Lithuanian Journal of Physics, Vol. **47**, No. 1, pp. 81–85 (2007) doi:10.3952/lithjphys.47113

MONOLAYER FILM ANALYSIS BY TOTAL INTERNAL REFLECTION ELLIPSOMETRY

V. Vaičikauskas and Z. Balevičius

Institute of Physics, Savanorių 231, LT-02300 Vilnius, Lithuania
E-mail: vikvai@ktl.mii.lt

Received 14 December 2006

The surface plasmon resonance (SPR) method combined with spectral ellipsometry was used to study the chemically formed octadecanthiol (ODT) monolayer on a gold film in Kretchmann configuration. Measurements were made with a commercial spectral ellipsometer GES-5 (SOPRA). The optical constants of an Au film and ODT at 1000 nm wavelength were determined by the best fit procedure from experimental data (Au: $n = 0.202$, $k = 5.970$ and ODT: $n = 1.4$, $k = 0$). Combination of the SPR method with advantages of phase measurements of ellipsometry demonstrated a substantial increase in sensitivity (more than one order of magnitude) compared with conventional ellipsometry.

Keywords: spectral ellipsometry, surface plasmon resonance, octadecanthiol

PACS: 87.80.y, 73.20.Mf, 78.66.Bz

1. Introduction

An increasing need for larger integration densities, and thus smaller feature sizes, has been the driving force of modern solid state electronics and sensorics. Ellipsometry and the surface plasmon resonance (SPR) techniques are widely used for determination of the refraction index n and the absorption index k of thin films. One of the most valuable peculiarities of ellipsometry is that one measures both the phase and the amplitude of elliptically polarized light reflected from surfaces. Phase methods are widely used in physics and measurement technology and in most cases are more sensitive than amplitude ones. The theory for internal reflection ellipsometry (IRE) is fully contained in the Fresnel formalism [1]. A more detailed analysis of IRE ellipsometry with experimental demonstrations was done by Arwin [2].

The ellipsometric angles ψ and $\Delta \equiv \Delta_p - \Delta_s$ are defined by

$$\tan\psi = |\rho|\,, \quad \Delta = \tan^{-1}\frac{\mathrm{Im}(\rho)}{\mathrm{Re}(\rho)}\,, \qquad (1)$$

where ρ is a complex reflection coefficient. These parameters depend only on the ratios or differences for the two main polarization directions. An angular change of $0.001\,^\circ$ can be measured with a state-of-the-art ellipsometer, and the minimum layer thickness that can be detected is of the order of ≈0.005 Å for visible wavelengths [3].

Spectral ellipsometry measurements of Abelès [4] have shown that the use of ellipsometric techniques together with SPR enables further information on the SPR to be gained, including information about the phase change. Recently, the SPR phase method has been successfully applied to a very sensitive measurement of the angle of incidence (0.2 arcsec) [5]. Monolayer sensitivity of interferometric surface plasmon resonance imaging has been demonstrated for self-assembled thiol on a gold substrate [6]. The computed SPR phase curves show that the refraction index changes as small as $3\cdot10^{-7}$ can be measured [7].

Only a few works about attempts to realize SPR and ellipsometry techniques in one set-up are known in literature. However, a combination of two different experimental methods sometimes gives very good results [6, 8]. Namely, successful combination of SPR and optoacoustic methods enabled sensitivity of 10^{-6} in the refractive index of gas [6]. In most measurements ellipsometry operates in the external reflection mode. However, operation in the internal reflection mode is also possible and has been used with a cell in an attenuated total reflection set-up to determine the optical constants of liquids at infrared wavelengths [9]. Evanescent field ellipsometry was applied to the investigation of swelling of polymer brushes [10]. Vaicikauskas et

ISSN 1648-8504

al [11] theoretically and experimentally showed advantages of the SPR phase method against the amplitude one using a very simple scheme of the rotating analyzer ellipsometer. They showed an increase in sensitivity of the ellipsometric method for thin film detection even up to two orders of magnitude when combined with the SPR technique. A two-beam differential scheme was used: one beam passed the attenuated total reflection (ATR) prism without SPR excitation, the second one at SPR excitation. Later Hooper [12] improved the measurement technique using the polarization modulation technique. The smallest refractive index change of 10^{-7} refractive index units, which is resolvable, was obtained. An optical heterodyne phase-shift detection scheme was applied to a very sensitive SPR phase measurement using the frequency-stabilized Zeeman laser [13]. Rekveld [14] used single-wavelength ellipsometry in the internal reflection mode to monitor the protein adsorption. Combination of ellipsometry and SPR techniques later was called the SPR-enchanced ellipsometry [15].

