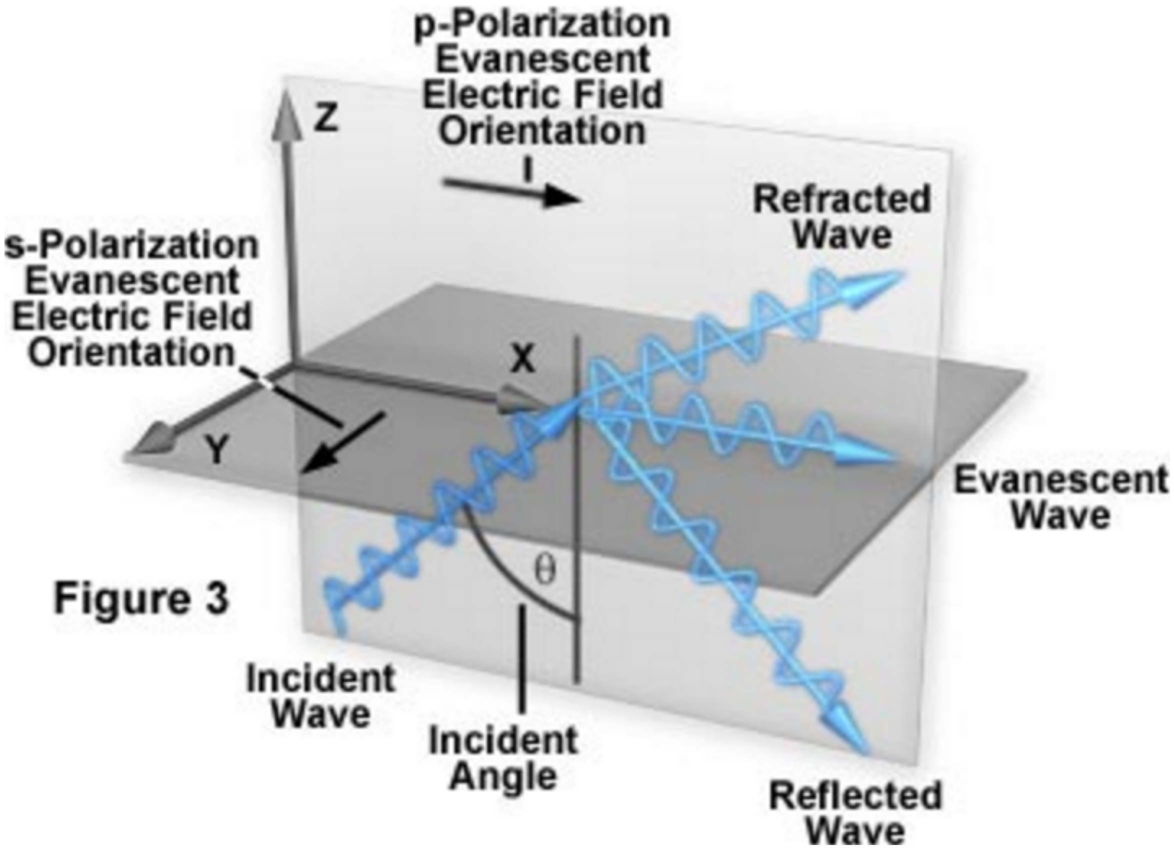
Surface plasmon excitation condition:
ε_d and ε_m should have opposite signs

In this case surface plasmon cannot interact with incident light, coming to metal film. And excitation of surface plasmon can be supported by total internal reflection using prism, diffractive grating or waveguide.

But only p-polarised light!

Why p-polarization?

Hybrid states of non-uniform surface waves and electron plasma in metal can be excited only by P-polarized light. E-vector is located in incident plane (xz), H-vector is directed along y axis.



Generation of surface charges requires electric field in both x and z components!

Plasma frequency of some metals

$$\epsilon(\omega) = 1 + \frac{i\sigma}{\omega\varepsilon_0} = 1 + \frac{i}{\omega\varepsilon_0}\left(\frac{\sigma_0}{1 - i\omega\tau}\right) \approx 1 - \frac{\omega_{p^2}}{\omega^2}$$

where

$$\omega_p = \sqrt{\frac{ne^2}{m\varepsilon_0}}$$

is called the ‘plasma frequency’.

Animation

Drude.mp4

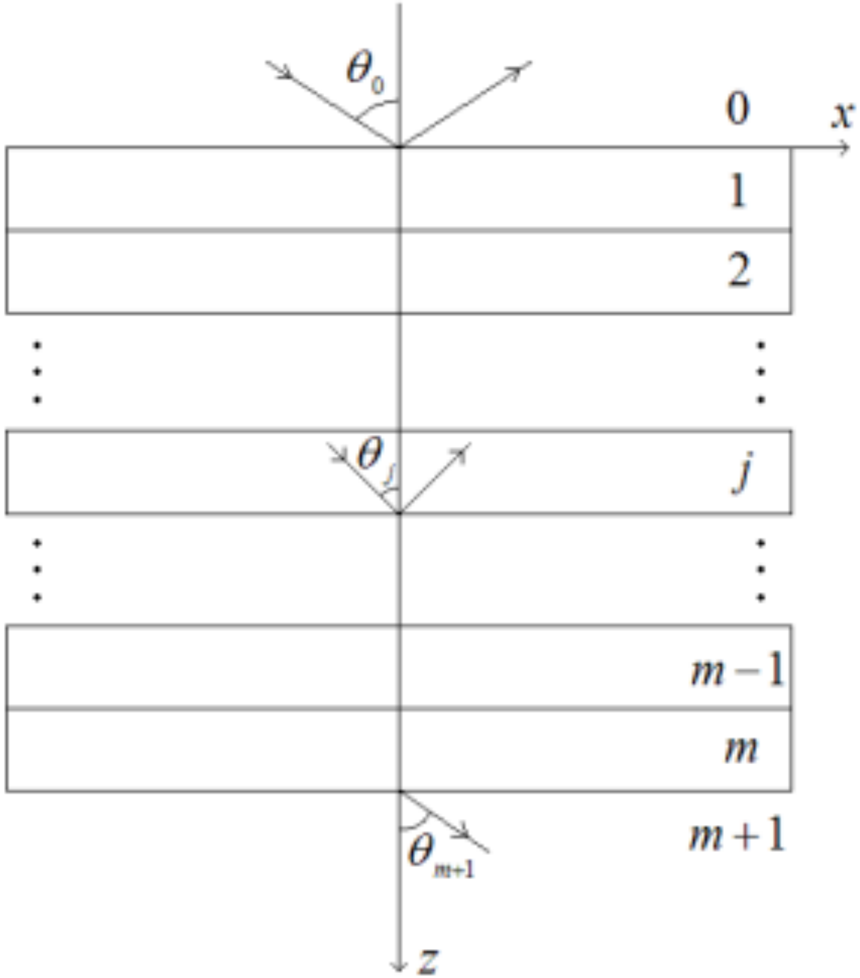
Surface Plasmon excitation

Animation

Surface_Plasmon_Polariton_(Surface_Wave).mp4

Theoretical description of SPR

Light distribution in many-layer system



Theoretical description of SPR

Electric Field distribution in many layer system

$$\begin{bmatrix} E^{+}(z_{01}) \\ E^{-}(z_{01}) \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \cdot \begin{bmatrix} E^{+}(z_{m(m+1)}) \\ E^{-}(z_{m(m+1)}) \end{bmatrix}$$

$E^{+-}(z)$ – Electric field propagating in direct and opposite direction
01 – first layer, m(m+1) – last layer

$$S = I_{01} L_1 I_{12} L_2 \ \dots \ I_{(m-1)m} L_m I_{m(m+1)}$$

S – scattering matrix, I – interface matrix, L – propagation matrix

$$I_{j(j+1)} = (1/t_{j(j+1)}) \begin{bmatrix} 1 & r_{j(j+1)} \\ r_{j(j+1)} & 1 \end{bmatrix}, \quad L_j = \begin{bmatrix} e^{i\beta_j} & 0 \\ 0 & e^{-i\beta_j} \end{bmatrix}$$

Theoretical description of SPR

$t_{j(j+1)}$ and $r_{j(j+1)}$ – Fresnel Amplitude coefficients of transmitted and reflected p-polarised light at j(j+1) interface

