

Characterizing Optical Thin Films (II)

This is a follow up article to the first article [1] in which we developed the mathematical tools to determine the optical properties of optical thin film materials from the measured spectral data for a single layer coating. In the previous article we also demonstrated that there was a very good correlation between the calculated optical properties and the design properties where the films were homogeneous and the precision of the data was very good, out to five decimal places. In the real world we do not make homogeneous films (i.e. they all have at least a little bit of inhomogeneity) and our spectral measurements are not accurate to five decimal places. In this article we will discuss the effects of inhomogeneity on the spectral performance of optical thin films, we will discuss techniques of making routine spectral measurements for characterization and we will demonstrate the results characterizing actual deposited thin film materials.

IAD ambient substrate temperature TiO₂ films can exhibit a fair amount of inhomogeneity as compared to films prepared at higher substrate temperatures. This may be due to the fact that during the deposition, the temperature steadily rises from a starting level to a higher temperature by the end of the run. For exceptionally long depositions the temperature might saturate before the run is completed and thus one would expect the index to also remain constant for the balance of the deposition. Also, pressure variations during film deposition will vary the refractive index. In order to study the effect of inhomogeneity, let's consider a TiO₂ film in which the refractive index steadily rises or decreases during the deposition. We could do this by several techniques. However simply dividing the coating up into a few segments with a step change in index is adequate.

The example chosen for this exercise is a 384 nm film divided into 26 equal thickness segments with the refractive index varying between sections by a constant amount (increments with a range of ± 0.03 and ± 0.06 where the mid-point or median index is that of the previous TiO₂ material used as an example in the first article [see Table III in the first article(1)]. The upper range of inhomogeneity far exceeds anything that you would expect to see in real life. It is included for illustration purposes only. Note that the film still has the same absorption properties (extinction coefficient) as the previous example.

By inspection we can see that there is very little change in the maximum reflectance for the odd orders in the interference pattern. This is good because it implies that the refractive indexes calculated by the means developed in the first article are still valid. However, there is a significant variation in the absolute reflectance at the even orders (minima in the interference pattern). In the perfectly homogeneous film, the reflectance at the interference minima would be exactly the same as the uncoated substrate. Inhomogeneity with an increasing refractive index will result in minima greater than that of the uncoated substrate and with a decreasing refractive index will result in minima that are less than that of the uncoated substrate. The greater the refractive index range, the greater the displacement of the reflection minima from that of the uncoated substrate.

Inhomogeneous TiO₂ Example

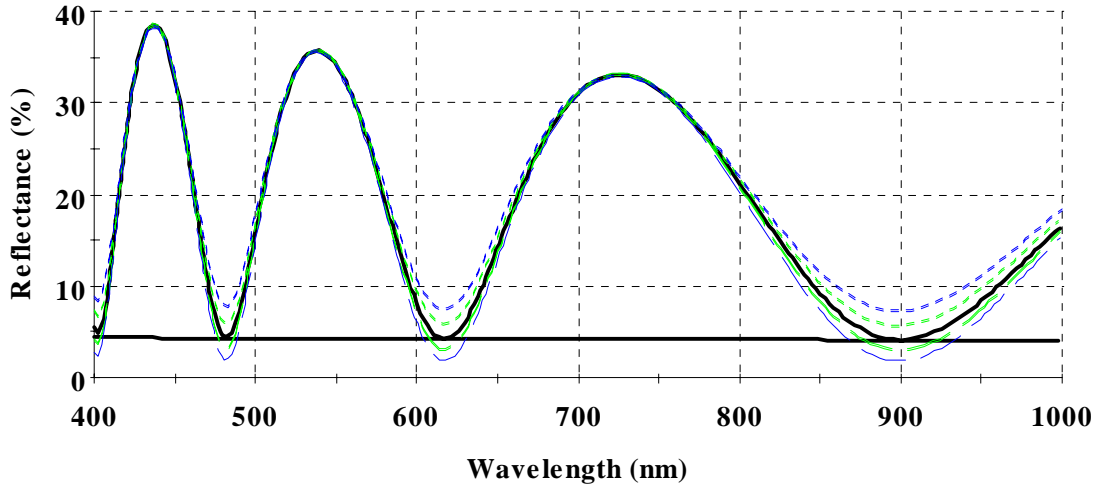


Figure 1. Plots of TiO₂ reflectance for inhomogeneity ranges of 0%, $\pm 0.03\%$ and $\pm 0.06\%$.

