Application Note # 171

Optical dispersion modelling of thin layers with multiwavelength MP-SPR

Optical dispersion is a characteristic change of refractive index of a material with wavelength. With Multi-Parametric Surface Plasmon Resonance (MP-SPR), the possibility to measure complete SPR curves at more than one wavelength allows assessment of dispersion constants to be measured of thin layers of a non-absorbing material. The more wavelengths are used, the better the estimation of the optical dispersion constants will be possible. Here optical dispersion measurement and analysis are given for poly-electrolyte multilayers (PEM).

Introduction

Optical dispersion is the change of refractive index (RI) with wavelength (λ). Various parametric functions have been used for describing the optical dispersion, of which the Cauchy and Sellmeier equations are the most common for dielectric materials. Out of these, the Cauchy equation is the most useful:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \ldots,$$

Where n is the refractive index, λ is the wavelength, and *A, B, C*, etc., are coefficients that can be determined for a material by fitting the equation to measured refractive indices at known wavelengths. The coefficients are usually quoted for λ as the vacuum wavelength in micrometers. In MP-SPR wavelength range (670-980 nm), the higher terms (*C, D,* etc.) are generally not significant, and a simple two-parameter equation ($n=A+B/\lambda^2$) can be used for dispersion modelling of most dielectric materials. Figure 1 and Table 1 illustrate the options available for MP-SPR instruments. The parameters estimated by curve fitting (using LayerSolver software for MP-SPR Navi™) are: *d* (thickness), *n* (real part of the RI) and *k* (imaginary part of the RI). The elucidation of a unique RI and thickness (*d*) of a thin layer is generally only possible with three wavelengths, because only then the amount of equations is equal to the amount of parameters (*d*, *A* and *B*). In this application note, some reference data is given with analysis of a PEM film with four wavelengths (4-WL).

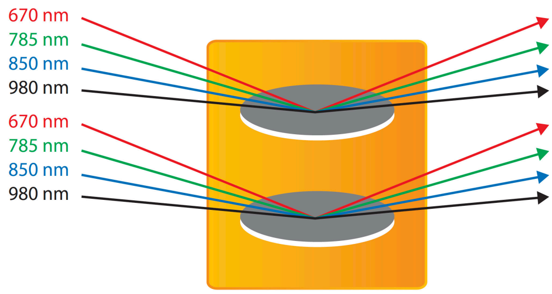

Figure 1. In a two-channel MP-SPR instrument, both channels are on a one sensor slide. Four wavelengths (4-WL) are measured simultaneously in each channel.

Materials and methods

Polyethylene imine (PEI), poly[styrene sulphonate] sodium salt (PSS) and poly[allylamine] hydrochloride (PAH) were obtained from Sigma-Aldrich. These polymers were diluted to a concentration of 0.1 mg/mL in water with 150 mM NaCl. As running buffer 150 mM NaCl was used. BioNavis standard gold sensors were used (SPR102-AU). The multilayers were formed by applying first a scaffold of PEI, then PSS and then PAH alternatively, as further detailed in the PEM kit available from BioNavis (SPR141-PE).

SPR sensograms were acquired in angular scan mode, as to collect the complete SPR curves at each timepoint. The thickness and RI were determined after each injection of PAH, in order to obtain the angular shift of each PEM bilayer (PSS+PAH) up to 8 bilayers. Data was analyzed with LayerSolver™ software (version 1.4), first fitting the blank sensor, and then after each bilayer setting the layer thickness as a global parameter for each wavelength and invoking the Cauchy fitting mode for the RI (Figure 2). Note that the constants *a* and *b* are to be set as global parameters too, as the RI is now derived from the wavelength via these parameters.

Table 1. Multiwavelength options for MP-SPR Navi™ instruments

Number of wavelenghts measuring in a single spot	What can be calculated			Pre-requisite
	thickness	RI	dn/dλ	
1 wavelength	☑*	☑*		dn/dλ and RI or thickness
2 wavelengths	☑	☑		dn/dλ
3 wavelengths	☑	☑	☑	—
4 wavelengths	☑	☑	☑	—

* With a single wavelength, one has to know refractive index of the layer in order to calculate layer thickness or vice versa.

BioNavis

email: info@bionavis.com
www.bionavis.com

Results and discussion

The sensogram of the PEM adsorption is depicted in Figure 3. At each bilayer step the total layer thickness and the Cauchy dispersion constants were calculated. Results were obtained by fitting the layers using simulation mode 2, which focusses on the minimum of the SPR peak. The SPR angle shift was almost linear with a step size of about 0.5 degrees for a bilayer (at 670 nm). Results of the fittings are shown graphically in Figure 4.

