Spectrophotometer accessories for thin film characterisation

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Abstract

The need for reliable measurement techniques for optical characterisation of thin films is growing. In the past, we have developed a manual tool for measuring directional optical properties with high accuracy. This tool is currently in use in over 40 laboratories for the characterization of coated window glass and optical filters. It has also proven to be a valuable instrument for thin film analysis by Variable Angle Spectroscopy.

An update on our latest developments includes an Automated Goniometer tool for Variable Angle Spectroscopy and BRDF/BTDF measurements and tools for measuring absolute reflectance and transmittance with the measurement spot at a fixed size and position on the sample.

Keywords: spectrophotometry, thin film analysis

1. Introduction

In the past decade, much of our work as been focussed on identifying and overcoming the sources of error present when making spectral optical measurements at oblique incidence [1,2]. This work has led to the development of new spectrophotometer accessories for Variable Angle Spectrophotometry (VAS) [3,4]. VAS 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.

On of the tools we have developed is a manual tool for measuring directional optical properties with high accuracy [3]. This tool (see Fig. 1) is currently in use in over 40 laboratories for the characterization of coated window glass and optical filters and has proven to be a valuable instrument for thin film analysis.

Performing directional optical measurements is not a simple task. Between scans, angles have to be changed and if necessary alignment adjusted. Avoiding mistakes requires the full attention of an experienced operator during the whole time. Often, many scans are required in transmittance and reflectance on both sides of the same sample. Needless to say that automation not only removes the burden of performing the time-consuming measurements manually but also offers more reliability.

Another requirement for obtaining input data for thin film analysis is that all measurement data need to be obtained on the same position on the sample. In the case of non-uniform layer deposition, not uncommon in R&D work, there is an additional requirement to obtain all data with the same spot size and geometry.

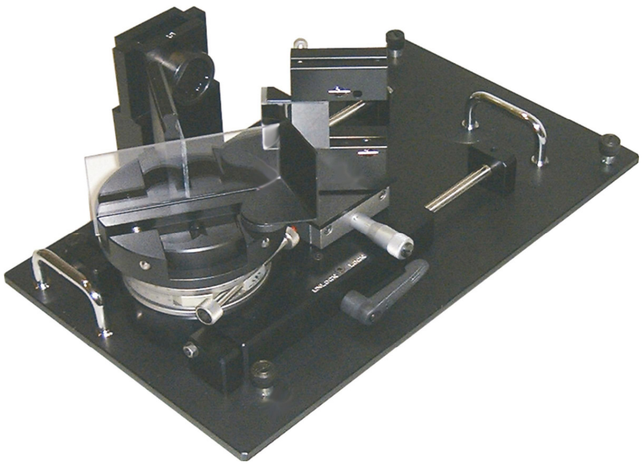

Fig. 1. The Directional Reflectance / Transmittance accessory currently sold by PerkinElmer (part nr. L631-0231) for the Lambda 800/900 and 850/950 spectrophotometers.

In the following sections we will discuss some of the new tools we have developed recently to provide adequate measurement solutions for thin film characterisation.

2. New tools for thin film characterisation

2.1 Automated Goniometer

We recently developed a new Automated Reflectance / Transmittance Analyser (ARTA) for the PerkinElmer Lambda 800/900 and 850/950 series UV/Vis/NIR spectrophotometers (see Fig. 2). It is an improved version of a tool that we designed earlier [5]. The ARTA is a stepper motor driven goniometer tool that uses an integrating sphere as detector.

Fig. 2. The Automated Reflectance / Transmittance Analyser (ARTA) installed in the PerkinElmer Lambda 950 spectrophotometer.

The sample holder is not fixed as in our earlier version [5] but is removable and can be adjusted to hold different sizes. The sample is positioned on a motorised rotation stage in the centre and the integrating sphere detector is either positioned behind the sample (at 180 degrees) for transmittance measurements or in front of the sample for reflectance measurements (at twice the angle of incidence) as shown in Fig.2.

