



## APPLICATION NOTE

### UV/Vis Spectroscopy

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## Measuring Absorptance ( $k$ ) and Refractive Index ( $n$ ) of Thin Films with the PerkinElmer LAMBDA 950/1050 High Performance UV/Vis/NIR Spectrometers

#### Introduction

An optical coating consists of a combination of thin film layers that create interference effects used to enhance transmission or reflection properties for an optical system. How well an optical coating performs is dependent upon the number of factors, including the number of layers, the thickness of each layer and the differences in refractive index at the layer

interfaces. The transmission properties of light are predicted by wave theory. One outcome of the wave properties of light is that waves exhibit interference effects. Light waves that are in phase with each other undergo constructive interference, and their amplitudes are additive. Light waves exactly out of phase with each other (by  $180^\circ$ ) undergo destructive interference, and their amplitudes cancel. It is through the principle of optical interference that thin film coatings control the reflection and transmission of light.

When designing a thin film, though the wavelength of light and angle of incidence are usually specified, the index of refraction and thickness of layers can be varied to optimize performance. As refraction and thickness are adjusted these will have an effect on the path length of the light rays within the coating which, in turn, will alter the phase values of the propagated light. As light travels through an optical component, reflections will occur at the two interfaces of index change on either side of the coating. In order to minimize reflection, ideally there should be a  $180^\circ$  phase shift between these two reflected portions when they recombine at the first interface. This phase difference correlates to a  $\lambda/2$  shift of the sinusoid wave, which is best achieved by adjusting the optical thickness of the layer to  $\lambda/4$ . Figure 1 shows an illustration of this concept.

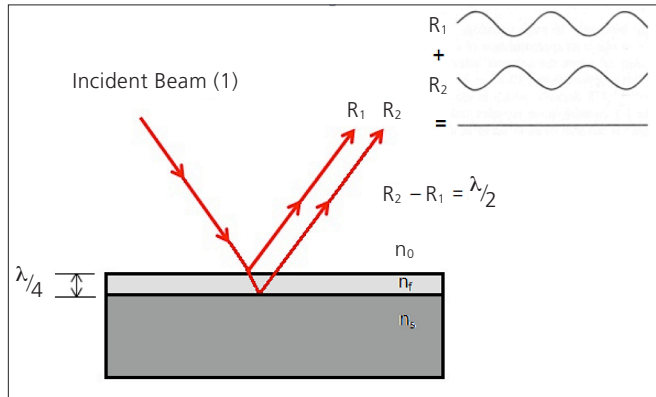


Figure 1. For an air ( $n_0$ ) / film ( $n_r$ ) interface, illustrated is the  $180^\circ$  phase shift between the two reflected beams ( $R_1$ ,  $R_2$ ), resulting in destructive interference of the reflected beams.

Index of refraction influences both optical path length (and phase), but also the reflection properties at each interface. The reflection is defined through Fresnel's Equation<sup>2</sup>, which provides the amount of reflection that will occur from the refractive index change at an interface at normal incidence:

$$R = \left( \frac{n_p - n_m}{n_p + n_m} \right)^2$$

The intensity of reflected light is not only a function of the ratio of the refractive index of the two materials, but also the angle of incidence and polarization of the incident light. If the incident angle of the light is altered, the internal angles and optical path lengths within each layer will be affected, which also will influence the amount of phase change in the reflected beams. It is convenient to describe incident radiation as the superposition of two plane-polarized beams, one with its electric field parallel to the plane of incidence (p-polarized) and the other with its electric field perpendicular to the plane of incidence (s-polarized). When a non-normal incidence is used, s-polarized and p-polarized light will reflect differently

at each interface which will cause different optical performances at the two polarizations.

Determining the refractive index,  $n$ , and the absorptance (absorption coefficient),  $k$ , of a coating are two important parameters in thin film research. In real materials, the polarization does not respond instantaneously to an applied field. This causes dielectric loss, which can be expressed by the complex index of refraction that can be defined<sup>2</sup>:

$$\mathbf{n} = n + ik$$

where:

$\mathbf{n}$  = the complex refractive index

$i$  = the square root of -1

$n$  = the refractive index

$k$  = the absorption index

Here,  $k$  indicates the amount of absorption loss when the electromagnetic wave propagates through the material. The term  $k$  is often called the extinction coefficient in physics. Both  $n$  and  $k$  are dependent on the wavelength. In most circumstances  $k > 0$  (light is absorbed).