The results (Figure 4) show that the Cauchy constants are slightly changing during the deposition process. The refractive index slightly decreases and the dispersion constant B increases. This might indicate that layers become more hydrated/swollen during the deposition: layers close to the gold are more compact than the outer layers.

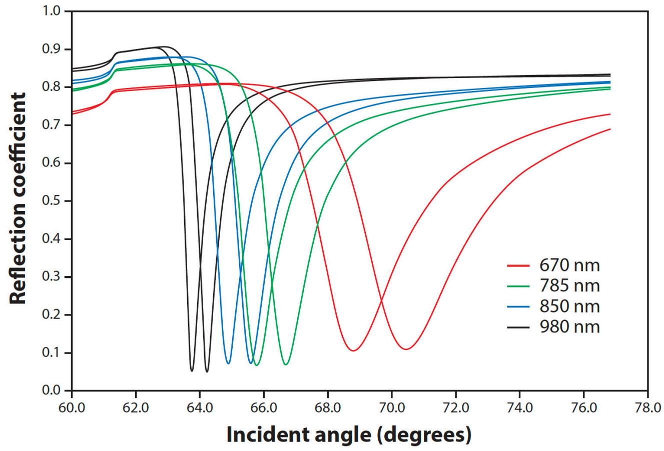

Figure 2. Complete SPR curves before and after PEM layers measured with four wavelengths (670, 785, 850 and 980nm).

Conclusions

MP-SPR instruments measure the complete SPR curve with multiple wavelengths of light allowing characterize layer unique thickness, refractive index and dispersion value, which are shown here on PEM layer. Tailored instruments can be equipped up to four wavelengths in each channel providing new insights to layer characterization. With the same instrument setup, also real-time and label-free interactions with the layer can be measured.

Detailed description of fitting procedure is available in a LayerSolver™ manual.

See also PEM layer characterization with linear (two wavelength) analysis in our Application Note #128.

Read also how 3 wavelength analysis was utilized to characterize lipid layers Soler *et al.*, ACS sensors 3 (11), 2018.

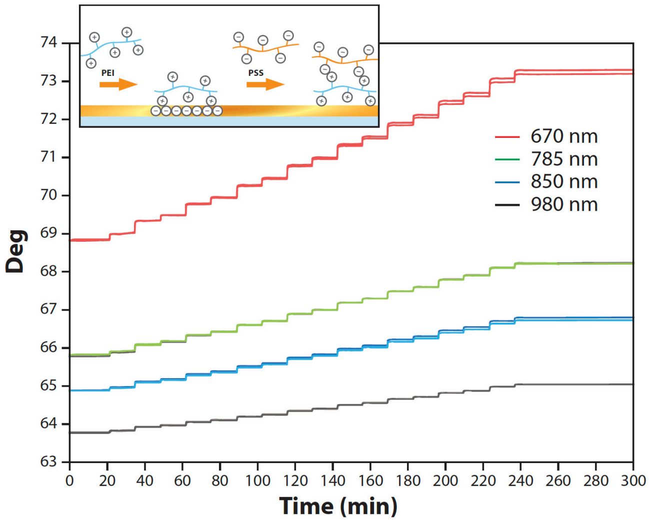

Figure 3. Sensograms of the SPR-angle for the formation of 8 bilayers of PEM at four wavelengths (670, 785, 850 and 980 nm).

Recommended instrumentation for reference assay experiments
MP-SPR Navi™ 200 OTSO, 210A VASA and 220A NAALI
Sensor surface: SPR102-AU
Software: MP-SPR Navi™ Controller, DataViewer, LayerSolver™ for MP-SPR Navi™

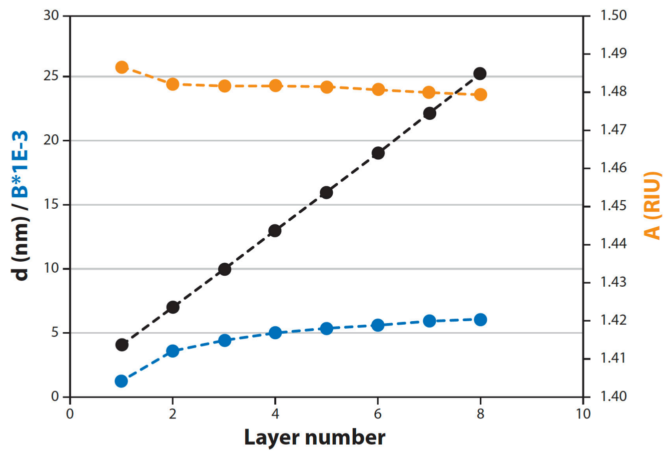

Figure 4. Obtained values for the thickness (d) and the Cauchy parameters A and B as a function of number of PEM bilayers.