Application Note # 111

Real-Time Characterization of Polyelectrolyte Multilayers with MP-SPR

Multi-Parametric Surface Plasmon Resonance (MP-SPR) was utilized for precise real-time characterization of polyelectrolyte multilayer build-up. Not only kinetics of adsorption was monitored but also thickness of the each deposited layer was calculated. Thickness of the layers increased exponentially from 1.5nm.

Introduction

Polyelectrolyte multilayers (PEM) are specific examples of Layer-by-Layer (LbL) nanofabrications, where well-defined nanoscale film structures are built on surfaces by selfassembly. PEMs are formed by sequential deposition of oppositely charged macromolecules that bind to each other by electrostatic interactions (Fig1). The layer buildup is dependent on many parameters, such as temperature, pH, ionic strength of the solutions, and the type of materials used for deposition, and these can also be used to control the structure and properties of the forming layer [1,2]. Materials like nanoparticles, carbon nanotubes, light, pH or temperature responsive polymers can be used to build PEMs with desired functionalities or properties. There a multitude of applications of PEMs in optics, sensing, filtration, coating, composite materials and drug delivery [1,2].

The thickness of a PEM is often of interest when studying the structure-property relationship of multilayer systems. Traditionally ellipsometry is widely used for determining optical thicknesses of nanoscale layers. However, in case of liquid phase applications the MP-SPR is a excellent technique as the optical detection is performed from the dry side of the sample in a so called Kretschmann configuration, while for example in ellipsometry the optical detection is done through the liquid phase. SPR allows also the use of opaque or highly scattering liquids, whereas in ellipsometry this will interfere with the measured signal.

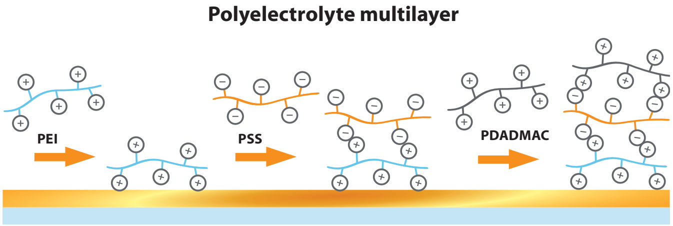

Figure 1. Polyelectrolyte multilayer build up on a gold sensor slide with electrostatic interactions.

PEI = poly(ethyleneimine), PSS = poly(styrenesulfonate) sodium salt, PDADMAC = poly (diallydimethylammoniumchloride)

SPR phenomenon is based on free electrons resonating at a metal surface, which are excited with light. There is an absorption maximum as a function of the angle of the incident light, and the SPR phenomenon is highly dependent on the dielectric constant near the metal surface. Any changes near the surface, such as deposition of new layer, change the angle of the absorption maximum. Due to the MP-SPR unique optical setup instrument can be utilized for determining not only affinity and kinetic of the interaction but also layer properties like thickness and refractive index.

Materials and Methods

A 0.15 M NaCl solution was prepared as a running buffer for the experiment. 1 mg/ml solutions of poly(ethyleneimine) (PEI), poly (styrenesulfonate) sodium salt (PSS) and poly (diallydimethylammoniumchloride) (PDADMAC) were prepared in the same buffer. A SPR sensor slide was cleaned by boiling it in a solution of 30% NH_4OH: 30% H_2O_2: H_2O (1:1:5) for 15 minutes and washed with deionised water and dried by using an aspirator.

The SPR Navi 200 in angular scan mode was used for studying the *in situ* PEM deposition. A flow rate of 25 µL/min, 4 minute deposition time and 11 minute wash periods were used. PEI, which binds to uncharged gold surfaces strongly, was injected first to render the gold surface positively charged. Then PSS and PDADMAC were sequentially deposited on the sensor slide.

Results and Discussion

MP-SPR allows real-time monitoring of polyelectrolyte multilayer build-up. The SPR peak minimum angle sensogram was used to study the dynamics of the PE-layers in the solution (Fig. 2). Figure 2 also shows that the adsorption of the PE-layers on the surface was relatively fast. The adsorption seems to take place in one quick step, and no desorption process takes place when the system is flushed with pure buffer.

Measured full SPR curves near the end of each wash period were used for calculating the layer thicknesses (Fig. 3). The modelling of the PEM layer thicknesses was performed by using the full SPR curve of the clean gold sensor slide as a reference point. A refractive index of 1.465 [3] was used for determining the thicknesses of the deposited PE-layers.