In this paper we will show how the absorptance, refractive index, and film thickness of thin films can be calculated from the spectral data.

## Experimental

To determine  $n$  and  $k$  a number of optical measurements are needed which require accessories to be added to the UV/Vis spectrometer. To calculate the absorption coefficient (re: absorptance, extinction) of a thin film the transmission and absolute reflectance spectra of the material needs to be acquired (it follows that the material cannot be opaque). Using a high performance LAMBDA spectrometer (LAMBDA 650/750/850/950/1050) an integrating sphere accessory, ideally the PE-Labsphere 150 mm Spectralon coated sphere, or the Universal Reflectance Accessory (URA) are ideal accessories for this determination. Though a smaller sphere may be used for these measurements, the accuracy level will decrease as the size of the sphere gets smaller. When the absorption gets low, smaller spheres may not have the inherent accuracy to be used. A number of other accessories can be used where absolute specular reflectance can be measured, accompanied by the transmission, such as the VN 8 degree absolute specular reflectance accessory.

Discussed in the next section are the procedures and some example results for calculating absorptance using a LAMBDA 1050 UV/Vis/NIR spectrometer fitted with a Labsphere Spectralon 150 mm InGaAs integrating sphere. Absorptance is light that is not transmitted or reflected by a material, but is absorbed. The equation  $T + R + A = 1$  describes the theory, where  $T$ =transmittance,  $R$ =reflectance, and  $A$ =absorptance.

## Measuring the Absorptance (k) of Materials

The procedure presented here will describe the accurate measurement of absorptance using the 150 mm Integrating Sphere accessory. A picture of the 150 mm integrating sphere (L6020204) installed in a LAMBDA 950 is shown in Figure 2, with a top down view of the schematic of the sphere beneath the picture. This accessory occupies the second sample compartment area (right side in picture) of the instrument, leaving the primary sample compartment free to accept liquid samples and other accessories.

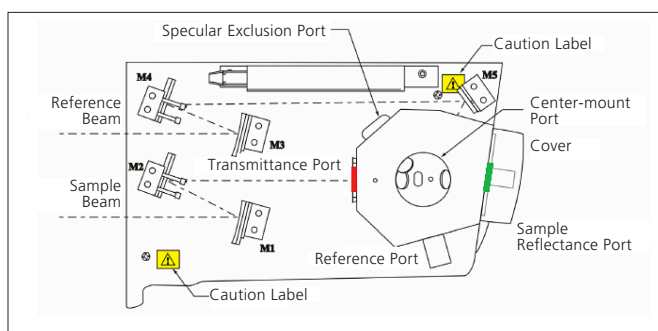
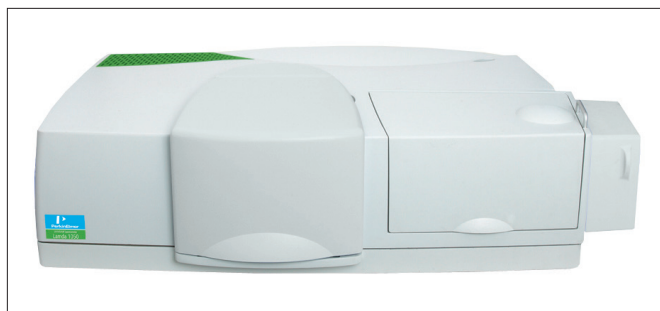


Figure 2. Picture of the 150 mm integrating sphere installed in a LAMBDA 950 with a top down view of the diagram of the sphere below. The red marked area is where transmission of the material is done, and the green area the reflectance of the material.

In addition to the integrating sphere accessory, this procedure requires a calibrated standard, either a calibrated Spectralon white reference plate, or a calibrated mirror. When measuring absorptance using the integrating sphere it needs to be noted that samples need to be clear (haze will cause problems with the calculation) and the coatings need to be applied to fairly thin substrates (i.e., glass slides are ideal). Coatings applied to thick substrates run the risk of some of the reflected light being clipped on the port on the return of the reflected light into the sphere.

