Application of Spectral Reflectivity to the Measurement of Thin-Film Thickness

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Abstract

The aim of this work is to investigate the application of the spectral reflectance technique to thickness measurement of highly localised semi-transparent coatings on miniature geometries, such as those used in the medical devices industry. The paper will describe the application of the technique to coatings on curved or non-uniform surfaces such as narrow-bore metal tubes and thin wires. The paper will describe the equipment used including a spectrometer with micro-focus attachment, and optical modelling software. This work also involved laser-drilling of the polymer films to allow complementary step-height measurements to be made. Special steps were also required to overcome problems in measurement due to the transparency of the thin films. Complementary techniques including white-light interferometry, which were used to benchmark the method, will also be described.

1. Introduction

When light is reflected from a thin film, the spectrum of the light is dispersed depending on the optical properties (absorption coefficient and refractive index) and thickness of the thin film. The effect is readily seen for example in an oil film on water. By capturing the reflected spectrum and comparing it with theoretical models based on the optical properties of the thin-film material, the thickness of the film can be calculated. This approach has been commonly applied to the measurement of ultra-thin dielectric films in the semi-conductor industry. The principal objective of this study is to explore the application of the technique to polymer films and complex cylindrical geometries.

Spectral reflectance at its simplest involves illuminating a sample with a broadband light source and analysing the spectral composition of the reflected signal. When the sample is flat with a layer or multiple layers of thin films deposited, the reflected signal will be modified due to light reflecting from the coating and the substrate interfering according to the optical properties (refractive index, n, and coefficient of absorption, k) of the layers and their respective thicknesses[1]. Figure 1 illustrates the effect diagrammatically. For a given material with a certain thickness, the reflected signal will carry interference modulations. For thicker films of the same materials, there will be a greater number of modulations in the reflected spectrum. The expected optical response, including the interference modulation, can be very accurately predicted using computer models. By comparing the predicted and measured response from a sample allows the input parameters to the model (n, k and film thickness, t) to be varied until the measured spectrum coincides (within preset error limits) with that predicted by the model. This approach can be used to determine the values of n, k and t, or where the optical properties are known, as an accurate determinant of t.

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Opto-Ireland 2002: Optics and Photonics Technologies and Applications, Werner J. Blau, John F. Donegan, Austin F. Duke, Brian D. MacCraith, James A. McLaughlin, Norman D. McMillan, Gerard M. O'Connor, Eon O'Mongain, Vincent Toal, Editors, Proceedings of SPIE Vol. 4876 (2003) © 2003 SPIE · 0277-786X/03/$15.00

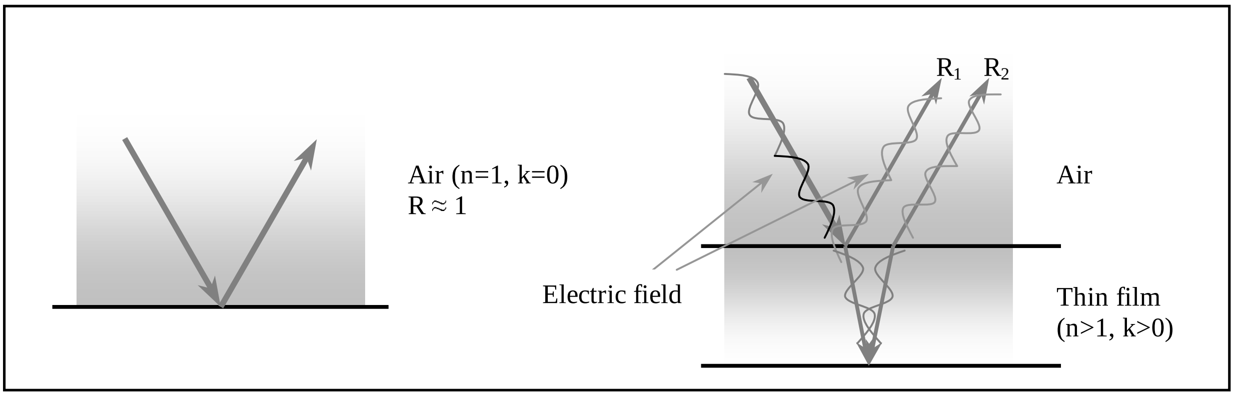

Figure 1. Modulations in the spectrum of the reflected signal occur due to interference between the light reflecting from the film surface, R_1 and light transmitted through the film and reflecting from the substrate, R_2.