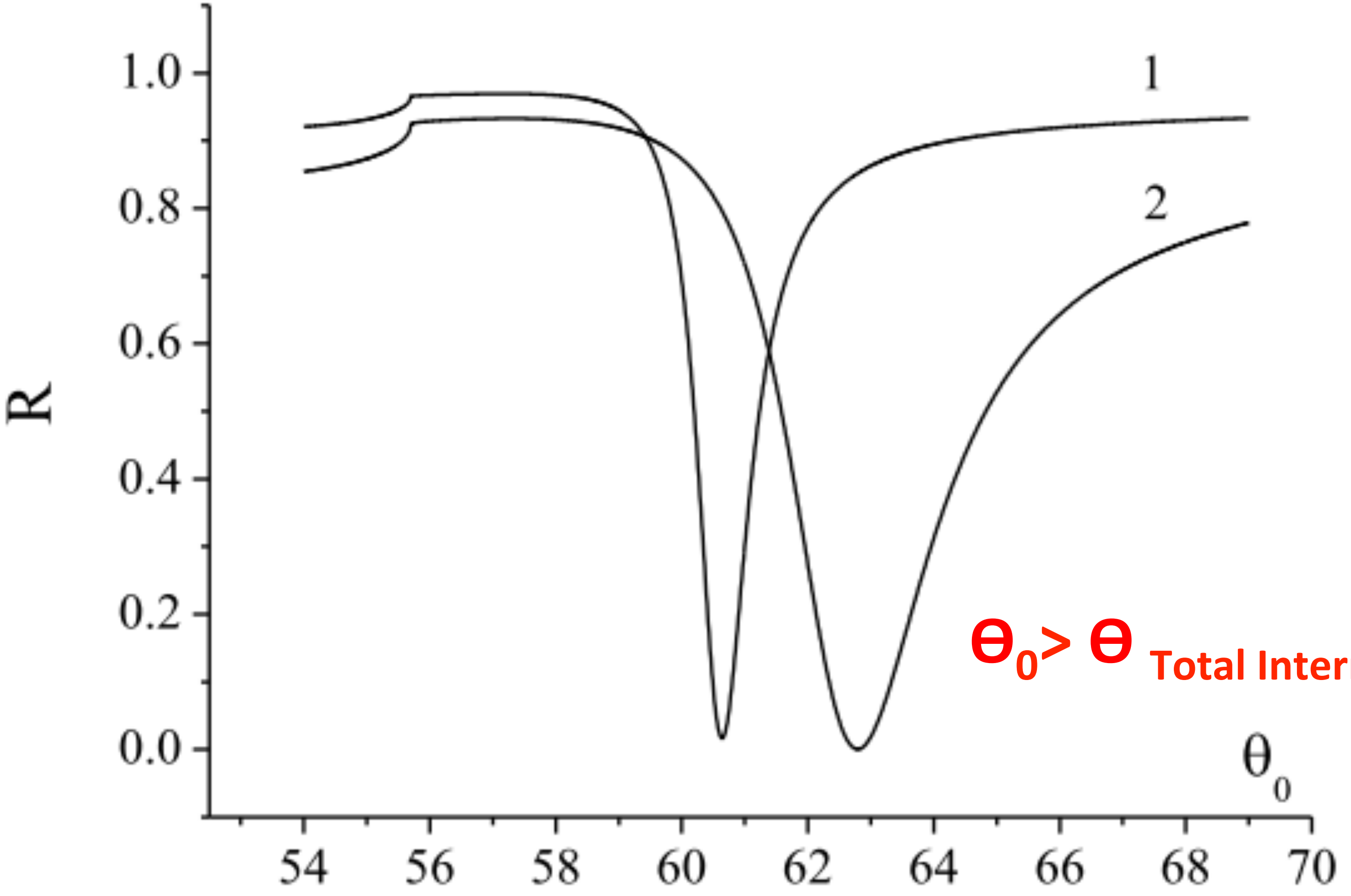
$$t_{j(j+1)} = \frac{2\widetilde{N}_j \cos\theta_j}{\widetilde{N}_{j+1}\cos\theta_j + \widetilde{N}_j \cos\theta_{j+1}}, \quad r_{j(j+1)} = \frac{\widetilde{N}_{j+1}\cos\theta_j - \widetilde{N}_j \cos\theta_{j+1}}{\widetilde{N}_{j+1}\cos\theta_j + \widetilde{N}_j \cos\theta_{j+1}}$$

Reflection of many-layer structure can be calculated using appropriate elements of matrix of scattering S

$$R = \left| \frac{S_{21}}{S_{11}} \right|^2$$

Theoretical description of SPR

Calculated reflection for angular scanning of many-layer SPR system based on thin Silver (1) and Gold (2) films



$\theta_0 > \theta_{\text{Total Internal Reflection}}$

Theoretical description of SPR

Taking into account Polarization and surface concentration of molecules
And applying Green Function as photon propagator:

$$E_i^{(R)}(\vec{k},z,\omega) = N_S G_{ij}^{(+,-)}(\vec{k},z,z_\alpha,\omega) \mathrm{X}_{jl}(\vec{k},\omega) E_l^{(0)}(\vec{k},z_\alpha,\omega)$$

Considering $E_p^{(R)} = R_p E_p^{(0)}$

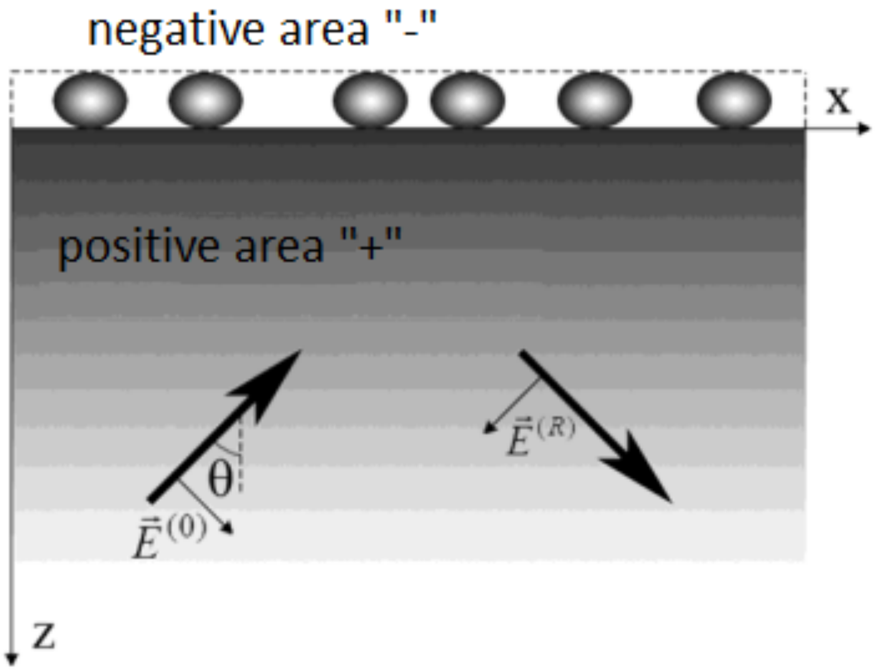
$$R_p^{(M)}(\theta,\omega) = G_{xj}^{(+,-)}(\vec{k},z,z_\alpha,\omega) N_S \mathrm{X}_{jx}(\vec{k},\omega) + G_{zj}^{(+,-)}(\vec{k},z,z_\alpha,\omega) N_S \mathrm{X}_{jz}(\vec{k},\omega) + \\ + \left[G_{xj}^{(+,-)}(\vec{k},z,z_\alpha,\omega) N_S \mathrm{X}_{jz}(\vec{k},\omega) + G_{zj}^{(+,-)}(\vec{k},z,z_\alpha,\omega) N_S \mathrm{X}_{jx}(\vec{k},\omega) \right] \cos\theta \sin\theta$$

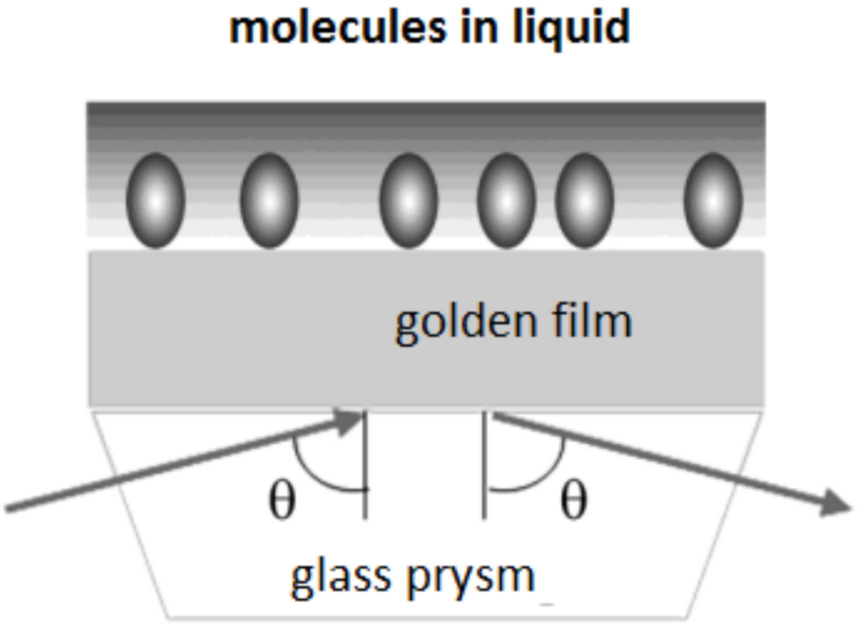
N-surface concentration of molecules, G_{ij} – photon propagator,
X_{ij} – permittivity of molecules, E – electric field, R – reflection

We should know permittivity of molecular layer!