### A. Measuring Transmission using the Integrating Sphere

The %T measurements have little considerations as long as the sample is large enough to cover the transmittance port of the sphere, and sample and reference beams are aligned properly. The sphere should be set for Total %R (Specular Exclusion Port plug in place). For sample sizes that are smaller than the instrument beam the Small Spot Kit Accessory (L6020211) might be necessary. In transmission the Correction settings in the method should be the same as shown in Figure 3, making sure the 0%T baseline option is checked.

### B. Measuring Reflectance with the Integrating Sphere

Reflectance measurements have a number of considerations. The reflectance needs to be measured in Absolute %R, which means the spectra are corrected for the reflectance of the reference material (**Light Spectral Reference**), as well as the dark level (0%R) of the sphere (**Dark Spectral Reference**). Though correction of spectra with calibration reference data can be done off-line in Microsoft® Excel®, UVWinLab™ V6 has the capability to define the calibration file in the method so that the reflectance spectral correction is performed automatically as data is being acquired in real-time (note: no calibration file is required for transmission data collection).

There are two common approaches for generating Absolute %R with an integrating sphere.

1. Use a **calibrated mirror**, either a primary (i.e., NIST, OMT) or secondary standard (PE # N1010504). The latter

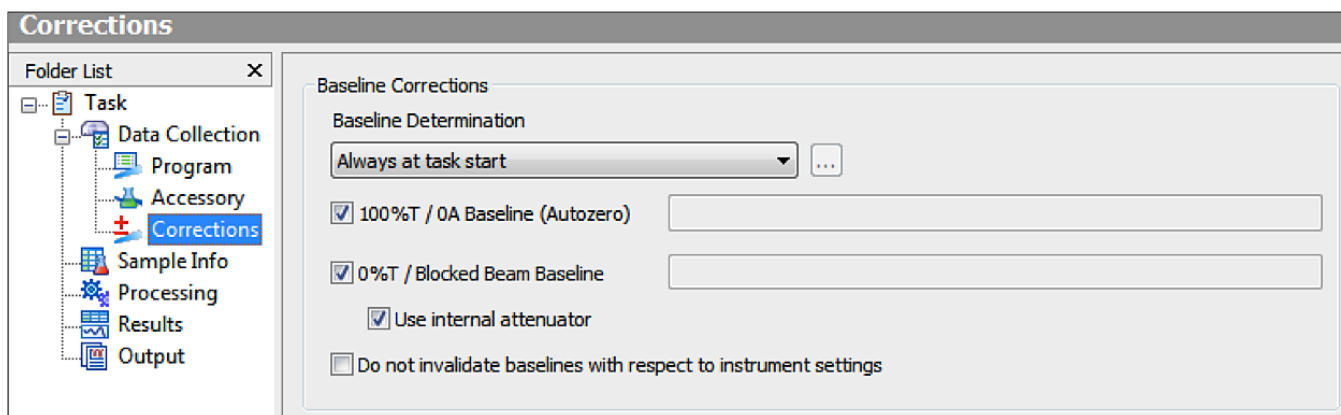


Figure 3. Corrections settings for a transmission scan with the sphere accessory.

is calibrated against a primary NIST traceable mirror, however the error tolerances are larger than with a primary mirror.

2. Use a **Labsphere Calibrated Spectralon Standard** (i.e., PELA 9058) having a specific calibration sheet for that standard.

Either which standard is used, the reflectance calibration data that comes with the standard needs to be converted to an UVWinlab V6 compatible file so it can be used in the method to automatically correct the spectral data. The procedure to do this is outlined in the application note **“Procedure for Creating %RC Correction Files in UVWinlab V6.docx”** (to obtain this paper contact your local PerkinElmer UVVis Product Specialist). Once the calibration data has been entered into an ASC file, this file can be copied to any location on the hard drive on to the computer operating the LAMBDA spectrometer, or alternatively it can be placed into the folder *“C:\Program Files\PerkinElmer\UVWinlab\6.0\Data\Corrections Data”* where the file will be registered automatically for method access.

When measuring reflectance for absorption determination, because the samples on the reflectance port also transmit light, it is important to correct for the dark level of the sphere. Without a sample in place on the reflectance port, due to minute scatter of the light beam traversing the length of the sphere and the inherent back scatter of light off the sphere cover, it is normal to see a sphere dark level in the range of a few tenths of a percent to nearly a percent above zero.