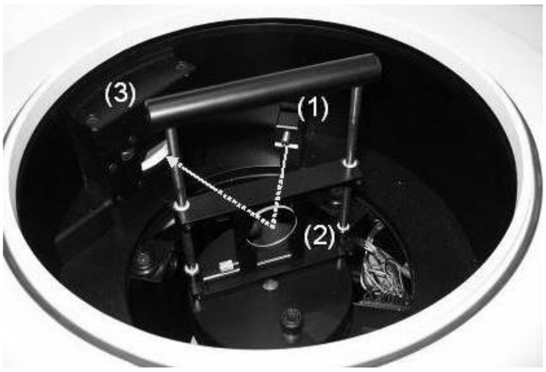

Fig. 2. Sample compartment of the ARTA: (1) sample beam periscope, (2) sample, (3) integrating sphere detector.

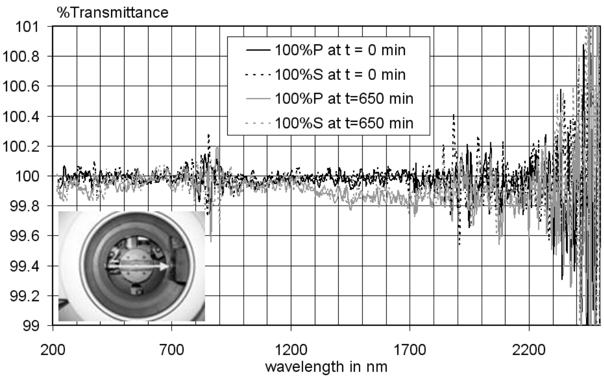

Fig. 4. 100% level measurement without sample, directly after Autozero calibration and after the accessory has been running for 650 minutes.

The reference beam of the spectrophotometer is guided through a mixed fibre bundle containing 50% UV/Vis fibres and 50% Vis/NIR fibres in order to obtain the whole UV/Vis/NIR range. The fibre bundle is connected to the movable integrating sphere detector. Since bending the fibres too strong can result in a change in the transmittance, the fibre bundle is mounted inside a flexible cable guide that controls and limits the bending.

The integrating sphere detector is made from Spectralon and has a 30 mm wide and 17 mm high rectangular entrance port. The sphere is equipped with a photomultiplier for the UV/Vis range and a Peltier cooled PbS cell for the NIR range. The integrating sphere is mounted in a large (320 mm diameter) drum that rotates in the horizontal plane along the same axis as the sample holder placed in its centre, driven by a second motorised rotation stage. The wall of this drum that forms the wall of the sample compartment is blackened for stray-light reduction. Without this feature, a systematic error can occur when reflection of a transparent sample is measured (transmitted beam reflected from the compartment wall). The results shown in Fig. 3 demonstrate the effectiveness of the wall coating to reduce stray-light.

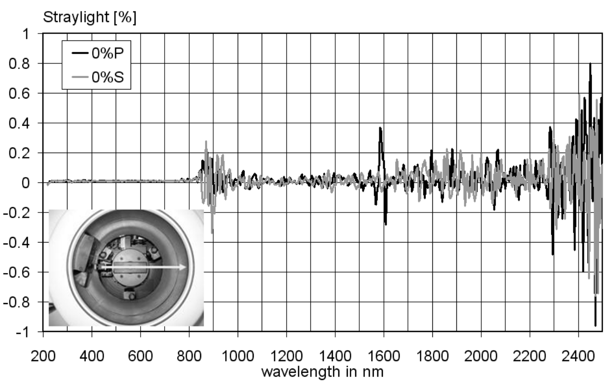

Fig. 3. Stray light (0% level) detected by the detector directly facing the position where the beam hits the compartment wall.

The nominal measurement range of the analyzer is 220 nm – 2500 nm (limited by the range of the fibre bundle and polariser. The results shown in Fig. 4 give an impression of the stability and noise level.