The minimum reflectance values at the even order wavelengths are shown in Table I. Also shown in Table I are the differences of the displacement in the reflections from the uncoated substrate (Δ_{xxx} , where xxx is the wavelength of the even order) due to inhomogeneity.

Table I

$\lambda(\text{nm})$	402 nm	Δ_{402}	617 nm	Δ_{617}	899 nm	Δ_{899}
uncoated	4.3702		4.2768		4.2103	
+6%	7.8347	3.4645	6.9857	2.7089	6.8397	2.6294
+3%	6.2886	1.9184	5.5576	1.2808	5.4543	1.2440
0%	4.8937	0.5235	4.2771	0.0003	4.2104	0.0001
-3%	3.657	-0.7132	3.194	-1.0828	3.146	-1.0643
-6%	2.5861	-1.7841	2.0911	-2.0911	2.1744	-2.0359

The Differences in the reflection are plotted as a function of the percentage of inhomogeneity in Figure 2. The film is basically non-absorbing at the two longer wavelengths and the change of reflectance from that of the uncoated glass are about the same percentage. Therefore at longer wavelengths where the film is non-absorbing it is possible to assign and calculate the degree of inhomogeneity. However at the shorter wavelength where the film is absorbing ($k \sim 0.0039$ @ 402 nm), reflected film minimum has been increased due to the absorption. In order to determine the degree of inhomogeneity, one would first have to determine the degree of absorption and take it into account. What we see is the fact that the entire difference curve has been shifted up. The amount of the additional shift seems to be proportional to the degree of inhomogeneity (0.79% for 6% inhomogeneity and 0.67% for 3% inhomogeneity and 0.52% for 0% inhomogeneity). Obviously it is much easier to estimate the degree of

inhomogeneity in the film using an even order in the interference pattern where the film is not absorbing.

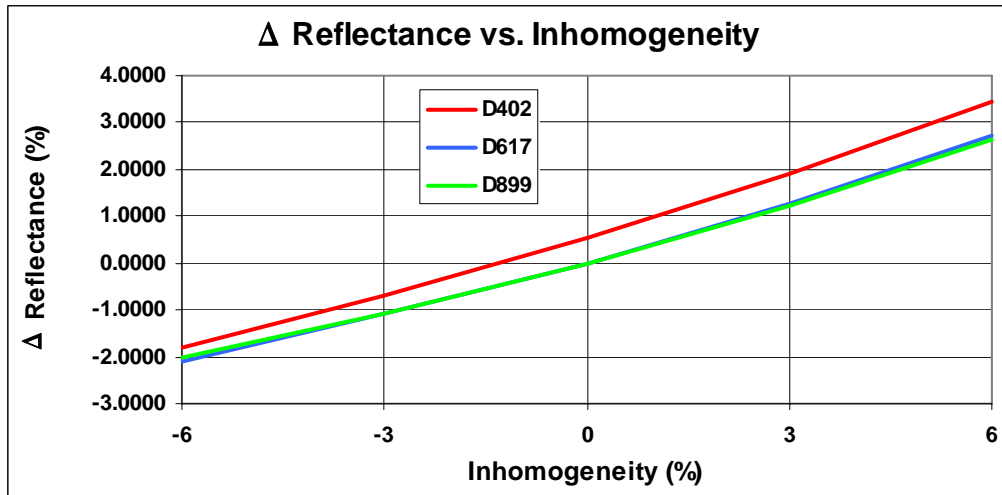


Figure 2. Shift in reflectance in the even order minima at different wavelengths for films of varying degree of inhomogeneity.