There are two ways of correcting for the sphere dark level for reflection of transmitting samples:

1. Acquire a new dark reference correction every time the method is run (the correction settings for this option are shown in Figure 4).
2. Perform dark reference correction from a stored file. The dark reference is measured and saved as a file so it can be assigned as the **Dark Spectral Reference** under the Correction menu (the correction settings for this option are shown in Figure 5).

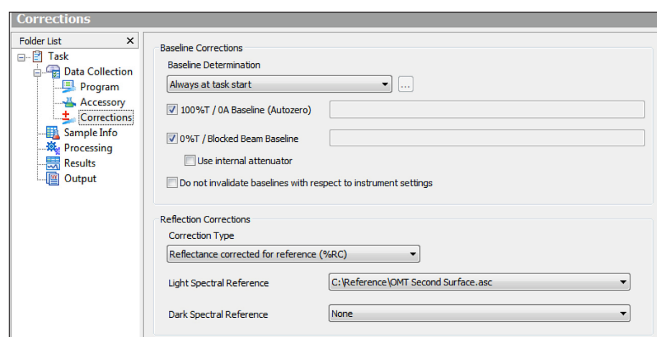


Figure 4. Reflectance corrections settings with the integrating sphere, where a dark reference correction is acquired before sample analysis. In this example, the “Light Spectral Reference” has been defined with an OMT primary

The setup for the option (1) requires that in the Corrections menu of the method, the options for both the **100%T/0A Baseline and the 0%T/Blocked Beam Baseline** are checked, but the option **Use internal attenuator** is left unchecked, as shown in Figure 4. Using this setup, when the correction prompt is given **“Block the beam and press OK to perform a 0%T/Blocked Beam correction”** the user will not actually block the beam, but rather will remove the Spectralon white plate from the reflectance port and replace the sphere cover.

Though it is fine to acquire the dark reference of the sphere in this manner each time 100% and 0% corrections are taken, it may be more convenient to acquire the dark current scan only once and then save this file so it can be assigned as the Dark Spectral Reference file in the Corrections menu. To acquire this file, make sure the white sample reflectance reference plate is removed, there is no sample in the beam, and replace the sphere cover. Start a scan over the widest wavelength range that will be used (i.e., 2500 to 250 nm is typical). When completed, right-click on the filename and select Save as ASC to any location on the computer, or save to *“C:\Program Files\PerkinElmer\UVWinlab\6.0\Data\Corrections Data”*, to add this correction file to the list of files in the method view.

To assign the calibrated mirror or calibrated Spectralon ASC files, and the dark current sphere file, to the UVWinlab method, select an ordinate mode of %R, click on the Corrections menu, under the Reflection Corrections section, select the Correction Type **“Reflectance corrected for reference (%RC)”**. Under the **“Light Spectral Reference”** setting, click the down arrow and then **“Select – Import”**. Browse to the location of the calibrated mirror or calibrated Spectralon ASC file, and assign this file to the field. Repeat this for the **“Dark Spectral Reference”** field. Note that when using a Dark Reference File correction, the option for **“Use internal attenuator”** is checked. Saving the method will store these correction file assignments.

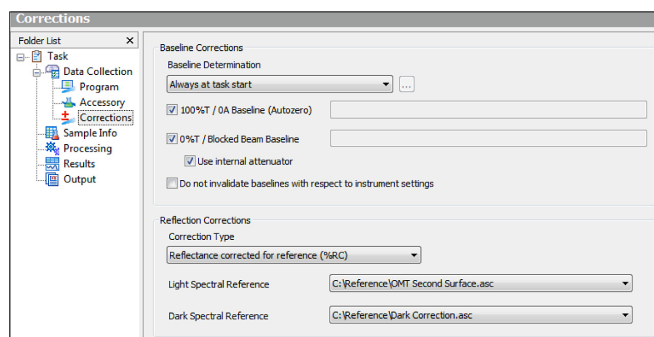


Figure 5. Reflectance correction settings where the dark reference correction is being applied from a stored spectral file.

Note that if using a calibrated Spectralon white reference, this plate is used in place of the sample regular Spectralon plate that is included with the sphere, and the regular reference plate is used on the reference port of the sphere.