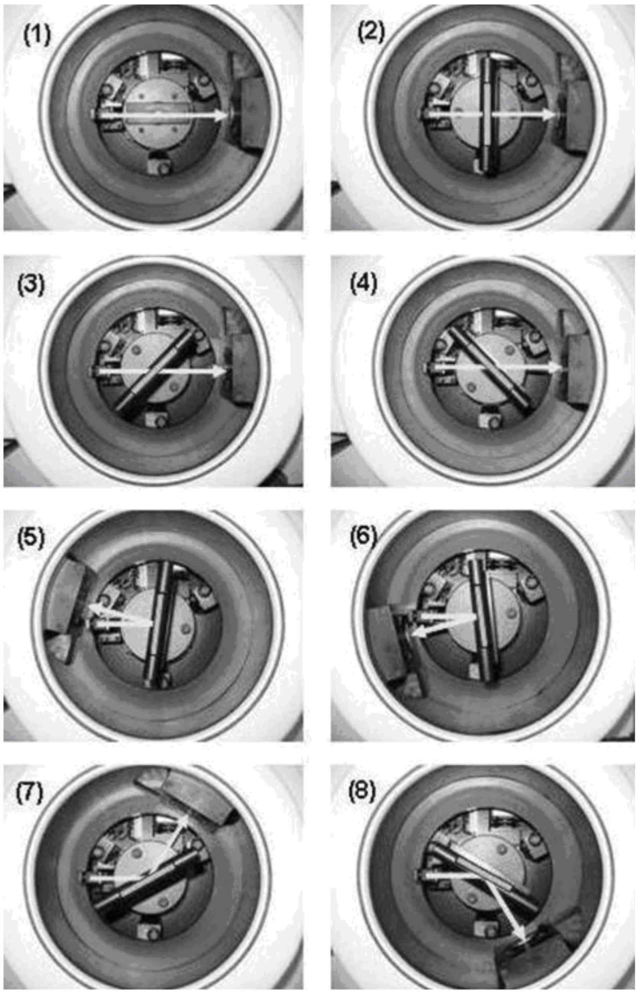

Fig. 5. Top view of the sample chamber with different measurement geometries: (1) Autozero mode (no sample installed), (2) transmission at 0°, (3) transmission at +45°, (4) transmission at -45°, (5) reflection at +8°, (6) reflection at -8°, (7) reflection at +60°, (8) reflection at -60°.

Various example of the measurement geometry are shown in Fig 5. The instrument is calibrated in the so-called Autozero mode Fig.5(1) without sample and detector in the 180° position. For transmittance the sample is inserted in the beam and the angle of incidence set with the sample rotation stage and the detector position at 180°.

For reflection measurements the angle of the detector rotation stage is set at twice the angle of the sample stage. The angular range is 10° - 350° (180° being the position directly behind the sample). The angular range for measurement of specular samples is 7.5° - 85° for reflectance and 0° – 85° for transmittance (depending on sample type and size).