Theoretical description of SPR

Illustration: reflection of light by molecular layer, located on the surface of thin Au film





$$R_p^{(T)}(\theta,\omega) = R_p^{(0)}(\theta,\omega) + R_p^{(M)}(\theta,\omega)$$

Thus, total reflection will be sum of Fresnel reflection, and reflection caused by polarization and concentration of molecular layer

For localized SPR: spherical particles. Mie theory.

$$\varepsilon'(\omega,R)=\varepsilon'_{bulk}(\omega)+\frac{\omega_p^2}{\omega^2+\frac{1}{\tau_{bulk}^2}}-\frac{\omega_p^2}{\omega^2+\frac{1}{\tau_{eff}^2(R)}},$$

$$\varepsilon''(\omega,R)=\varepsilon''_{bulk}(\omega)+\frac{\omega_p^2}{\omega}\left(\frac{\tau_{eff}(R)}{\omega^2\tau_{eff}^2(R)+1}-\frac{\tau_{bulk}}{\omega^2\tau_{bulk}^2+1}\right)$$

Au:

$$\tau_{eff}(R)=\left(\tau_{bulk}^{-1}+A\frac{V_F}{R}\right)^{-1}$$

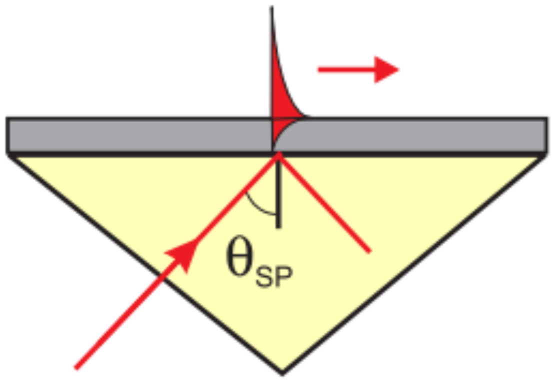
$\omega_p=1.37\times10^{16}$ rad/s, $\tau_{bulk}=9.3\times10^{-15}$ s $V_F=1.4\times10^{6}$ m/s

$$n_1(\omega,R)=\sqrt{\frac{1}{2}\left(\varepsilon'(\omega,R)+\sqrt{\varepsilon'^2(\omega,R)+\varepsilon''^2(\omega,R)}\right)},$$

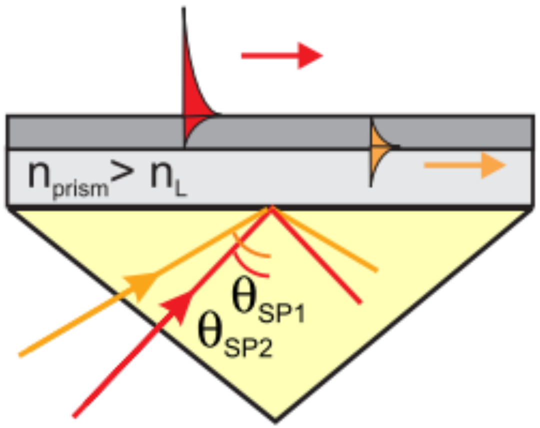
$$k_1(\omega,R)=\sqrt{\frac{1}{2}\left(-\varepsilon'(\omega,R)+\sqrt{\varepsilon'^2(\omega,R)+\varepsilon''^2(\omega,R)}\right)}$$

SPP Excitation configuraion geometry

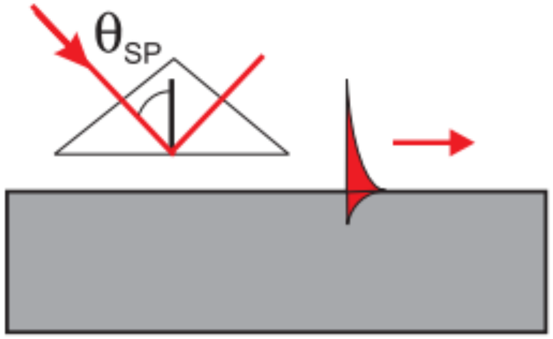
Kretschmann

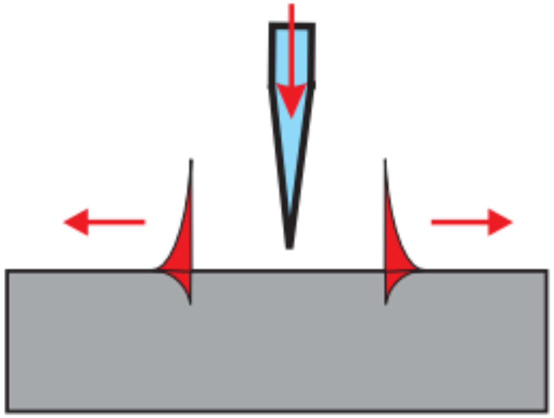


two-layer Kretschmann

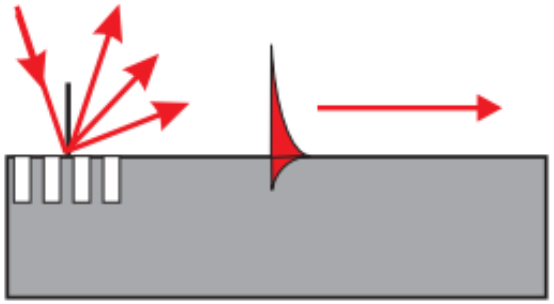


Otto

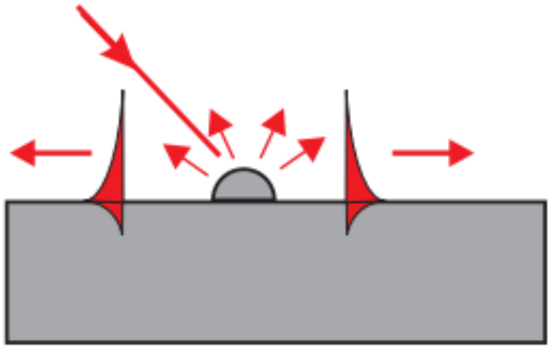




with a SNOM-probe



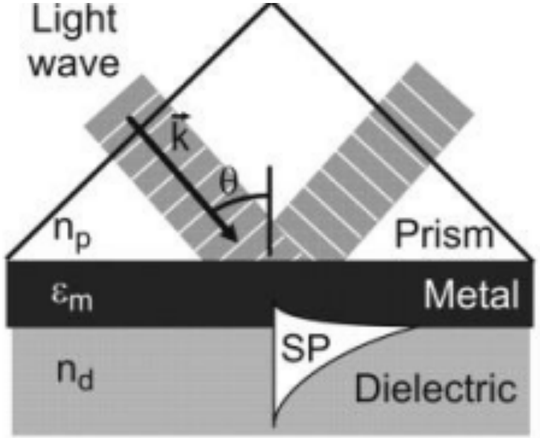
diffraction on a grating



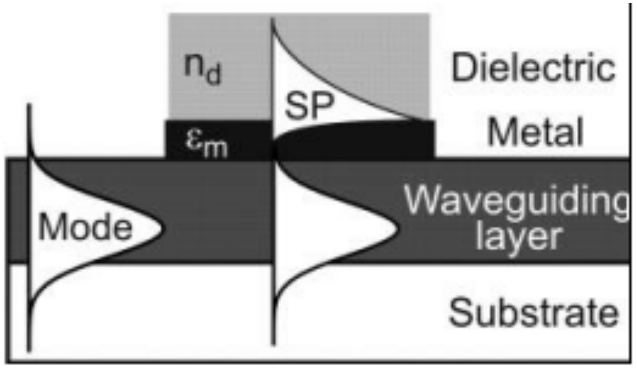
diffraction on surface features

A.V. Zayats et al. / Phsics Reports 408 (2005)

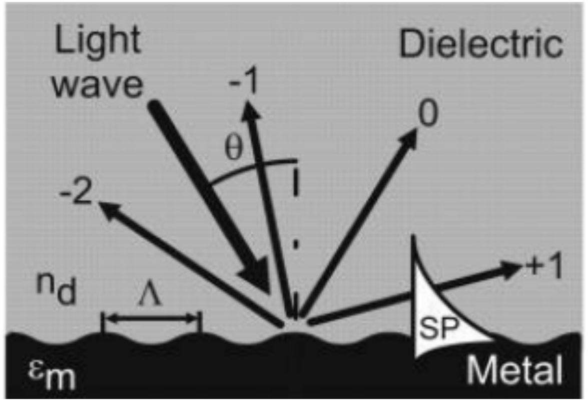
Coupling of light to surface plasmon



Prism



waveguide



diffraction grating

Type of Modulation

Angular Modulation – Excitation by monochromatic wave by changing the incidence angle.
Surface Plasmons are observed as a dip in the angular spectrum of reflected light. Sensor output – the incidence angle yielding the strongest coupling .