### C. Example of Determining the Absorptance (k) of a Sample

When both the %T and the %R files have been acquired, the Processing section of the method can be used to calculate the absorptance of the sample. A single equation is required.

$$(100 - \text{Transmittance} - \text{Reflectance}) / 100$$

Shown in Figure 6, are the %T and %R scans of a sample transmission and reflectance spectra of thin film crystalline silicon deposited on a glass slide, for characterization of its semiconductor properties, acquired with a LAMBDA 1050 with 150 mm InGaAs Integrating sphere accessory.

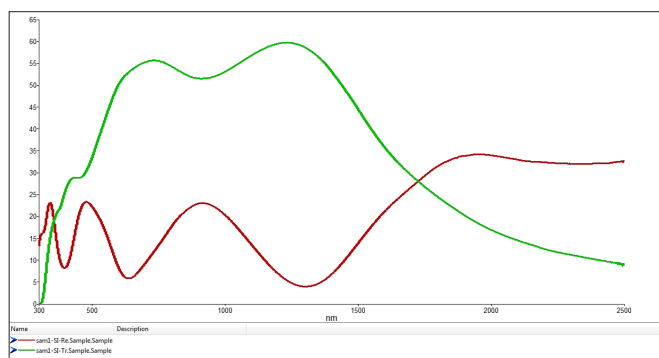


Figure 6. Transmission (green) and reflectance (red) spectra of thin film crystalline silicon acquired for absorptance determination.

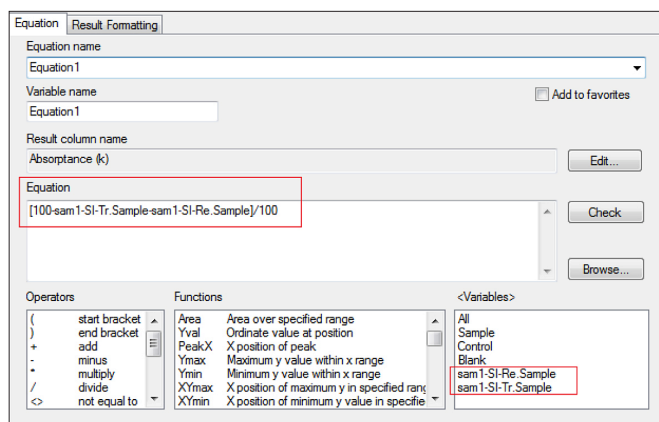


Figure 7. Equation (boxed) programmed into the Processing section of UVWinLab to calculate absorptance (k). The filenames assigned for the %T and %R measurements are variables.

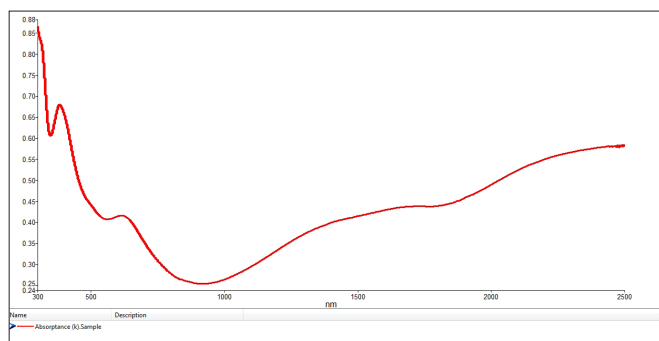


Figure 8. Equation calculated absorptance (k) from the %T and %R spectra shown in Figure 6.

Under the Processing section of the method a single equation can be entered to calculate the extinction as shown Figure 7. The result is shown in Figure 8.

### Measuring the Refractive Index (n) of Materials

Numerous mathematical approaches exist to calculate the refractive index and film thickness from transmittance and reflectance spectra of thin films. Three approaches will be discussed here, all within the capabilities of the high performance LAMBDA spectrometers and UVWinlab software.

1. Using the **Ri** and **Tcalc** equation functions under the Processing editor of UVWinlab V6
2. Calculating refractive index from transmission or reflectance spectra acquired at two different angles of incidence
3. Calculating refractive index and thin film thickness using formulas from either the reflectance or transmittance spectra where no interference fringe pattern is available

Each of these approaches will be discussed in detail below.

