Multiple wavelengths, multiple angles surface plasmon resonance measurements

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Abstract

We present the use of multiple wavelengths, multiple angles surface plasmon resonance data for unambiguously determining the optical index and thickness of a 15-50 nm thick dielectric layer deposited on a 50 nm thick gold layer. The surface plasmon resonance is generated from a UV-VIS spectrophotometer, providing accurate wavelength information. The position of the plasmon peaks as a function of wavelength and angle to the incoming light beam is fitted to a model of multiple planar layers in which the unknown optical index and thickness of the dielectric layer are parameters. We apply this technique to evaporated tantalum pentoxide, leading to an optical index assumed to be constant in the 500-1000 nm range of 2.55±0.1.

1. Introduction

Surface plasmon resonance (SPR) is increasingly used in biosensors applications for identifying thin layer thicknesses and overlayer coverage[1,2]. The theory predicting the resonance condition when the plasmon wavevector and the incoming light source wavevector match is well understood[3]. The in-plane component k_p of the wavevector must verify the condition

$k_p = \frac{\omega}{c}\sqrt{\frac{\varepsilon_{di}\varepsilon'_{met}}{\varepsilon_{di}+\varepsilon'_{met}}}$, where ω is the light source pulsation, c the velocity of light, ε_{di} the dielectric constant of the layer deposited on the metallic surface and ε'_{met} its imaginary part[4]. The in-plane component of the wavevector must match that of the incoming light source: $k_x = \frac{\omega}{c} n_p \sin(\theta)$ where n_p is the optical index of the glass supporting the metallic layer and θ the angle of the incoming light source relative to the normal of the layer.

All commercial instruments use, to our knowledge, curves of the reflected intensity *v.s.* angle at a single wavelength (670 nm for the Ibis II from Holland Biomaterials, 760 nm for Biacore instrument, 840 nm for Texas Instrument's Spreeta system) and either assume the optical index of biomolecules to be known and extrapolable ($n_{proteins} \simeq 1.41$ in most cases) or calibrate their instrument using an independent technique applied to a limited range of species (e.g. Biacore using radioactive labeling[8]). The assumption on the optical index which is required for analyzing single wavelength SPR measurements is a major drawback when unknown samples are used[12].

De Bruijn *et al.*[9,10] have previously analyzed the limitations of SPR measurements and described iterative algorithms for identifying these properties in a more general context (requiring multiple measurements with various thicknesses of layers made of the unknown dielectric material).

We here display multiple wavelengths, multiple angles measurements[5] as an unambiguous means to identify both the thickness and optical index of an unknown dielectric layer. A major advantage of this technique is that it provides simultaneous and accurate measurements of the thickness of thin layers (20-50 nm) and the optical index of that dielectric layer with an estimated uncertainty of ± 0.05.

2. Experimental setup

The setup presented here (Fig. 1) is a cost-effective means of obtaining multiple wavelengths and angle-dependent curves for locating the SPR reflected intensity minimum and deducing from these experimental data an unique pair of optical index and thickness values. We

illustrate this method for a thin film of tantalum oxide[6]. Indeed, the very high optical index of this material (1.9 to 2.1 as reported in the literature[7]) makes most commercial instruments ineffective for observing the SPR dip in the reflected intensity since they are designed for the limited purpose of detecting biological species and do not provide a wide enough angle range for such an exotic application. Furthermore, the very thin layers we are interested in ($< 100\ nm$ thick) strongly limit the available analysis methods. We use an Shimadzu UV-1601PC UV-Visible spectrophotometer as a variable wavelength converging light source (angle of the light beam: 7^o). We introduce a half-cylinder glass prism (with optical index: 1.518) in place of the sample holder and use an Hamamatsu S3399 photodiode for measuring the reflected intensity in a Kretschmann SPR configuration, the resulting voltage being measured by an HP3457A multimeter and transmitted via GPIB to a personal computer. Although the convergence angle of the light beam is very large, the convolution effect on the reflected intensity *v.s.* angle curve is not a major limitation since the peak is very broad for tantalum oxide on a thin gold layer. The limited sensitivity range of the photodetector limits our investigations to the wavelength region of 500 nm to 1000 nm, while the manual rotation stage (Melles Griot, USA) on which the half-cylinder prism is fitted provides all angles from 0^o to 90^o with $\pm 2^o$ resolution.

