Multi-Parametric Surface Plasmon Resonance – A new technique to determine thickness and refractive index of thin and thick layers

Michael Robinson*, Johana Kuncova-Kallio**, Niko Granqvist***, Janusz W. Sadowski**

* BioNavis Ltd, Washington (DC), phone: 410 923 0062, email michael.robinson@bionavis.com
** Oy BioNavis Ltd, Tampere, Finland, email: janusz.sadowski@bionavis.com
***Univeristy of Helsinki, Faculty of Pharmacy, Department of Biopharmaceutics and Pharmacokinetics, niko.granqvist@helsinki.fi

ABSTRACT

We present a new method for measuring thicknesses and refractive indeses of ultra-thin, thin and relatively thick films by using multi-parametric surface plasmon resonance (MP-SPR). The layers measured can be organic, inorganic, metallic, and it is also possible to follow interaction kinetics of interaction components with all these materials.

Keywords: SPR, thickness, refractive index, nanolayer, material characterization

1 INTRODUCTION

We present a new method for the determination of thickness and refractive index of thin and thick layers. For the past 20 years SPR has been routinely used for biomolecular interaction analysis. [1] Now, Multi-Parametric Surface Plasmon Resonance (MP-SPR) broadens the application range to biophysical studies, and biomaterial studies, such as ceramic and polymer coating characterizations and biocompatibility studies. [2,3] Thickness and refractive index can be measured both on nanolayers (Å-100 nm) and on thick layers (350 nm – microns). With additional wavelengths, a singular solution can be found without known RI or thickness. [4] Materials that can be measured include metals, semiconductors and dielectrics, such as Al2O3, SiO2, hydrogels, nylon, cellulose, PS, PP, PET and more [2-6].

2 TECHNOLOGY

The MP-SPR technology is based on surface plasmon resonance phenomena, which is achieved using Kretschmann configuration with rotating light source. This set-up scans the angular area of 40 to 80 degrees, providing RI range of 1.0 to 1.4. In a single wavelength mode, the resulting SPR full curves can then be fitted using a known RI of the measured material and Fresnel formalism. However, in multiple wavelength mode, when the material is scanned with at least two different wavelengths, both thickness and RI can be experimentally determined [4].

2.1 Ligth Non-Absorbing Samples

Determining thickness and optical properties on nanoscale layers with optical techniques has been challenging. In optical methods used to provide both thickness and optical properties, the basic theory and calculations are not able to distuinguish between the thickness and refractive index and result in a continuum instead. [4, 6] Therefore, it has been mandatory (a) to know

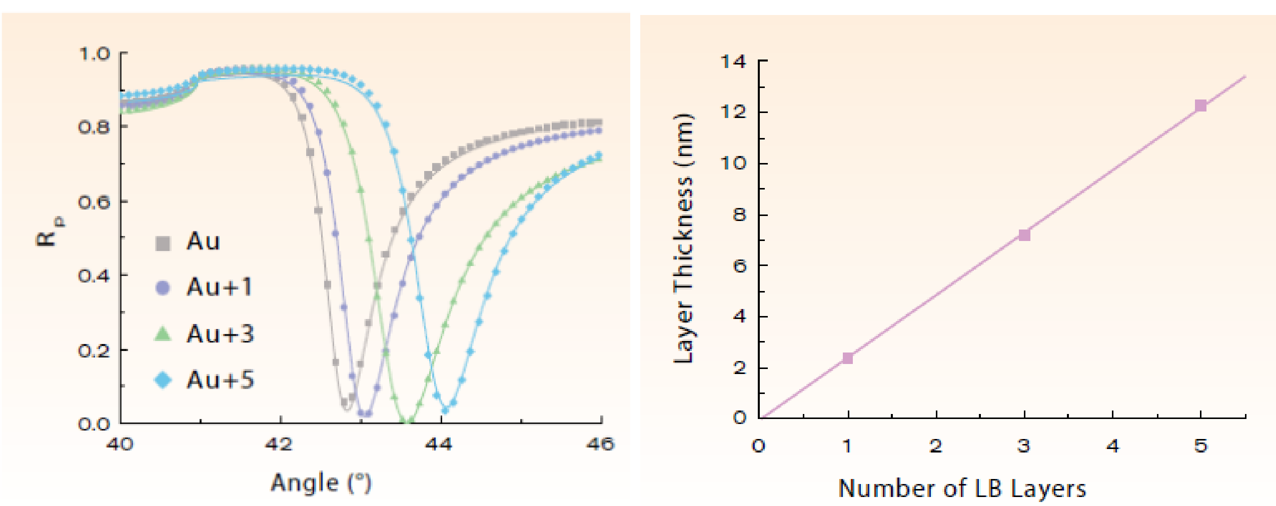

Fig. 1 Left: Measured full SPR curves of Au-coated sensor slide with 1, 3 and 5 layers of LB-layers. Right: After fitting of the curves, the thickness of the layers can be determined.

either parameter, or (b) measure at many conditions that result in a big enough difference to the optical properties of the whole system [4, 6].