#### 1. Calculating Refractive Index and Film thickness using the built-in Ri and Tcalc Equation Functions

Thin films in the thickness range of about 0.1 to 10 microns can exhibit a constructive-destructive interference pattern as a function of wavelength. If the film thickness is known, the refractive index can be calculated using the built-in **Ri** equation function under the Processing section of the software. Conversely, if the refractive index is known, the film thickness can be calculated using the **Tcalc** function. The equations programmed into these functions are shown in Figure 9<sup>2</sup>.

$$t = \frac{N(\lambda_1 \times \lambda_2) c}{2((\lambda_1 - \lambda_2) ((n^2 - \sin^2 a)^{1/2}))}$$

$$n = \left[ \left( \frac{N(\lambda_1 \times \lambda_2) c}{2(\lambda_1 - \lambda_2) t} \right)^2 + \sin^2 a \right]^{1/2}$$

where:

- $\lambda_1$  = maximum wavelength
- $\lambda_2$  = minimum wavelength
- $N$  = number of fringes
- $n$  = refractive index
- $a$  = angle of incidence
- $c$  = conversion factor to angstroms

Figure 9. Film thickness and refractive index equations programmed into the **Tcalc** and **Ri** equation functions of UVWinlab.



To calculate film thickness and refractive index the user enters the required data, including the wavelength range, the refractive index (or film thickness), the number of fringes, and angle of incidence in the equation formats for Tcalc and Ri shown below.

Film thickness (**Tcalc**) and refractive index (**Ri**) preprogrammed equations:

#### Tcalc

Tcalc[<spectrum>, range start x, range end x, Refractive Index, Number of Fringes(-1=Auto), Angle of Incidence, result unit 1=Å/2=µm, Peak Threshold (optional)]

#### Ri

Ri[<spectrum>, range start x, range end x, Sample Thickness, Number of Fringes (-1=Auto), Angle of Incidence, Thickness Unit 1=Å/2=µm, Peak Threshold (optional)]

In the example shown in Figure 10, a polycarbonate protection lens having a thin film anti-abrasion coating with a nominal film thickness of 6 microns is shown.

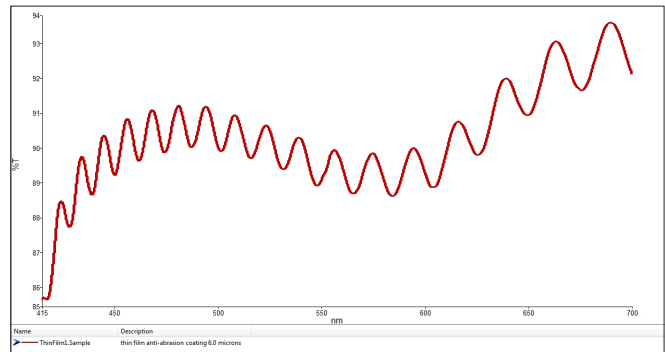


Figure 10. Spectra acquired from a lens having a thin film anti-abrasion coating, showing a characteristic constructive-destructive interference pattern.

In this example a film thickness of 6.00 microns was entered in the Ri function under the Processing section of the method, and a refractive index of 1.467 was calculated between 675 and 548 nm (6 fringe peaks. Conversely, the film thickness was calculated by entering a refractive index of 1.467. The results from these calculations are put into the Results table, as shown in Figure 11.

	Sample ID	Description	Thickness (microns)	Refractive index (n)
✓ 1	ThinFilm1.Sample	thin film anti-abrasion coating 6.0 microns	5.973	1.467

Figure 11. Film thickness and refractive index calculated by the Ri and the Tcalc functions of UVWinlab for the lens sample in Figure 10.

## 2. Calculating Refractive Index from Spectra Measured at Two Different Angles of Incidence

For samples that exhibit an optical thin film interference pattern it is possible to calculate the refractive index by acquiring the transmittance or reflectance spectra at two different angles of incidence, and entering the shift observed in the interference pattern into an equation (Figure 12). For this measurement a variable angle transmission or a variable angle specular reflectance accessory is required. This can be a relative (i.e., B0137314) or absolute variable angle (i.e., Universal Reflectance Accessory – URA L6020202) reflectance accessory. Additionally, because light impinging on the sample at oblique angles will be transmitted or reflected in two orthogonal planes, s-polarized or p-polarized, either a Common Beam Depolarizer (CBD) is recommended, or a polarizer drive unit fitted with a polarizer crystal allowing measurement at a known angle of polarization.

