SPECTROSCOPIC ELLIPSOMETER AS A SENSOR BASED ON SURFACE PLASMON POLARITONS

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1. Introduction

Surface plasmon resonance (SPR) is an effect occurring on metal/dielectric interfaces. When the matching condition is fulfilled, surface plasmon polaritons can be excited. Although the first observation of SPR on diffraction grating was made by and R. M. Wood alreadey in 1900 [1], in the 80's of 20th century only it founds wider application as biosensor. Due to the high sensitivity of SPR to interface quality, SPR sensors could register presence as well as structural change of monomolecular layer on the metallic surface. Such sensors are commercially fabricated and used mainly in the fields of surface biochemistry. Kinetics coefficients, adsorption constants, binding constants, and other parameters important in the surface chemical processes can be measured using these equipments [2].

In this work we show a possibility to utilise the spectroscopic polarimeter (ellipsometer) Horiba Jobin-Yvon MM-16 as SPR based sensor. Although an ellipsometer is over-equipped for such purpose, if someone wants to measure slow surface chemical processes, ellipsometer could help. While many wide-used ellipsometers cannot measure layers thinner than 1 nm, SPR can also enhance their capabilities. The ability of such device to measure time dependent measurement with characteristic times larger than 10 s are also shown.

2. SPR and ellipsometry

Usually, SPR excitation is observed as reflectivity dip when the condition of excitation is fulfilled [3]:

$$k_{\parallel} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_{\mathrm{d}}\varepsilon_{\mathrm{m}}}{\varepsilon_{\mathrm{d}}+\varepsilon_{\mathrm{m}}}} \qquad (1)$$

where $k_{\parallel}$ is the SPR wave vector component parallel to the interface surface, ε_{d} and ε_{m} are dielectric constants of the dielectric and metalic material, respectively.

The optimal condition is reached by setting an appropriate angle of incident to match the dispersion relation Eq. (1). Another way is to find available wavelength (frequency) of incident light at fixed angle of incidence. The first case is the basic principle of commercial SPR based sensors. One needs just monochromatic polarized source (He-Ne laser) and two-arm goniometer. The second, wavelength matching scheme, needs wide spectral source, polarizer and monochromator. The angle matching concept is better in many aspects, e.g. faster measurement and high angle sensitivity of goniometer. On the other hand, spectroscopic ellipsometer is equipped with stabilized wide spectral source, polarizer and analyzer; and monochromator with CCD can acquire whole spectrum at once in relatively short time. The shortest measurement time of Horiba Jobin-Yvon MM-16 is 2 s. The processes with characteristic time constant from about 10 s could be studied.

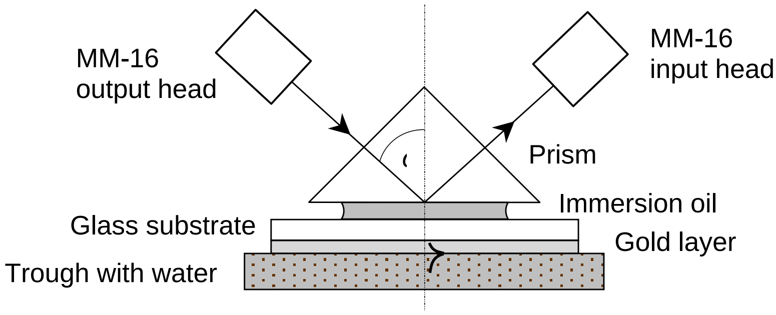

Fig. 1 *Kretchman configuration of SPR excitation by spectroscopic ellipsometer MM-16.*

The output of one polarimetric measurement is spectrally dependent 15 elements of the Mueller matrix. Reflectiviy R_p of p-polarized incident light is related to the Mueler matrix by the following expression [4]:

$$R_p = \left(m_{11} - m_{12} - m_{21} + m_{22}\right)/2 \tag{2}$$

where m_{ij} are corresponding elements of the first block of the Mueller matrix. In standard ellipsometry, a pair of ellipsometric parameters Δ and ψ is the usual output. Their meaning is clear from the ellipsometric equation [5]:

$$\frac{r_p}{r_s} = \tan\psi \exp(\mathrm{i}\Delta) \tag{3}$$

where r_p and r_s are the amplitude reflectivities of the measured sample for s-polarized and p-polarized light respectively. Since the SPR excitation is realized through evanescent wave in the total internal reflection, the r_s is close to 1, so we can write

$$r_p = \tan\psi \exp(\mathrm{i}\Delta) \qquad \text{and} \qquad R_p = |r_p|^2 = \tan^2\psi \tag{4}$$

The SPR excitation is a resonant process, the incident light is in resonance with plasmon polariton. That is why Δ serves as a phase of complex variable r_p in resonance and changes rapidly. This is useful to enhance the SPR measurement sensitivity. Except of finding the resonant λ_R, for which R_p achieves minimum, one can find so-called „work point“ at the linear part of spectra and measure change of Δ. The commercial SPR sensors work with the first derivation of angle spectra of R_p. The advantage of ellipsometry is that the measurement gives directly the phase parameter Δ. Therefore, we need no differentiation of measured data, which could lead to quite serious difficulties in the case of any noise presence.

