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# Surface plasmon polaritons as sensor system

Skoršepová Terézia · Elektrotechnika

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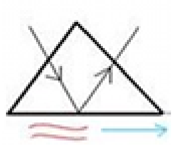


Surface plasmon polaritons are an optical phenomenon on the interface metal and dielectric. This optical phenomenon is very sensitive to the quality of metal´s surfaceand it is able to detect small changes of the surface. The first capture consist of theoretical description of the surface plasmon polaritons and Dispersion relation. The second chapter of the paper describes experimental measurement. This experiment was implemented without adsorption dodekathiol and cyklodextrin.

**Introduction**

Surface plasmon polaritons were described at beginning of 20th century. Increased interest in this optical effect rose in last decades. Results of previous research show a wide range of applications in the optics and in sensors. Surface electromagnetic waves – surface plasmons (SPP) are electromagnetic waves that we are not able to detect as electromagnetic oscilation. They originate on the interface metal- dielectric. We can them characterize as multiple electron oscilations with energy in the coduction band. The intensity decreases exponencially with increasing distance from the interface. For this reason is electromagnetic field SPP limited only at metal surface surrounding. SPP are formed by charge in metal and by electromagnetic field in both interfaces. [1]

Since 1902 till 1912, John Hopkins noticed on diffraction grating with deposited metal layer by which was polarized light incidented on this layer, that there are bright and dark anomalous reflexes. This anomalous was explained by Lord Rayleight, in 1907. His interpretation was based on the dispersion of electromagnetic field in outgoing waves area. Furthermore, he interpreted, that this phenomenon appears only by the polarization, where is electric’s field intensity vertical to the incident interface. Later he showed that this anomalous is observing by the p- polarization, if the vector of electric’s field intensity is not vertical to the incident interface. In this case were SPP observed only on the diffraction grating with deeper grooves.

During 1950s, it was given large attention to SPP problem. It was realiyed few measurements concentreated on the decline of energy respectively energy losses in gas and on the thin foil. These measurements led Pines and Bohm to idea that energy losses are caused by surface plasmon oscillation respectively it are induced by plasmon. Further research showed that occurrence of surface plasmons is affected by presence of any film or impurity on the surface samples. This effect was described as formation of evanescent field on the metal’s surface. In the year 1970 was this effect described as evanescent waves, where they are described as important aspect by analyse and by research of ultrathin metal layers. [2]

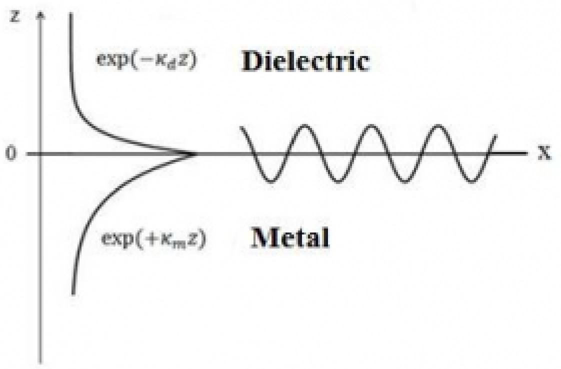
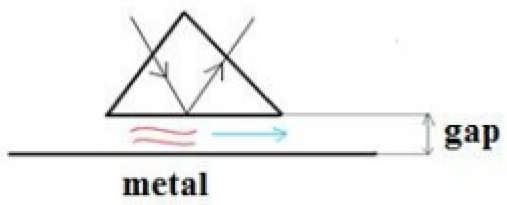


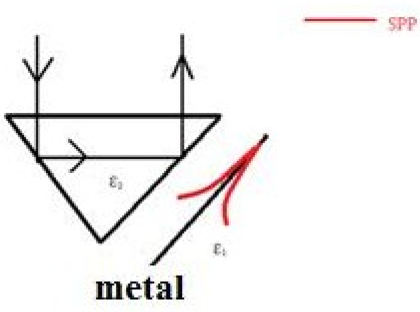

*Fig. 1 Surface plasmon moves along interface and exponentially expires with distance from the interface [3]*

**Configurations for excitation SPP**

There are various configurationsthat are capable to generate and measure surface plasmon polariton. As an example we can mention optical prims that use total reflection of incident electromagnetic emission, optical reticles, optical fibres or optical waveguide. By surface plasmons excitation by maens of optical prims are used two configurations. By those are Kretchman and Otto configuration. Otto configuration consists of optical prim, air gap and metal layer. The difference between Otto configuration and Kretchamn configuration is only in that that by Kretchman configuration is metal layer directly applied to the one side optical prim. A applicable usage of Otto configuration is in the SPP studies, where are examined media in the solid phase. Kretchman configuration allows more effective SPP excitation.