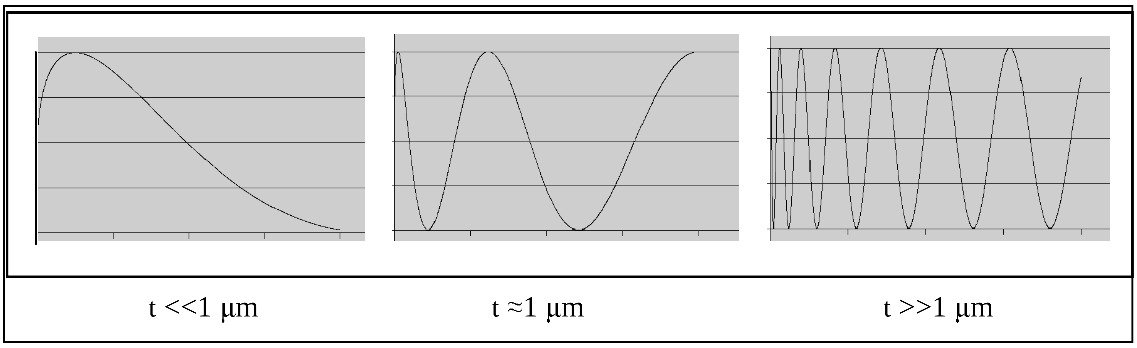

Figure 2. Variation in spectral reflectance with increasing film thickness.

2. Experimental Methods

The standard reflectance probe (Filmetrics Inc. F20 Reflectance Probe) used in the measurement of thin films on flat uniform substrates uses a fiber-delivered beam of light with a 3 mm spot size. The fiber used for light collection is usually bundled with the light delivery fibers. The captured signal is analysed in a compact spectrometer using a photo-diode or a ccd array. The measured spectrum is then compared with a theoretical spectrum for the sample under test using a model generated with inputs from a library of material optical properties within the instruments software.

The application of the spectral reflectance technique to small or curved samples brings certain difficulties; light delivery and collection is carried out via a microscope objective and so an on-line vision system is usually required for alignment of the sample under the beam. The sample must also be positioned normal to the light source. This is an issue with curved samples like stents. The micro-spot set-up used in this work consisted of a LabRam Infinity dispersion spectrometer manufactured by JY-Horiba. The system is based around a confocal microscope with multiple laser and white-light illumination capability. A 50x objective generating a 10 micron spot size on the sample and a spectral range between 500 and 750 nm were selected.

The surface profilometer used was a Zygo Newview 100 scanning white-light interferometer. This system generates contour lines in the form of interference fringes on the surface of a sample and then scans vertically, recording the location of the contour lines with vertical position[2]. The instrument can be used to make thin film thickness measurements if it has access to a step from the surface of the film to the substrate. For fully coated samples, a step can be generated by masking an area of the sample during coating. This has the difficulty of possibly modifying the coating thickness in adjacent areas, particularly at the step edge. Alternately, laser ablating an area of the coating can provide a clean, representative step, so long as the laser can ablate the coating material without damaging the substrate. A compact argon fluoride (ArF) excimer laser was used in this work. The short laser ArF wavelength at 193 nm interacts photochemically with the polymer coating, giving rise to a so-called 'cold' process- ablating the coating material without any thermal damage to adjacent areas. The power density of the laser is low enough to avoid damaging the metal substrate.

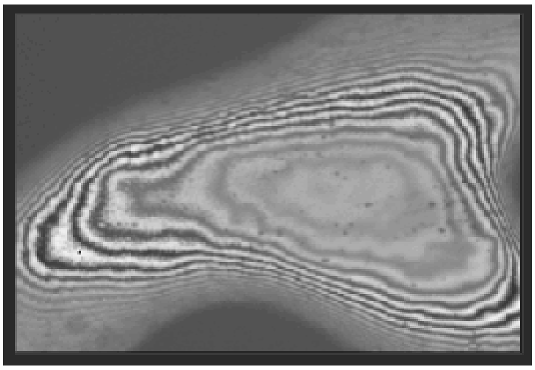

Figure 3. Interference fringes on the surface of a stent. These fringes form contour lines which are used to measure the surface form.

A difficulty arises however in trying to use white-light interferometry for profilometry purposes and spectral reflectance for film thickness measurements on the same samples. The spectral reflectance technique relies on interference between reflected signals from the coating and substrate, while this same effect undermines the accurate determination of step height in profilometry measurements. The profilometer effectively sees a ghost image of the substrate beneath the coating and, if the substrate is more reflective than the coating (as is the case with the polymer-metal system), the reflection from below the coating can dominate, leading to a small negative step being recorded, as opposed to the expected positive step. The negative step is due to the increased optical path length travelled by the light through the coating, compared to the light which reflects from the substrate in the ablated area, as illustrated in figure 4a and b.

