Optical analysis of coatings by variable angle spectrophotometry

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Abstract

Variable angle spectrophotometry (VAS) involves measurement of transmittance and reflectance as a function of the angle of incidence, wavelength and polarisation. This provides a means for analysis that yields the thickness and optical constants of the individual layers in multi-layer coatings, as well as other parameters that can be related to optical material properties. In the past decade, VAS has evolved into an accurate tool for optical characterisation of coatings, with many advantages over ellipsometry.

The paper describes the tools for measurement and analysis developed by the author for the UV/Vis/NIR and IR wavelength ranges. Examples are given for single- and multilayer stacks with materials like ZnO, Cr, ITO and SiO_2.

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1. Introduction

For many decades, a spectrophotometer has been a standard instrument in most laboratories where optical materials are being characterised. Although mostly used for determining filter characteristics and reflectance and transmittance spectra, a spectrophotometer has also been used as a tool for the determination of the refractive index and layer thickness of coatings. A comparison of different methods is given by Arndt et al. [1]. Most of these methods determine a complex refractive index at one wavelength at a time, using the optical properties measured at this wavelength. An exception is the more advanced Inverse Synthesis method that was already used in the 1980s by Dobrowolski et al. [2]. Their method is based on comparing near-normal reflectance and transmittance spectra that are measured at different angles and polarisation, with similar spectra that are calculated using a thin film optical model of the coating in which the optical constants of the materials are described by dielectric functions. Non-linear regression is used to minimise the difference between measured and calculated spectra by varying the values for the thickness of the layers and the parameters of the dispersion models, resulting in their best estimates.

Over the years, the inverse synthesis method has mostly been applied in spectroscopic ellipsometry (SE), where it is used to obtain the coating parameters by fitting measured and calculated spectra of the ellipsometric Y and D functions. In the last two decades, this technique has grown into widely accepted and powerful tool for coating analysis [3].

Although an inverse synthesis method based on transmittance and reflectance spectra obtained by variable angle spectrophotometry (VAS) has advantages over the method based on spectroscopic ellipsometry, the latter became the dominant method. The main reason for this is that although determination of the optical properties for normal or near normal incidence is part of a standard procedure for most laboratories, measurements at oblique incidence are much more difficult and experimental results from different laboratories often disagreed [4].

In the past decade, considerable progress has been made in identifying and overcoming the sources of error present when making spectral optical measurements at oblique incidence [5,6]. This has led to the development and commercialisation of new spectrophotometer accessories for the measurement of reflectance and transmittance at oblique incidence [7,8]. Using these accessories, which already are in use in many laboratories, it has become possible for these laboratories to perform state-of-the-art high-accuracy VAS measurements.

A comparison of the properties of VAS and SE for optical characterisation of coatings is given in Table 1. SE is in general

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Table 1
Comparison of the two methods SE and Vas

	Spectral ellipsometry	Variable angle spectrophotometry
Measurement accuracy	Δ: 0.2%–0.3%	R_c, R_g: 0.2%–0.5%
	Ψ: 0.2%–0.5%	T: 0.1%–0.3%
Layer thickness sensitivity		
$d<5$ nm	++	+
5 nm$<d<$500 nm	++	++
$d>500$ nm	+	++
Optical constant sensitivity		
n	++	++
Low k	−	++
High k	++	++
Flexibility	+	+++
Information content	++	+++
Performance/Price ratio	+	++

more accurate in determining the thickness of extreme thin layers (<5 nm) because of the sensitivity of the phase difference D for small variations in the optical thickness. However, for thick layers (>500 nm) VAS often seems to give more reliable results.

In determining the optical constants, both methods perform equally well except in the case of the imaginary part k of the complex refractive index of low absorbing materials (low values of k). For this reason, SE is often combined with transmittance data produced by a spectrophotometer in order to provide a spectrum that is sensitive for absorption.

