SPR APPROACH FOR DETERMINATION OF TEMPERATURE WATER REFRACTIVE INDEX ALTERATIONS

APLIKACE METODY SPR PRO STANOVENÍ TEPLOTNÍCH ZMĚN INDEXU LOMU VODY

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Abstract

The paper is devoted to surface plasmon resonance (SPR) technique applied to the specification of refractive index deviation. The main idea is concentrated to specify the possibilities of SPR for the study of water refractive index changes influenced by temperature. Special attention was devoted to the comparison of experimental results with theoretical predictions.

Abstrakt

Článek je zaměřen na techniku povrchových plazmonů (surface plasmon resonance - SPR) aplikovanou ke studiu změn indexu lomu. Hlavní část je věnována možnostem SPR pro studium změn indexu lomu vody vyvolaných posuvem teploty. Speciální pozornost je zaměřena na porovnání experimentálních výsledků s teoretickými modelovými výpočty.

Key words: Surface Plasmon Resonance - SPR, Reflectivity, Refractive Index.

1 INTRODUCTION

Since surface plasmon resonance (SPR) was observed by Wood in 1902 [1, 2], the physical phenomenon of SPR has found its way into practical applications in sensitive detectors, capable of detecting sub-monomolecular coverage. Physical interpretation of the phenomenon was initiated by Lord Rayleigh [3], and further refined by Fano [4], but a complete explanation of the phenomenon was not possible until 1968, when Otto [5] and in the same year Kretschman and Raether [6] reported the excitation of surface plasmons. The pioneering work of Otto, Kretschmann, and Raether established a convenient method for the excitation of surface plasmons and their investigation, and they introduced surface plasmons into modern optics. Application of SPR-based sensors to biomolecular interaction monitoring was first demonstrated in 1983 by Liedberg et al. [7].

SPR instrumentation can be configured in various ways to measure the shift of the SPR-dip. In general, three different optical systems are used to excite surface plasmons: systems with prisms, gratings and optical waveguides. Instruments with a prism coupler are most widespread [8]. In this configuration, a prism couples p-polarized light into the sensor coated with a thin metal film. The light is reflected onto a detector, measuring its intensity, using a photodiode or a camera. In instruments with a grating coupler [9], light is reflected at the lower refractive index of substrate [10]. Besides the grating couplers, some instruments apply optical waveguide couplers [11].

SPR belongs to modern optical methods that during the last decade found the assertion in the detection and analysis of solid and liquid materials. The extreme sensitivity of SPR to small changes in refractive index (up to 10^{-8}, [12]) is used primarily in sensors, expecially as very sensitive detectors of various substances in biology and chemistry, determining thicknesses of layers adsorbed on metal surface or to study the kinetics of chemical reactions [13].

At Institute of Physics VSB-TU of Ostrava it was decided to extend experimental possibilities of laboratories by the SPR setup. This was achieved by modification of one of present instruments. Some measurements of liquid samples have been done by excitation of SPR method. The results are present for the specimen of NaCl melted water. The results confirmed the possibility of spectral SPR measurements with high precision.

2 THEORY

The propagation constant of plasmon wave is always higher than that of electromagnetic wave in the dielectric and thus the plasmons cannot be excited directly by an incident optical wave at metal-dielectric interface. Therefore the wave vector of the incident optical wave has to be enhanced to match that of plasmon wave. This momentum change is commonly achieved by prism couplers, diffraction gratings, or waveguides in planar structures. When surface plasmon wave is induced it manifests itself as a significant loss in reflectivity at specific angle [14]. In this paper, we apply the Kretschmann-Reather configuration: coupling prism, metal thin film, and inspected medium (Fig.1).

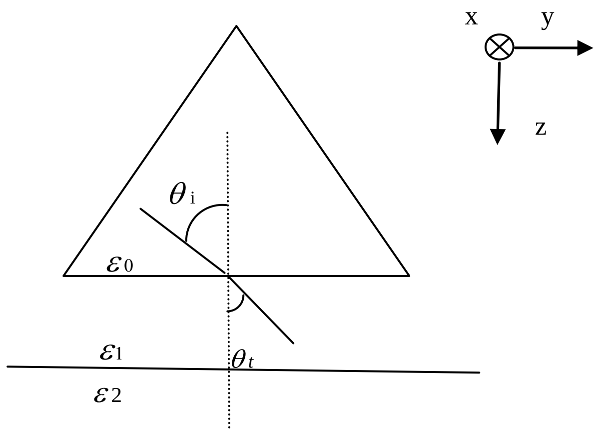

Fig. 1 A prism / metal / water-Kretchmann SPR configuration

For our case of three layered media, the reflection coefficient can be modified as:

$$r_{012} = \frac{r_{01} + r_{12}\exp(-2ik\beta d)}{1 + r_{01}r_{12}\exp(-2ik\beta d)} \tag{1}$$

where r_{01} and r_{12} represent the reflection coefficients on the boundaries 0-1 and 1-2, the parameter d specifies the gold thin film thickness, and k is wave number in vacuum, respectively.