Wavelength Modulation – Excitation by collimated polychromatic light.
Surface Plasmons are observed as a dip in the wavelength spectrum of reflected light. Sensor output – the wavelength yielding the strongest coupling.

Intensity Modulation – Excitation by single incidence angle and wavelength by changing the intensity of light.
Sensor output – the intensity of light yielding the strongest coupling .

Phase Modulation – Excitation by shift in phase of the light wave at a single incidence angle and wavelength.

Table. Analytical parameters of different types of SPR sensors

Type of Modulation	Intensity Measurement	Angular spectroscopy	Frequency spectroscopy	Phase shift measurement
Typical resolution (RIU)	10^{-5}	5×10^{-7}	10^{-6}	4×10^{-8}
Typical width of dynamic range	0.05	0.1	>0.1	5×10^{-4}
Typical Sensitivity	15000%/RIU	200 Deg/RIU	10000 nm/RIU	100000 Deg/RIU
Potential to increase sensitivity	High	Mid	Mid	High

Sensitivity of SPR sensors

$S = \Delta A / \Delta n$

$A = \varphi, \lambda, I, \Phi$ (Angular, spectral, Intensity and Phase modulation)

Depends on surface morphology of sensors!

For spectral modulation:

Surface	Nanorhombs	Nanospheres	Nanopyramides	Needles
S	267 nm/RIU	44 nm/RIU	400 nm/RIU	703 nm/RIU

Figure of Merit (FOM)

$FOM = S_{nm/RIU} / FWHM_{nm}$

FWHM – full width at middle height

For spectral modulation:

Surface	Nanorhombs	Nanospheres	Nanopyramides	Needles
FOM	2.22		4.2	0.8

Ways to increase sensitivity

Angular Modulation	add diffractive grating, temperature and noise stabilization
Wavelength Modulation	use Furie spektrometers, multi-channel sensing (2x10^{-7} RIU)
Intensity Modulation	2 light sources with different wavelength (2 x10^{-6} RIU)
Phase Modulation	Interfarence pattern analysis, Ellipsometry(3.7 x10^{-8} RIU) , Heterodynes (2.8 x10^{-9} RIU)

Universal Methods:

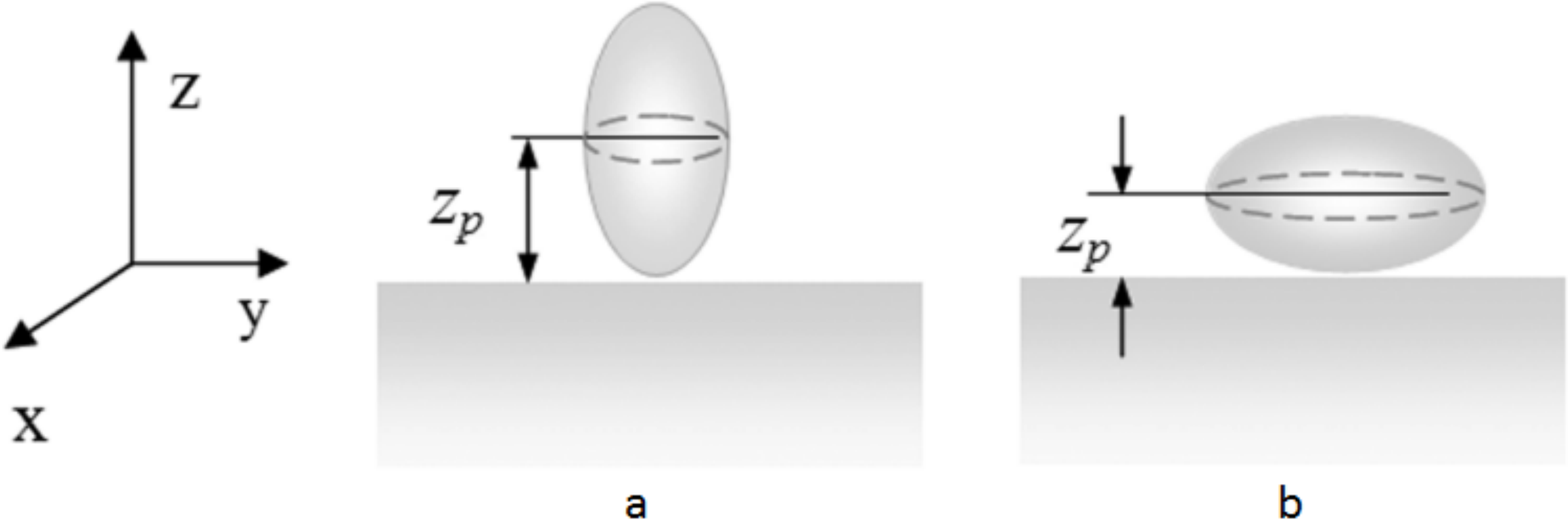
Dielectric nano coating
Using graphene
Nanoparticles
Magnetit (Fe_2O_3)

Increasing productivity

Multichannel systems

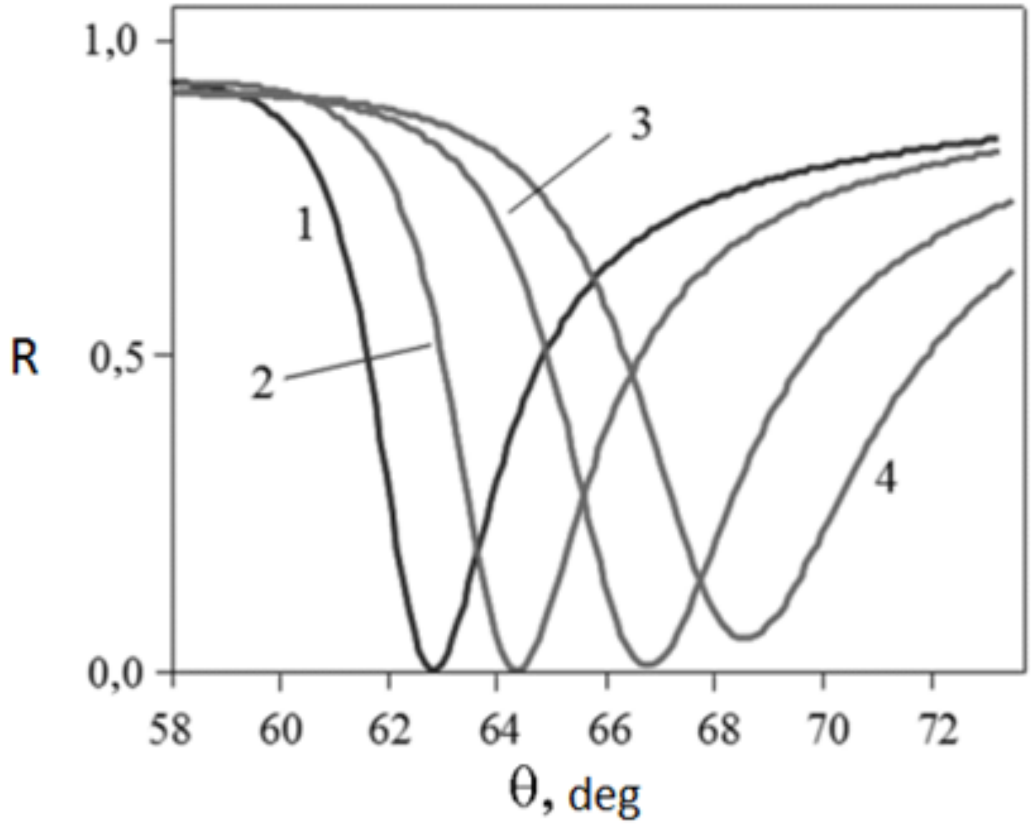
SPR Imaging

Influence of forms of molecules on SPR curve



Protein molecule on a surface: a – extended ellipsoid, b – shortened ellipsoid

Influence of forms of molecules on SPR curve



Calculated SPR curves, depends on form of molecules.

