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Total Internal Reflection Ellipsometry under SPR Conditions: In-Situ Monitoring of the Growth of Poly(*N*-isopropylacrylamide) (PNIPAAm) Brushes

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Summary: Total internal reflection ellipsometry (TIRE) under surface plasmon resonance (SPR) conditions represents a powerful characterization technique combining the conveniences of spectroscopic ellipsometry with SPR. Besides the very high sensitivity to small changes in the optical constants (up to 10 times more sensitive than conventional ellipsometry), the possibility to investigate media of different optical densities or even opaque media makes this analytical method very convenient for different sensing applications. This article presents an example of application of TIRE under SPR conditions for the continuously in-situ monitoring of the growth of covalently tethered poly(*N*-isopropylacrylamide) (PNIPAAm) chains on a gold surface.

Keywords: poly(*N*-isopropylacrylamide); spectroscopic ellipsometry; surface plasmon resonance; thin films; total internal reflection ellipsometry

Introduction

Optical methods such as ellipsometry and surface plasmon resonance (SPR) spectroscopy are well established analytical techniques for the characterization of thin films.[1–3] Due to the high sensitivity to small changes in film thickness and optical constants, both methods have become suitable for the precise study of chemical and biological sensing processes on a solid surface.

Especially ellipsometry has become a very popular analytical instrument in this context.[1,3,4] This method is similarly sensitive as SPR spectroscopy but has the advantage that both the relative amplitude ratio ($tan\Psi$) and the relative phase difference (Δ) are measured; hence, the film thickness d and the refractive index n are accessible if an appropriate optical model is applied.[1,3] However, its application is limited by experimental difficulties of the light beam passing through the investigated ambience.[5–12] For instance, the composition dependent variations of the medium refractive index and local inhomogeneities (turbulences, bubbles) can seriously affect the experimental data, especially during in-situ investigations of the kinetics of chemical reactions within the surface layer.

The relatively novel analytical technique of total internal reflection ellipsometry (TIRE) under SPR conditions combines the advantages of spectroscopic ellipsometry and SPR spectroscopy.[5–12] Besides a highly elevated sensitivity (up to 10 times higher than traditional external reflection ellipsometry)[7] another advantageous fact is that the light beam does not directly penetrate the ambience which enables measurements in different gaseous and even opaque media.

This work presents the unique applicability of TIRE under SPR conditions for the investigation of chemical reactions on a gold surface. In this regard, the growth of poly(*N*-isopropylacrylamide) (PNIPAAm) brushes (polymer chains which are on one end covalently tethered to a surface) is continuously monitored in-situ.

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Experimental Part

Materials

If not otherwise stated all applied solvents and chemicals were purchased from Sigma-Aldrich and used as received without further purification.

Special glass slides (BK7) which were covered on one side with a thin (2 nm) Cr layer to improve the adhesion of a 25 nm semi-transparent Au coating were purchased from Dresdner Transferstelle für Vakuumtechnik e.V. The surface roughness (rms) of the gold deposited glass slides was in the order of magnitude of 0.1 nm as determined by AFM. The surface roughness is therefore much smaller than the applied wavelength range and hence perturbing light scattering can be neglected. To allow polymer growth on the surface the Au layer was selectively coated with a suitable bifunctional self-assembled monolayer of substance (1). The molecule bears a surface binding thiol group to bind to the gold substrate and an atom transfer radical polymerization (ATRP) initiator group (bromo-*iso*-butyric acid) to subsequently commence the surface initiated polymerization as described previously by Jones *et al.*[13] (Figure 1). In order to deposit a monolayer of the initiator, a clean gold coated glass slide was immersed into a 1 mM ethanolic solution of the sulfide initiator (1) for 24 h and subsequently rinsed with an excess of ethanol leading to the selective formation of the initiator-functionalized gold surface (2). The ellipsometrically observed thickness of the initiator layer (~1 nm with n fixed to the bulk value of 1.45 at 632 nm) and the appearance of a carbonyl band at 1740 cm^{-1} in the IR spectrum confirmed the successful surface modification.