Accurate SE measurements are obtained by measuring the change in polarisation that occurs when a beam of light is directly reflected by the coated surface at large angles (>50°) where the effect of polarisation becomes large. Preferably, reflected light from the back of a transparent substrate has to be excluded. VAS does not have this limitation and in contrary to SE, VAS can also be used for measuring the coating properties when the coating is on the back of a transparent substrate (or laminated between two substrates). VAS is therefore a more flexible technique.

The amount of information that can be obtained with VAS is also much more that with SE. With SE only two spectra are obtained for each angle of incidence with angles usually limited between 50° and 75°. With VAS, up to six (6) spectra per angle of incidence can be obtained on a coated glass substrate: the transmittance T, the reflectance of the coated side R_c and the reflectance of the glass side R_g, each of these measured for P and S polarisation. The angular range is also larger, often 0°–75° for T and 8°–75° for R_c and R_g [7,8]. Therefore, with VAS, more complex multi-layer coatings can be analysed.

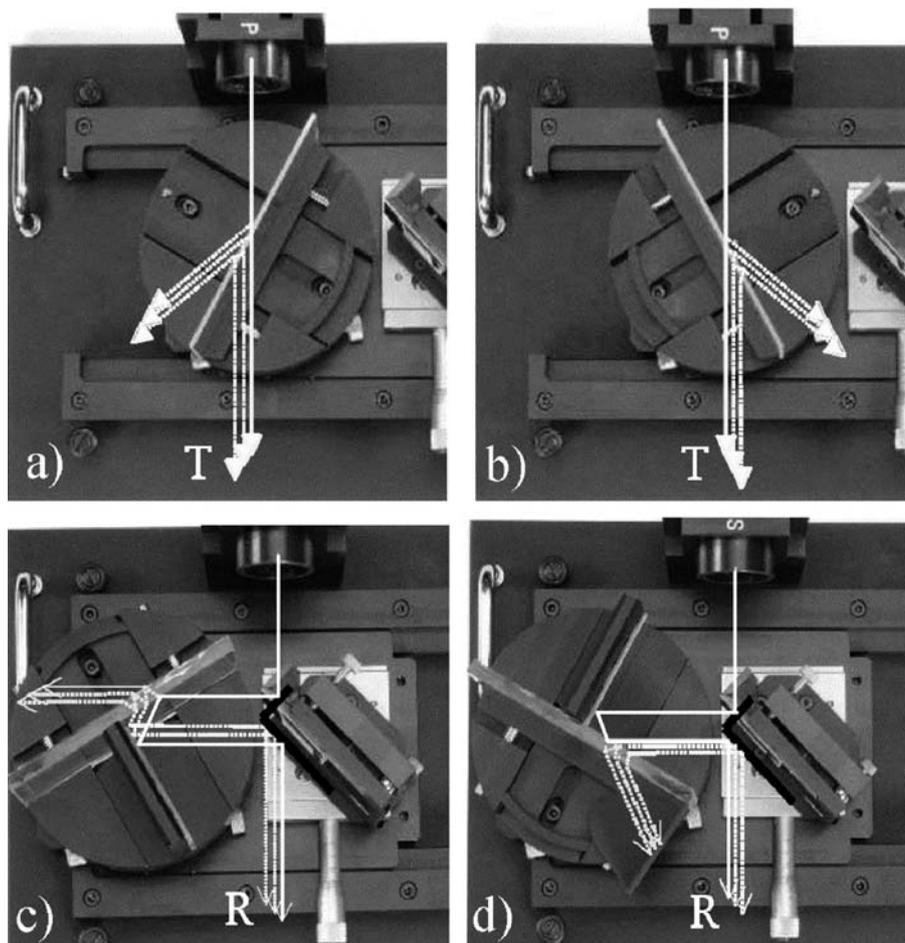
Fig. 1. Different top views of the directional reflectance/transmittance accessory. (a, b) Transmittance at +60° and −60° incidence, respectively; (c, d) reflectance at +60° and −60° incidence, respectively.