In this work we experimentally realized the advantages of two techniques when combined into one set-up: the localization of the electromagnetic field in SPR geometry and the possibility of reflected wave phase measurement by ellipsometry. Drastic changes in the SPR amplitude and phase were measured in the angular scan mode using a spectral ellipsometer. Very good sensitivity for analysis of monolayer films on metal was demonstrated.

2. Experimental set-up

2.1. Samples

The procedure of sample fabrication was the following. We used the BK7 glass prism as a substrate for the Au film evaporation. At first, we precisely determined the refraction index n_p of the prism from the total internal reflectance angle measurement in glass / air interface ($n_\mathrm{p} = 1.5075$). Then, we thermally evaporated a thin Au film, the thickness of which was measured using a profilometric technique and from the SPR curve measurements as well. After that, an octadecanthiol (ODT) layer was chemically formed on the evaporated gold film by incubating the sample prism hypotenuse in 0.1 mM solution of ODT during 24 hours.

2.2. Optical sketch

A schematic view of total internal ellipsometry with plasmon excitation (Kretchmann configuration) is shown in Fig. 1. The GES-5 type (SOPRA, France) rotating-polarizer spectral ellipsometer with extended spectral region up to 2.0 μm was used for determination of principal ellipsometric angles ψ (Psi) and Δ (Delta). A 75 W collimated xenon lamp mounted in the air-cooled module was used for SP excitation when light passed the ATR prism. The polarizer and analyzer both made of high quality Roshon prisms were mounted on hollow axis stepper motors. In our measurements the analyzer angle was fixed at 45 °. Collimating optics ensured beam divergence of about 1 mrad. Both arms of the goniometer are computer-controlled and the position repeatability of both arms was $\pm 0.01\,^\circ$. The incident angle range could be selected from 7 to 90 °. It allowed a precise angular scan of the SPR curve at fixed wavelength as well as a spectral scan at the plasmon resonance angle. The wavelength accuracy was 0.2 nm at infrared wavelengths. Simulation of sample spectra was accomplished using WinElli II software. The ATR prism was put on an adjustable sample holder of the ellipsometer (Fig. 1).

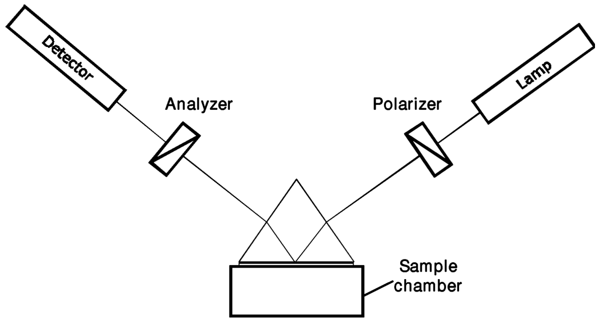

Fig. 1. Scheme of surface plasmon excitation with ellipsometer.

3. Results and discussion

The experimental curves of ellipsometric parameters ψ and Δ are presented in Figs. 2 and 3. At first, we made spectral measurements of ψ and Δ on a gold film. The resonant feature of surface plasmon was observed at 1 μm wavelength seen as a wide minimum in the curve of the reflection spectrum. After that, we fixed this wavelength of the ellipsometer and performed the angular scan of the SPR curve. After the best fit procedure of curve *1* in Fig. 2 using noncommercial "Thin Films" software, a complex refraction index and thickness of Au film were obtained at 1 μm wavelength: $n = 0.202$, $k = 5.970$, and thickness $d = 35.2$ nm. The estimated thickness was the same as that measured by the profilometric technique. An even better curve fit was obtained when the additional 0.3 nm gold oxide Au_2O film ($n = 1.5$, $k = 0$) was introduced on gold surface.