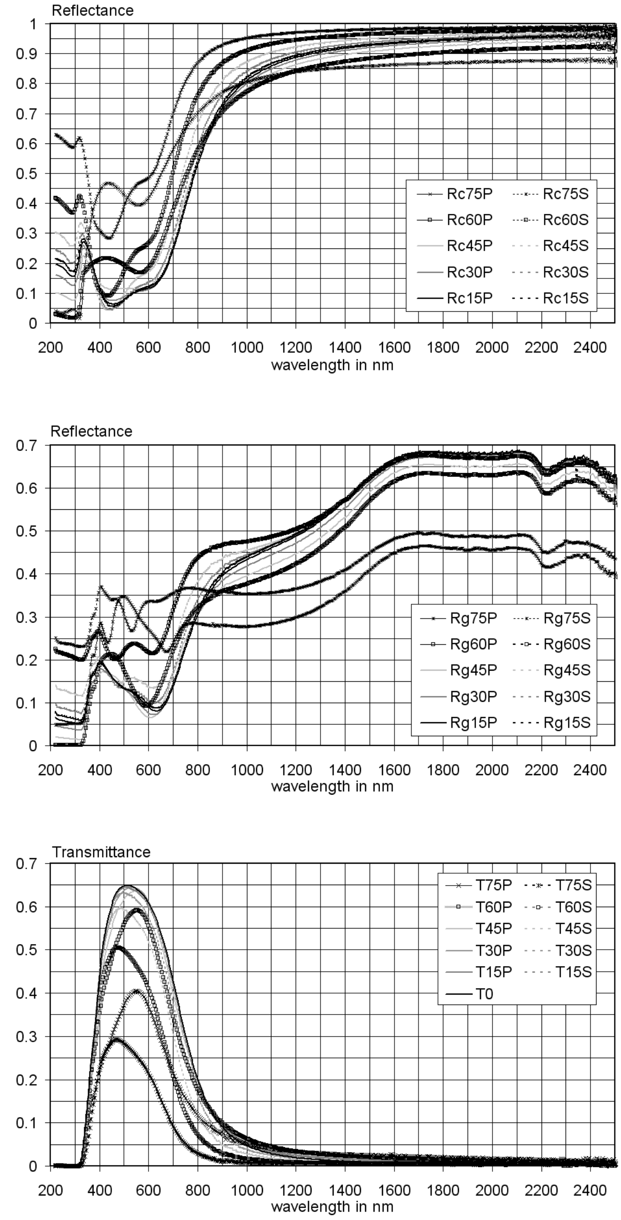

Fig. 6. Measurements performed by the ARTA in a single task. The results are the transmittance (T) and reflectance measured on the coated side (Rc) and glass side (Rg) of a Ag coated window glass sample measured with P and S polarised radiation at different angles of incidence.

An example of results obtained on a coated window glass sample are shown in Fig. 6.

The ARTA is also capable of measuring BRDF/BTDF and Angular Resolved Scattering. For this purpose, the detected solid angle can be controlled by a variable slit in the entrance port of the integrating sphere detector. This feature is useful for investigating the surface morphology of Transparent Conductive Oxides (TCO) used for solar cells. A key technology to increase cell efficiency in thin-film solar cells is optimization of the light trapping effect [5]. The ARTA has proven to be a useful tool in comparing different materials and processes. An example of such a measurement is shown in Fig. 7.

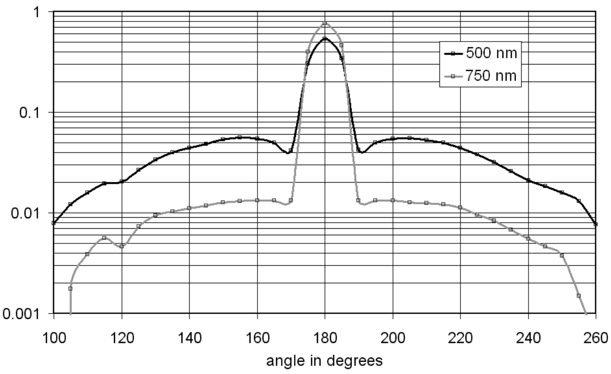

Fig. 7. Angular Resolved Scattering measurement of radiation transmitted by a TCO coated solar cell cover glass sample.

2.3 Absolute Reflectance/Transmittance accessories for the MIR range

In this section we will briefly discuss some of the tools we have developed for the Mid Infrared (MIR). The first one is an accessory capable of performing Reflection and Transmittance measurements with the same spot-size and beam geometry without moving the sample. The accessory is designed for the PerkinElmer Spectrum GX FTIR spectrophotometer (see Fig. 8). The measurement principle is based on a movable detector arm (see Fig.8).

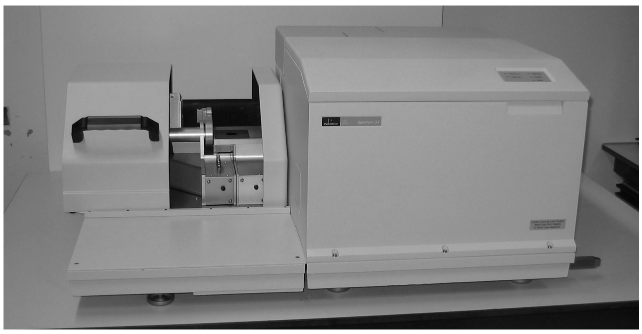

Fig. 8. Our Absolute 10° Reflectance/ Transmittance accessory installed in the Spectrum GX FTIR.

