Multiple angle of incidence, spectroscopic, plasmon-enhanced, internal reflection ellipsometry for the characterization of solid-liquid interface processes

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ABSTRACT

A semi-cylindrical lens in Kretschmann geometry combined with a flow cell was designed for a commercial rotating compensator ellipsometer to perform internal reflection spectroscopic ellipsometry measurements, while allowing the use of multiple angles of incidence. A thin glass slide covered with a gold film was mounted between the half-cylindrical lens and a small-volume flow cell ensuring an improved sensitivity for protein adsorption experiments. The performance of the system was investigated depending on the angle of incidence, wavelength range and thickness of the gold films for surface plasmon resonance enhanced ellipsometric measurements, and a sensitivity increase was revealed compared to ellipsometric measurements with standard flow cells, depending on the measurement parameters and configuration. The sensitivity increase was demonstrated for fibrinogen adsorption.

Keywords: Ellipsometry, Bioellipsometry, Internal reflection, Plasmon enhanced ellipsometry, Protein adsorption

1. INTRODUCTION

Optical methods are of primary importance for the development of sensors and measurement techniques to characterize solid-liquid interfaces. Techniques utilizing waveguides, surface plasmon resonance (SPR) or ellipsometry are being developed and improved intensively.[1–3] Currently, the sensitivity of ellipsometry is less than waveguide or SPR sensors by several orders of magnitude. Moreover, it provides spectroscopic information which helps to build complex optical models and to measure complex structures in a more quantitative way.[4] Ellipsometry has mainly been used in a configuration measuring the surface through the liquid using flow cells.[4,5] There have been further configurations proposed and demonstrated, which measure from the substrate side, mainly in order to utilize plasmon enhancement.[6–11] We used a semi-cylindrical lens with the Kretschmann geometry to use spectroscopic ellipsometry in a broad wavelength range at different angles of incidence, and studied the performance of the tool for different gold layer thicknesses. A detailed sensitivity study is under preparation.[12]

2. SETUP OF MULTIPLE ANGLE OF INCIDENCE KRETSCHMANN ELLIPSOMETRY

We designed a flow cell covered by a semi-cylinder made of BK7 glass. The diameter of the semi-cylinder is 51 mm. A 0.5 mm thick glass slides covered by plasmonic gold layers were attached index-matched to the cylinder from the bottom, with the gold-covered side facing down, pressed against the o-ring of the flow cell. The gold layers were evaporated in a thickness range from 10 nm to 50 nm. Below the gold layer, 2 nm of Cr_2O_3 was

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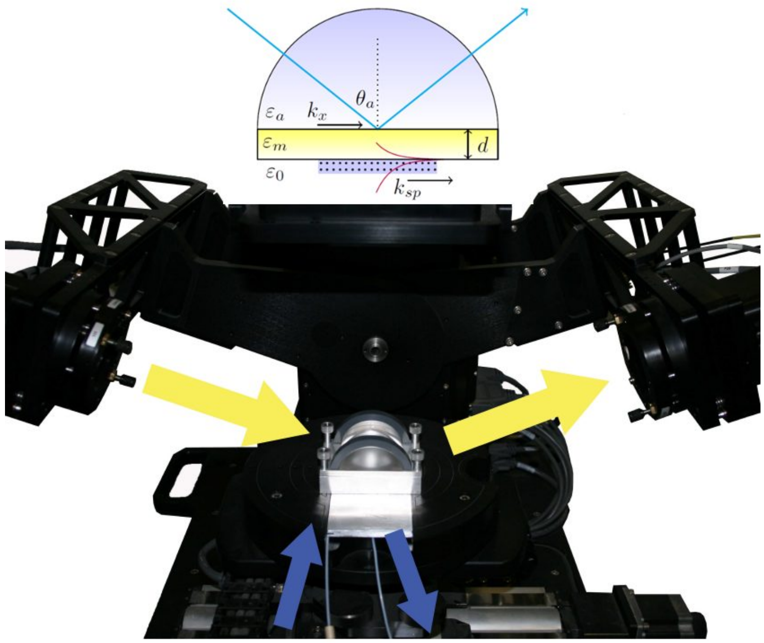

Figure 1. Photograph of the flow cell with the semi-cylinder placed on the mapping stage of the ellipsometer. A schematic drawing of the beam path in the cylinder is shown on the top of the graph.

evaporated to enhance the adhesion of gold. The volume of the cell is approximately 10 μl. The small cell is advantageous not only because smaller amount of expensive materials has to be used for the experiment, but also because the transient fluid mixing effect is shorter when switching from one solution to the other.