And we can define the value of β mentioned in (1):

$$\beta = N_1 \cos\theta_1 . \tag{2}$$

Because surface plasmon waves are generated at p-polarization waves, we can write:

$$r_{01} = \frac{N_1\cos\theta_i - n_0\cos\theta_1}{N_1\cos\theta_i + n_0\cos\theta_1}, \tag{3}$$

$$r_{12} = \frac{n_2 \cos\theta_1 - N_1 \cos\theta_2}{n_2 \cos\theta_1 + N_1 \cos\theta_2}.$$

$n_0, N_1, n_2, \theta_i, \theta_1, \theta_2$ represent the refractive index of prism, gold, and measured medium, incident angle, complex refractive angle in the gold, and transmission angle, respectively. In the SPR experimental configuration, the thin gold film located on the prism is frequently applied. The refractive index of metallic layer can be expressed in complex number:

$$N_1 = n_1 - ik_1 = n_1(1 - ip_1) \tag{4}$$

where $p_1 = \frac{k_1}{n_1}$.

And write the reflectivity for our experimental arrangement:

$$R_p = r_{012} \bullet r_{012}*, \tag{5}$$

where $r_{012}*$ means complex conjugate to r_{012}.

The real refractive angle θ_t in metallic medium can be expressed from the requirement of the continuity of the tangential field components at the interface 0-1:

$$\cos\theta_t = \frac{n_1 q(\cos a + p_1 \sin a)}{\sqrt{n_0^2 \sin^2\theta_i + n_1^2 q^2 (\cos a + p_1 \sin a)^2}}. \tag{6}$$

The values q and a in (4) are related to the incidence angle θ_i and metallic parameters:

$$q^2 \cos 2a = 1 - \frac{n_0^2 (1 - p_1^2) \sin^2\theta_i}{n_1^2 (1 + p_1^2)^2}, \tag{7}$$

$$q^2 \sin 2a = -\frac{2 p_1 n_0^2 \sin^2\theta_i}{n_1^2 (1 + p_1^2)^2}.$$

As an example the reflectivity for p-polarized light at 632.8 nm has been computed for our three-layered structure for the following parameters: n_0 = 1.7231 (SF 10 prism), n_1 = 0.1838 – i3.4310 (gold film), and temperature modified refractive index of water (n_2 = 1.32 – 1.34). The value dependence of R_p reflectivity influenced by the angle of incidence (θ_i) for three different refractive indices of ambient medium is demonstrated on Fig. 2.

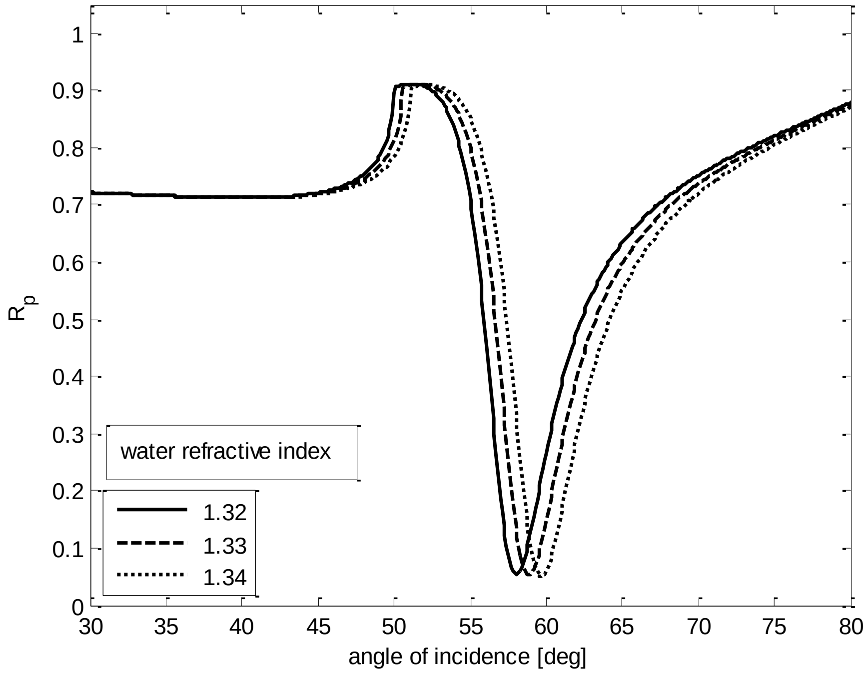

Fig. 2 Reflectivity R_p versus incidence angle θ_i for three different refractive indices of ambient medium