For surface initiated polymerization under ATRP conditions, the synthetic procedure described by Edmondson *et al.* was applied.[14] The monomer *N*-isopropylacrylamide (NIPAAm, 97%) was dissolved in a water/methanol mixture (50:50 v:v) and thoroughly deoxygenized by several ''freeze-pump-thaw'' cycles. Afterwards, a deoxygenized mixture containing the catalyst CuBr (>99.999% trace metal basis) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%) as ligand was carefully added.

To initialize the polymerization, a modified gold coated glass slide (2) was mounted in the SPR flow cell (Figure 2) and continuously exposed to the reactive NIPAAm solution. The polymerization starts immediately after getting into contact with the ATRP initiator. After a reaction time of a few hours, the excess of injected monomer solution was poured in cold diethyl ether in order to verify that polymerization only proceeded at the modified gold substrate (3) and not in solution due to free initiator or temperature initiated polymerization. However, no indication for precipitated none-tethered PNIPAAm was observed over the course of the experiment.

Instrumentation

The applied experimental setup in this study is build on the basis of a commercial spectroscopic ellipsometer (M2000 VI, J.A Woollam Co. Inc.), operating in visible/near IR spectral range of 370–1700 nm and exploiting the rotating compensator principle. The SPR flow cell was designed for a special Kretschmann geometry (Accurion

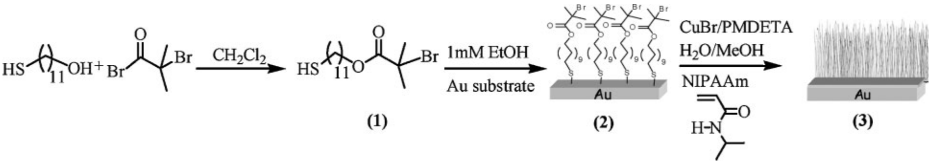

Figure 1.

Simplified scheme of the applied synthetic procedure for the preparation of covalently tethered PNIPAAm chains.

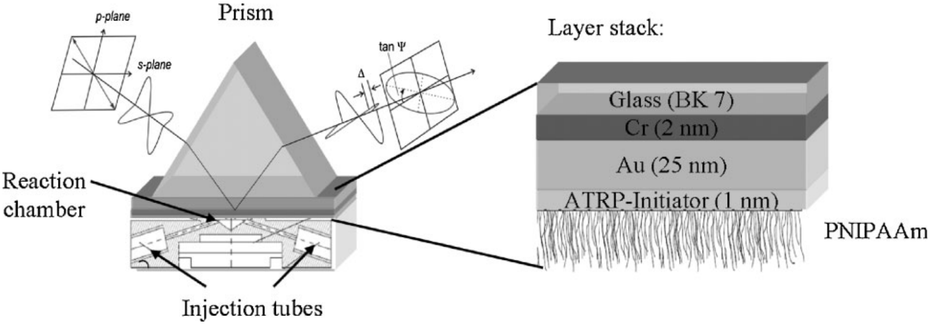

Figure 2.
SPR flow cell using the Kretschmann geometry as applied for TIRE under SPR conditions (*left*) and corresponding layer stack (*right*).

GmbH) containing an equilateral triangle (68°) prism (BK7 from Hellma Optik GmbH) which provides coupling of the light beam into the thin gold film (Figure 2).

The light beam, which was generated from a xenon lamp, passes the optical components of the ellipsometer device and is afterwards refracted into the glass prism (BK7) of the SPR flow cell which is in closed optical contact (index matching fluid, n ~ 1.518 at 23 °C) with the modified gold coated glass slide (2). The SPR flow-cell has input and output tubes enabling the continuous injection of different solutions (reactive NIPAAm solution for polymerization and pure solvent for rinsing). Polymer growth was achieved by mounting the initiator modified substrate (2) in the SPR geometry followed by continuous rinsing (~1 ml/min) with reactive NIPAAm solution at 24 °C.