A similar effect can also be seen in the transmission plot of the inhomogeneous example (see Figure 3) where we plot the transmission of a plate coated one side. The transmission of the coated plate at the multiple QWOT thickness wavelengths is not affected very much by the inhomogeneity. Therefore the refractive index calculated at these wavelengths will be fairly accurate. However, the transmission at the HWOT wavelengths is affected significantly with the decreasing refractive index films having a higher transmission and the increasing refractive index films having a lower transmission than the transmission of the homogeneous film.

Inhomogeneous TiO₂ Example

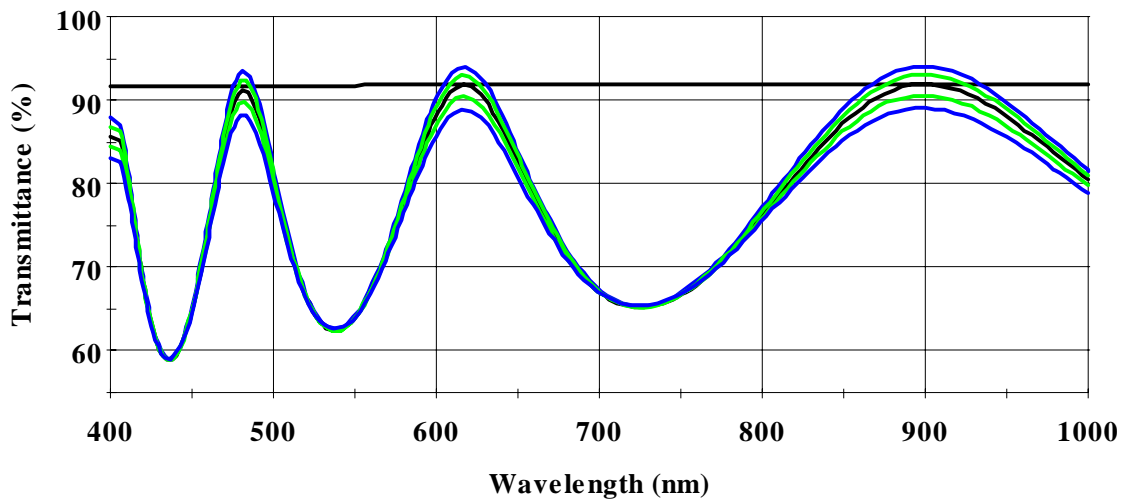


Figure 3. Plots of TiO₂ coated plate transmittance for inhomogeneity ranges of 0%, ±3% and ±6%.

If we take the transmission and the reflection values of the coated plate for the -3% inhomogeneous example and compute the refractive index and the extinction coefficient of the film by the technique developed in the first article of this series, we will get exactly the same values as for the homogeneous film. Therefore the technique presented previously is still valid. Most thin film analysis programs commercially available for thin-film analysis have the capability of taking measured spectral data and extracting the optical properties of the films. The spectral transmission and reflection data for the -3% inhomogeneous example were imported into the Essential Macleod software package [2] and the OptiChar software package [3] (part of the Optilayer package) and the optical properties of the film determined. A comparison of the results of the refractive index extraction (mean refractive index) using the method outlined here-in, labeled as MathCad for the worksheet used to generate the data, and the results from the Essential Macleod and the OptiChar characterization are plotted in Figure 4. As can be seen, there is a very good agreement between the techniques.