3 EXPERIMENTAL ARRANGEMENT

Apparatus is based on Gaertner L119 ellipsometer which has been previously modified to fully automatic, computer controlled operation [15, 16]. A simplified scheme of the setup with variable angle is displayed in Fig. 3. Wavelength selectable HeNe laser serves as a light source, irradiating on wavelengths of 543, 594, 604, 612, and 633 nm, respectively. Before reaching the sample the light is polarized by Glan-Thompson prism and part of the light is reflected on the beamsplitter to the reference detector. The intensity of the light reflected from the sample is measured by the other detector attached on traversable arm.

The second setup is shown in Figs. 4 and 5. The Xe lamp serves as a light source, in this measurement the wavelength is variable and angle is fixed. The USB650 Red Tide Spectrometer with wavelength range 350-1000 nm is applied.

Kretchmann-Raether configuration for exciting surface plasmons is used [17]. The samples with prism coupler are placed on a rotation stage allowing to set incidence angles with precision of some arc seconds. Our experimental arrangement enables to analyse solid state samples or liquid ones using flow cell.

The setup is operated by a personal computer and the whole measuring procedure is fully automatized.

Control software, including graphic interface, was created in LabWindows/CVI (National Instruments Inc.) development environment.

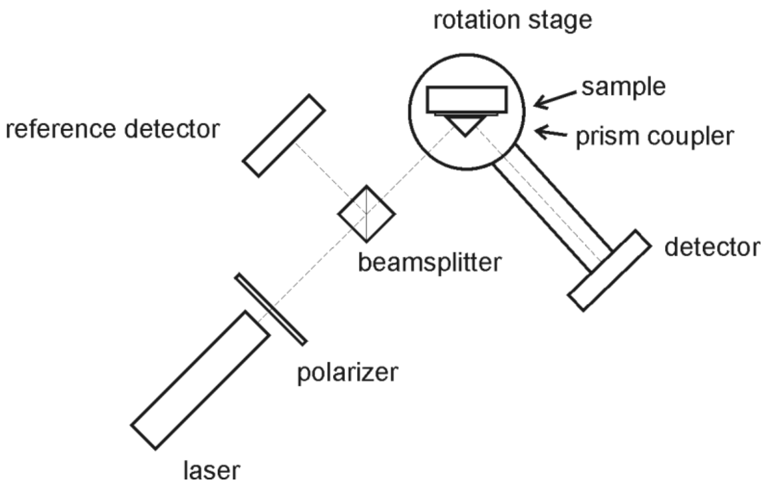

Fig. 3 Scheme of experimental geometry with variable angle

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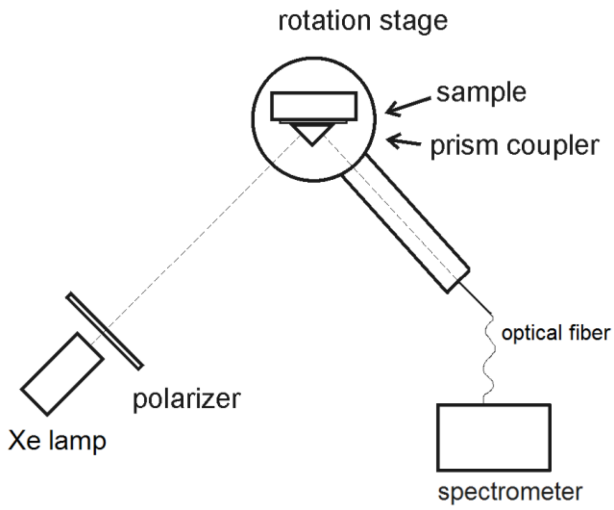