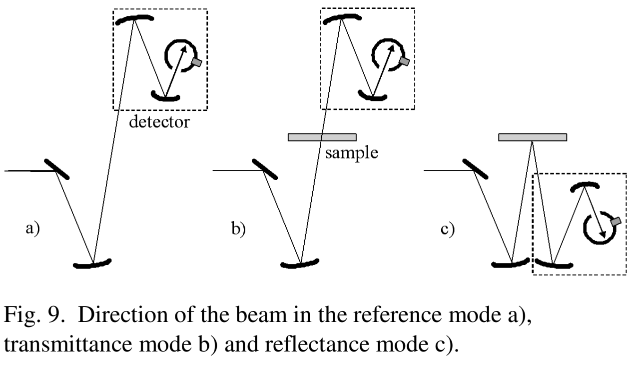

Fig. 9. Direction of the beam in the reference mode a), transmittance mode b) and reflectance mode c).

For a 100% reference measurement the detector arm is in the upward position (Transmittance mode) to capture the beam from below (see Fig. 9). A transmittance measurement (at 10° incidence) is performed by placing the sample in the beam on the horizontal sample plate. A reflectance measurement is performed by rotating the detector arm 180° to capture the reflected beam. A 25 mm diameter integrating gold sphere is used as a detector to reduce the sensitivity for misalignment. Since no calibrated reference sample is necessary the measurement is absolute!

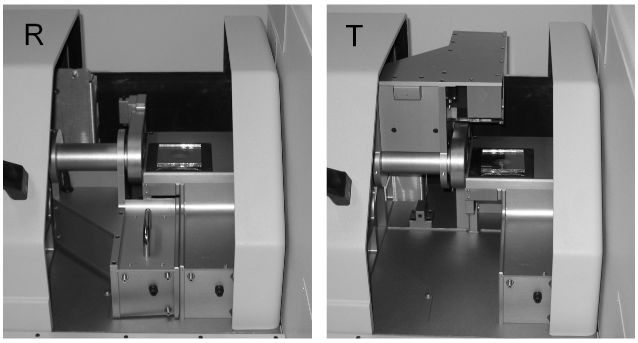

Fig. 10. The accessory in Reflectance (R) and transmittance (T) mode with a glass sample in position,

The accuracy was determined by measuring a certified (NPL) bare gold mirror in the following sequence (after performing a background calibration first):

$$R_0,\ M_1, R_1,\ M_2, R_2,\ M_3, \ldots\ldots,\ R_9,\ M_{10}, R_{10}$$

in which R is a reference measurement (T mode without sample) and M the measurement on the mirror (R mode). The reflectance of the mirror was determined by dividing the average value of the mirror measurements by the average of the reference measurements.

The mirror was certified in the range 500 – 4000 cm-1 with a calibration uncertainty of 0.3%. The deviation from the NPL certified value is shown in Fig. 11. The ordinate scale is in wave numbers (wavelengths per cm) which is common for IR spectrophotometers.

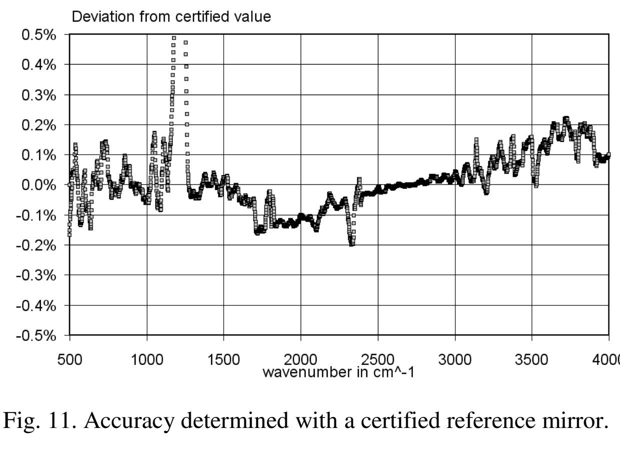

Fig. 11. Accuracy determined with a certified reference mirror.

