Application Note # 127

Determining thickness and refractive index of metal and metal like ultrathin films using MP-SPR

MP-SPR can also be used to measure metal and other highly light absorbing thin films with high accuracy. These can be utilized for example in developing new materials, processes or quality control.

Introduction

Mutliparametric surface plasmon resonance (MP-SPR) can be applied as a method to determine thickness and refractive index of a number of materials not easily measured using optical techniques. Metals and metal-like compounds such as Au, Pt, Ag, Cu, Al, and TiN can be deposited directly on glass substrate and measured from subnanometer to hundred nanometers as a single SPR peak, depending on the optical properties of the material [1,2]. This can be applied further for example in determining different mono- and multilayers from different coating methods such as chemical vapor deposition (CVD), atomic layer deposition (ALD), sputtering, spin coating, etc.

The most common methods for measuring thin film thickness and optical properties are ellipsometry and more advanced spectroscopic ellipsometry. While both ellipsometry and MP-SPR are optical methods, ellipsometry measures through the material and has limited capability for measuring non-transparent samples [3], which most conducting materials are. For Plasmon generation needed for MP-SPR this is not as crucial issue. Also multilayer films, such as thin films with an adhesion layer, are challenging for ellipsometric methods [3], while they are clearly distinguishable with surface plasmon measurements as they change the overall shape profile of the SPR angular spectra measured in MP-SPR [1,4].

In this example CVD deposition quality and thickness magnitude inside the CVD reactor has been studied using MP-SPR. As nanosciences advance, the demand for determining the process quality and variance in the deposition become increasingly important issues, and it is crucial to know and control these parameters for successful applicability of the coatings.

Materials and Methods

The evaporation chamber experiments were performed with SATIS CR 725 (Satis Vacuum Ag, now Satisloh). The sensors were fixed on one of the arms of the substrate holders in different radial positions (see Fig. 1) to determine position dependence of the deposition. The substrates were pure glass SPR sensor slides. During the deposition process, 2 nm of Cr (adhesion layer) were deposited followed by 50 nm (nominal) of Au. The deposition was performed twice with slight adjustment to the deposition time.

The sensors were measured before and after the deposition with SPR Navi 200-L instrument (BioNavis Ltd) at 670 nm (single wavelength mode) in the angular scan -mode. The measurements were performed in ambient atmosphere in air and at 20 °C temperature. The resulting full SPR curves were fitted for the layer thickness and complex RI using Fresnel formalism [1] using Winspall v.3.02 (Max Planck Institute for Polymer Research, Germany). All metal layer parameters were set as floating variables in the analysis, and the fitting was repeated with different starting values.

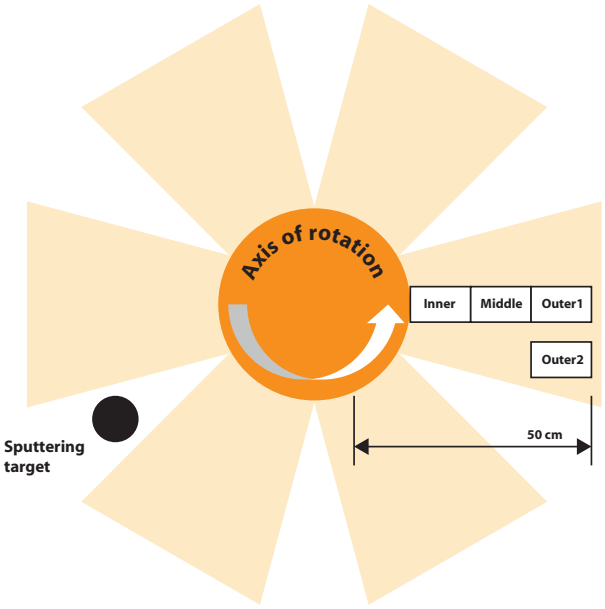

Figure 1. Schematic of the CVD deposition chamber and the sensor position inside the chamber.

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Results and Discussion

Measured SPR curves of the deposited sensors from both batches are shown in Fig. 2 and the analyzed thicknesses in Table 1. The difference in the horizontal direction of the arm was almost 10 nm (over 50 cm arm length). This was most probably due to the location of the sputtering target in the chamber (Fig. 1) as the areas closer to the center in closer vicinity of the target due to the circular structure of the reactor. The conformity in the radial direction was 0.2 nm in both batches. This is reasonable, as the arms are rotating and each sensor with at the same radius from center has approximately identical exposure to the target. Also the outer ring sensors clearly exhibited peak broadening that fitted with increasing roughness in the gold layer [1], and therefore also showed poorer deposition quality than the inner and middle ring.