*(a)*




*(b)*

*Fig. 2 (a) Otto configuration, (b) Kretchman configuration [3]*

**Dispersion relation**

Dispersion relation is characteristic parameter for SPP definition . By deriving dispersion relation came from Maxwell equations and from continuity of electromagnetic field on the interface. SPP is surface wave, so E and H declines with distance from the interface as: $e^{-\kappa dz}$ (z > 0) and $e^{\kappa mz}$ (z < 0). If we consider TM polarization, so H is parallel with metal's surface, then by the x and z factor intensity E is valid: [1]

$$\frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} = i\omega\mu_0 H_y \qquad (1)$$

$E_x$ has to be continuous function. Consequently, we can tell , that condition of SPP existenceis:

$$\frac{\kappa_d}{\varepsilon_d} + \frac{\kappa_m}{\varepsilon_d} = 0 \qquad (2)$$

Whereas is valid $\kappa_d > 0$ and $\kappa_m < 0$.This term has solution only if $\varepsilon_m < 0$. Therefore SPP incipient only on the interface metal/ dielectric. Consequently, we determine dispersion term for the SPP by means of wave vector SPP $k_\parallel$. Dispersion term of the SPP is:

$$k_{||} = \omega\sqrt{\varepsilon_0\mu_0}\sqrt{\frac{\varepsilon_d\varepsilon_m}{\varepsilon_d+\varepsilon_d}} \qquad (3)$$

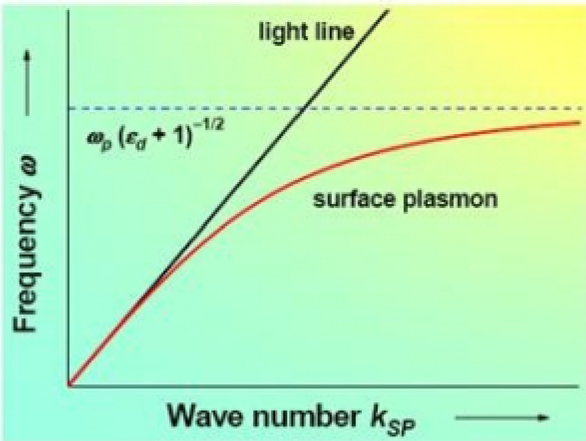



*Fig. 3 Dispersion term [4]*

**Experiment**

Theoretical models verification of surface electromagnetic waves behaveing is able by means of the experiment that we are able to monitor even small changes in minimum reflectivity shift of reflected light by the plasmon polariton excitation. By us realized experiments are focused on excitation of surface electromagnetic waves on the interface dielectric/metal/water or another liquid with nearby refractive index water refractive index. Bz these experiments employ source of electromagnetic emission in the spectral scale from 430 nm to 850 nm by constantlly set up the angel.

The base of the sensor system with using the surface plasmon polaritons is polarimeter Horiba Jobin Yvon MM -16 which is determined to the fast characteristic of thin layers for the research and for quality control of measured sample, for the wide range of materials such as semiconductor, solders as well as organic thin layers. Polarimeter Horiba Jobin Yvon MM – 16 is easily and simply controlled device. Liquid crystals technology provides high accuracy of measurements for ellipsometry angels Δ and ψ in their full scale by one measurement. Each head of the polarimeter has one liquid crystal, two LC modulators from which each has two possible phase of polarization . Whole spectral scale is possible to gain in the time under two second by very high definition. To achieve relevant results is needed stability of device, but also stability of the whole experiment. We realized measurement of long stability by means of etalon sample $SiO_2$.