There are a number of potential routes around this problem. The first is to position the profilometer objective so that the lower extent of its scan is above the apparent depth of the ghost reflection. This will only work where the coating thickness is thick enough to allow the appropriate positioning of the objective. The second approach is to use the knowledge (or an estimate) of the optical properties of the coating to estimate the real thickness of the coating from the apparent thickness measured (see figure 4 below). Thirdly, the sample can be coated with a thin film of gold, eliminating the ghost reflection and providing uniform reflectivity from both the coating and the substrate in the ablated region. The gold is deposited in a vacuum evaporation chamber to a depth of a few tens of nanometres. This will eliminate the spectral modulation effect, so obviously this approach must be implemented after other measurements have been made.

In the top picture (figure 4a, below), the difference between the path lengths travelled is simply t_1**,** the thickness of the film**.** When the light reflects from the substrate below the coating, the recorded thickness t_2 is negative. The optical path travelled by the ray to the reflection from the coated substrate is n.t (n is the refractive index). The distance travelled by the ray to the uncoated substrate is t. The difference between the two (the measured thickness, t_2) is,

$$n.\mathbf{t_1} - \mathbf{t_1} = \mathbf{t_1}.\ (n - 1) = \mathbf{t_2} \qquad (1)$$

Therefore,

$$\mathbf{t_1} = \mathbf{t_2} / \ (n-1) \qquad (2)$$

Thus if the refractive index is known, the actual thickness can be calculated from the measured negative step. The problem with this approach in this instance is that it fails to provide the absolute thickness measurement required of a complementary technique and so gold coating the area will eliminate this potential ambiguity.

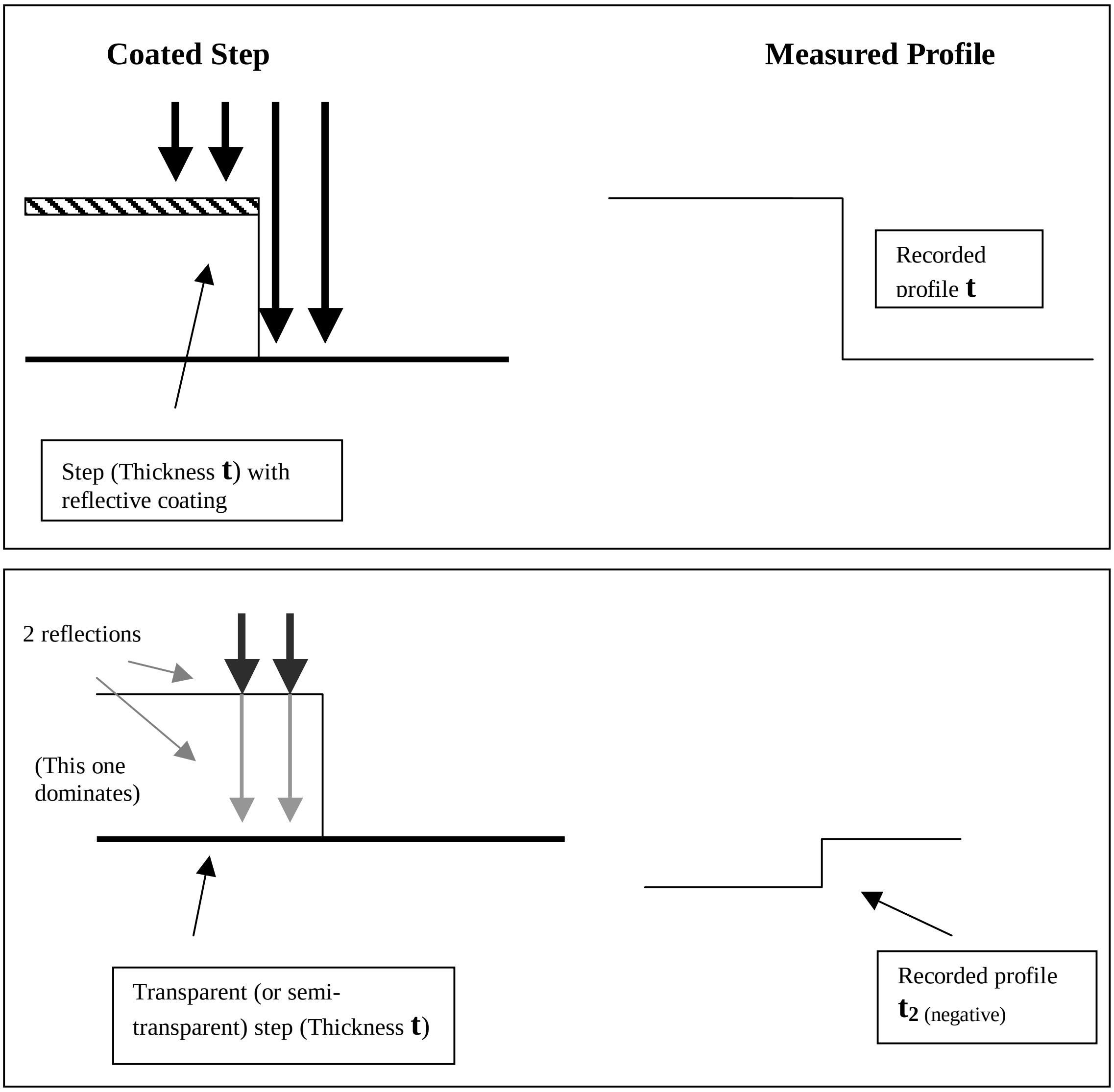

Figure 4a (top) Diagram illustrating the measurement of opaque film thickness by the profilometer and 4b. illustrating the effect of a ghost image on the thickness of a semi-transparent film.