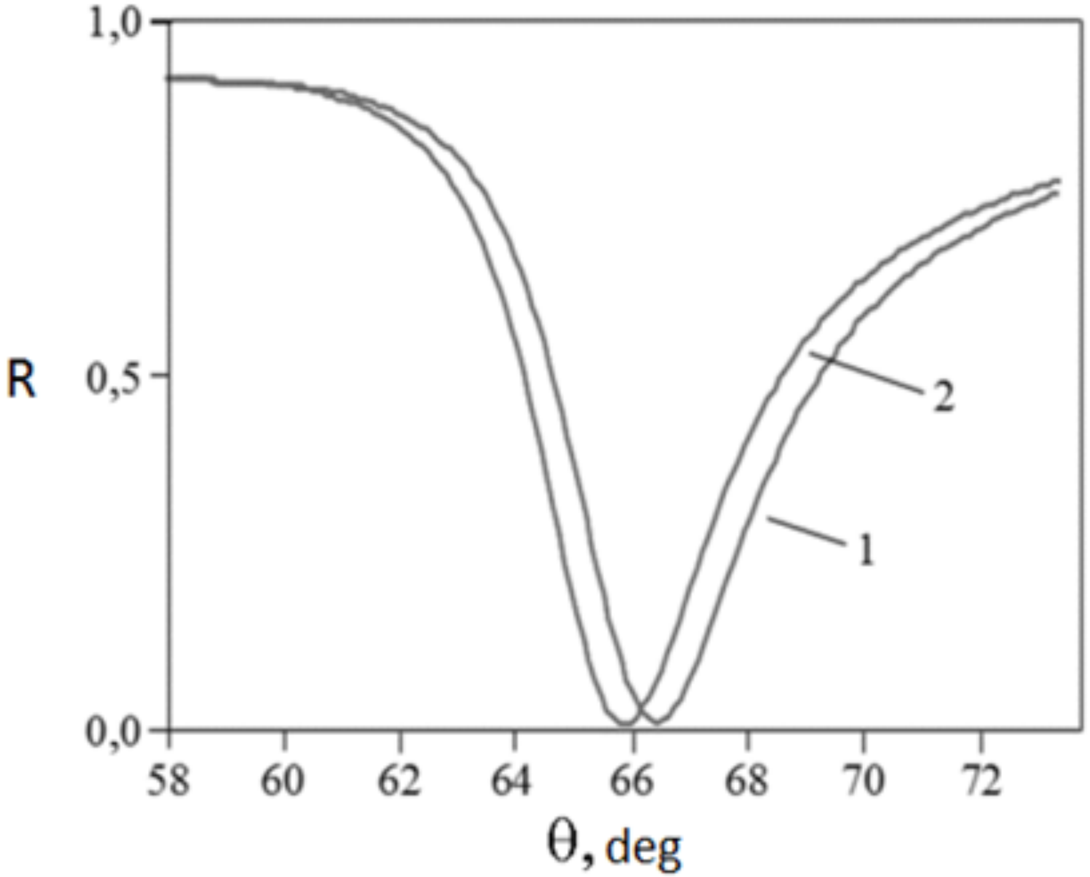
1 – empty surface, Θ_{min}=62.747;

2 – shortened molecules, ζ=2.0, Θ_{min}=64.262

3 – extended molecules, ζ=0.12, Θ_{min}=66.585

4 - extended molecules, ζ=0.11, Θ_{min}=68.302

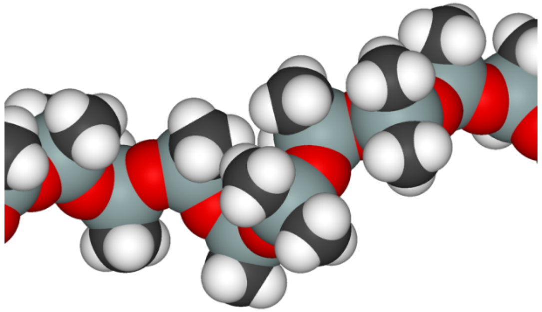
Influence of forms of molecules on SPR curve

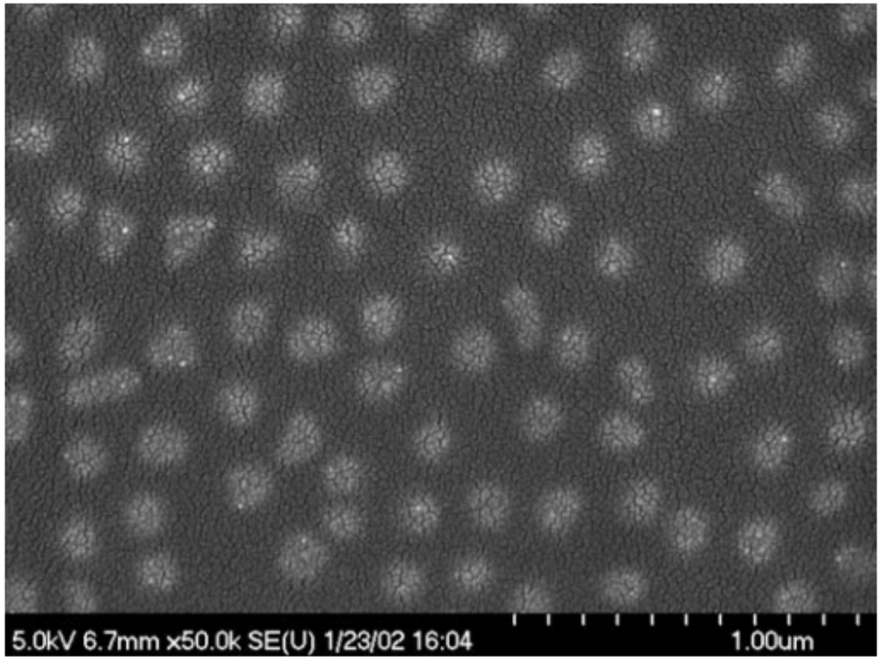


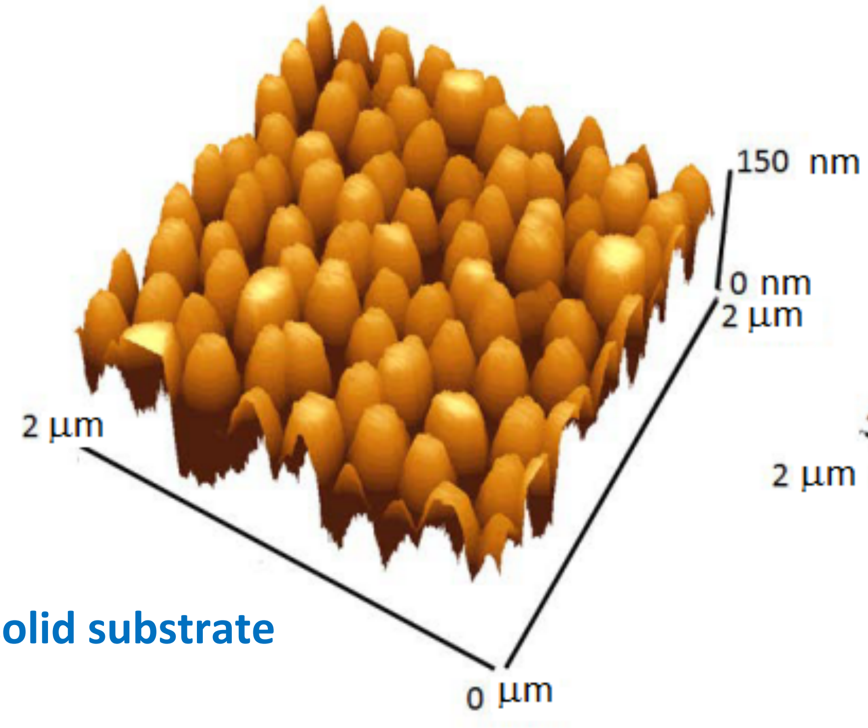
Calculated SPR dependences on structure of molecular film, consists from extended (ζ=0.12) and shortened (ζ=2.0) molecules.
Part of extended molecules: f=1 (curve 1, Θ_{min}=66.282)
And f=0.5 (curve 2, Θ_{min}=65.777)