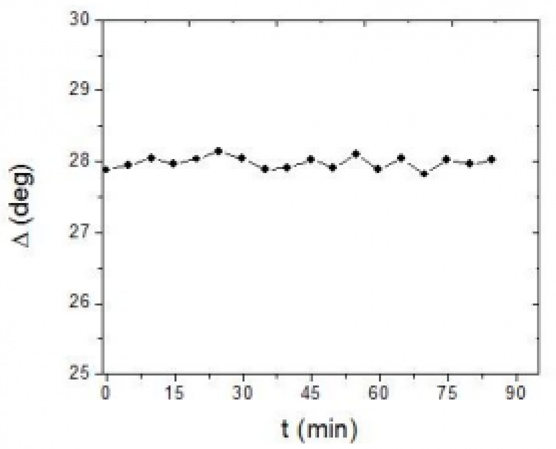



*Fig. 4 Measurement of long stability to the etalon sample $SiO_2$*

On the picture 4 is a graphical dependence of change elipsometric parameter Δ in dependence on the time. The measurement last for 90 minutes. The change of parameter Δ is shifting on the scale of ±0,31°. Mean square deviation computed from measured data is 0,083°, mean square deviation was determined by mean of formula:

$$\sigma_{x,n} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_n - x_i)^2} \tag{4}$$

**Experiment realization**

The base of the sensor system with using the surface plasmon polaritons is polarimeter . Angles, that we are able to achieve with our polarimeter, are not sufficient to generate SPP by pass-over air/metal. We use by realization of this experiment Kretchman configuration. Whereas deficient angels to the SPP excitation allow us not using air pass-over, measurement were realiyed in special case with water.

We put on the case optical prims and glass sample with thin gold layer, it is possible to apply various metals for example Ag or Pt, In our experiment we used only gold layer. We put the case with optical prims on the polarimeter’s stool polarimeter so that incident electromagnetic waves are incident in the middle of this configuration. Entire measurement is controlled by PC. To observe Kretchman configuration sample with gold layer is on the optical prims optical deposited by means of immersion oil. It is showed a schematic setting of the experiment on the Picture 5 by which were measurements realized. [5]

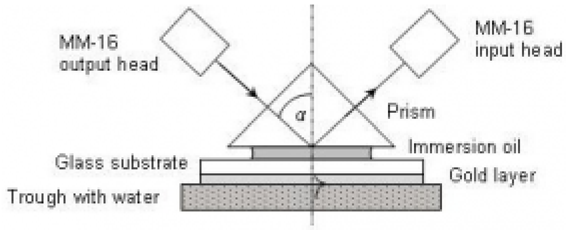



*Fig. 5 Kretchman configuration of SPR excitation by using spectroscopic ellipsometer MM-16.[6]*

We analyse measured data by parameter $R_p$, where we follow minimum shift of excited surface electromagnetic wave. By analysing ellipsometric parameter Δ we choose one wavelength from measured spectrum and we follow point shift in the vertical direction. In some cases we are able to evaluate better small changes, that we follow by the measurement, by parameter Δ, as by evaluating minimum position of excited plasmon. We determine parameter Rp by formula:

$$R_p = (m_{11} + m_{12} + m_{21} + m_{22})/2 \quad (5)$$

Where elements $m_{11}$, $m_{12}$, $m_{21}$, $m_{22}$ are elements Mueller matrix. [5]

**Excitation SPP with Kretchman configuration**

The first measurements were excitations of SPP by the different angels in the angel scale from 90° to 77° and in spectral scale from 430 to 850 nm. We tie in, by immersion oil, on oprical prim glass thin plate with thin gold layer. Immersion oil has near reflectivity index as a glass BK7. Materials used to optically tying in have to have identical or bigger reflexivity index as optical prim or any optical element. Excitation of surface plasmon polariton was by the interface electromagnetic waves through the air – optical prim– gold layer – distilled water in the teflon case with capacity 2 ml.

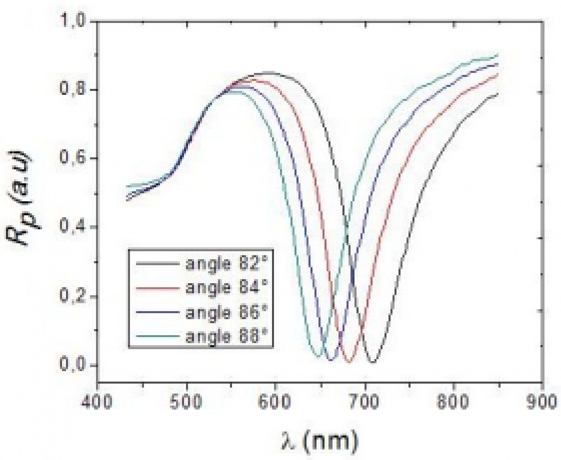



*Fig. 6 Depedency of $R_p$ on wavelength in dependence on the angle displacement. As s liquid we used distilled water.*