The thicknesses of the PEM were plotted against the layer number (Fig. 4). The layer thickness increases following an exponential growth pattern when excluding the first layer, which is of a different polymer (PEI). Similar behaviour has also been reported for PEMs measured by ellipsometry [3]. It should be noted that the RI and layer thickness are interchangeable parameters in the SPR experiments for organic layers. Because the PEMs are not dense confined layer structures, the RI of the layer is not constant throughout the whole layer. This effect is emphasized for a small number of PE-layers, because the interface does not have a sharp transition [1,2]. The PEMs have been reported to smooth surfaces greatly when deposited [1], and part of the growth can come from the fact that the surface roughness is being "bridged" during deposition of the first few layers before the inherent roughness of the PEM pair is reached [1].

Conclusions

MP-SPR is an excellent tool for *in situ* monitoring of polyelectrolyte multilayer build-up. Apart from monitoring only the kinetics of adsorption, also thickness of each deposited layer can be calculated from full SPR curve. In addition, MP-SPR can be used for assemblies that have complex refractive index or when using turbid solutions and it would also be ideal to monitor LbL assembly of metallic nanoparticles. MP-SPR and polyelectrolyte layer characterization can be utilized in a variety of research areas, e.g. optics, material research, coatings as well as drug delivery.

With MP-SPR instrument equipped with additional wavelength it is also possible to determine both unique refractive index (RI) and thickness of deposited layers without prior knowledge of the material RI. For this, see BioNavis Application Note 128.

References:

[1] Hammond P. T., Adv. Mater. 2004 (16), 1271-1293

[2] Decher, G., Science 2007, 277, 1232-1236

Recommended instrumentation for reference assay experiments
SPR Navi™ 200, 210A or 220A with additional wavelength (-L)
Sensor surfaces: Au, other metal or inorganic coating
Software: SPR Navi™ Control, SPR Navi™ DataViewer, SPR Navi™ LayerSolver

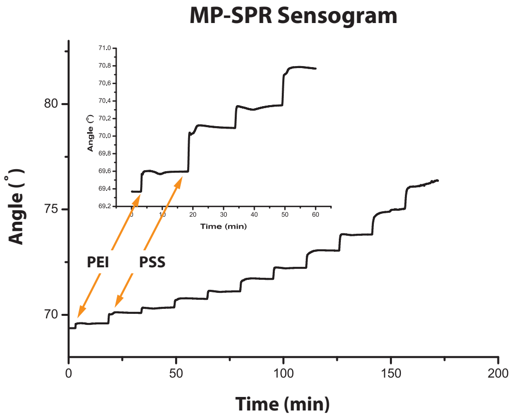

Figure 2. SPR minimum angle plotted against time for the PEM-assembly. The inset shows a magnification from the beginning of the assembly.

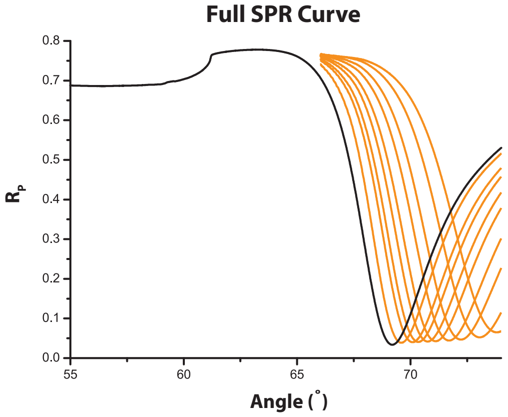

Figure 3. SPR curve of pure gold sensor slide in buffer (black curve), and curves with increasing number of PE-layers from left to right (orange curves; first PEI layer, after that alternating PSS and PDADMAC).

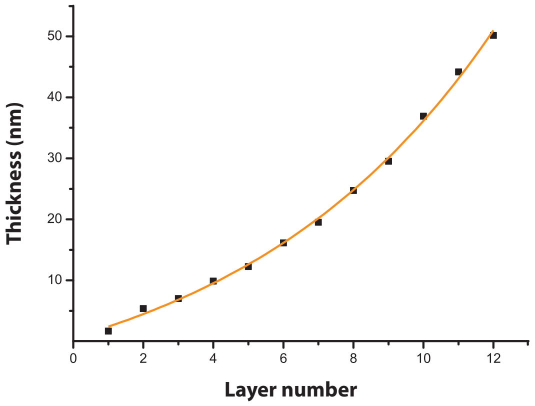

Figure 4. Calculated layer thickness plotted against layer number. (Odd number PDADMAC and even PSS layer) There is a first-order exponential relationship between the points.