VIS-optical spectroscopy
revealing the dynamics of physical processes

In the field of thin films characterization, the VIS optical spectroscopy is an important tool to investigate the layer thickness, optical constants as refractive and absorption indexes. Knowing the nature of the materials that form the layer structure, information on the chemical composition and/or structure can be obtained from the optical constants. The method here presented has been extensively described elsewhere[1]. The aim of this work is to introduce briefly to the reader an extraordinary powerful tool. Because, as a Hawaian proverb says: "no rain, no rainbow!".

1. What?

A simple VIS-optical spectroscopy setup consists of a white light source whose beam light is sent on the sample to be investigated and a detector, which generally is a spectrometer in visible optical range (400nm – 850nm). The sample is a thin layer (solid or liquid) deposited on a substrate. It is important that two reflection beams: one at the air/sample interface and the other one at the sample/substrate interface (Figure 1a), will interfere at the detector surface. According to the classic optics, the result of the interference will be a figure of interference with fringes (Figure 1b).

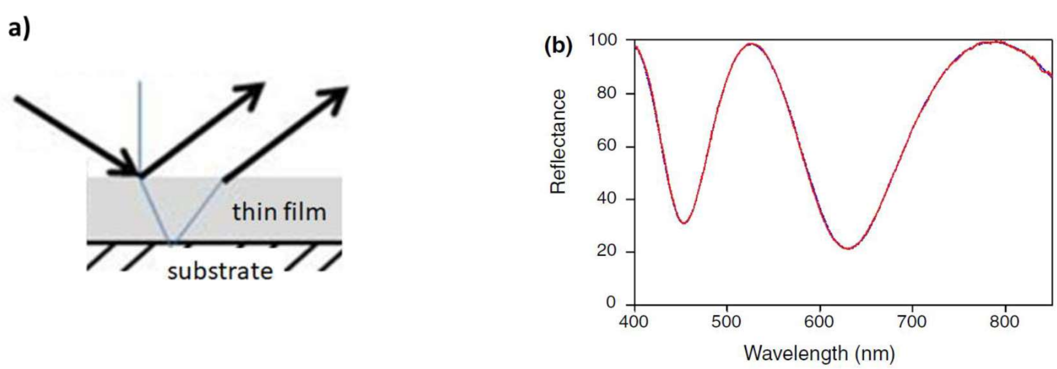

Figure 1. a) Schematically the light beams interacting with the thin film sample within a VIS optical spectroscopy setup; b) Fringes of interference for a thin layer of 550nm

The fringes are "bread" for a specialist in optical spectroscopy: analyzing them interesting details about the layer composition and/or structure are revealed. Mathematically this is a problem with one equation (the refection spectrum) and usually three unknowns: the layer thickness, d, the refractive index, n, and the absorption index, k. The latter two unknowns may be connected between them via the Kramers - Kroning relations, but the difficulty is that we need the dispersion of one parameter (n, or, k) on the whole optical spectrum. The

[1] N. Tomozeiu, J. Coat. Technol. Res. **16** (6) 1571-1580 (2019), https://doi.org/10.1007/s11998-019-00218-1

message is that we need the help of other type measurements for method calibration, or a good understanding of the material properties as a function of their structure / composition. A simple example is given hereunder: the same material was deposited on the same substrate but in one run-deposition, respectively in two, with stop and restart the deposition. In *Figure 2* are shown very clear the differences in the reflection spectrum as measured (in red color) and as fitted (in blue color) with the same program, without considering the interface generated by the stop time during deposition.