(a) Full SPR curve itself contains highly sensitive information of the deposited layers, and accurate thickness can be calculated if the RI is known [Fig1] [4]. When one of the parameter has to be known, most of the techniques rely on refractive indeces from literature. These can, however, vary for the same material, such as Al2O3 with RI 1.76394 or 1.65682 [7] Moreover, new materials can be only approximated as their RI is not known yet. These assumptions can cause large uncertainty in the result.

(b) However, if the measurement is performed with one ore more wavelengths, it is possible to determine both the RI and thickness from one measurement simultanously [4]. Similar measurements can also be performed using two media far enough from each other by their RI (i.e. water and air), for similar results [6]. MP-SPR, measuring with two media or two wavelengths, enables determination of both RI and thickness and therefore, provides more accurate information of the same sample from the same measurement.

2.2 Ligth Absorbing Samples

In the cases where the refractive index of a material is complex (light-absorbing, such as metal organic framewoks (MOF), semiconductors or organic solar cell dyes, the thickness and refractive index have an unique answer instead of a continuum. With MP-SPR measuring the full SPR, this property can be exploited and allows us to

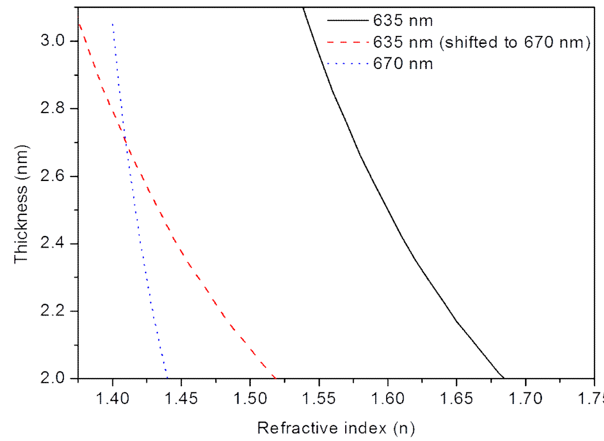

Fig. 2: Refractive index (RI) and thickness can be determined from two measurements, each at different wavelength. Black line – sample measured at 635 nm, blue dashed line – sample measured at 670 nm, red dashed line – measurement at 635 nm shifted to 670 nm. At the crossing point, a unique singular solution is obtained both for thickness and RI.

determine the uniques RI and thickness for a nanolayer. [Fig3,Fig4].

2.3 Thick layers

A commonly known property of SPR is, that the evanescent field created and probed by SPR reaches only approximately one half wavelength into the measuring media, and that the sensitivity of the field decays exponentially. However when the layer on top of SPR coating is thicker than the half-wavelength of the SPR