3. Experiment and Results

We have used Kretchman's configuration in our experiments (Fig. 1). The equipment consists of optical right-angle BK-7 prism, immersion oil, 50 nm gold layer on BK-7 glass substrates and teflon trough (2 ml). Light source and detector provided spectroscopic polarimeter Horiba Jobin-Yvon MM-16 with motorised goniometer. The range of angles is 45 to 90 degrees. Spectral rage is 430 nm – 850 nm.

Fig. 2 shows the long-term measurements of SPR with destilated water. Open trough meaurements are plotted in the left panel. Systematical shift of Δ indicates that the measurement is not stable. This could be caused by evaporation of water resulting in the changes of temperature of water. The right panel of Fig. 2 depicts measurement with closed trough. No significant systematic shift is present. Standard deviation of Δ is σ_Δ = 0.62°. This value is considered to be the reference value in the estimation of the SPR measurements

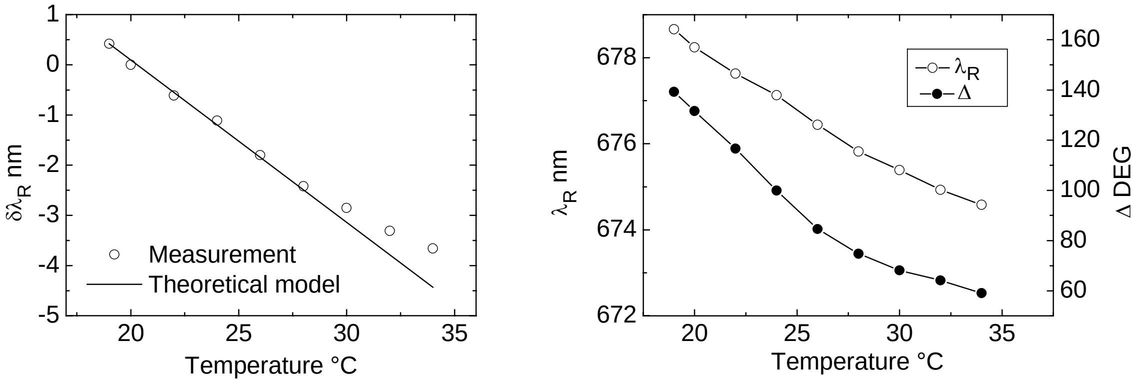

Fig. 3 *Dependence of the resonant wavelength of SPR on the temperature of water. Andgle of incidence was 83°, Δ was measured at 677 nm*

accuracy. The standard deviation of λ_R is extremely small, σ_λ = 0.4 nm, an order of magnitude below the spectral resolution of the ellipsometer (2 nm). We conclude that the equipment is stable.

Results of the thermal measurements are shown in Fig. 3. The left panel shows the comparison of measurement and theoretical model. We put into the trough water with temperature 35 °C and let it cool to the room temperature (19 °C). The temperature of water was measured by digital thermometer. The reason of the differences between measurement and analytical calculation at higher temperatures is that the theoretical model took into account only the temperature and refractive index of water, meanwhile, in the real experiment also glass substrate and the prism are partially heated.

From the left panel of Fig. 3 the gradient of Δ near room temperature can be estimated: $\partial\Delta/\partial T$ = 15 °/K. With connection to the long-term measurement and the standard deviation of Δ, our device is able to measure temperature change of water $\sigma_T = \sigma_\Delta(\partial\Delta/\partial T)$ = 0.043 K. The temperature gradient of refractive index of water near the room temperature is $\partial n/\partial T = -8.0\times10^{-5}$ K^{-1} [6]. It follows that the smallest detectable change of refractive index is $\sigma_n = 3.3\times10^{-6}$.