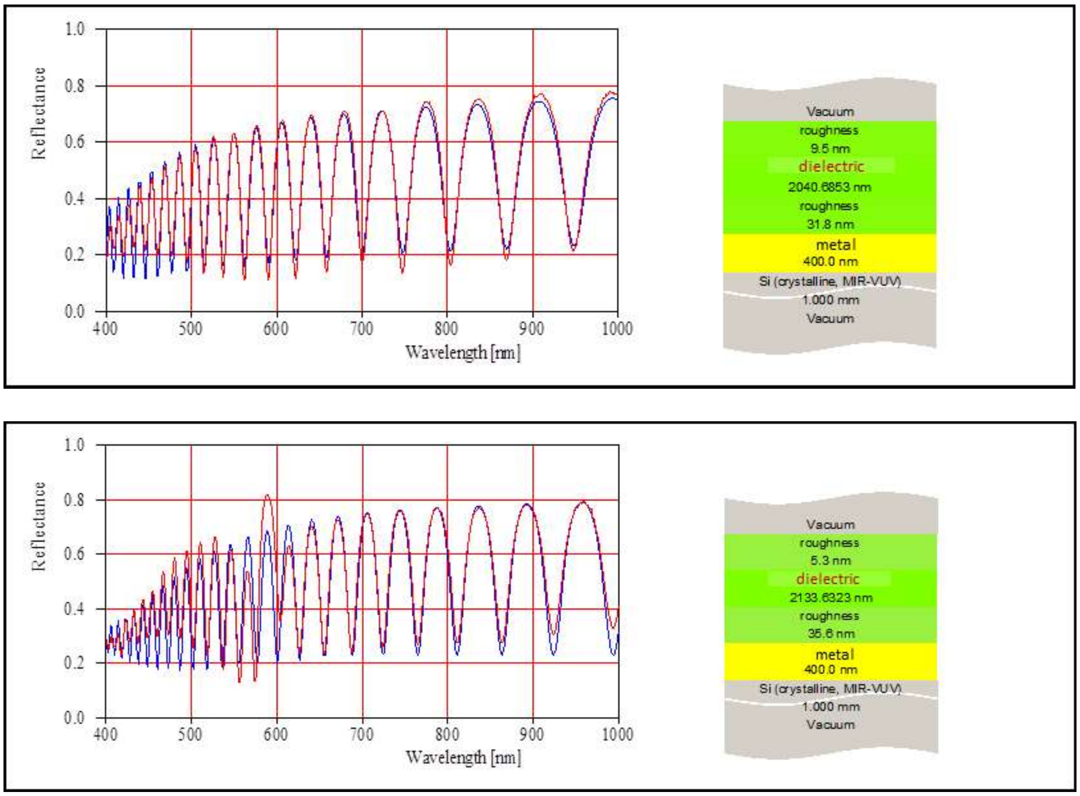

Figure 2. The same sample deposited under the same conditions but with different strategies in time deposition: top – one run deposition, bottom- with interruption during deposition – a multi-layered structure.

2. VIS reflectometry and water evaporation: an example of application

Let consider a sample formed from complex aqueous mixture (e.g. water, polymeric colloids). It is important that the two interfaces of the liquid sample where the beam light is reflected are parallel planes. For this, it is necessary that the liquid will totally wet the substrate surface (contact angle null) and the substrate surface has a well-known reflection coefficient. This is why, the sample holder of the liquid layer is build-up on crystalline silicon (c-Si) from polymeric material so that layers of different thickness up to 20μm can be made (see Figure 3). The measurement beam light is sent on the sample via an optical fiber and the reflected light is collected using another optical fiber; this reflected light is the input in a spectrometer that reveals the reflectance spectrum. The measurement is driven by an on-line computer and it can be repeated with a well-defined periodicity.

The temperature of the sample-holder, which can be varied using a heater, is revealed by a thermocouple. Also the relative humidity within the measurement chamber and the ambient temperature are monitored.

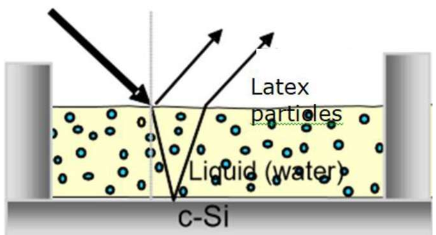

Figure 3. The sample holder for VIS reflectometry measurements of liquid samples (water + polymeric particles)

The optical interference between the beams reflected at the two interfaces of the liquid (air at the top and c-Si at the bottom) will result in a spectrum of reflection with fringes. In *Figure 4*a such a spectrum is shown: in red color the measured one and in blue color the simulated spectrum using the SCOUT program[2].

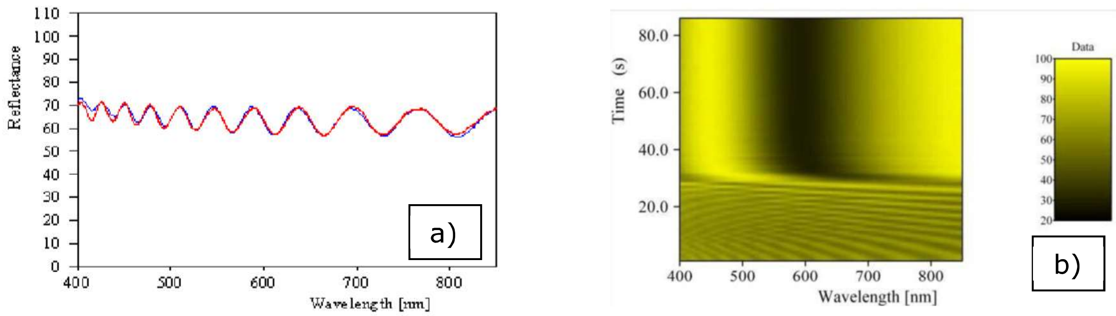

Figure 4. a) The reflection spectrum measured for a layer of water at room temperature and rh=48%; b) The water evaporation revealed by the color 3D plot: the color scale represents the reflectance value, the Ox axis is the wavelength and the Oy axis is the time.

Measuring such reflection spectra with periodicity, a color-scale 3D like plot, is obtained as that showed in **Error! Reference source not found.**b . Knowing the periodicity of measurements and the number of the spectrum, the evolution of the reflectance spectrum in time is easily revealed. The measured fringes shift in time towards small values of the wavelength, which is equivalent with reducing the layer thickness (water evaporation). When this process ends the spectra are identical in time, and vertical columnar structures are generated as it is shown in **Error! Reference source not found.**b for t>28sec.

The layer thickness at the beginning of the experiment was 2776.9 nm and at the end it remains 292.5 nm after about 30 sec.

[2] Wolfgang Theiss, http://www.wtheiss.com W. Theiss, Hard- and Software, 2010 (online)

Having the recorded spectra, the layer thickness values can be calculated using the spectrum simulation technique. From here, the evaporation rate and the dynamics in time of the evaporation process are simple to study. More about this can be found in our published paper in Journal of Coatings Technology and Research (2019) https://doi.org/10.1007/s11998-019-00218-1

3. Instead of conclusions

The VIS optical reflectometry is a tool of investigation versatile, relatively simple to buildup and use, but it needs experience to analyze and correctly interpret the results. I am a great fan of it because I had solved many problems using it when the samples have been thin solid films of semiconductors or dielectrics, or complex aqueous samples.