Very close values of optical constants were obtained from curve *1* in Fig. 3.

The formation of the octadecanthiol monolayer on a gold film caused a slight shift (by about 0.1 °) of the SPR curve towards higher angles, corresponding to curve *2* in Figs. 2 and 3. From the best fit procedure using earlier determined optical constants of a gold film we obtained optical constants for the ODT monolayer: $n = 1.4$, $k = 0$, and $d_{\mathrm{ODT}} = 2$ nm.

Calculations show that the presence of the dielectric layer on the gold film qualitatively changes the character of the SPR field. There is a redistribution of SPR field energy, and the additional maximum emerges in the distribution function for the Poynting vector. Since a larger part of the SPR energy becomes localized in the dielectric film, the sensitivity of the method increases significantly. We have found that the SPR amplitude method gives the same optical constants as the SPR phase method when the films are in the tens of nanometre range, or thicker. However, it is important to point out that the SPR phase method for films in the nanometre and subnanometre range is more sensitive due to peculiarities of measurements in the time domain. It is also clear that ellipsometric measurements outside the resonance region (below 42 ° or above 43.5 ° angle of incidence) would give much smaller reflection and phase changes. Comparison of relative changes in Δ and ψ values at 42 and 42.6 ° indicates a 15 and 32 times higher change in these values under SPR excitation (Figs. 2 and 3). If measurements are performed in the external reflection ellipsometric mode instead of the internal one, the change in the Δ value is very difficult to measure even at the pseudo-Brewster angle of incidence.

The obtained optical constants and thickness of octadecanthiol should be compared with those obtained by using other techniques. The formation of organic monolayers on gold has been well investigated during the recent two decades. Various monolayer characterization techniques such as contact angle measurements, Fourier transform infrared spectroscopy, X-ray and Auger electron spectroscopy, ellipsometry, and electrochemistry have been employed in the rigorous investigation of monolayer properties. The mechanism of self-assembly has been investigated for both vapour phase [16] and solution-based [17] systems. As the study of atomic force microscopy performed by Xu et al [17] indicates, initially ODT molecules are fixed on Au by thiol (−SH) groups. The adsorbed molecules lie on the Au film with their axes parallel to the substrate. When the surface adsorption reaches saturation, due to a two-dimensional phase transition, the molecules start to "stand up", forming small monolayer islands. This process proceeds until nearby islands coalesce, forming a continuous monolayer. In the "stand-up" phase the molecules have a tilt angle of about 30 ° to the surface normal. The monolayer formation process occurs in a matter of minutes, and a complete well-ordered SAM can be achieved in a few hours. However, we did not find values of the refraction index of ODT in literature, whereas the thickness obtained by us corresponds to the size of the ODT molecule indicating a complete formation and compactness of the monolayer.

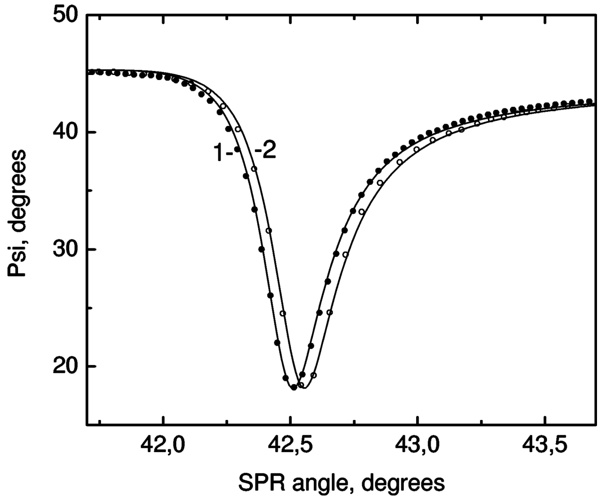

Fig. 2. Angular dependence of ellipsometric angle Psi of 35.2 nm Au film on BK7 glass (*1*, filled circles) and with ODT ($d = 2$ nm) film (*2*, open circles), $\lambda = 1000$ nm.