Using elastic substrate

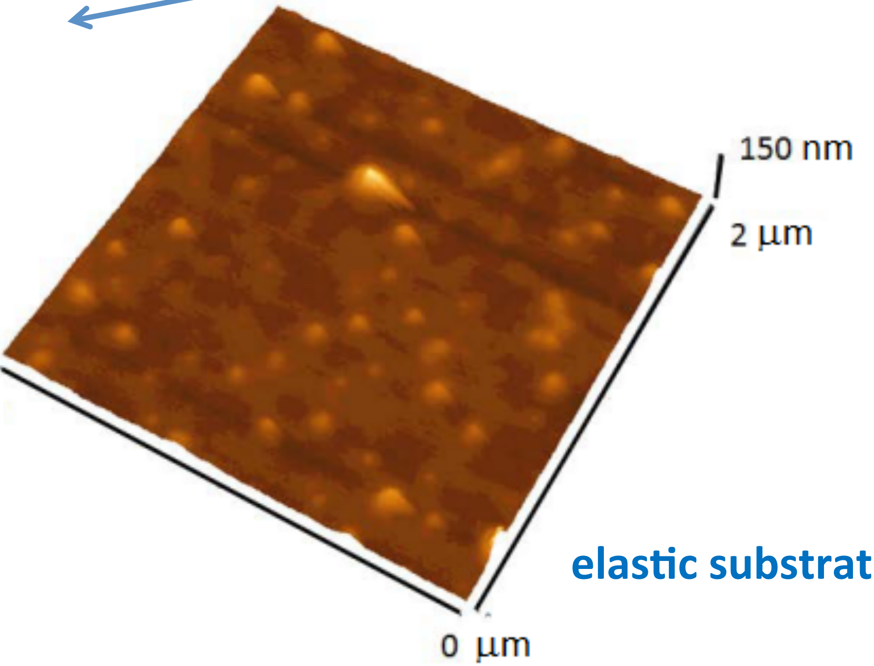
Tuning the shape and position of LSPR curve by changing surface concentration of nanoparticles - Poly(dimethylsiloxane) - PDMS







solid substrate

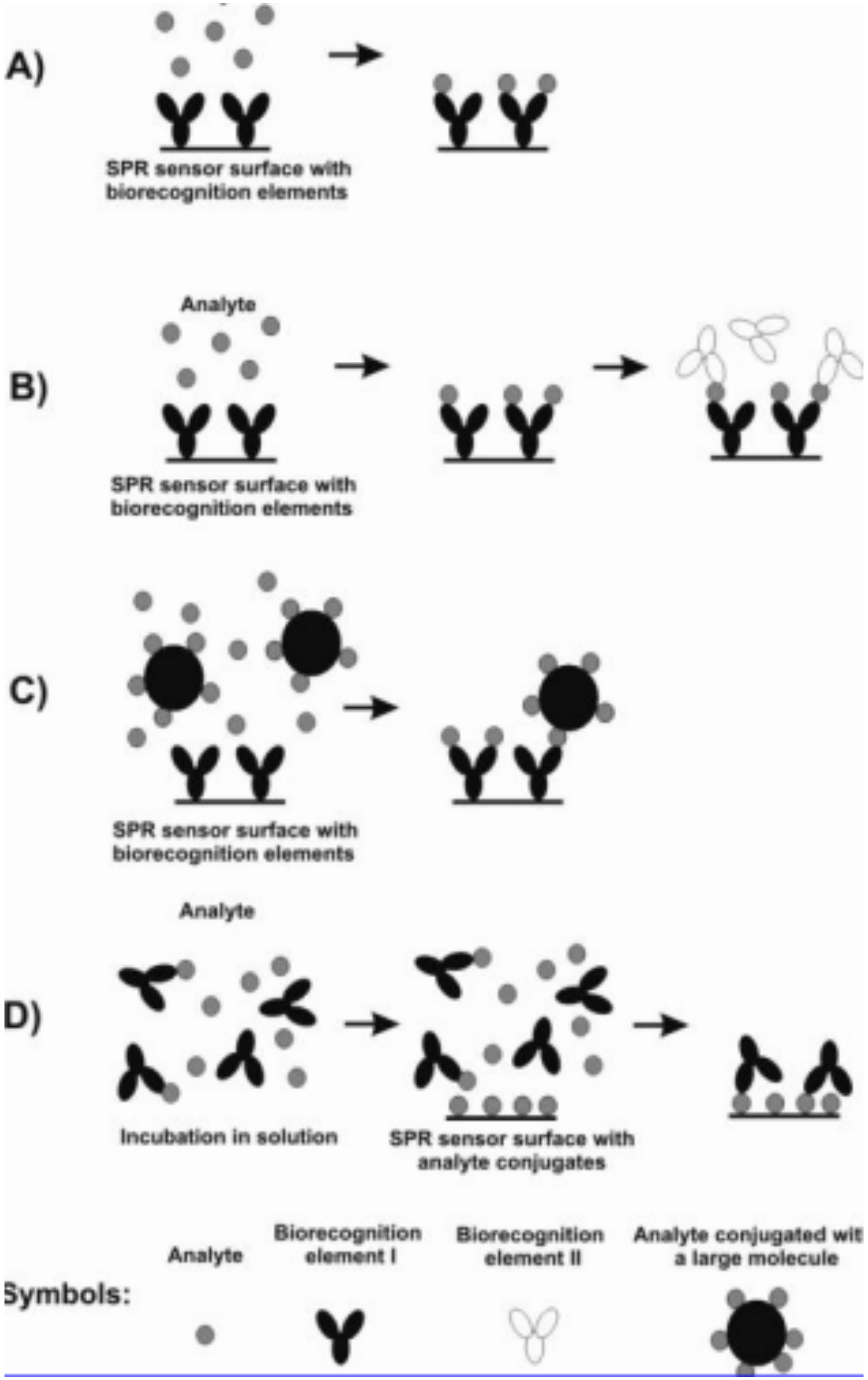


elastic substrate

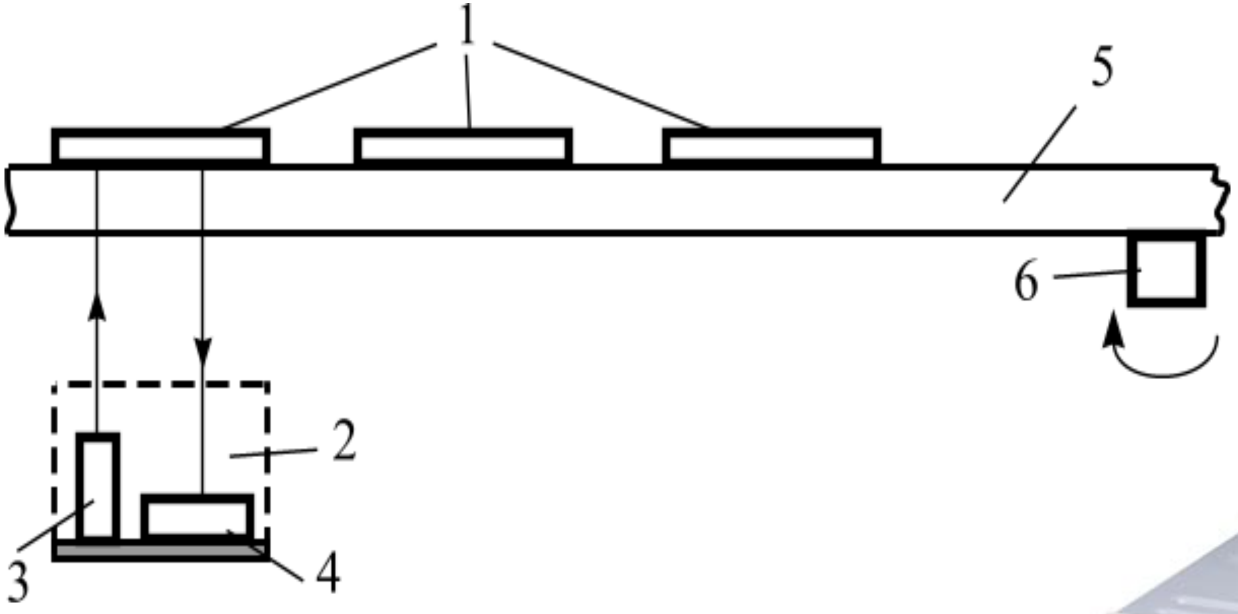
SPR sensing of biomolecules

Main detection formats used in SPR biosensors:

(A) direct detection;
(B) sandwich detection format;
(C) Competitive detection format;
(D) inhibition detection format