An example of a sample measurement is shown in Fig. 12. The sample is this case was a thin uncoated glass sample which proved to be opaque for wave numbers below 2000 cm^{-1}.

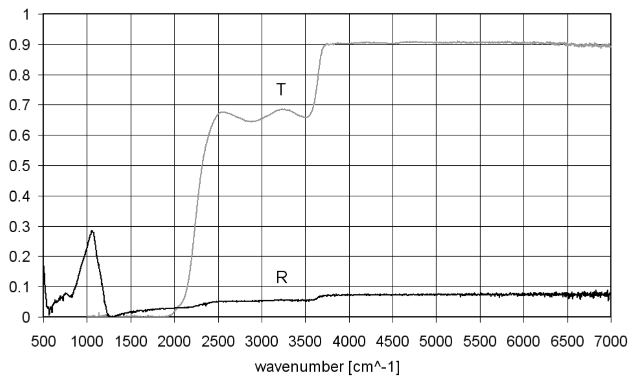

Fig. 12. Reflectance (R) and transmittance (T) measured on a 1 mm clear float glass sample.

Another tool we have developed for the Spectrum GX is shown in Fig. 13. This accessory measures the square of the reflectance of flat specular samples having reflectance values > 20%, like reflectance standards, laser mirrors, optical solar reflectors, beam-splitters, etc..

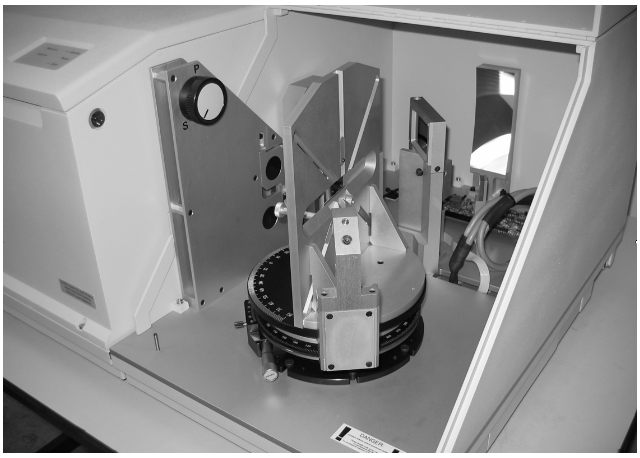

Fig. 13. Directional IV accessory for measuring absolute reflectance of highly reflecting materials at angles of incidence in the range 10° – 80°.

The accessory uses output port one of the Spectrum GX (right compartment, rear position). We call this an IV accessory, after the shape of the beam in reference and sample modes (see Fig. 14).

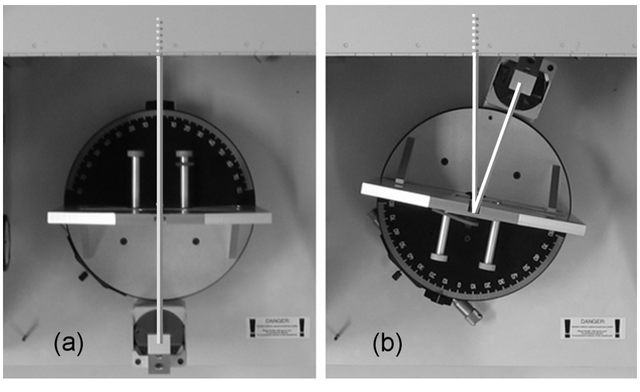

Fig. 14. Top view of the sample stage, showing the optical path of the beam in the I-mode (a) and V- mode with sample (b).

The measurement principle of the IV reflectance accessory is based on a combination of two measurements. The 100% scale calibration is performed in the so-called I-mode without the sample and the sample is measured in the V-mode in which the beam additionally interacts twice with the sample. The ratio of the two scans produces the square of the sample reflectance. This method is an absolute one since a calibrated reference is not needed.