On graph is evidence of minimum´s SPP movement depending of angle. Measurement runs through by the constant angle, in the whole spectral scale, it is evaluated in dependence of the wavelength, what allow to us polarimeter Horiba Jobin Yvon. By the angle 82°is minimum of surface plasmon polariton by the wavelength 707 nm. Minimum of SPP is by the angle 88° by the wavelength 647 nm. Therefore can we see, that surface plasmon polariton is very sensitive to the angles changes. Even by change 6° is SPP minimum shifted by over 60 nm.

**SPP excitation in the various liquids**

In this case, we used to surface plasmon polariton excitation three different liquids: methanol, ethanol and distilled water. The measurements run through by the constant angle 83°.

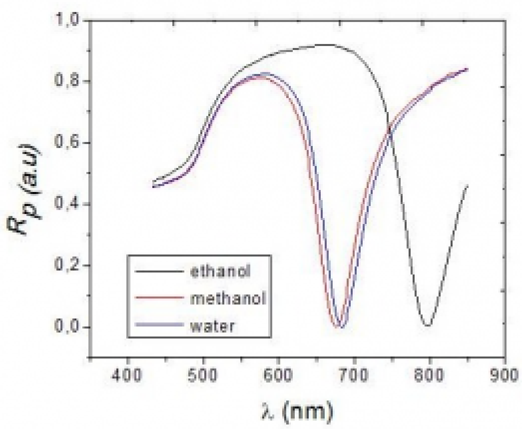



*Fig. 7 SPP comparison by the using different liquid: methanol, ethanol, water for the angle 83°*

On the graph is dependency of wavelength and parameter $R_p$. The blue line draws measurement, where was as liquid employed distilled water. SPP minimum for angle 83°is by the wavelength 683 nm, which was determined by the fit line with parable. Refractive index of distilled water by the wavelength 683 nm is 1,331. Refractive index of methanol by the same wavelength is 1,322. Whereas they are two different materials with near equal refractive index, by the equal wavelength are SPP process very similar, but are not identical.

**Dodekathiol adsorption on the gold surface**

Dodekathiol is chemical substance which is adsorbated on sample surface as intermediary by the laying on a multilayer on substrate. It is sensitive to the contact with air and humidity. Dotekanthiol is insoluble in the water and reacts violently with water vapour. It easily oxidizes on the disulphite and it is incompatible with oxidizers, reducers and alkaline metals. Adsorbated layer of dodecathiol on the sample is around 1 nm. Therefore is not possible to find out by ellipsometric measurement if this layer was laid on the sample, because our ellipsometer has resolution approximately 1 nm.

Alternative measurement is verification of adsorbated layer of dodecanthiol by the contact angle, then verification of surface wettability. It means, if was on the sample laid on a layer, then will change contact angle. It will be smaller than by the layer without dodecanthiol. Monitoring of adsorbtion is possible even with observation of surface electromagnetic wave shifting in dependence on time. [7]

Monitoring of adsorbtion of dodecanthiol on gold layer is possible with surface electromagnetic waves by monitoring of time in dependence on adsorbtion. As we discussed above, SPP are extreme sensitive to surface changes. We can register adsorbtion of dodecantiol on the gold layer with resonance of wavelength. Software DeltaPsi2 allows explanatory chart of ellipsometry parameter. If we make dependence of parameter Δ change to time, throughout which ran dodecanthiol adsorbtion on the sample with gold layer by the one wavelength we getdevelopment of this parameter shift.

Experiment was conducted in the laboratory conditions. Sample with gold layer was in the first step cleansed in the chloroform and subsequently set for 30 minutes under UV lamp, whereby was deprived contamination. The solution of ethanol with dodecantiol was mixed in proportion 2,8 µl of dodecantiol on the 20 ml ethanol. It is approximate $1{,}2 \times 10^{19}$ molecules of dodecantiol in the solution 1 mmol/l. The measurement ran as excitation surface plasmon, nobbut we used as liquid solution ethanol with dodecanthiol. Measurements were repeated every minute. It was necessary, during measurement, to fill up solution with pure ethanol, whereas ethanol is volatile substance and it quickly evaporates. Filling up with pure ethanol had not effect on the concentration of dodecanthiol particles in the solution used to absorption.