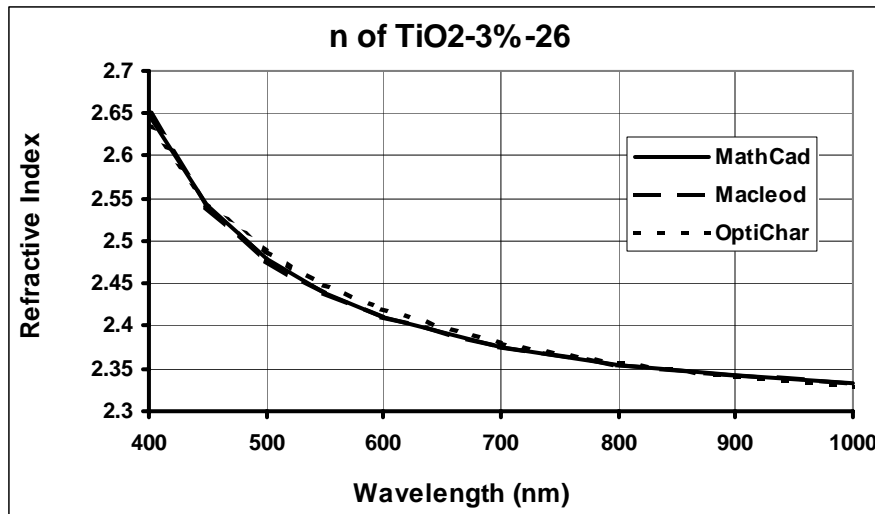


Figure 4. Refractive index comparison of -3% inhomogeneous TiO₂ film as extracted by three methods.

The method being presented in this series and the commercially available software packages also determine the thickness of the films and the level of inhomogeneity. The thickness of the film as determined by the characterization are 1) MathCad 383.2 nm, 2) Essential Macleod 383.3 nm and 3) OptiChar 383.8 nm. All are very close to the 384 nm design thickness used to generate the data. For inhomogeneity the results are 1) MathCad -3% (from Figure 2, not contained in the worksheet), 2) Essential Macleod -3.1% and 3) OptiChar -2.9% (where the $-$ sign indicates decreasing refractive index from the substrate/film interface to the film/air interface).

The example used in the first article to illustrate how to take measured data and extract the optical properties of a film was done so from calculated film spectra of a homogeneous film with reflection and transmission measurement accurate to 8 decimal places. The resulting optical properties for refractive index and extinction coefficient extracted were accurate to about 4 decimal places. In this article we have shown that the accuracy is equally good for a well defined inhomogeneous example. In the real world, spectroscopic data is not accurate to 5 or 6 decimal places so that the optical properties

obtained will not be accurate to 4 decimal places. To complicate things further, optical thin films are rarely homogeneous. Therefore the optical properties obtained from the prescribed formula will be the mean refractive index and the extinction coefficient. The inhomogeneity of the refractive index can then be inferred from the example developed here-in.

We are now in a position to take a real life example and extract the optical properties. However, before doing so we will review the relationships developed in the first article. Basically the refractive index is calculated for the odd order wavelengths from the reflectance maximum using the following formula:

$$nf_{\lambda} = ns_{\lambda} \left(\frac{1 + \sqrt{Rf_{\lambda}}}{1 - \sqrt{Rf_{\lambda}}} \right)^{0.5} \quad (1)$$

where: nf_{λ} is the refractive index of the film at wavelength λ .
 ns_{λ} is the refractive index of the substrate at wavelength λ .
 Rf_{λ} is the reflectance of the film at wavelength λ and the interference order is odd.

Equation 1 is applicable to reflection data measured directly or to values obtained from the transmission data. I feel that the direct reflection measurements are most accurate but like to calculate the refractive index from both the reflection and the transmission data. Regardless it is necessary to make the transmission measurement in order to calculate the extinction coefficient. Most people make the transmission measurement using an open sample path as a reference. This is quite adequate when the substrate is non-absorbing. If the substrate has a little bit of absorption in the wavelength range being measured, accuracy would be improved by having an identical uncoated sample in the reference beam or by auto-zeroing using the uncoated clear sample. If measuring a coated sample against a clear sample is used, it is necessary to first multiply the measured transmission by the decimal equivalent of the transmission of the clear sample to get the actual measurement of the coated sample in air. Once the measurement of the coated sample in air is obtained it is necessary to calculate the transmission from air into the substrate on the coated side of the sample. This is done using the following formula:

$$Tf_{\lambda} = \frac{Tp_{\lambda}^2}{Tu_{\lambda} - Tp_{\lambda} + Tu_{\lambda} * Tp_{\lambda}} \quad (2)$$

where: Tf_{λ} is the transmission through the film (coated side) into the substrate.
 Tp_{λ} is the transmission of the plate (coated on one side) in air.
 Tu_{λ} is the transmission from air into the uncoated side of the plate.