Fig. 4 Scheme of spectral experimental arrangement

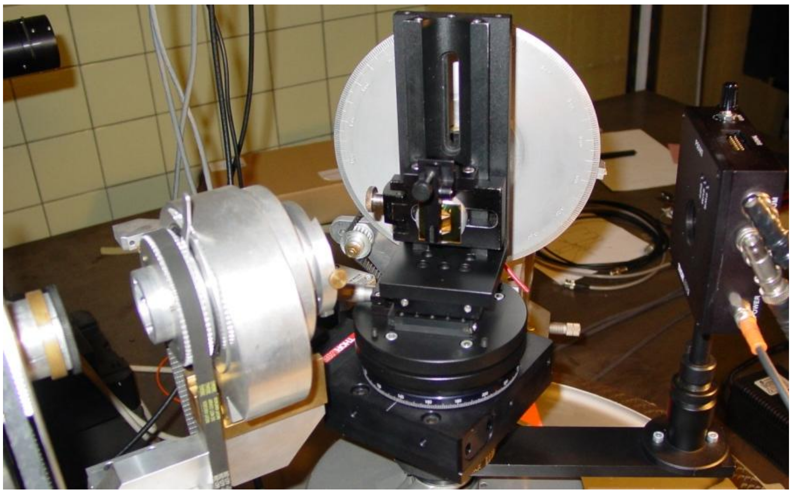

Fig. 5 Detail of experimental setup. Rotation stage with sample (in the middle)

4 EXPERIMENTAL RESULTS

The experiments have been realized by a modified arrangement of the Gaertner ellipsometer [18]. To generate plasmon waves the spectral experimental setup with SF 10 prism coated by nano gold film has been applied. During measurement the incident angle of incoming plane wave was fixed to 63 degrees (to the normal of the prism base). The wavelength of the incoming light was in the band from 550 nm to 820 nm. The temperature refractive index dependence of the water was studied by heated chamber for liquid samples. The temperatures have been changed from 27.8 ºC to 46 ºC. The experimental results – the spectral dependences of reflectivity for different temperature values are demonstrated on Fig. 6.

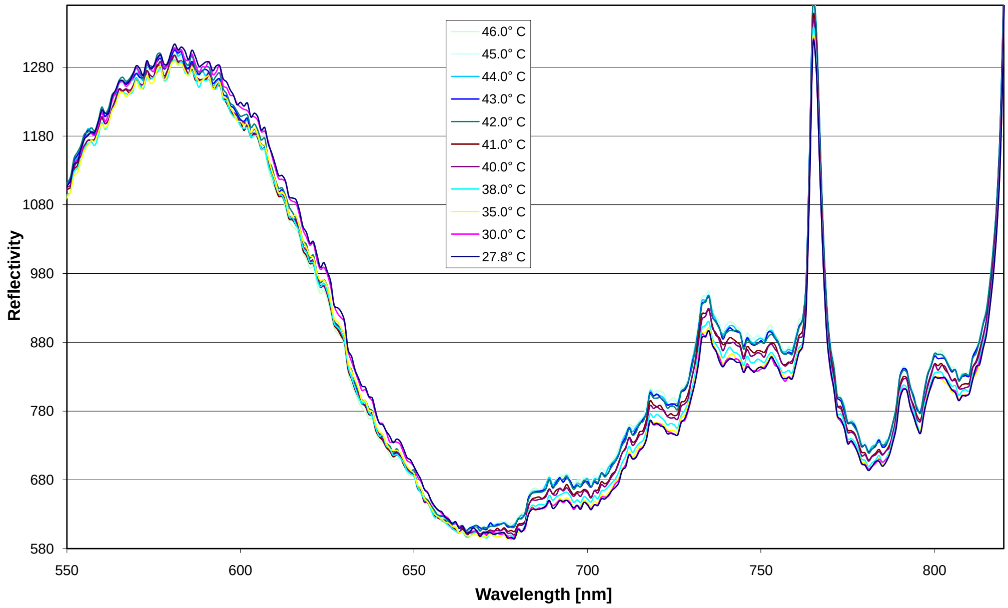

Fig. 6 Spectral SPR reflectivity as function of water temperature

5 CONCLUSIONS

The influence of the temperature on water refractive index has been described by various authors – e. g. [19]. The published values of the temperature derivate dn/dT of the mentioned refractive index at 632.8 nm for room close temperature are in the range (-96 to -106) x 10^{-6} K^{-1} [19, 20, 21]. These values are in the frame of SPR sensitivity. In our experimental arrangement the 1 ºC temperature shift of liquid sample generated the reflectivity feedback of about 0.25 % (Fig. 6). It is in good accordance with the theoretical prediction (Fig. 2). SPR technique can be in this case successfully applied to the temperature dependence specification of optical parameters of water.