The ellipsometric data were modelled using the WVASE32® software (J.A Woollam Co. Inc.) with the corresponding optical constants of Au, Cr and BK7 from the database. The optical constants of the reactive NIPAAm solution in the visible spectral range were determined by means of an external measurement using a multi-wavelength refractometer (DSRα from Schmidt + Haensch GmbH & Co). The refractive index of PNIPAAm was fixed to the bulk value of about 1.45 at 632 nm in order to be able to accurately fit especially the early polymer growth where layer thickness is still very small.

Theoretical Backround

Ellipsometry measures the change of the polarization state of a light beam reflected from a surface. The relation between the ellipsometric angles $\tan\Psi$ (relative amplitude ratio) and Δ (relative phase difference) is expressed by the fundamental equation of ellipsometry:[1,3]

$$\rho = \frac{R_p}{R_s} = \tan\Psi \exp(i\Delta) \qquad (1)$$

Herein, ρ is the complex-valued ratio of the Fresnel reflection coefficients R_p and R_s for light polarized parallel (p) and perpendicular (s) to the plane of incidence. It depends on the optical properties and composition of the layer stack, on layer thicknesses, morphology and on surface roughness. Hence, ellipsometry is exploited as a non-invasive (if the sample is not light sensitive) analytical method of thin films and interfaces. Ellipsometry is an indirect, model based technique which needs an appropriate optical model. Applying an appropriate model, the film thickness d and optical constants (e.g. complex refractive index $N(\lambda) = n(\lambda) - ik(\lambda)$, with n = refractive index and k = extinction coefficient) can simultaneously be calculated from a spectroscopic ellipsometric data set (if film thickness $d > 10\,\mathrm{nm}$[1]).

The main difference between total internal reflection ellipsometry (TIRE) under SPR conditions and conventional external reflection ellipsometry is in the way of the light beam penetrates the sample and hence in the order of layers (Figure 3). In the case of traditional external reflection ellipsometry, the light beam enters the sample from the ambient side, whereas for TIRE under SPR conditions a reversed layer stack is present (light beam comes from the glass side). The surface plasmons are generated in a thin metal film (e.g. Au, Ag, Cu). Finally, TIRE measurements are based on measuring the intensity of a light beam reflected at an interface for which the refractive index of the less optically dense (reflecting) medium is n_2 and for the more dense (incident) medium is n_1. If the angle of incidence is larger then the critical angle Φ_c defined by

$$\sin \Phi_c = \frac{n_2}{n_1} \tag{2}$$

the light beam is not transmitted into the second medium, but total internal reflection occurs. To give an example, Φ_c is 42° for a glass/air interface, whereas for a glass/water interface Φ_c is 63°. Although most of the incident light is reflected on the surface, an evanescent field/wave penetrates the second medium which can excite surface plasmons from a deposited metal layer at the interface. These surface plasmons used in all SPR based techniques to monitor small changes on the surface are strongly sensitive to the dielectric constant of the surrounding medium. At this point it should be mentioned that TIRE itself does not require the SPR effect, moreover it has general applicability and can be applied for instance for iron, titanium layers.[5] However, in terms of sensitivity SPR enhancement is very much beneficial.

Results and Discussion

Inhomogeneous media (e.g. due to turbulences, bubbles or composition dependent variations of n during chemical reactions)