Assuming that the film is non-absorbing, the reflection (based on the transmission) is:

$$Rf_{\lambda} = 1 - Tf_{\lambda} \quad (3)$$

The refractive index can then be calculated from Rf_{λ} using equation 1. In a perfect world, the refractive index as calculated from the transmission data and from the reflection data would be the same. In the real world, due to inaccuracies in measurements, they will not be the same but they should be close.

Figure 5 shows the transmission and reflection plot of a TiO_2 film deposited with ion assist. The black lines are the transmission of a clear uncoated microscope slide and reflection from the polished side of a frosted back microscope slide. The red line is the transmission of a clear slide coated one side and the blue line is the reflectance off the frosted back slide. The spectral scans were made using a Perkin Elmer λ 900. This plot is made from stored measurement data files and the known reflection of the frosted back slide and transmission of the clear slide. This particular film has 2 problems at about 861 nm. There is a significant drop in the transmission data at the grating interchange and the reflectance data is fairly noisy ($\pm 0.6\%$).

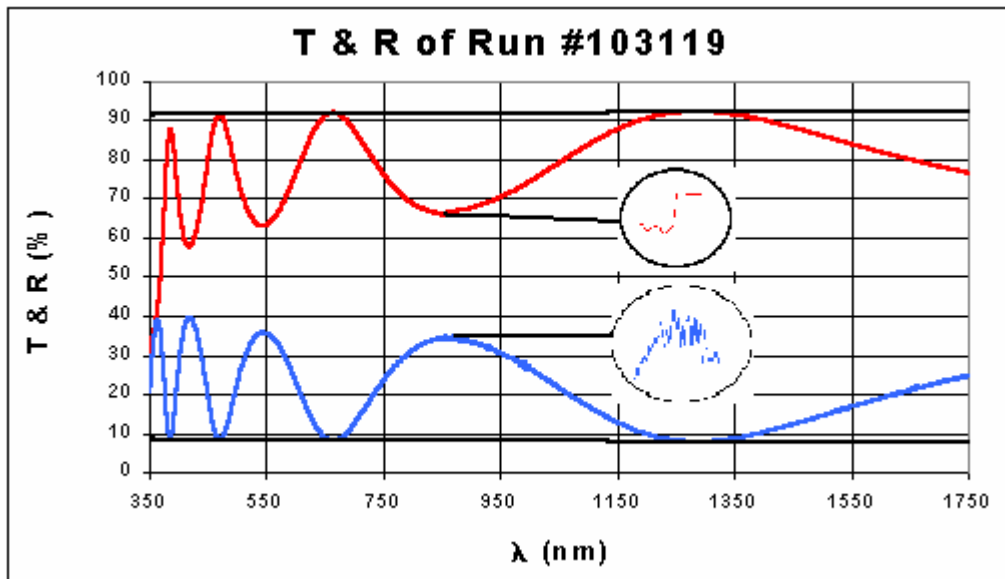


Figure 5. Plot of measured transmission and reflection data for a TiO_2 film on glass.

Table II shows the data and the results of calculations made using the relationships reported here-in. The wavelengths and data values are taken from the peak selection software supplied with the PE λ 900. This software is relatively crude, finding the peaks from the absolute high or low value without aid of any curve smoothing. Therefore the absolute peak is affected by the instantaneous noise. The wavelength values have been rounded to the nearest nanometer and the transmission values to the nearest 0.01% (the same rounding will be used for the reflection data). We normally determine the optical properties of materials from spectral data using a math program that allows setting up a work sheet form that only takes a few minutes to do a complete evaluation. We have also done this using Excel spreadsheet. The uncoated clear glass microscope slides have been carefully measured against a BK7 reference and characterized. This data is used to determine the reflection reference and the index of the substrate, as it is needed in the calculations. The dispersion equations for the reflectance, transmission and refractive index of the glass are incorporated in the mathematical and Excel spreadsheets.