Procedure:

1. Using a variable angle transmittance or variable angle specular reflectance accessory measure at two different angles of incidence.
2. Obtain the fringe pattern at each angle.
3. For each angle of incidence, measure the spacing between adjacent fringes.
4. Use the following formula to calculate the refractive index (ref. 4):

$$n = ((\sin^2\theta_1\Delta v_1^2 - \sin^2\theta_2\Delta v_2^2) / (\Delta v_1^2 - \Delta v_2^2))^{1/2}$$

where  $\theta_1$  and  $\theta_2$  are the two different angles of incidence, and  $\Delta v_1$  and  $\Delta v_2$  are the fringe spacing for adjacent fringes measured at angles  $\theta_1$  and  $\theta_2$  respectively (note: if entering wavelength values the result is multiplied by  $10e^7$ ).

Figure 12. Formula to calculate refractive index from thin film spectra at two different angles of incidence.

The Universal Reflectance Accessory (URA) was used to acquire the absolute reflectance data at two different angles of incidence of a silicon nitride coated semiconductor wafer. Like the 150 mm integrating sphere accessory, the URA fits into the second sample compartment area of the High Performance LAMBDA spectrometer (Figure 13). A close-up of the URA is shown below. Samples are laid horizontal over the beam port for measurements, and the motorized accessory will drive to the angles programmed.



Figure 13. The Universal Reflectance Accessory (URA) fitted into a LAMBDA 950. The URA is a programmable motorized absolute reflectance with an angle range of 8-68 degrees.

The parameter setup screen and the sample table entries for the measurements are shown in Figure 14. Once the angles are programmed, all angle changes and corrections proceed automatically without operator intervention.

Sample ID	Description	Type	CBDep	Width	Length	Angle
✓ 1 Sample1-15	15 degree	Sample	On	5.0	5.0	15.0
✓ 2 Sample1-45	45 degree	Sample	On	5.0	5.0	45.0

Figure 14. Universal Reflectance Accessory parameter page and associated sample table to acquire absolute reflectance data at 15 and 45 degrees angle of incidence, using a beam size of 5x5 mm (length x width). When the run is started all angle changes and corrections are done automatically.

In the example shown in Figure 15 is a silicon nitride coated semiconductor wafer on silicon which was scanned in reflectance at a 15 and a 45 degree angle of incidence. The interference patterns are clearly observed, and the adjacent peak wavelength separation can be measured easily.

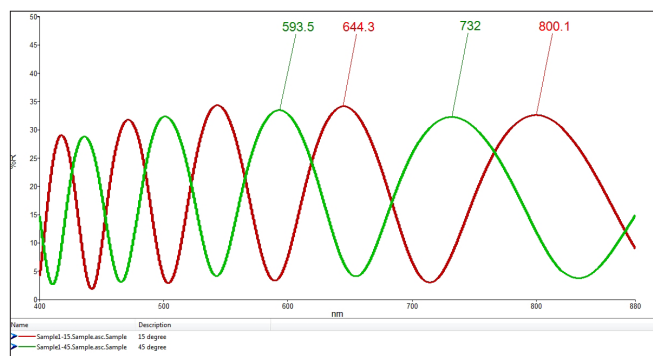


Figure 15. Silicon nitride thin film coating on a silicon substrate semiconductor wafer scanned in absolute reflectance at two different angles of incidence (red = 15°, green = 45°) using the URA accessory.

Using the peaks at 800.1 and 644.3 for 15°, and 732.0 and 595.5 for 45°, deltas of 155.8 nm and 138.5 nm were calculated respectively. After entering the equation in Figure 12 into the Processing section of UVWinLab a refractive index of 2.22 was calculated for this sample. The equation output is shown below:

1	Equation1	24273.64
2	Equation2	0.1971
3	Equation3	19182.25
4	Equation4	0.954981
5	Equation5	0.954981
6	Equation7	-0.757836
7	Refractive Index (n)	2.22