Furthermore, VAS does not require an additional instrument to obtain reflectance, transmittance and other filter characteristics that form the specifications for coated optical products. With SE, these specifications can only be determined by model calculations, which are less suitable for quality control. For this reason, VAS is also a more economical method.

In the following sections, we will discuss the use of VAS for determining the thickness and optical constants of multi-layer coatings.

2. Variable angle spectrophotometry

2.1. Measurements

Measurement of directional transmittance and reflectance is complicated by polarisation effects and by the occurrence of secondary shifted beams. These secondary beams, due to inter-reflections and reflections from the back of the sample, are shifted with respect to the optical axis, resulting in multiple mutually shifted images on the detector. Proper detection therefore requires the use of an integrating sphere [7] of which the entrance port (larger than the diameter of the spectrophotometer beam) serves as an under-filled uniform detector. Another important issue is the accuracy of the angular setting, which is a weak point of most commercial spectrophotometer accessories. Based on an investigation of the problems involved with this type of measurement [5], measurement procedures and new spectrophotometer accessories for VAS have been developed by the author, taking into account all major measurement problems [7,8].

2.2. VAS in the UV/Vis/NIR region

For measurements in the wavelength region 250 nm–2500 nm, a PerkinElmer Lambda 900 UV/Vis/NIR Spectrophotometer is used in our Optical Measurements & Testing Lab. For VAS, this instrument is equipped with a directional reflectance/transmittance accessory [7] and a 60-mm integrating sphere as detector.

Fig. 1 shows four different top views of the accessory. Pictures (a) and (b) show the measurement geometry in transmittance mode for 60° incidence in two directions. Taking the average of these two measurements results in a compensation of systematic errors and calibration of the zero position of the rotation stage [7]. The rotation stage has an angular accuracy of 5′ (0.083°). The polariser is shown in *P* polarisation. The arrows indicate the transmitted and reflected primary and secondary beams.

Similar pictures of the accessory in the reflectance mode are shown in Fig. 1c and d. In Fig. 1d, a baffle is placed behind the sample to prevent the radiation that is transmitted by the sample from reaching the detector.

A detailed description of the accessory can be found in the work of van Nijnatten [7]. The reflectance measurements are performed relative to a reflection standard, which is calibrated using a Directional VW absolute reflectance accessory that was specially developed for this purpose [5].

As an example, we will discuss the analysis by VAS of a 3-layer $TiO_2/Cr/TiO_2$ coating on a 2-mm glass substrate. According to our coating department which produced the sample by E-beam evaporation, the thickness values of the layers based on previous experience were approximately 40 nm and 60 nm for the top and bottom TiO_2 layers and 10 nm for the Cr layer, respectively.

For the analysis of this sample, 9 spectra were measured in the wavelength range 300 nm–1200 nm, T, R_c and R_g at (near-) normal incidence and at an oblique incidence for P and S polarisation at 60° (T) and 45° (R_c and R_g). The reason that these angles are not the same is that at the time of the measurement the highest accuracy for directional reflectance was obtained at 45°.

The analysis was performed using commercial available software (CODE version 2.4, W. Theiss Hardware and Software). The agreement between the measured and calculated spectra is shown in Fig. 2.