Using our construction, the mechanical unit with the flow cell and the cylinder can be placed onto the mapping stage of our rotating compensator Woollam M2000DI spectroscopic ellipsometer to a reproducible position (Fig. 1). The advantage of the semi-cylindrical arrangement is that the incidence of light is perpendicular to the surface of the cylinder at each goniometer position (i.e. for each angle of incidence on the sample). Therefore, in a well-aligned case, neither of the ellipsometric parameters of Ψ and Δ (amplitude and phase, respectively, of the reflection coefficients of light polarized parallel (r_p) and perpendicular (r_s) to the plane of incidence) has to be compensated and calibrated for the aberration caused by non-normal incidence.

The M2000DI ellipsometer has a wavelength range from 193 nm to 1690 nm. However, the part of the spectrum below approximately 350 nm is cut by the BK7 glass. Additional to the capability of a plasmon enhanced measurement, a major advantage of measuring from the glass substrate is that there is no cut-off in the infrared side of the spectrum, i.e. the wavelengths up to 1690 nm can be utilized, in contrast to a cut-off above 1000 nm when measuring through water in a conventional cell.

3. ANALYSIS OF ANGLE OF INCIDENCE AND SPECTRAL RANGES AS WELL AS THE THICKNESS OF THE GOLD LAYER

In case of plasmon resonance, r_p goes to zero. From the ellipsometric point of view, this appears as a vanishing absolute value of the complex reflection coefficient, $|r_p/r_s|$ (also denoted as $\tan(\Psi)$ in the terminology of ellipsometry). $|r_p/r_s|$ maps are shown for different wavelengths and angles of incidence in Fig. 2. The sharpest resonance is observed for the gold thickness of 40 nm, which decreases for thicker layers (see the 50-nm case in the figure) due to the increased absorption, and broadens for thinner layers (see the 20-nm case) due to radiation loss. Plasmon dispersion curves are also plotted (as described in the caption) for refractive indices of glass shifted by 0.0125 – already indicating a large sensitivity to the refractive index values at the interface of the plasmonic layer. Note that the instrument with the constructed cell can measure down to the angle of incidence of 45°.

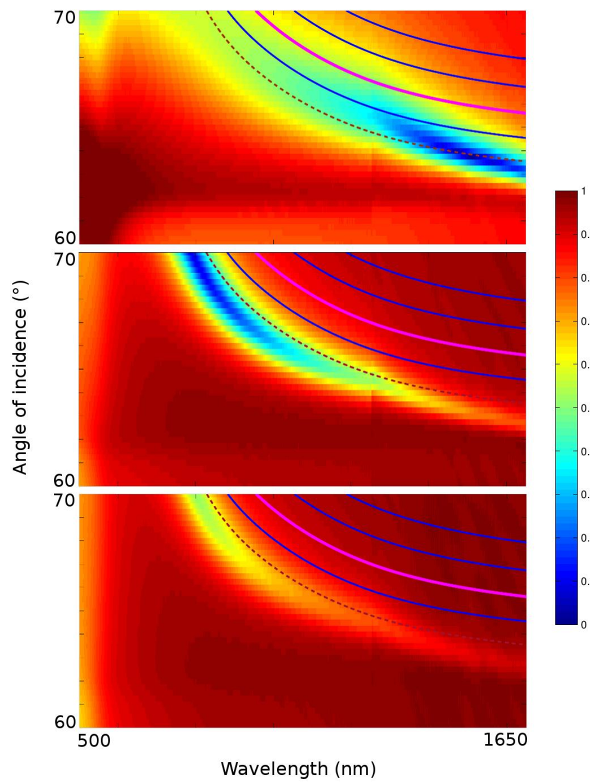

Figure 2. $|r_p/r_s|$ values measured on the layer structure of BK7/Cr_2O_3/Au/Air for different Au layer thicknesses shown in the bottom right corner of each sub-graph (with the BK7 glass and air being the ambient and the substrate, respectively). The thickness of the Cr_2O_3 layer for adhesion enhancement was 2 nm. The lines correspond to plasmon dispersion curves calculated using the equation of $\theta = asin(sqrt\{\epsilon_m N_2^2/[\epsilon_m + N_2^2]\}/N_1)$, where N_1 and N_2 are the refractive indices of the glass and the liquid, respectively, whereas ϵ_m denotes the real part of the dielectric function of the gold layer. For the different curves, N_1 is shifted by 0.0125.