Table II

Order (m)	λ_m (nm)	T (sample) (decimal)	T (clear slide) (decimal)	T_f equ. 2	R_f equ 3	R_s	n_m equ 1	n *
2	1285	.9224	.9202	.9608	.0392	.0415	1.503	2.294
3	865	.6666	.9197	.6866	.3134	.0418	2.317	2.317
4	665	.9202	.9190	.9591	.0409	.0422	1.512	2.375
5	554	.6283	.9182	.6463	.3537	.0426	2.446	2.428
6	471	.9153	.9174	.9547	.0453	.0431	1.532	2.523
7	418	.5743	.9165	.5897	.4103	.0436	2.641	2.612
8	386	.8760	.9157	.9129	.0871	.0440	1.677	2.757

* See comments in text concerning relationship between the order n, d and λ .

The refractive index calculations (next to the last column) are valid for the quarter wave optical thickness (odd orders). The calculation is not valid at the half wave optical thickness (the even orders). Actually, for a perfect film, the refractive index calculation at the odd orders should be exactly that of the uncoated substrate. If a film is absorbing and/or is inhomogeneous, the reflectance will be different than that of the uncoated substrate. This film is slightly inhomogeneous with a decreasing refractive index as can be seen by the film reflectance being lower than that of the uncoated substrate for the second and fourth orders. At the shorter wavelengths absorption in the film causes the even order reflectance to increase and, even though the film still has the same inhomogeneity, the resultant reflectance is greater than that of the substrate.

It is possible to calculate the refractive index at the even order wavelengths because of another relationship between the order, refractive index, thickness and wavelength in the interference pattern. That relationship is (equation 16 in the first article(1)):

$$d = \frac{m\lambda_m}{4n_m} \qquad n_m = \frac{m\lambda_m}{4d} \qquad (4)$$

Where d is the film thickness and m, n and λ are as defined before.

The third order was used in the first relationship above to calculate the film thickness 280 nm ($3*865/4*2.317 = 280$). Then the refractive index for each of the even orders was calculated from the second relationship using a 280 nm film thickness. We now have a refractive index for the even orders.

A similar analysis of the optical properties of this film were done for the reflection data and recorded in Table III.

Table III

Order	λ_m	R_s	R_f	n_f	n
2	1276	0.0415	0.0382	1.499	2.261
3	872	0.0418	0.3244	2.350	2.318
4	665	0.0422	0.0427	1.519	2.356
5	547	0.0426	0.3464	2.423	2.423
6	471	0.0431	0.0445	1.529	2.504
7	420	0.0436	0.3987	2.600	2.605
8	386	0.0440	0.0482	1.547	2.736

The reflectance data shows similar degrees of inhomogeneity as the transmission data at the longest wavelength. Note that the differences in the film transmission/reflection from the uncoated substrate at the half waves is .0022/.0033 @ ~1276 nm. The reflectance at the other even orders is slightly greater than the uncoated substrate due to slight absorption. The -0.33% difference in reflectance corresponds to about or less than -1% inhomogeneity in the film.

Having measured the transmission and the reflectance we are now in a position to calculate the extinction coefficient of the film. The relationship is shown in equation 5. One would assume that the wavelengths for the maximum and minima in the transmission and reflection scans would be the same. This would be true if the films are

$$k_f = \frac{\lambda}{2\pi d_f \left(\frac{n_s}{n_f} + \frac{n_f}{n_s} \right)} * \frac{1 - R_f - T_f}{T_f} \quad (5)$$

non-absorbing. If they are slightly absorbing, then there will be a small difference in the peak positions. For the example (Run # 103119) we are using in our illustration, the spectral scans were made on two different samples. Therefore we would anticipate a difference in peak positions even though the area scanned was in somewhat the same position in the tooling. Equation 5 assumes that the reflection and transmission data is at the same wavelengths and is at a peak in the pattern. In order to make the calculation, we assume that the wavelengths are those obtained from the transmission spectra and use the reflection data for the same order at that wavelength. The data and calculation results are recorded in Table IV.