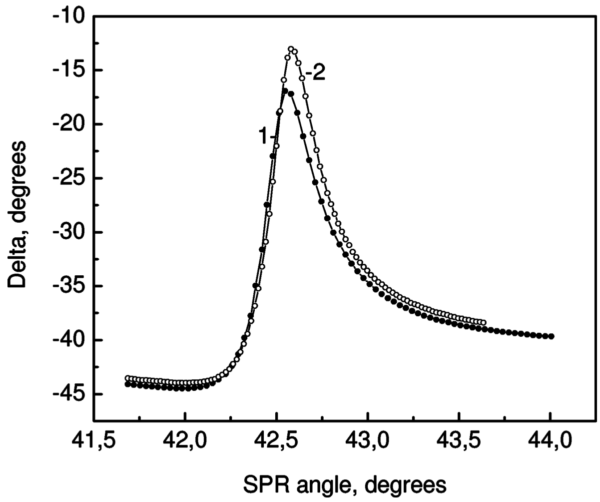

Fig. 3. Angular dependence of ellipsometric angle cos Δ of 35.2 nm Au film on BK7 glass (*1*, filled circles) and with ODT ($d = 2$ nm) film (*2*, open circles), $\lambda = 1000$ nm.

4. Summary

The system prism / Au / octadecanthiol in the Kretschmann configuration was investigated using a commercial GES-5 spectral ellipsometer. Using both amplitude and phase SPR methods the optical constants of the gold and octadecanthiol monolayer films were determined. The physical origin of high sensitivity arises from the peculiarities of the SPR field distribution. The enhancement of the SPR field at the interface has a maximum at the SPR minimum angle where reflectance $R_p \approx 0$. However, under such circumstances the signal-to-noise ratio of the reflected beam intensity measurements is strongly reduced. On the other hand, the phase change near the resonance conditions is very large. Our estimates show that if the wavelength and metal film parameters are optimally selected, the attainable sensitivity should increase by more than one order of magnitude (in our case 15 times in the Δ value and 32 times in the ψ value). Results with the ODT monolayer have demonstrated that the total internal reflection ellipsometry technique could be applied to *in vivo* analysis of oligomolecules, biomolecules, polymers, and in biosensor technology, as well as in the study of interfacial chemical reactions and physical processes.

Acknowledgement

The outlined experiment is a part of program "Infrared laser spectrometric remote atmospheric pollution sensing systems" (LISATNAS) supported by the Lithuanian State Science and Studies Foundation, contract No B-12 / 2003.

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MONOSLUOKSNIŲ TYRIMAS VISIŠKO VIDAUS ATSPINDŽIO ELIPSOMETRIJA

V. Vaičikauskas, Z. Balevičius

Fizikos institutas, Vilnius, Lietuva

Santrauka

Naudojant spektrinį elipsometrą GES-5, atlikti sistemos prizmė / auksas / oktadekantiolis (ODT) Kretschmann'o konfigūracijoje spektriniai tyrimai. Matuojant amplitudę bei fazę, nustatytos aukso ir ODT sluoksnių optinės konstantos bei storiai. Plazmonų rezonanso elipsometrijos metodo jautrį monosluoksniniams storiams nulemia paviršinių plazmonų lauko pasiskirstymo ypatybės. Paviršinių plazmonų lauko pasiskirstymo maksimumas yra dviejų aplinkų, t. y. metalo ir dielektriko, riboje. Tačiau, esant tam tikroms sąlygoms, kai atspindžio koeficientas artimas nuliui, amplitudinių matavimų signalo ir triukšmo santykis žymiai sumažėja. Kadangi rezonanso sąlygomis atspindėtos bangos fazė taipogi labai keičiasi, tai fazinius matavimus galima panaudoti ir optinėms konstantoms nustatyti. Matavimai parodė, kad, tinkamai parinkus žadinamos bangos ilgį bei metalo sluoksnio storį, galima padidinti metodo jautrį daugiau nei viena eile. Tyrimai su ODT monosluoksniu parodė geras perspektyvas visiško vidinio atspindžio elipsometriją panaudoti tiriant oligomolekules, biomolekules, polimerus bei paviršines chemines reakcijas ir fizikinius procesus metalų paviršiuje.