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REFERENCES

[1] Wood R.W., *Philos. Mag*., 1902, 4, 396-402

[2] Wood R.W., *Philos. Mag*., 1912, 23, 310-317

[3] Lord Rayleigh, Proc. R. *Soc. London, Ser. A*, 1907, 79, 399

[4] Fano U., J. Opt. Soc. Am., 1941, 31, 213-222

[5] Otto A., Z.. Phys., 1968, 216, 398-410

[6] Kretschmann E. and Raether H., Z.. *Naturforsh*., Teil A, 1968, 23, 2135-2136

[7] Liedberg B., Nylander C. and Lundstorm I., *Sens. Actuators*, 1983, 4, 299-304

[8] Kretschmann E., Z.. *Phys*., 1971, 241, 313-324

[9] Wassaf D., Kuang G., Kopacz K., Wu Q. L., Nguyen Q., Toews M., Cosic J., Jacques J., Wiltshire S., Lambert J., Pazmay C. C., Hogan S., Ladner R.C., Nixon A. E. and Sexton D. J., Anal. *Biochem*., 2006, 351, 241-253

[10] Perez-Moralesa M., Pedrosab J. M., Munoza E., Martin-Romeroa M. T., Mobiusc D. and Camachoa L., *Thin Solid Films*, 2005, 488, 247-253

[11] Ctyroky J., Homola J. and Skalsky M., *Opt. Quantum Electron*., 1997, 29, 301-311

[12] Slavik R., Homola J., *Ultrahigh resolution long range surface plasmon-based sensor*, Sensors and Actuators B 123, 2007, 10-12

[13] Homola J., Yee S. S., Gauglitz G., *Surface plasmon resonance senors: review*, Sensors and Actuators B 54, 1999, 3-15

[14] Raether H., *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*, Springer, Berlin 1988, ISBN 3-540-17363-3

[15] Lesňák M., Luňáček J., Talik A. , Hlubina P., Pištora J., *Úprava elipsometru Gaertner L119 a jeho použití pro studium tenkých vrstev*, Jemná mechanika a optika 2, 2007, p. 40-42, ISSN 0447-6441

[16] Višňovský Š., Yamaguchi T., Pištora J., Postava K., Beauvillain P., Gogol P., *Undirectional propagation in planar optical waveguides*, ISBN 80-248-1186-3, VŠB-TU Ostrava 2006

[17] Raether H., Surface *Plasmons on Smooth and Rough Surfaces and on Gratings*, Springer, Berlin 1988, ISBN 3-540-17363-3

[18] Talik A., Lesňák M., Vlašín O., Pištora J., *Design and realization of SPR setup for measuring method*, Geoscience Engineering 54, No. 1 (2008), ISSN 1802-5420

[19] Schiebener P., Straub J., Levelt Sengers J. M. H., Gallagher J. S., J. Phys. Chem. Ref. Data 19, 1990, 677

[20] Kaye G. W., Laby T. H., *Tables of Physical and Chemical Constants*, Longman Group, London 1986

[21] Hauf W., Grigull U., *Optical Methods in Heat Transfer*, Academic Press, New York 1970

RESUMÉ

Článek je zaměřen na techniku povrchových plazmonů (surface plasmon resonance - SPR) aplikovanou ke studiu změn indexu lomu. Hlavní část je věnována možnostem SPR pro studium změn indexu lomu vody vyvolaných posuvem teploty a na porovnání experimentálních výsledků s teoretickými modelovými výpočty.

Modelový přístup studia reflectivity na vícevrstevnatém rozhraní byl realizován na bázi Yehova maticového formalismu. Experimentální část probíhala v prvním případě na modifikované elipsometrické sestavě firmy Gaertner pro pět vlnových délek interagujícího světla He-Ne laseru: 543 nm, 594 nm, 604 nm, 612 nm a 632.8 nm. Ve druhém případě byla aplikována xenonová lampa a měření byla prováděna spektrálně v pásmu 550 až 850 nm. Teplota vody v měřicím boxu se měnila v intervalu 27.8 ºC až 46 ºC.

Teplotní gradient indexu lomu vody se uvádí v pásmu (-96 až -106) x 10^{-6} K^{-1}. Dosažené experimentální výsledky prokázaly velmi dobrou kompatibilitu s teoretickými modelovými přístupy a potvrdily možnost využití experimentální techniky plazmonových vln ke studiu teplotního gradientu indexu lomu vody.