For the optical constants of the glass, values previously obtained on a similar glass were used and the thickness of the glass was included in the list of fit parameters. If for instance the absorption of the glass under investigation is in reality 1% lower than that of the glass from our database, the effect on the optical properties is compensated by lowering the thickness by 1%.
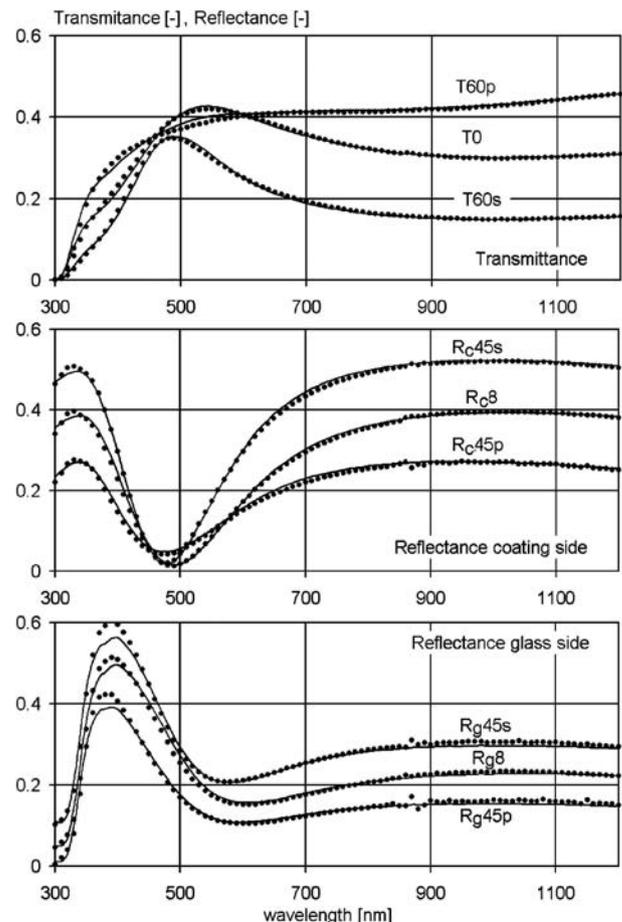

Fig. 2. Measured (markers) and calculated (lines) reflectance and transmittance spectra of the $TiO_2/Cr/TiO_2$-coated glass.
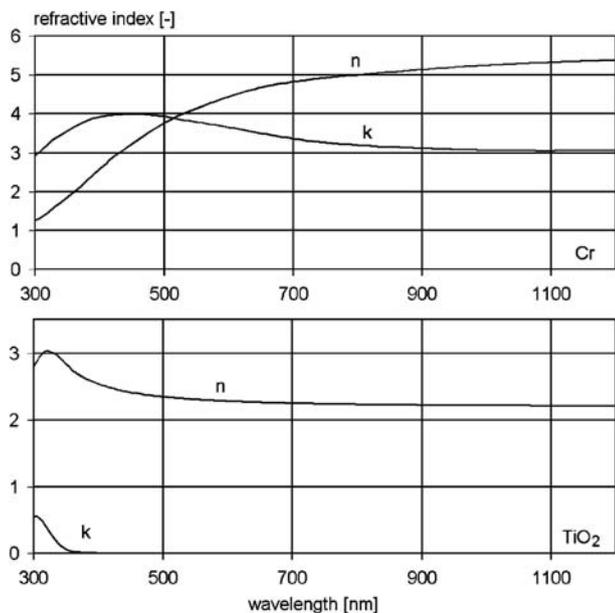
Fig. 3. Optical constants of the Cr and TiO_2 layers.

Fig. 5. Measured (markers) and calculated (lines) reflectance and transmittance spectra of the $ZnO/SiO_2/ITO/SiO_2$-coated glass.

The spectra of the optical constants of the TiO_2 and Cr that resulted in the calculated spectra of Fig. 2 are shown in Fig. 3. The actual stack description that was produced by the VAS analyses is 2.1 mm glass/64.4 nm TiO_2/9.4 nm Cr/43.8 nm TiO_2.

The dielectric function model for the optical constants of the thin Cr layer was a combination of a harmonic oscillator with Gaussian band shape and a polynomial correction for the imaginary part with altogether 7 parameters. A similar model with the polynomial expression in the real part was used for the TiO_2 layer. The total number of parameters in the fit was 17.