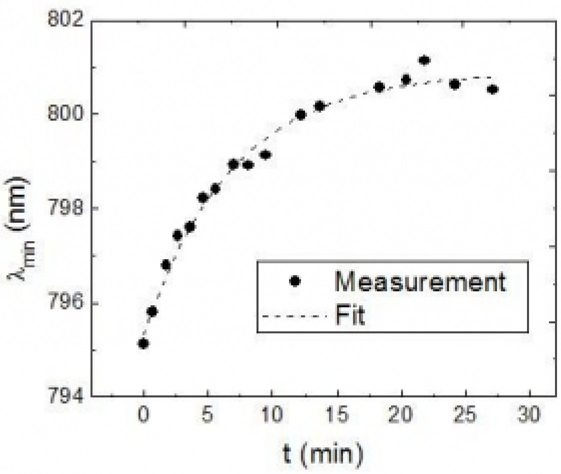



*Fig.8 Dependence of position's change of R_p minimum on time by the laying on dodecanthiol in ethanol*

On the figure 7 is dependence position's change of R_p minimum on time in comparison with fit of this dependence. Data were fitted with exponential function: $y=y_0- A \exp^{(-t/\tau)}$. Where the refraction parameters are: $y_0=(801\pm0{,}15)$ nm, $A=(5.58 \pm0.18)$ nm, $\tau=(6{,}92\pm0{,}61)$ min. By the analyses we proceed equally as in previous measurements. Measurement ran 40 minutes. By the analyses of resonance λ surface plasmon polariton we observed we systematic shift by 8 nm.

**Adsrorbate of cyklodextrin**

Cyklodextrins are in the water dissolvable oligosaccharides and polysaccharides. The term dextrin means degrading product of amyloid with content of reducing sugars. Dextrins are expressed as amyloids. They are final product of thermo- chemical amyloid processing. They are coloured with iodine according to chain length. For example, amylodextrines are blue, erytrodextrines are red and achrodextrines are colourless, in this sequence declines also their molecular weight. [8]

We are able, with surface plasmon polaritons, to follow time dependence of cyklodextrine adsorbtion mono SH – BCD on the gold layer. The measurement was realized in the Kretchman configuration on the gold layers by the angle 83° in whole spectral range of polarimeter Horiba Jobin Yvon MM- 16.

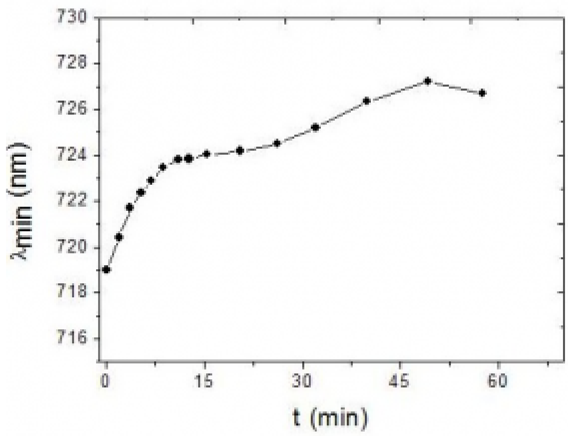



*Fig. 9 Time dependence of resonance λ by SH – BCD adsorbtion on the gold layer surface*

Measurement was realized by constant angle 83° in the time interval 60 minute. The aim of measurement was observation of excited surface plasmon polariton shift by adsorbtion of cyklodextrine SH – BCD on the gold layer. On the figure 8 is systematic shift of SPP position. From measurement result we are able to point out that there give out to cyklodextrine adsorbtion on the gold surface of the sample. Hereby, we are able to observe by the means of surface plasmon polariton absorbtion of dodekathtiol.

## Conclusion

The problematic of surface plasmon polariton is broad and comprehensive. In this paper we wanted to dedicate SPP excitation with utilitization of Horiba Jobin Yvon MM- 16 and to verification of their sensitive by very small condition change, for example by the small change of temperature or by the using different liquid with a very similar refractive index such as distilled water and also to follow directly by the measurement behaviour of surface electromagnetic waves by the adsorbation another substance on the metal surface. These experiments are only beginning and the first steps by the construction of complete sensor system with utilitization surface electromagnetic waves.

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