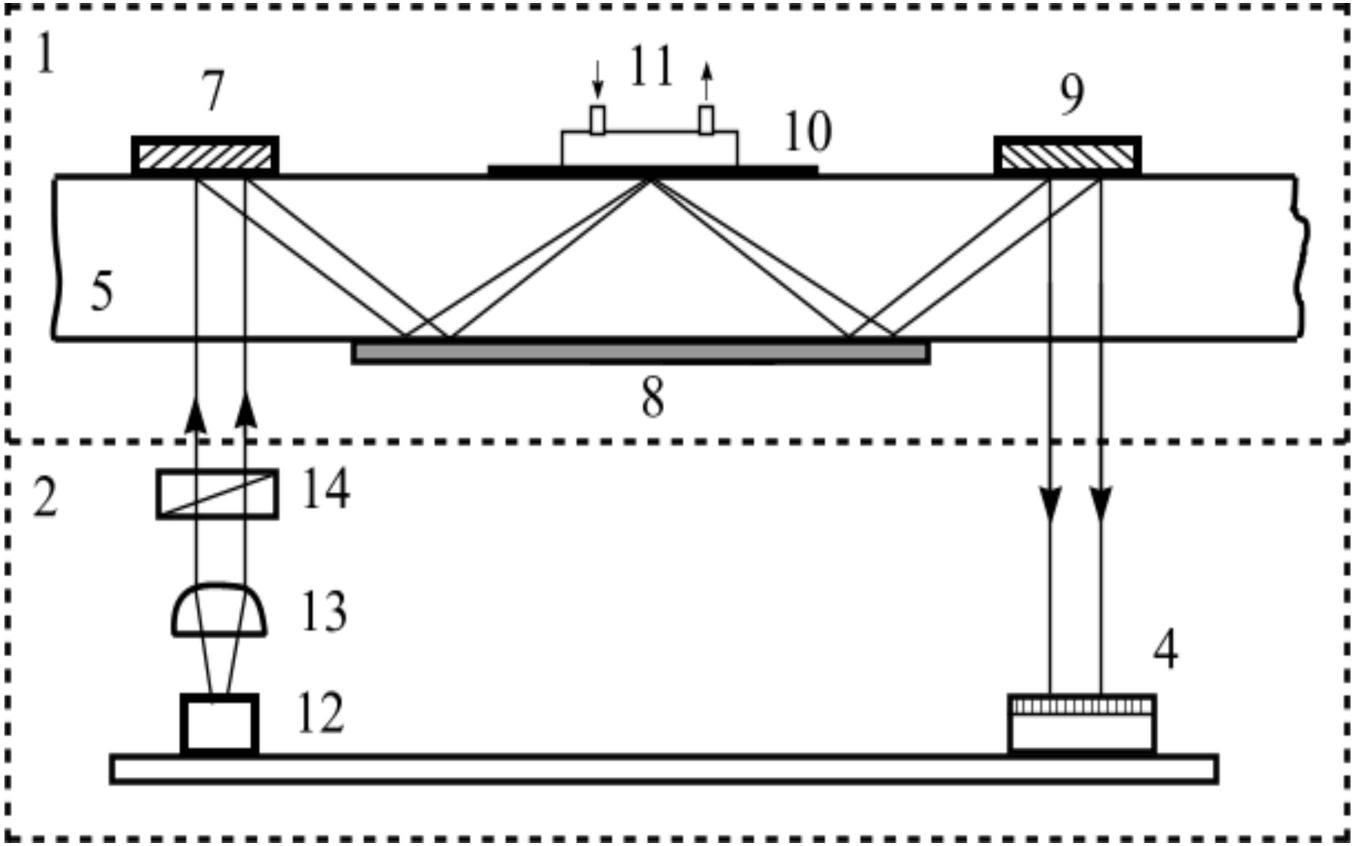


SPR sensor in disc format



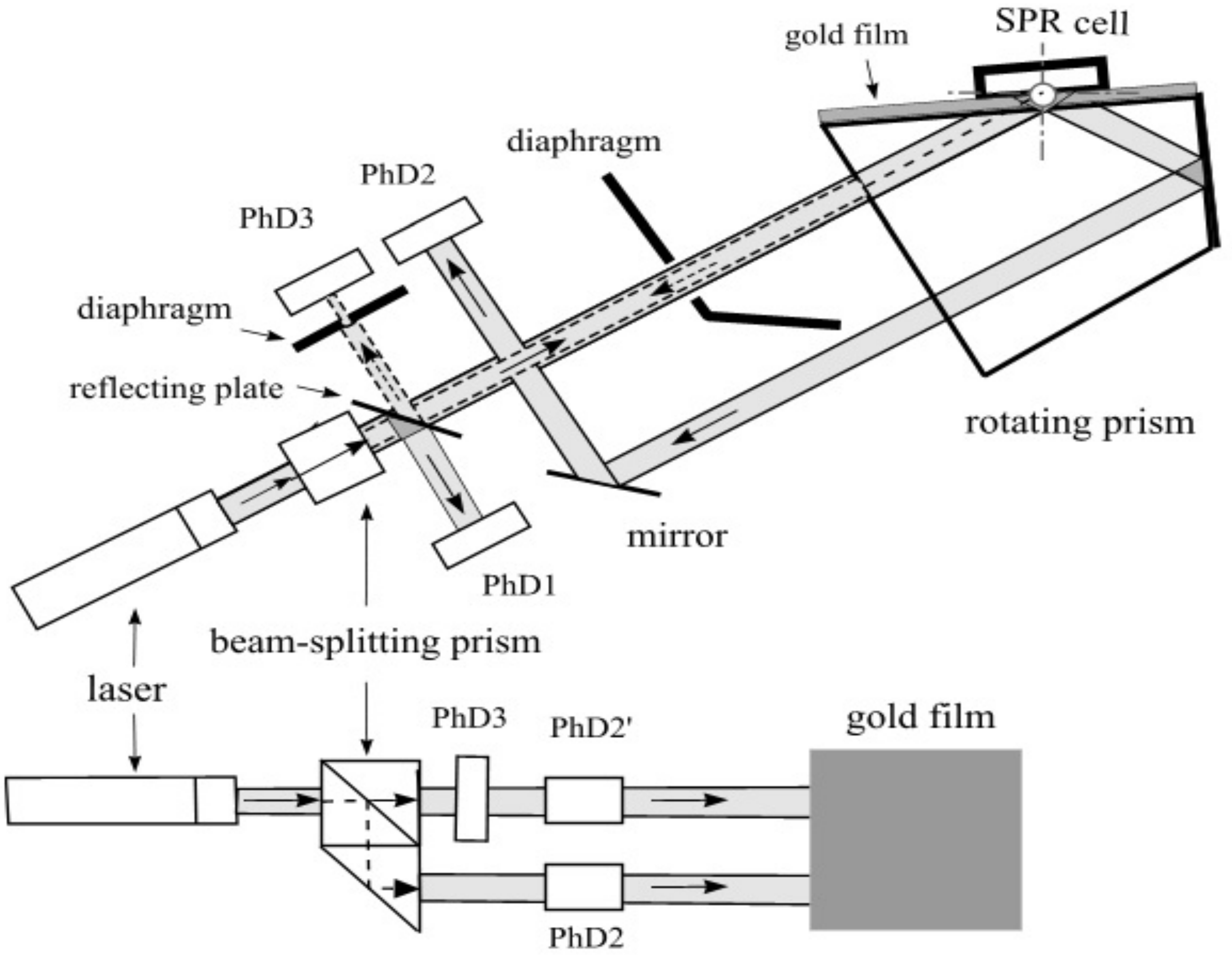
Block-diagram of a multielement SPR sensor in a disk format: 1 – sensor part of a transducer, 2 – optical part of a transducer, 3 – illuminating system, 4 – detector of light reflected from the sensor unit, 5 – rotating polymeric disk, 6 – rotation axis.

SPR sensor in disc format



Sensor unit (1) is mounted on polymeric rotating disk (5) and consists of integrated diffraction elements (7,9) and film-like metallic working element (10) placed between them. The metallized gratings of the surface relief (with a linearly varying parameter) focus the incident light on metal film (10) and transfer the reflected light onto detector (4) with the use of optical mirror (8). The flow-through cuvette for the supply of sample (11) under study contacts with metal film (10). Optical unit (2) includes illuminating system (3), which contains a source of monochromatic light (12), collimator (system of lenses) (13), polarizer (14), and light detector (4) in the form of a block of light diodes.

Plasmon-6 with angular scanning system



Optical scheme of a two-channel "Plasmon"-type device

To register the emission, we used three light diodes: "PhD1" controls the incident emission power, "PhD2" registers the reflected light, and "PhD3" realizes the absolute calibration by angle, by fixing the time moment of the maximum reflection of light from the front face of the prism with the use of a diaphragm 100 μm in width.