This example illustrates the advantage of having the possibility of including the reflectance measured from the back of the substrate, which represents the properties of the reversed stack. A coating like this would be difficult to analyse with SE since the absorbing Cr layer reduces the sensitivity of the measurements for the properties of the underlying 64-nm TiO_2 layer.
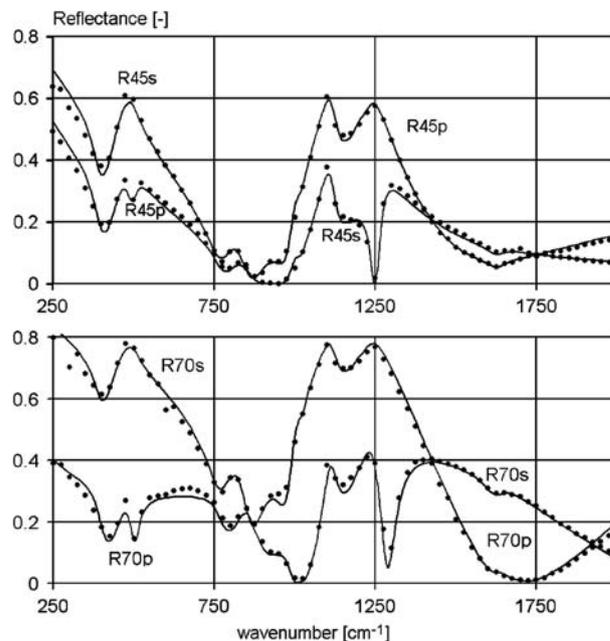
2.3. VAS in the IR region

For measurements in the wavelength region 2000 nm–56,000 nm, a PerkinElmer 983 IR Spectrophotometer is used in our lab. For VAS, the instrument is equipped with a directional reflectance accessory of which a top view is shown in Fig. 4.

The reflectance measurements are performed relative to a gold mirror that has been calibrated against IR reflectance standard certified at 10° incidence. Its reflectance at oblique incidence was for P and S polarised radiation calculated using

$$R_P(\theta) = R(10°)\frac{\rho_P(\theta)}{\rho(10°)} \tag{1}$$

in which ρ is the reflectance calculated using optical constants of gold from our software's database and the subscript P refers to the polarisation state.
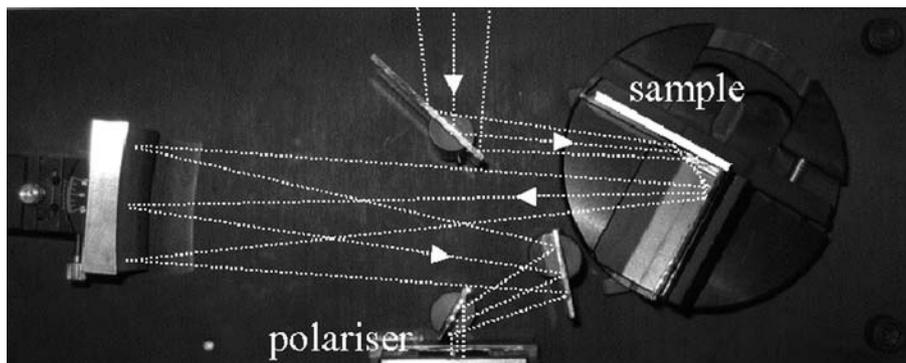

