Application Note # 128

Determine Layer Unique Refractive Index and Thickness using MP-SPR

Multi-Parametric Surface Plasmon Resonance (MP-SPR) can be used to determine unique thickness and refractive index (RI) of ultrathin films without prior knowledge of the RI or the thickness of the layer. Polyelectrolyte multilayer was measured using MP-SPR two wavelength method and analysed by LayerSolver™ software module. Thickness of 5 bilayers was found to be 16.8nm and RI 1.48 at 785nm.

Introduction

In optical methods, refractive index (RI, n) and thickness (d) are interdependent variables. Pairs of correct answers exist for each particular measurement, according to a hyperbolic function. Traditional optical methods, such as ellipsometry, require prior knowledge of either RI or thickness from other sources for accurate characterization of dielectric layers. Differences between the solutions are so small that they cannot be determined in practice, even though theoretically unique solutions exist. [1] However, RI of material varies for different immobilization techniques, thickness, concentration, even moisture and pH in some cases and that is why values from the literature are not sufficient to accurately assess thicknesses. Thickness and RI are important properties for many thin film coating industrial applications, such as insulation layers and antifouling coatings, but also for biological and biomaterials basic research, such as determining lipid bilayer properties.

Surface Plasmon Resonance (SPR) is a phenomenon based on free electrons resonating at a metal surface. Typically the excitation energy source is laser light. Multi-Parametric SPR (MP-SPR) measures light absorption as a function of the angle of incident light. Maximum absorption is achieved at maximum plasmon excitation. The plasmonics is highly dependent on the dielectric constant near the metal surface. Any changes near the surface, such as deposition of a new layer, change the angle of the absorption maximum. The MP-SPR Navi™ instruments are uniquely capable of recording a whole SPR curve using multiple wavelengths. This enables precise thickness and refractive index characterization for wide range of materials such as metals (see Application Note #127), ceramics, or polymers.

Two methods for thickness and RI characterization are presented, 1)measuring in two different media (2M) with a high RI difference, such as air and water [1, 2], and 2) measuring with two different wavelengths (2W) of light [2], such as 670 and 785 nm. The two media method is only suitable for materials which are stable in both media and do not swell or change conformation when environment changes. Two wavelengths method is suitable for all materials. The recent publications in the area show that these two presented methods can be applied to measurements the properties of thin films from 3 Ångströms up to microns [4,5].

Materials and methods

Typical working protocol to determine thickness and refractive index (RI):

1. Capture a background of the SPR sensor slide. The whole SPR curve (angle range from 40-78 degrees) is measured at two wavelengths before coating is performed.
2. Coat the sensor slide with the sample material *in situ* or *ex situ*. Suitable *ex situ* material deposition methods can include sol-gel, Langmuir-Blodgett, CVD, ALD, or other thin film methods.
3. Capture a sample layer: Whole SPR curve of the sample is measured with two wavelengths after the layer deposition.
4. Analyse data with MP-SPR Navi™ LayerSolver™.

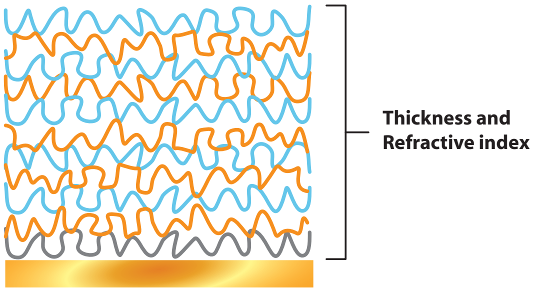


Figure 1. Polyelectrolyte multilayer was deposited on a sensor slide *in situ* and layer thickness and refractive index were determined.

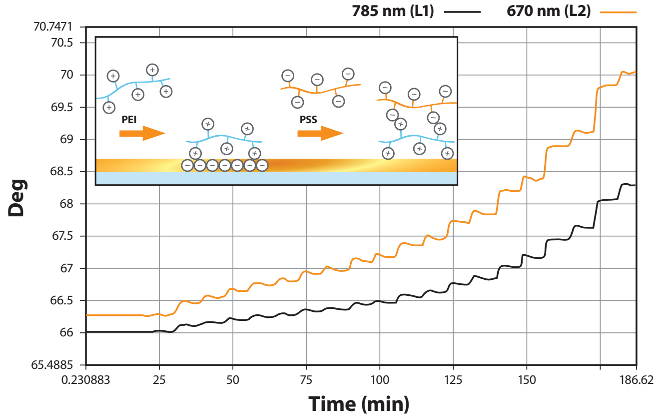


Figure 2. Polyelectrolyte multilayer build-up monitored in real-time using MP-SPR.

In this example polyelectrolyte multilayer was deposited *in situ* onto the standard gold sensor slide (Fig.1, Fig2). First layer was a positively charged poly(ethyleneimine) (PEI), and after that bilayers of negatively charged poly(sodium4-styrenesulfonate) (PSS) and positively charged poly(allylamine hydrochloride) (PAH) were deposited. 0.15 M NaCl, 20 mM Tris with a pH of 7.4 was used with 50µL/min flow rate at 20˚C [4]. The thickness after each layer can be determined (Fig.3).

Optical fitting software MP-SPR Navi**™** LayerSolver**™** was used to model the measured SPR curves (Fig.5). The Software varies RI and thickness values to obtain RI – d continuum answers for both of the wavelengths. One of the curves is shifted with the optical dispersion (dRI/dλ) relation of the material to correspond to the other wavelength (Fig.4). The values for the intersection point of the shifted and measured curves present unique solutions for both the RI (n) and d of the sample.