### 3. Calculating Refractive Index Using Formulas From Either the Reflectance or Transmittance Spectra

Besides providing information on the absorption of a sample, transmission and reflectance spectra can be used to calculate the refraction indices of a sample. If the absorption is high with no or minimal interferences the sample refractive index  $n_f$  can be calculated using the equations below<sup>1</sup>:

$$n_s = \frac{\sqrt{M + \sqrt{M^2 - n_s^2}}}{T_{max}} \quad 1$$

$$\text{where } M = \frac{2n_s^2}{T_{min}} - \frac{n_s^2 + 1}{2}$$

If interferences are determined, from the maxima in the transmission spectra the refractive index of the substrate can be derived by the following equation. Note this formula only applies to cases where absorption of the substrate is negligible:

$$T_{max} = \frac{2n_s}{n_s^2 + 1} \quad 2$$

$$\text{where } n_s = \frac{1 + \sqrt{1 - T_{max}^2}}{T_{max}}$$

If the absorption is low and there are no or minimal interferences the sample refractive index can be calculated from the transmission minima by using the following formula:

$$R = \left( \frac{n_f - 1}{n_f + 1} \right)^2 \quad 3$$

$$\text{where } n_f = \frac{1 + R + \sqrt{R}}{1 - R}$$

Since the absorption of thin film coatings is usually not uniform as a function of wavelength, ranging from low to high absorption, the formulas above can be applied to the appropriate sections of the spectra for a valid calculation of refractive index.

Shown in Figure 16 are the transmission and reflectance spectra of thin film crystalline silicon deposited on a glass slide, for characterization of its semiconductor properties. Shown in Figure 17 is the absorbance spectrum. In the area between 1800 and 2500 nm the absorption was significant, so the first equation above (1) above was used to calculate

the refractive index over that part of the spectrum. Again, the equation was entered into the Processing section of UVWinlab.

Shown in Figure 18 are the calculated refractive indices at a select number of wavelengths, with a mean refractive index of 4.87 calculated from 2500 to 1800 nm.

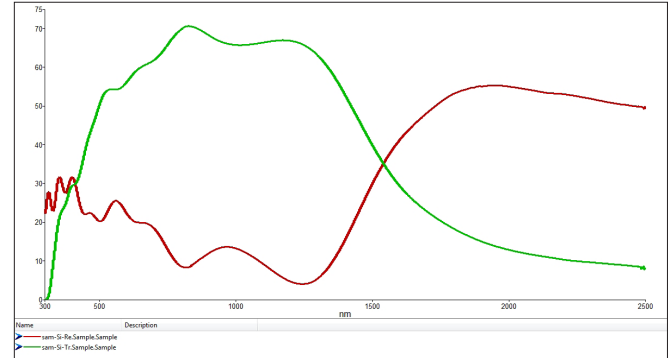


Figure 16. Transmission (green) and reflectance (red) spectra of thin film crystalline silicon deposited on a glass slide.

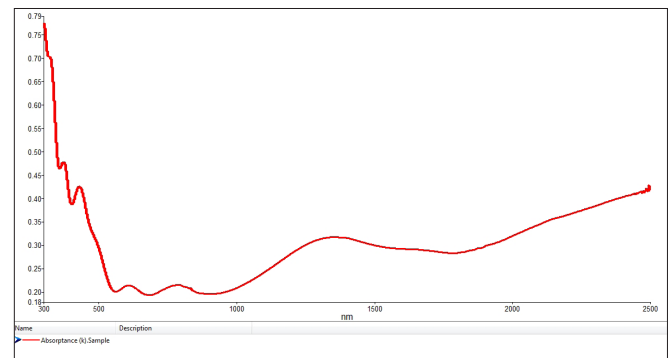


Figure 17. Absorbance spectrum calculated from the spectra in Figure 16.

Sample ID	Description	Ri (2500) nm	Ri (2300) nm	Ri (2000) nm	Ri (1800) nm	Mean (Ri) 2500-1800 nm
✓ 1	Sam-Si-Re Sample crystalline silicon on glass	4.95	5.10	5.08	4.36	4.87

Figure 18. Refractive index calculated over the range of 2500-1800 nm using the first equation (1) above from the reflectance spectrum (Figure 15) of thin film crystalline silicon deposited on a glass slide. The equation was programmed into the Processing section of UVWinlab and a mean refractive index of 4.87 was determined.

### Conclusion

The reference grade high performance LAMBDA 1050 when fitted with the proper accessories becomes an ideal tool for the determination of optical thin film constants. In this paper procedures were described for the determination of refractive index ( $n$ ), absorbance ( $k$ ), and film thickness for thin films. The 150 mm InGaAs integrating sphere and the Universal Reflectance Accessory proved to be ideal accessories for acquiring the data for the examples presented in this paper.



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