Figure 3 shows the difference in the Ψ and Δ ellipsometric angles between the cases of measuring with and without an adsorbed fibrinogen layer. For thicknesses below 40 nm, the resonances become broader and the sharp peaks of large differences (most pronounced for the thickness of 40 nm) at the plasmon resonance conditions get broadened due to radiation loss.[8,10] Note that because of measuring in a large wavelength range simultaneously, the overall sensitivity, when fitting whole spectra for complex optical models, are not necessarily higher for resonant gold layer thicknesses. An analysis of wavelength ranges and plasmon layer thicknesses will be published elsewhere.[12]

Figure 4 shows the adsorption curve of fibrinogen using both standard and Kretschmann flow cells when measuring through the liquid at a fixed angle of incidence of 75°.[5] Both adsorptions are made on a gold surface. The change of the Δ value is approximately an order of magnitude larger in case of the internal reflection plasmonic configuration than in a standard flow cell. The thickness of the fibrinogen layer is about 5 nm, the change of Δ during the formation of this layer is about 30°, whereas the repeatability of both measured ellipsometric values of Ψ and Δ are typically in the range of 0.05°. As a consequence, the variation in Δ for a 5-nm fibrinogen layer is almost three orders of magnitude larger than the repeatability of its measurement.

CONCLUSIONS

A total internal reflection plasmonic flow cell in the Kretschmann geometry has been demonstrated. The effect of different plasmonic gold layer thicknesses has been investigated. It was shown that the sharpest resonance is obtained for layer thicknesses close to 40 nm. However, because of measuring and fitting in a broad wavelength

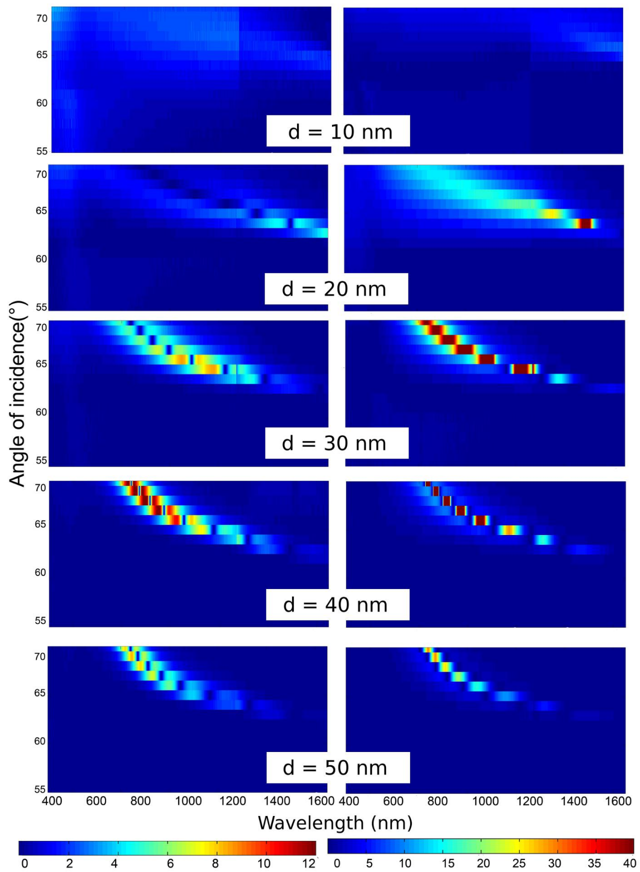

Figure 3. Differences in the Ψ and Δ ellipsometric angles (in degrees) measured with and without an adsorbed fibrinogen layer for different gold layer thicknesses (denoted by d on the graph).

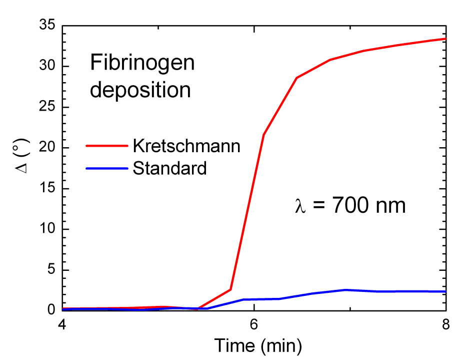

Figure 4. Ellipsometric angle Δ in degrees as a function of time measured during fibrinogen adsorption in standard and Kretschmann configurations.

range simultaneously, and measuring not only the amplitude but also the phase difference of the TE- and TM-polarized reflections, the ideal measurement range for a complex, multi-parameter optical model applied in a broad spectrum is not necessarily only the resonance value of the angle of incidence, wavelength, and gold layer thickness. A detailed sensitivity study will be published elsewhere.[12]

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