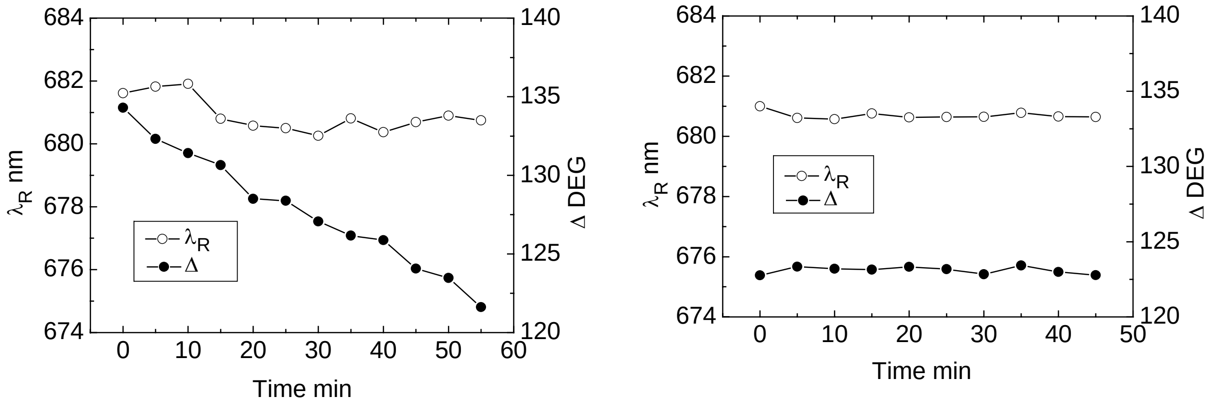

Fig. 2 *Long-term measurements with open trough (left) and closed trough (right). Angle of incidence was 83°, Δ was measured at 680 nm.*

Demonstration of the device potential is shown in Fig. 4. The time dependence of SPR resonant wavelength during adsorption of dodecanethiol on gold surface was measured using 1 mmol/l solution in ethylacohol. The molecule is an alkyl chain consisting of 12 carbons and one SH (thiol) group. Sulfur can bind gold via covalent bound and creates compact monolayer of surfactant. SPR change is caused by its gradual growth. Even if the

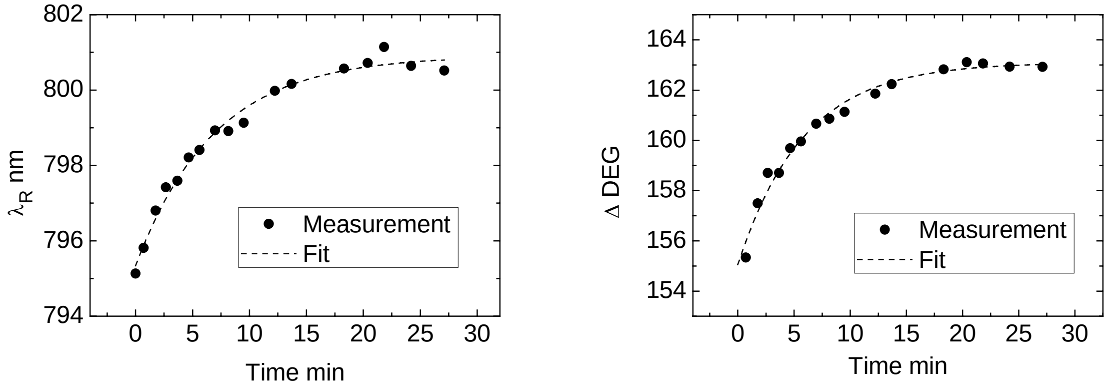

Fig. 4 *Adsorption of dodecanethiol measurements by SPR. Angle of incidence was 83°, Δ was measured at 788 nm. Data are fitted by exponential function* $y = y_0 - A\exp(-t/\tau)$*. The parameters for reflectivity minima (left):* $y_0 = (801 \pm 0.15)\,\mathrm{nm}$, $A = (5.58 \pm 0.18)\,\mathrm{nm}$, $\tau = (6.92 \pm 0.61)\,\mathrm{min}$ *and for* Δ *(right):* $y_0 = (163 \pm 0.27)\,°$, $A = (8.05 \pm 0{,}37)\,°$, $\tau = (5.85 \pm 0.72)\,\mathrm{min}$

time curve can be fitted by exponential function, the time parameter $\tau \approx 6\,\mathrm{min}$ is strogly affected by diffusion of dodecanthiol in liquid solution.

4. Conclusion

We have presented SPR based sensor measurements using spectroscopic ellipsometer. In the vicinity of the SPR resonance λ_R, we observed rapid changes of Δ, while is still linear in λ. Changes of refractive index 3.3×10^{-6} of water have been detected. The first long time experiments revealed the need to equip the device by thermally isolated closed SPR cell. The ellipsometer is sensitive enough to measure time dependent dodecanethiol monolayer adsorption. For studying other chemical parameters, advanced equipment must be used, as flowing closed thermaly stabilised cell.

Acknowledgement

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