Results and discussion

The two wavelength method is based on the fact that the refractive index wavelength dependency (dRI/dλ) can be approximated to be linear for relatively small wavelength changes (few hundred nm), and that the value is similar to similar materials, while the RI itself can be quite different. For example for organic materials and polymers the (dRI/dλ) is approximately 10^{-4} - 10^{-5} nm^{-1} (at 700 nm) [3].

The thickness for a polyelectrolyte multilayer consisting of five layers was successfully determined to be 16.8 and RI 1.481 at 785nm with the two wavelength method. Thickness after each layer and even up to 120 bilayers can be determined using MP-SPR [4].

Conclusions

The MP-SPR two wavelength method using the MP-SPR Navi™ instruments enables effective and accurate optical characterization of ultrathin films without prior knowledge of the material properties. Layer properties can be determined in air and in liquid without any change in the instrument setup and layer thickness up to few micrometres thick layers can be measured. The method can be applied in research of advanced coatings, functional materials, biologically active materials and also fundamental biochemical research. In addition, the method is suitable for multilayer structures.

References:

[1] W. M. Albers and I. Vikholm-Lundin, Nano-Bio-Sensing, 1st ed, Chapter 4, Springer 2010

[2] H. Liang, et al., Sensors and Actuators B: Chemical, 149(1), 212-220, 2010

[3] S. N. Kasarova et al., Optical Materials, 29, 1481-1490, 2007

[4] Granqvist et al. Langmuir, 29, 8561 – 8571, 2013

[5] Capasso et al. OncoImmunology 2015

Recommended instrumentation
for reference assay experiments

MP-SPR Navi™ 200 OTSO, 210A VASA, or 220A NAALI with additional wavelength (-L)

Sensor surfaces: Au, other metal or inorganic coating

Software: MP-SPR Navi™ Control, DataViewer and LayerSolver™

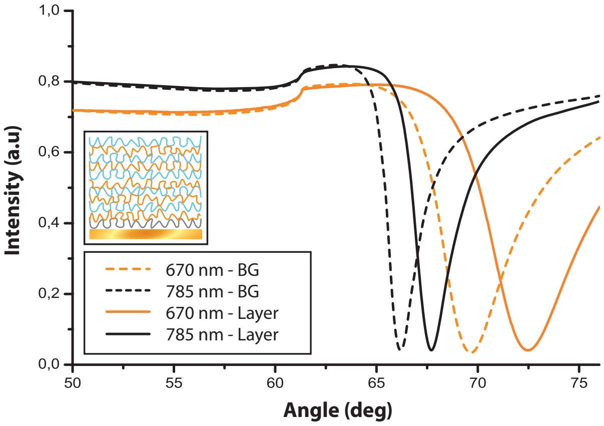


Figure 3. MP-SPR curves of 5 *in situ* deposited polyelectrolyte multilayers measured at 670 nm (orange) and 785 nm (black) wavelengths. The dashed lines are background and solid line are with the deposited layer.

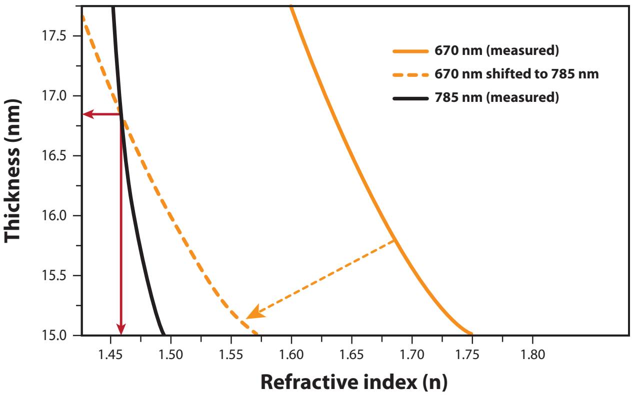
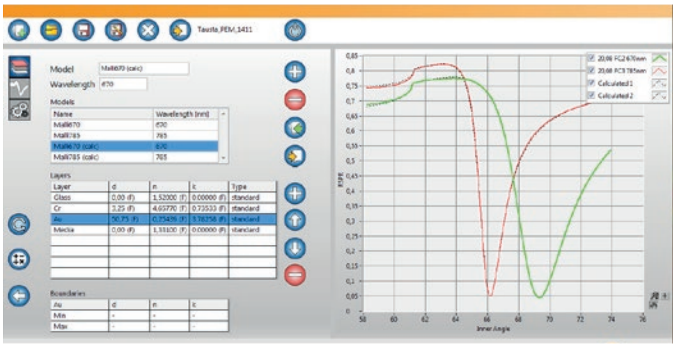


Figure 4. Illustration of the two wavelength analysis principle. Black and orange line are RI – d continuum answers for both of the wavelengths. Dashed line is sifted curve based on the dRI/dλ value, which enables a unique solution for the thickness and RI.



Model Mall670 (calc)
Wavelength 670

Models

Name	Wavelength (nm)
Mall670	670
Mall785	785
Mall670 (calc)	670
Mall785 (calc)	785

Layers

Layer	d	n	k	Type
Glass	0,00 (F)	1,52000 (F)	0,00000 (F)	standard
Cr	3,25 (F)	4,65770 (F)	0,73533 (F)	standard
Au	50,75 (F)	0,23439 (F)	3,78258 (F)	standard
Media	0,00 (F)	1,33100 (F)	0,00000 (F)	standard

Boundaries

Au	d	n	k
Min	-	-	-
Max	-	-	-

Figure 5. MP-SPR Navi™ LayerSolver™ can be used to fit measured SPR curves to determine thickness and RI of the deposited layer.