Table IV

Order	l	T_f	R_f	n_s	n_f	k
2	1285	0.9608	0.0382	1.512	2.295	0.00035
3	865	0.6866	0.3244	1.514	2.317	0.00000
4	665	0.9591	0.0427	1.517	2.375	0.00000
5	544	0.6463	0.3464	1.521	2.429	0.00157
6	471	0.9547	0.0445	1.524	2.523	0.00010
7	418	0.5897	0.3987	1.528	2.613	0.00203
8	386	0.9129	0.0482	1.531	2.757	0.00395

It is obvious that there is a problem in calculating the extinction coefficient. The k values at the multiple QWOT wavelengths are significantly larger than the k values at the multiple HWOT wavelengths. We do not know the reason for this. However, we suspect that the k values calculated from the HWOT reflectance and transmission are more accurate. To support or refute this, we go back to the Essential Macleod and OptiChar software and calculate the optical constants as was done for the in the previous “good” examples. The results for the refractive index are shown in Figure 6 and for the extinction coefficient are shown in Figure 7.

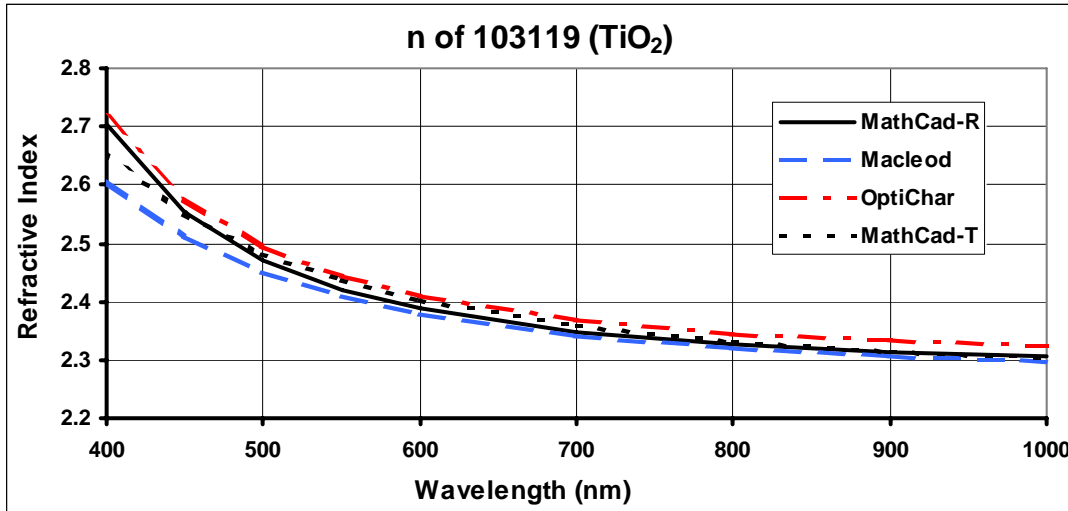


Figure 6. Refractive index calculation by three characterization methods; 1) black-MathCad, 2) blue-Essential Macleod and 3) red-OptiChar.

As expected, the above refractive indexes are in fairly close agreement. The film thickness as calculated using each method are also in close agreement (280 ± 2 nm). The extinction coefficients are in close agreement where they are greater than .0002 and in less agreement where they are in the range of or less than .0001. The varying results from 600 nm to 900 nm is probably caused by having measured data with insufficient accuracy (i.e. the discontinuity in the transmission data at 861 nm and the noise in the reflectance data on either side of 861 nm).