These measurements provide better insight into the process and can be used to tune different steps within the process. Based on these measurements, the process can be adjusted, and positioning of product substrates tune inside the reactor. For extremely delicate coatings it could also be beneficial to similar internal standard setup of sensors instead of maximum yield of products in order to ensure the quality of the product.

Conclusions

MP-SPR is suitable for process optimization of coating processes. For thin films, almost any materials (including multiple layers) can be measured and thickness and refractive index determined from the single SPR peak measurements. It is especially useful for control of functional coatings, where material properties change with the thickness of the material (such as coatings for food processing, biosensors, drug release), for multilayer structures (multiple layers of materials with different RI, such as in manufacturing process development, organic solar cells), for active materials (change of properties in different pH, temperature, electric field), for instance.

MP-SPR empowers multidisciplinary research between life sciences and material sciences. 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 [5].

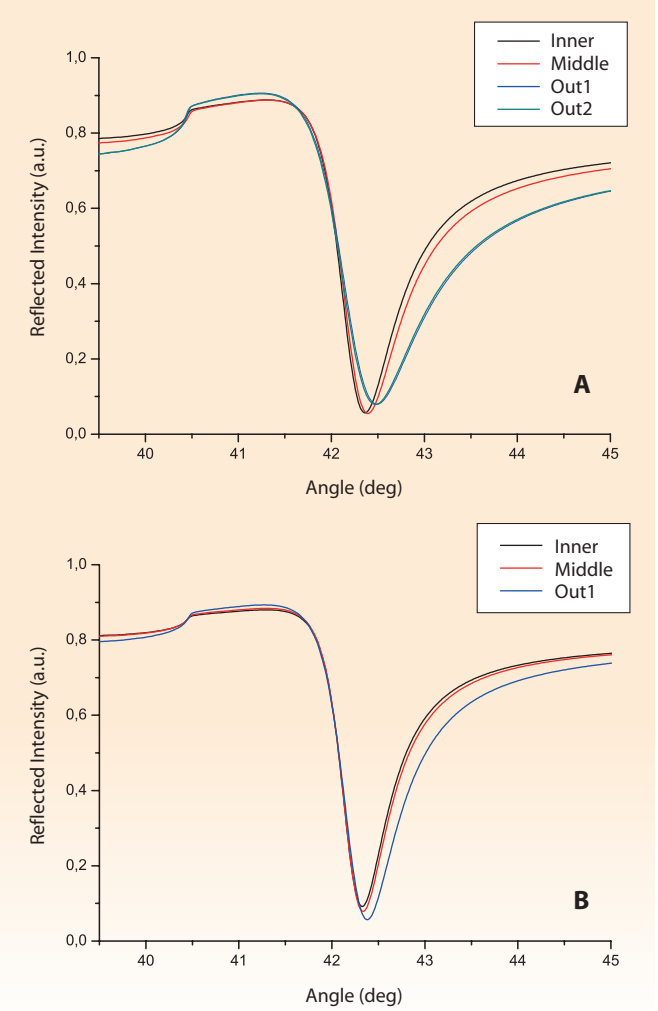

Figure 2. a) Measured SPR curves of sensors deposited in batch1. b) Measured SPR curves of sensors deposited in batch2.

		Inn	Middle	Out1	Out2
Batch1	Cr	1,1	1,1	1,1	1,1
	Au	50,4	49,0	39,2	39,4
Batch2	Cr	1,1	1,1	1,1	
	Au	53,9	53,0	49,4	

Table 1. Calculated metal layer thicknesses for batches1 and 2.

[1] Sadowski et al. Optical Engineering, 1995, 34 (9), 2581-2586
[2] Sadowski, et al. Biosensors & Bioelectronics 1991, 6, 439-444,
[3] Hilfiker et al., Thin Solid Films 2008, 516, 7979-7989
[4] Albers and Vikholm-Lundin, Nano-Bio-Sensing, 1st ed, Chapter 4, Springer 2010
[5] Liu et al., Langmuir 2010, 26 (12), 9565–9574

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