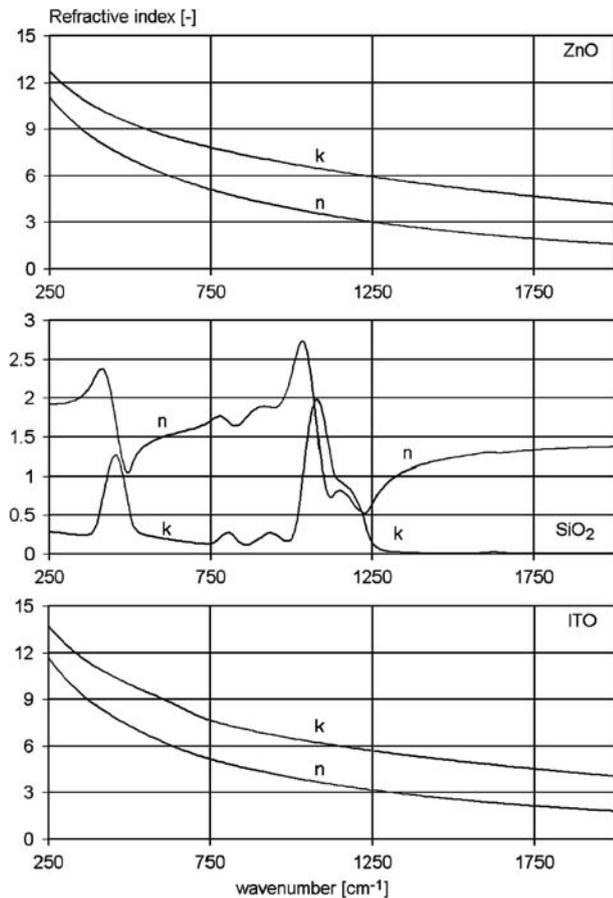Fig. 4. Top view of the TNO directional IR reflectance accessory for the PerkinElmer 983 Spectrophotometer.

Fig. 6. Optical constants of the ZnO, SiO$_2$ and ITO layers of the coating.

The rotation stage of this accessory has an angular accuracy of 5′ (0.083°). Other contributions to the uncertainty in the angle of incidence on the sample are due to a slightly tilted beam and an unknown offset the angular setting. As a result, the "true" angle of incidence θ is given by

$$\theta = a\theta' + b \tag{2}$$

where θ' is the angular reading from the rotation stage and a and b are constants ($a \sim 1$ and $b \sim 0$). By including these constants as fit parameters in the thin film analysis, the systematic error in the angle of incidence can be found and corrected.

As an example, we will discuss the analysis of a 3-layer coating that was deposited on a ZnO$_2$-coated flat glass substrate. The 3-layer coating was produced by E-beam evaporation and consists of two SiO$_2$ layers with approximate thickness of 1000 nm separated by approximately 50 nm ITO. The optical constants of the glass substrate and the (679 nm thick) ZnO coating were determined earlier. An Extended Drude model with frequency-dependent damping constant was used for modelling the optical constants of ITO. The optical constants of SiO$_2$ were adequately modelled by 9 harmonic oscillators with Gauss-distribution of resonance frequencies to account for local variations in the disordered SiO$_2$ system.

For the analyses, 4 reflectance spectra were measured in the wave number range 250 cm^{-1}–2000 cm^{-1} (corresponding to a wavelength range of 5 μm–40 μm), at incident angles of 45° and 70°, P and S polarisation.

The angle calibration parameters a and b of Eq. (2) were included in the list of fitting parameters in the analysis, in addition to the thicknesses and the optical constants of the SiO$_2$ and ITO layers. A total number of 45 parameters were fitted in the analysis.

The final agreement between the measured and calculated spectra is shown in Fig. 5. The spectra of the optical constants of the ZnO layer and the SiO$_2$ and ITO that resulted in the calculated spectra of Fig. 5 are shown in Fig. 6.

The actual stack description of the 3-layer coating that was produced by the VAS analyses is 1122.5 nm SiO$_2$/47.4 nm ITO/ 1048.4 nm SiO$_2$.

3. Conclusion

Spectrophotometer accessories and methods were developed for the accurate measurement of directional reflectance and transmittance of coated substrates. These accessories turn a spectrophotometer into a valuable tool in the optical characterisation of coatings, providing a means for analysis that yields the thickness and optical constants of the individual layers in multi-layer coatings, as well as other parameters that can be related to optical material properties.

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