In addition to (near-) normal incidence, the accessory is capable of performing measurements under oblique incidence as well. Two forms of the V -mode are possible, representing "positive" and "negative" angles of incidence as shown in Figure 15.

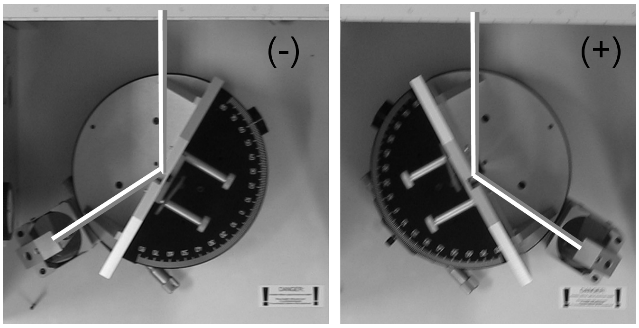

Fig. 15. Measuring under “negative” (left) and “positive” (right) angles of incidence.

The ability to perform measurements at both “positive” and “negative” angles, gives the user the possibility for compensating for systematic errors related to beam-shift effects and angular accuracy, by taking the average of these two types of measurements.

A schematic drawing showing the various optical components and the optical path of the beam in the reference mode (without sample) is given in Fig. 16.

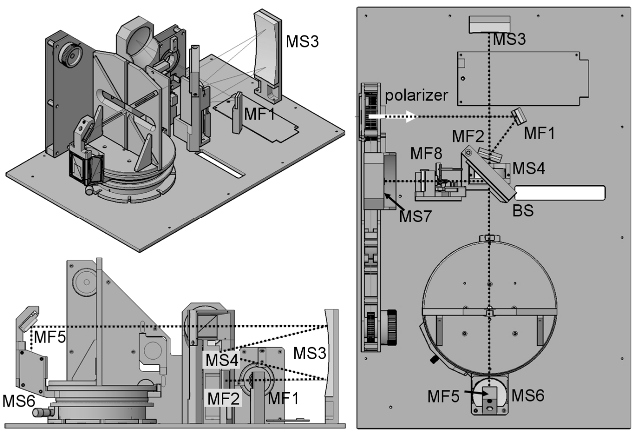

Fig. 16. Schematic drawing of the IV accessory.

The beam entering the accessory compartment fist passes the polarizer, is redirected via mirrors MF1, MF2, MS3, MS4 and again MS3, passes through the beam splitter BS and the sample holder, reflects on MF5, MS6 and again on MF5, goes back through the sample holder (along the same optical path), is 90 degrees reflected by the beam splitter BS towards mirror MS7 and is finally directed towards the detector by mirror MF8.

The sample holder is mounted on a rotation stage to set the angle of incidence. Mirror combination MF5 and MS6 form a retro-reflector. It forms an image of the sample spot onto itself and is designed to compensate for misalignment and sample tilt (Radius of spherical mirror MS6 is equal to its optical distance from the sample).

Although the accessory was optimised for the range 3300 cm^{-1} – 5000 cm^{-1}, where the combined standard uncertainty of the measurement is as low as 0.002, the workable range is at least down to 500 cm^{-1} (20 µm).

As an example we show our results obtained on a commercial low-e (single Ag) coated window glass which we measured at different angles of incidence (see Fig. 17).

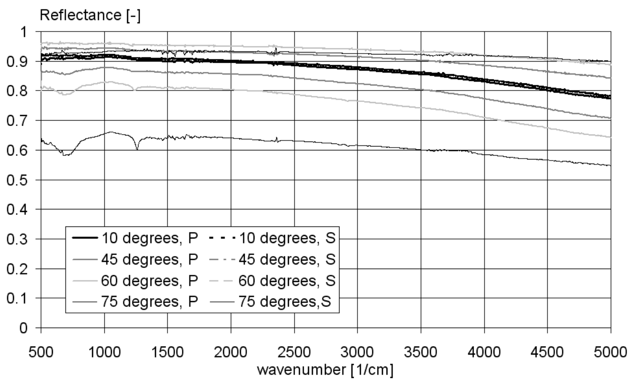

Fig. 17. Reflectance of a low-e coated window glass, measured with our IR IV accessory at different angles and polarisation.