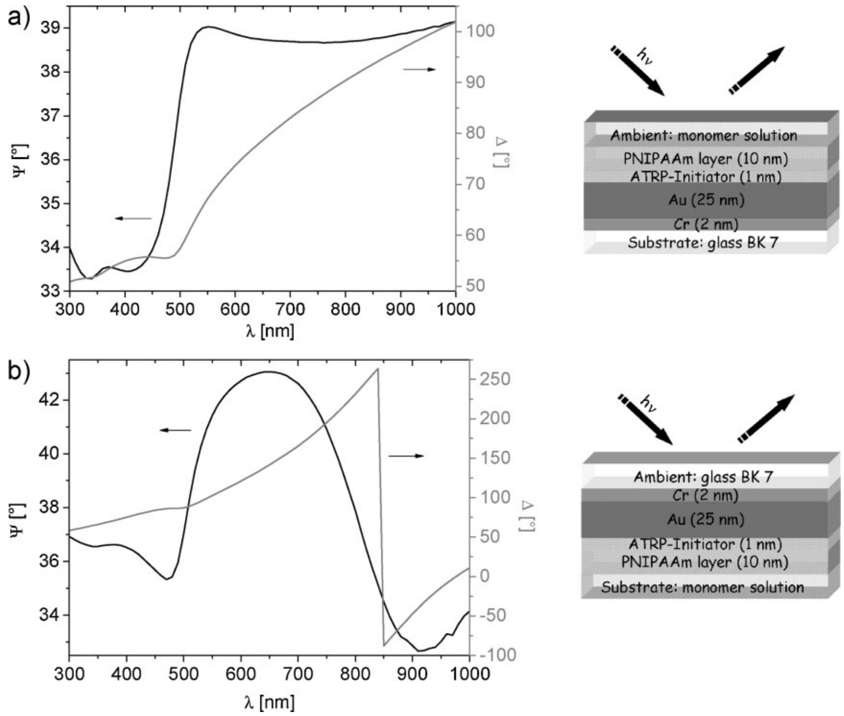

Figure 3.
Simulated results ($\Psi(\lambda)$ and $\Delta(\lambda)$) of *a)* traditional external reflection ellipsometry and *b)* TIRE under SPR conditions with the corresponding layer stacks.

seriously affect the ellipsometric data measured in conventional external reflection mode. The focus of this work is to demonstrate how to overcome such experimental difficulties using TIRE under SPR conditions. The applicability and the versatility of this technique is shown on a representative example; the continuous in-situ monitoring of the growth of covalently tethered PNIPAAm chains on a gold surface.

In order to demonstrate the differences between TIRE under SPR conditions and traditional ellipsometry the ellipsometric angles were calculated "straight-forward" by solving the fundamental equation of ellipsometry (Eq. 1). For these calculations the optical model based on the layer stack shown in Figure 3 was applied. Completely different behaviour of the ellipsometric $\Psi(\lambda)$ and $\Delta(\lambda)$ spectra was observed in the case of TIRE under SPR conditions in comparison to traditional external reflection ellipsometry. Figure 3a shows typical $\Psi(\lambda)$ and $\Delta(\lambda)$ spectra in external reflection according to the shown layer stack; Figure 3b shows typical SPR curves obtained by TIRE measurements with a pronounced sharp drop in the phase of Δ (from 260 down to -90) due to plasmon resonance at SPR conditions. One can benefit from the sharp drop in $\Delta(\lambda)$ and its very high sensitivity to very small changes on the gold surface. Nabok *et al.* have demonstrated in their work that such an experimental setup is about 10 times more sensitive than conventional ellipsometry.[7]

For reasons of clarity as well as the much higher sensitivity of $\Delta(\lambda)$ in comparison to $\Psi(\lambda)$, only $\Delta(\lambda)$ measured by TIRE under SPR conditions is further presented and discussed in this article. However, for all experiments both ellipsometric angles in dependence of λ were recorded. In order to initiate the experimental investigation the flow cell was thoroughly rinsed with a methanol / water mixture until no air bubbles were visible in the setup anymore. Afterwards, the ellipsometric angles were continuously determined while the reactive NIPAAm solution was injected. The polymerization immediately starts when the reactive solution gets in contact with the ATRP initiator on the surface leading to an instantaneous shift of the minimum in $\Delta(\lambda)$ to higher wavelengths (Figure 4). After about 200 min, the shift is less pronounced indicating the termination of the reaction. Hence, the polymerization was interrupted by carefully rinsing the cell with an excess of solvent (MeOH and H_2O).

Taking advantage of the plasmon resonance, the sharp drop in $\Delta(\lambda)$ as a function of reaction time is plotted (Figure 4). The polymerization kinetics obtained from this "raw" data are indicating a non-linear ("non-living") polymerization process.