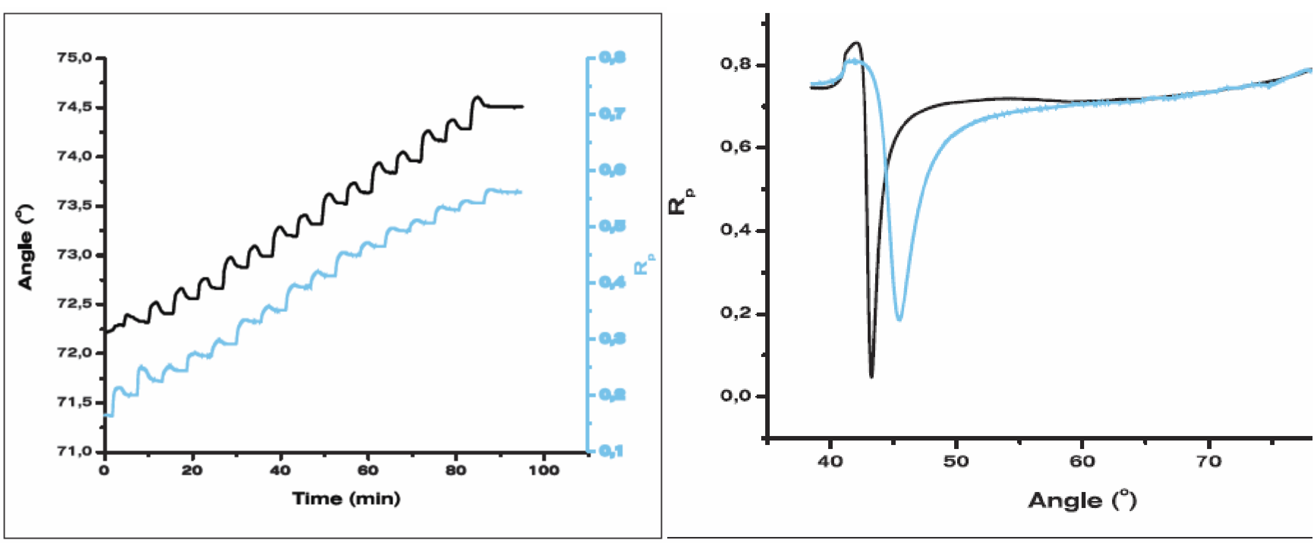

Fig. 3 Left: Multiple injections of Metal organic framework (MOF) from copper and trimesic acid. An angular shift can be detected with each layer addition from either the peak minimum (black) or fixed angle intensity (blue). The fixed angle intensity looses linearity in fabrication of thick layers. Right: The full SPR curve shows that there is not only growth of the material, but also change in light absorbance. (SPR peak minimum shifts up.)

exitation light, a different optical phenomena, called SPR waveguide is created [8]. This phenomena can also be effectively used to measure layers thicker than the SPR field, or to measure reactions in or above the new thick layer [Fig5]. When more than one of the waveguide peaks are visible, there exists an unique answer to the thickness and RI of the material. This method works only for dielectric materials, like most polymers and glasses, as even a small amount of light absorption will diminish the waveguide peaks and larger amount prevent measurements completely.

3 FUTURE PROSPECTS

MP-SPR empowers multidisciplinary research between life sciences and material sciences. Biochemists are moving from molecule-molecule interactions to molecule-material interactions, as seen in drug encapsulation or development of diagnostic kits. On the other hand, material science and, especially nanotechnology, is moving towards functional materials, including encapsulation of biomaterials, nanoparticles and more. MP-SPR is a promising new technique, which provides more information both on the material properties, such as thickness and refractive index, and also on the reactions between the sample and the material, such as binding kinetics [2].

REFERENCES

[1] Crescenzo *et al.*, *Journal Cellular and Molecular Bioengineering 2008, 1 (4), 204–215*
[2] Liu *et al.*, *Langmuir 2010, 26(12), 9565–9574*
[3] Liu *et al, Langmuir, 27 (16), 9769–9780 (2011)*
[4] Liang *et al.*, , *Sensors and Actuators B: Chemical 2010, 149(1), 212-220*
[5] Orelma *et al.,Biomacromolecules (2011) 12 (12), 4311–4318*
[6] Albers and Vikholm-Lundin, *Nano-Bio-Sensing, 1st ed, Chapter 4, Springer 2010*
[7] www.refractiveindex.info (20.3.2012)
[8] Lévesque *et al.*, *Applied optics, 1996 (33), 34, 8036-8040*

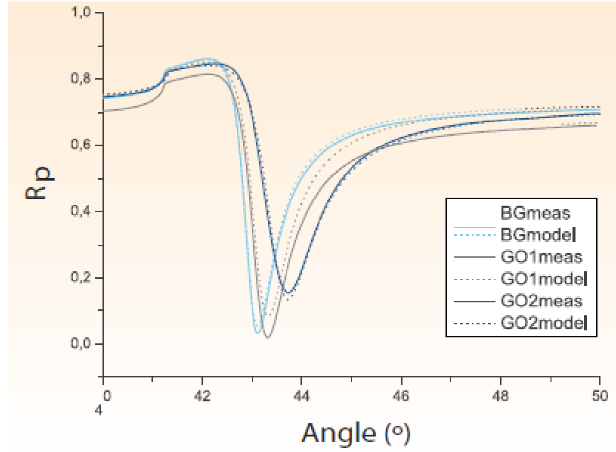

Fig. 4: Full SPR curves of thin graphene films made with two different method, and their respective optical models. BG = Au-coated sensor slide, background; GO1 and GO2 = graphene films.

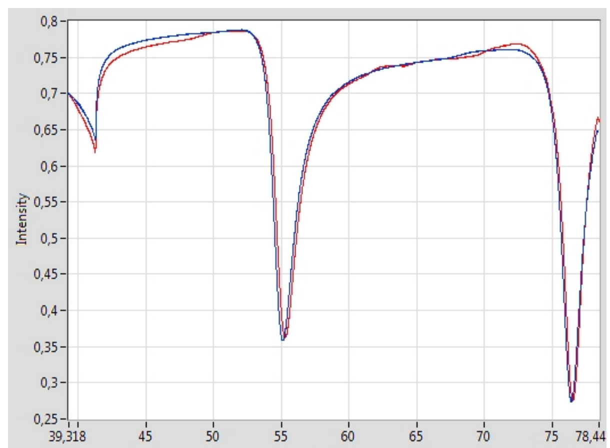

Fig. 5: SPR waveguide phenomena created on a PS-PMMA copolymer spin coated on a gold SPR sensor. Thickness of the material has to be more than half of the light source wavelength in order for this phenomena to occur – here 800 nm.