2.2 Absolute 8° Reflectance/Transmittance accessory for the UV/VisNIR range

The last new tool we will briefly discuss is similar to the accessory shown in Fig. 8. It is an accessory for the UV/Vis/NIR range, capable of measuring Absolute reflectance and transmittance with accuracy < 0.2%, Angle of incidence at 8° and a wavelength range of approximately 200 nm – 2500 nm. The accessory has a horizontal sample plate and all optics are protected by a cover to prevent accidental contamination (see Fig. 18). The optical path in transmittance and reflectance modes is shown in Fig. 19.

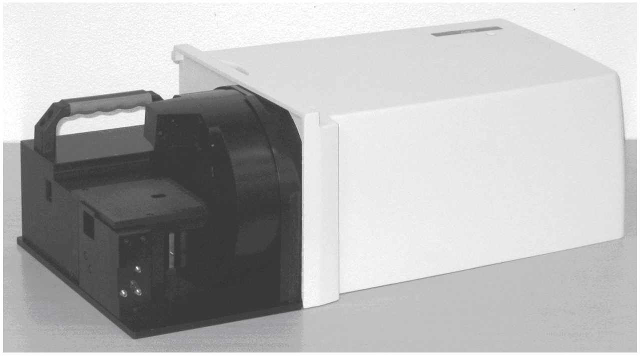

Fig. 18. Absolute Reflectance/Transmittance accessory for the PerkinElmer Lambda 950 spectrophotometer.

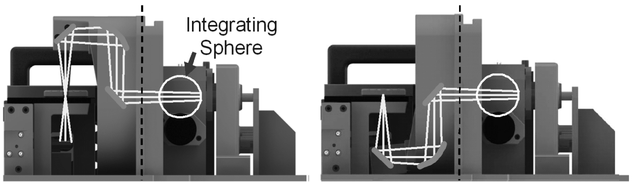

Fig. 19. Optical path of the beam between sample and detector sphere in transmittance (left) and reflectance (right).

In Fig. 20 we show results obtained for one of our reference mirrors which has been calibrated at 8° incidence using a VW accessory. The results demonstrate excellent agreement between the two methods.

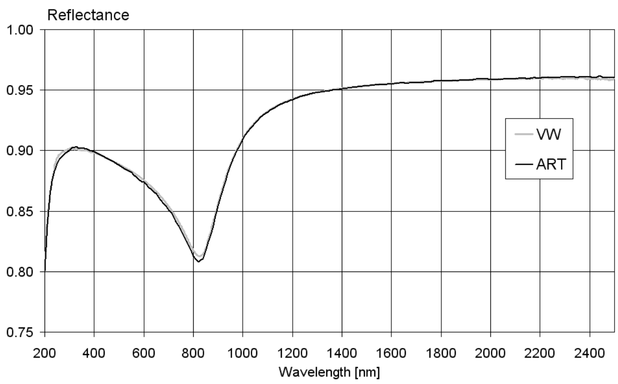

Fig. 20. Comparison of the reflectance of a second surface reference mirror, measured with the VW and ART accessories.

5. Conclusion

Various new tools have been described for the accurate characterisation of thin films by spectrophotometry in the UV/Vis/NIR and MIR ranges. Examples of measurement results have been given to demonstrate their performance.

Automation of directional optical measurements for Variable Angle Spectrophotometry has increased the reliability and significantly reduces the time required for the operator to be involved with the measurement.

References

[1] P.A. van Nijnatten, Proc. WREC, Part I (2000) 300.

[2] M.G. Hutchins et.al., Thin Solid Films, 392 (2001) 269.

[3] P.A. van Nijnatten, Solar Energy, 73 (2002) 137.

[4] P.A. van Nijnatten, Thin Solid Films, 442 (2003) 74.

[5] M.B. van Mol, Y. Chae, A.H. McDaniel, M.D. Allendorf, Thin Solid Films, 502 (2006) 72.