The SPR is generated by an evaporated Ti/Au layer 5 and 55 nm thick respectively on top of which various thicknesses of tantalum oxide have been deposited (e-beam evaporation).

3. Results

The minima of the SPR dip in the reflected intensity *v.s.* wavelengths curves have been measured for a wide range of angles, *i.e.* 35 to 85 degrees in our case for which the dip is within the accessible wavelength range as shown in Fig. 2. The graphs in this figure display the reflected intensity normalized by a reference curve taken at an angle for which no plasmon resonance is expected. We then manually iterate our Matlab-based simulation software which provides the reflected light intensity for all required set of wavelengths and

angle. The simulation software accurately simulates a stack of planar interfaces, while we consider the optical index of pure dielectrics (imaginary part of the optical index null) to be constant over the whole wavelengths range and we do take the variable (complex) optical index of gold into account over the wavelength range using the tabulated values provided in Ref.[11].

Only one single pair of optical index and thickness of the unknown layer provides an accurate fit of the experimental data as shown in Fig. 3. We observe the fitted thicknesses of tantalum oxide to closely match the expected thickness as monitored by the quartz crystal microbalance during the deposition process. However, the optical index is surprisingly high, in the 2.5 to 2.6 range, when compared to the values reported in the literature[7]. This explains why other optical means of measuring the thickness (Sopra MOS 4DG ellipsometer) reported inaccurate values (data not shown): the standard optical index values (in the 2.2 to 1.8 range for wavelengths ranging from 250 nm to 850 nm respectively) provided to the fitting software were not accurate for our layers.

The fits can be seen in Fig. 3 not to perfectly match the measurements for the lower wavelengths. This slight discrepancy might be attributed to our assumption that the optical index of the dielectric layer (tantalum oxide) is constant over the wide (500 to 1000 nm) wavelength range which might be partially invalid.

We independently checked the accuracy of the SPR results by looking at the cross section of two of the samples by transmission electron microscopy (TEM). The two thicknesses measured on the resulting images (Fig. 4) match well with the thickness information provided by the quartz crystal microbalance used for monitoring the deposited mass during the evaporation process as well as the fits of the SPR data.

4. Conclusion

We have presented a means of precisely determining both the thickness and optical index of a thin dielectric layer using multiple wavelength surface plasmon resonance. The technique

is easily reproducible since the variable wavelength source is a widely available UV-VIS spectrophotometer. Sweeping the wavelength at which the SPR is generated removes one of the main limitations of SPR for quantitative measurements, namely the assumption on the optical index of the dielectric layer. The measurement technique was shown reliable by independent thickness estimate by TEM.

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FIGURES

Fig. 1. Experimental setup: the light coming from the UV-VIS spectrophotometer comes from the right, enters the cylindrical prism, reflects on the Ti/Au coated glass slide on which various thicknesses of tantalum oxide were deposited, and the reflected intensity is monitored by a photodetector positioned in the output beam.

Fig. 2. Raw experimental data: measurements were performed in a UV-VIS spectrophotometer by scanning the wavelength range from 500 to 1000 nm while the angle of the sample to the incoming light beam was varied by discrete 5^o steps from 35^o to 80^o. Estimated sample thicknesses: 18 nm (top-left: two independant measurements, full and dashed lines), 25 nm (top-middle), 35 nm (top-right), 39 nm (bottom-left), 50 nm (bottom-right).

Fig. 3. Comparison between the simulated reflected intensity as a function of angle and wavelength (the SPR reflection dip is visible as a black curve on the graph) and the experimentally measured position of the SPR dip (as observed on curves in Fig. 2). Top-left: 17 nm/n = 2.55. Top-right: 24 nm/n = 2.55. Bottom-left: 35 nm/n = 2.6. Bottom-middle: 39 nm/n = 2.45. Bottom-right: 50 nm/n = 2.50. The position of the graphs displaying simulation results match those of the experimental data shown on figure 2.

Fig. 4. Independent estimate of the thickness of tantalum oxide on 18 nm (right) and 39 nm (left) nominal thickness samples using TEM. The multiple-wavelength SPR technique was also used on these two samples to accurately measure the thickness and optical index as shown in Figs. 2 and 3.