Plasmon-6 with angular scanning system

Refractive index measurement range	1.0 – 1.43
Detection limit of refractive index variation	0.00005
Angle-of-incidence setting precision	10 angular sec
Maximum angular scan	17º
Total measurement time of a single resonant curve	3 sec
Maximum time resolution of kinetics measurements:	≤ 3 sec
Maximum time resolution for Tracing measurement mode	1 sec
Maximum time resolution for Slope measurement mode	0.2 sec
Number of optical channels	2
Light source	GaAs laser (λ=650 nm)
Additional ADC input (optional)	±5V
Overall dimensions of the measurement unit	215x130x100 mm
Weight	2.5 kg
Computer connect	COM port, USB
Control and data processing software Windows	95/98/ME/XP/7

Conclusions

SPR methods allows to detect changes of n up to 10^{-8} RIU

Good for measurement low concentration

Various configurations available

Possibility to detect non-organic and organic gas and liquid solutions including cites, viruses, proteins etc.

Non-expensive technology

Possibility to use multichannel detection

Effectivity of CD Disc format biosensors

Special thanks

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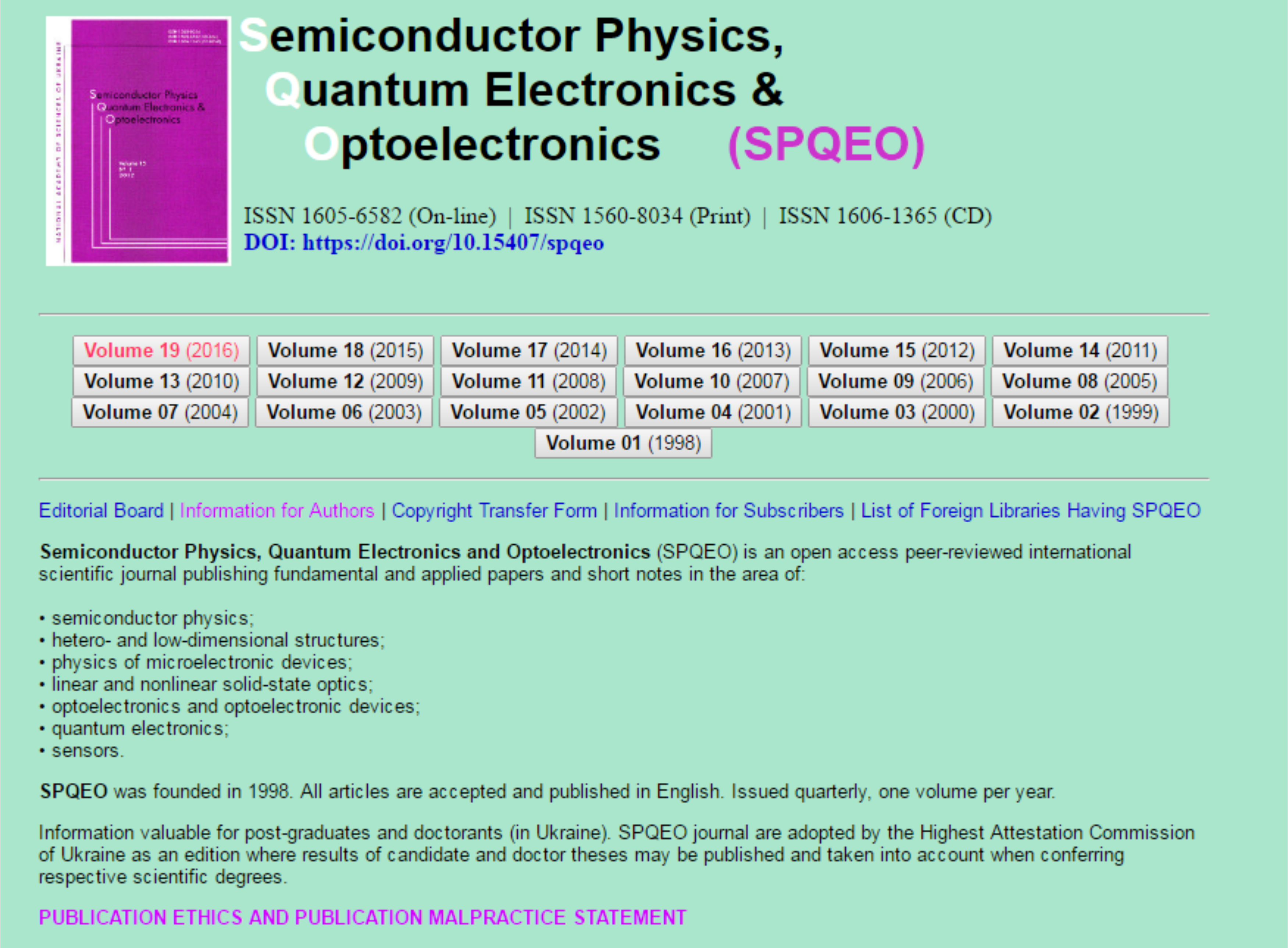

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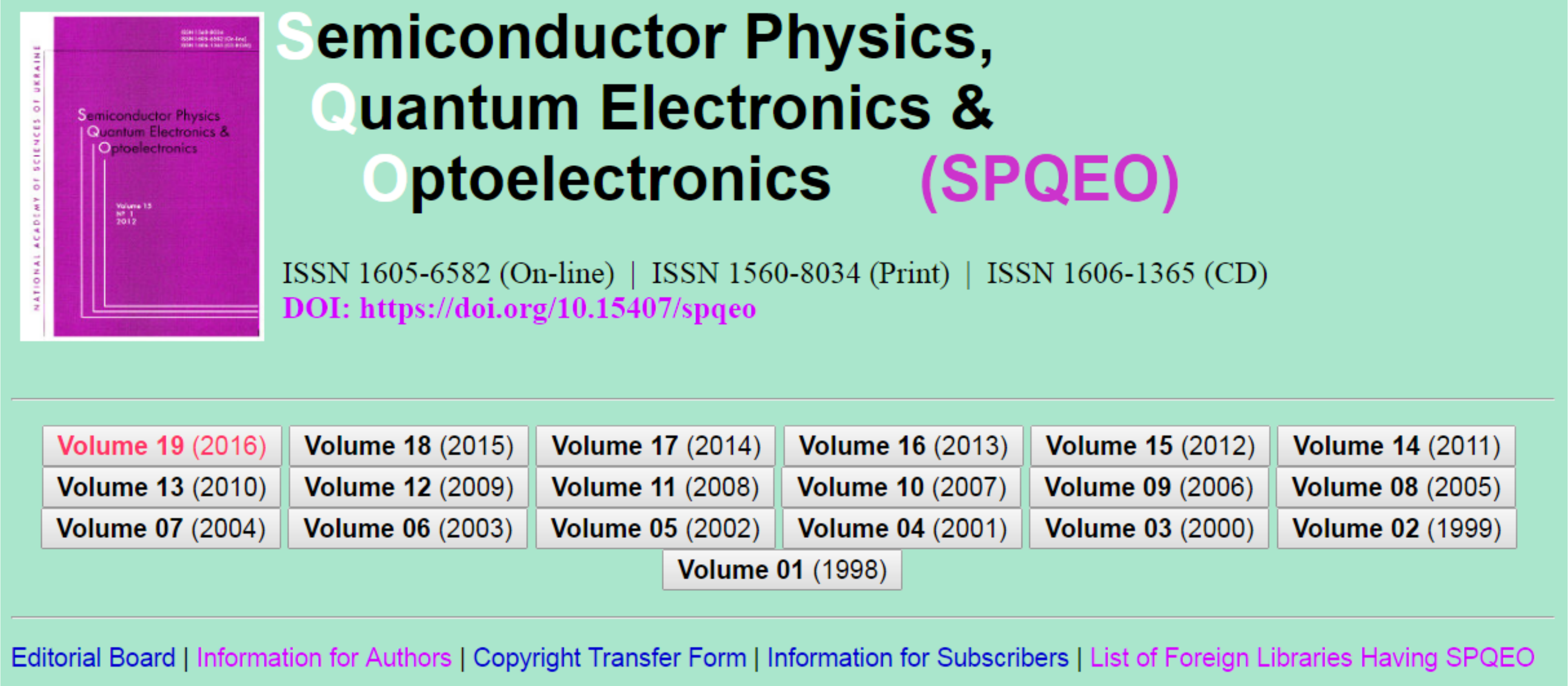

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