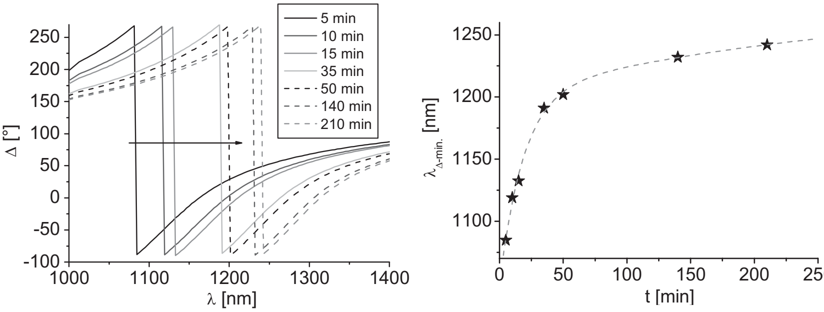

Figure 4.
Polymerization kinetic after injection of monomer solution to the modified gold substrate (3). A representative series of $\Delta(\lambda)$ spectra using TIRE (*left*) and the position of the Δ minimum $\lambda_{\Delta\text{-min.}}$ as a function of reaction time (*right*). The dashed line is a guidance for the eyes and represents the best fit of the experimental data. For reasons of clarity only some representative $\Delta(\lambda)$ spectra are shown.

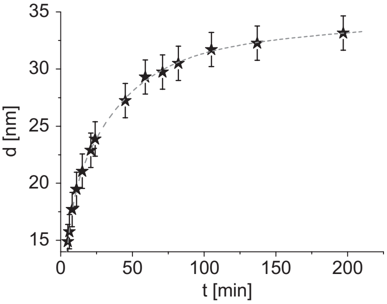

Figure 5.
PNIPAAm brush thickness changes in dependence of the polymerization time.

Besides the direct evaluation of $\Delta(\lambda)$ influenced by plasmon resonance as demonstrated in Figure 4, it is more informative to evaluate the layer thickness and optical constants of the growing PNIPAAm chains by means of a physically reasonable optical model. The applied model for the fit procedure is based on the layer stack presented in Figure 3b. From both kinetic diagrams it is obvious that after about 25 min the linear trend of the curve, indicating an ideal "living" polymerization process, is interrupted. This is most likely due to termination reactions (e.g. radical recombination, disproportionation etc.) and a plateau value is reached after 100 min with a maximum PNIPAAm brush thickness of about 33 nm. Such polymerization kinetics are known from the literature.[15] The reason for that can be found, *inter alia*, in the restricted reactivity of the PMDETA ligand and the used solvent mixture (H_2O/MeOH). Furthermore, it cannot completely be excluded that small amounts of oxygen have penetrated the experimental setup during the reaction which would slow down the reaction due to the formation of less reactive peroxy radicals on the polymer chain end.

In order to control the accuracy of TIRE under SPR conditions as well as the subsequent fitting procedure, external reflection ellipsometry was applied to characterize *ex-situ* the layer stack before ($t = 0$ min) and after polymerization ($t = 197$ min). For both external measurements the presented results of TIRE under SPR conditions could be verified within an experimental error of ± 2 nm or less.

Conclusion

The high sensitivity of TIRE under SPR conditions makes it convenient where very small changes in the environment of the gold surface (in the molecular range) shall be detected, e.g. in sensing applications. Another advantage is the possibility to investigate inhomogeneous or even opaque media which is problematic or simply not feasible with traditional external reflection ellipsometry. In this regard, the polymerization kinetics of NIPAAm at ATRP conditions is the first time monitored in-situ by means of TIRE under SPR conditions. Typical non-linear polymerization kinetics reaching a plateau value at a PNIPAAm thickness of about 33 nm were found for the applied reaction system. Such an experimental setup permits both, the control of systematic synthesis of well defined polymer brushes and the monitoring of e.g. their sensing behaviour in dependence of different media.

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