

## Application Note # 111

# Real-Time Characterization of Polyelectrolyte Multilayers using Surface Plasmon Resonance

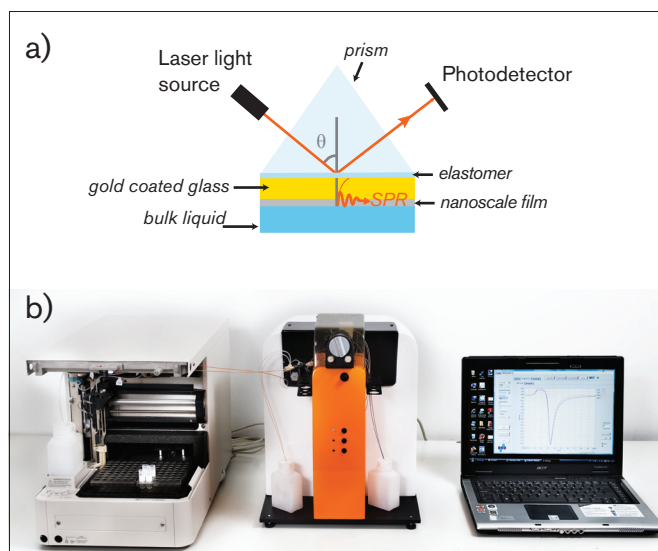
This note demonstrates that the KSV SPR 200 instrument enables precise real-time characterization of polyelectrolyte multilayer buildup.

## Introduction

Polyelectrolyte multilayers (PEM) are specific examples of Layer-by-Layer (LbL) nanofabrications, where well-defined nanoscale film structures are built on surfaces by self assembly. PEMs are formed by sequential deposition of oppositely charged macromolecules that bind to each other by electrostatic interactions. The interaction is nonspecific, which expands the variety of materials that can be utilized in the nanofabrication. 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 are 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 SPR is a better technique as the optical detection is performed from the dry side of the sample in a so called Kretschmann configuration (Figure 1a), while for example in ellipsometry the optical detection is done through the liquid phase. Hence, SPR even allows the use of opaque or highly scattering liquids, whereas in ellipsometry this will interfere with the measured signal. QCM can also be used to measure the thickness of nanoscale films in liquid phases. However, as QCM is an acoustic technique it determines nanoscale film thicknesses indirectly from mass and energy loss changes. The mass/thickness values obtained by QCM also include any embedded liquid in the nanoscale structure, while the SPR provides the so called dry thickness of the nanoscale structure. Hence, SPR and QCM data will complement each other, and optimally both techniques should be used in order to completely characterize a nanoscale film structure like PEM. However, in this application note we will focus on presenting how the surface plasmon resonance (SPR) technique can be used to measure PEM deposition *in situ* in liquid phase.

SPR is based on free electrons resonating at a metal surface, which are excited with visible or near infrared light. There is an absorption maximum as a function of the angle of the incident light. The SPR is highly dependent on the dielectric constant near the metal surface, and any changes near the surface changes the absorption maximum angle. *In situ* measurements also provide information on the kinetics of the studied systems, which can be important for process optimization.



**Figure 1.** a) Optical configuration of the KSV SPR 200 instrument with a rotating laser. An index matching elastomer is used as optical index matching between the prism and the sensor slide. b) KSV SPR 200 equipped with an autosampler accessory.

## Experimental

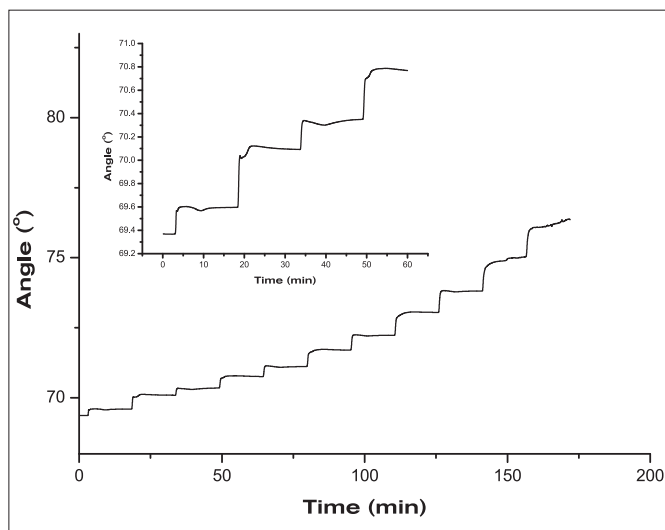
A 0.15 M NaCl solution was prepared as a running buffer for the experiment. 1 mg/ml solutions of poly(ethyleneimine) (PEI), poly(styrenesulfonate) sodium salt (PSS) and poly(diallyldimethylammoniumchloride) (PDADMAC) were prepared in the same buffer.