The Essential Macleod software package uses an envelope method and makes adjustments in the data while extracting the optical constants. These adjustments seem to result in a real but moderate level of absorption in the longer wavelengths. The OptiChar software seems to be doing a curve fitting that results in low extinction coefficients at most longer wavelengths, except in the 861 nm region where there is a known problem with the data of the example. The method we are proposing results in a measured value of .00035 at 1285 nm, which we would normally conveniently ignore as an abnormality in the data. All three methods will produce much closer results when there is good measured data ($R+T \leq 0$ and no discontinuities), as was demonstrated in the earlier perfect example.

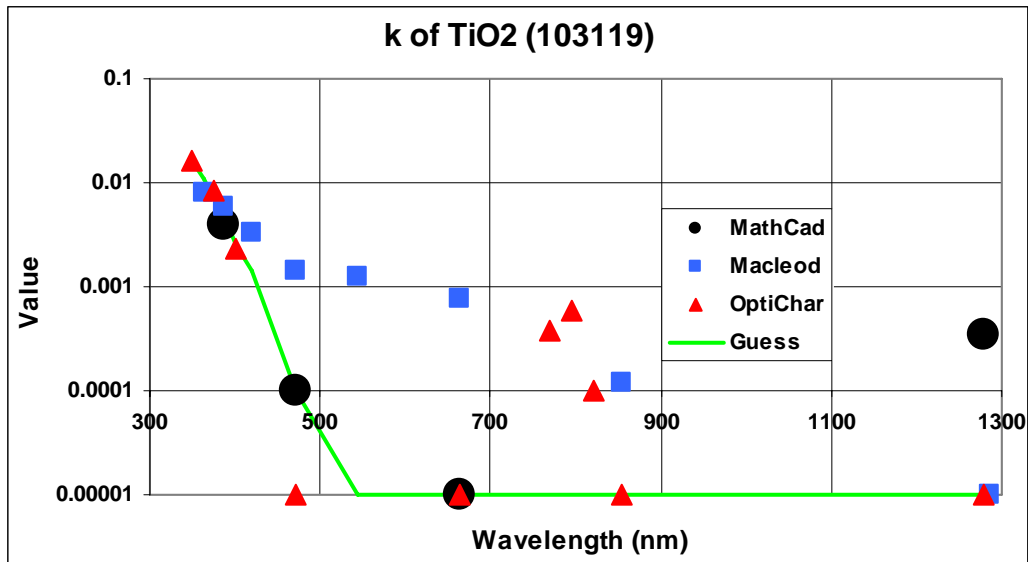


Figure 7. Extinction coefficient calculation by three characterization methods; 1) black - MathCad, 2) blue - Essential Macleod and 3) red - OptiChar. Note: zero values were plotted as 0.00001.

Also included in the above plot is a green line showing what the author would use as the extinction coefficient for the film. This example shows the difficulty in determining the optical properties of film materials from spectral data, especially when there are obvious problems with the data. Data extracted by the three methods shown are in very close agreement when the measured data is good and accurate. When the measured data is not good, then the results will vary depending on how the data is manipulated in the individual packages. Most commercially available thin film analysis packages have the capability to extract the optical properties of thin film materials from spectral data.

The purpose of these 2 articles was to show an alternative method for extracting the optical properties of thin films from measured data. As indicated previously, all of the calculations shown in this article can be done using an EXCEL spreadsheet. If you are interested in obtaining a copy of this spreadsheet, it can be downloaded from the Denton Vacuum Web page (titled: "n-paper") www.dentonvacuum.com.

References:

- 1) D. E. Morton, Characterizing Optical Thin Films (I), Vacuum Technology and Coating, **2**, No. 9, September 2001, p. 24-31.
- 2) Thin Film Center, Inc. 2745 E. Via Rotonda, Tucson, AZ 85716-5227 Ph: 520-322-6171 FAX: 520-325-8721. <http://www.thinfilmcenter.com>
- 3) DeBell Design, 619 Teresa Lane, Los Altos, CA 94024 Ph: 650-948-9480. <http://www.optilayer.com>.