An SPR sensor slide was cleaned by boiling it in a solution of concentrated  $\text{NH}_3\text{OH} : 30\% \text{H}_2\text{O}_2 : \text{H}_2\text{O}$  (1:1:5) for 15 minutes and washed with deionised water and dried by using an aspirator.

The KSV SPR 200 was equipped with an autosampler accessory for studying the PEM deposition (Figure 1b). A flow rate of 25  $\mu\text{L}/\text{min}$  and injection volume of 100  $\mu\text{L}$  were used, with 15 minute interval between the samples, corresponding to 4 minute deposition time and 11 minute wash period. 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. The PEM build-up process was monitored *in situ* by using the angular scan mode.

## Results

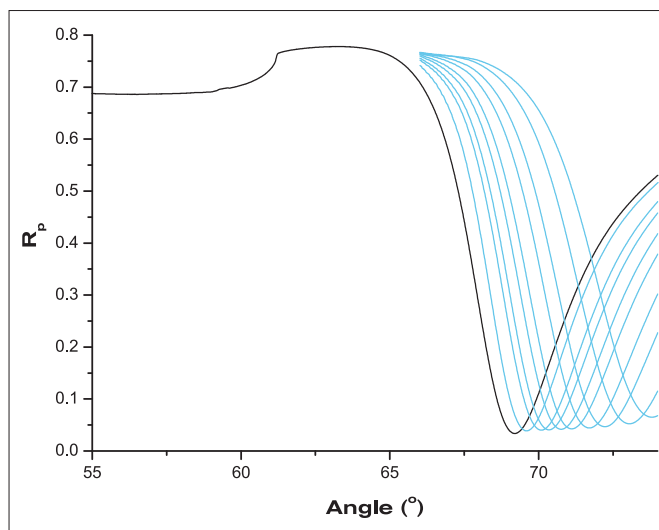
The SPR minimum angle was plotted against time in order to study the dynamics of the PE-layers in the solution (Figure 2). Figure 2 also shows that the adsorption of the PE-layers on the surface was relatively fast. The adsorption seems to take place in one quick step, and no desorption process takes place when the system is flushed with pure buffer.



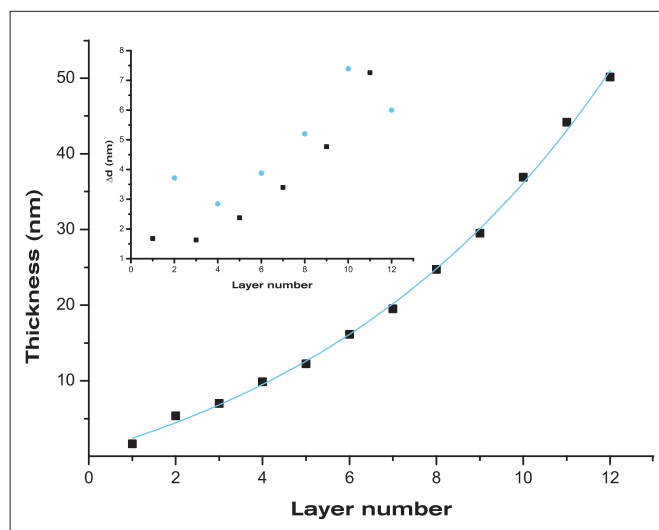
**Figure 2.** SPR minimum angle plotted against time for the PEM-assembly. The inset shows a magnification from the beginning of the assembly.

SPR-spectra near the end of the wash period were used for calculating the layer thicknesses (Figure 3). The modelling of the PEM layer thicknesses was performed by using the SPR spectrum of the clean gold sensor slide as a reference point. The actual modelling was done with the Winspall software version 3.02. 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, as well as the change in thickness for each layer (Figure 4 and inset respectively). 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 do 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].

- (1) Hammond P. T., *Adv. Mater.* 2004 (16), 1271-1293
- (2) Decher, G., *Science* 2007, 277, 1232-1236
- (3) Halthur T. J., Elofsson, U. M, *Langmuir* 2004 (20), 1739-1745
- (4) Schasfoort, R. B. M., Tudos, A. J., *Handbook of Surface Plasmon Resonance*, RSC 2008



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



**Figure 4.** Modelled layer thickness plotted against layer number. (Odd number PDADMAC and even PSS layer) There is a first-order exponential relationship between the points. The inset is change in thickness ( $\Delta d$ ) versus layer number. (PDADMAC layers black and PSS layers red)

## Conclusions

We have successfully shown how the KSV SPR 200 instrument can be used for *in situ* monitoring of a liquid phase LbL assembly process between PDADMAC and PSS. Apart from only monitoring the kinetics of adsorption, the KSV SPR 200 instrument also give the possibility to collect full SPR spectra with absolute angle information enabling the determination of layer thicknesses. This method can also be used for assemblies that have complex refractive index or when using turbid solutions, as these parameters can be taken into account when modelling the layer properties. The method described would also be ideal to monitor LbL assembly of metallic nanoparticles.