3. Results and Discussion

Two sets of samples were studied. The first was a set of three polymer-coated silicon chips, approximately 1 cm sq. that would act as a reference. These samples were flat and so the coating could be put down in a very uniform fashion and could be measured on the Filmetrics system (using the large spot size). The polymer coatings on two of the samples were pigmented, to simulate the presence of additives within the coating. Visual inspection of these samples indicated that the coating thickness was not uniform and varied across the sample. The measurements performed on these samples were: Large area spectral reflectance, Micro-spot spectral reflectance and laser ablation (of the coating) followed by surface profile measurements.

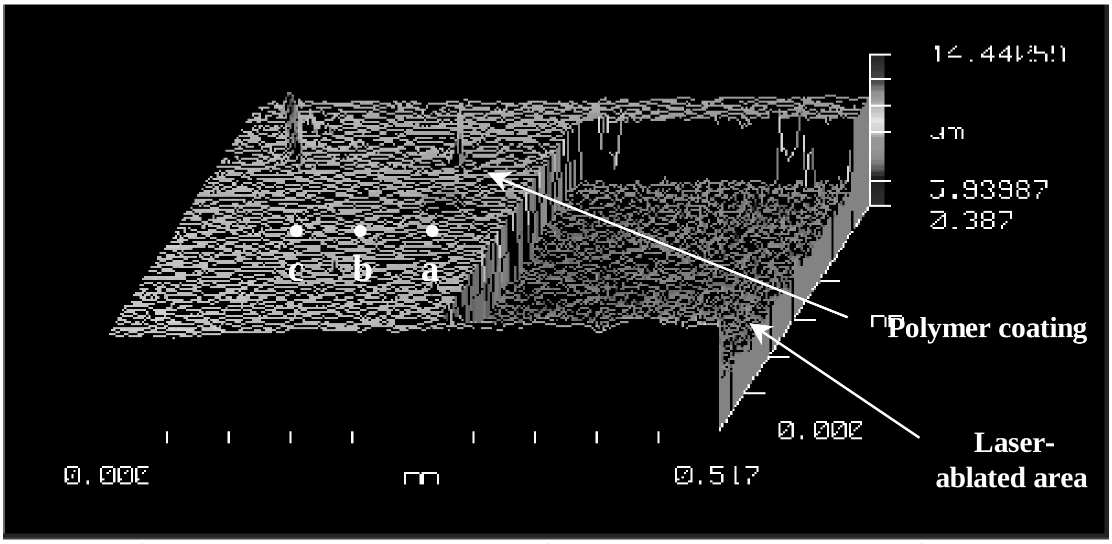

Figure 5a. Profilometer output showing 3-d projection of laser- ablated area and the location of the three micro-spot measurement points, a, b and c.

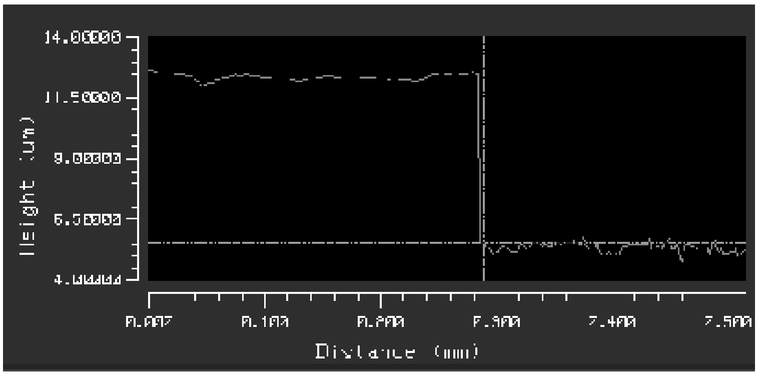

Figure 5b. Profilometer output showing cross-sectional profile of the coating step.

3.1 Large area spectral reflectance:

Measurements were made in three areas of the sample. The variation in thickness across the samples 1 and 2 is in accordance with visual inspection, where the colour of the coating went from clear to deep purple, indicating a variation in thickness.

Sample	Area 1	Area 2	Area 3
Sample 1- 90:10 PU:GV mix	2628	4302	6925
Sample 2- 50:50 PU:GV mix	2501	3808	4119
Sample 3- 100% PU	12870	14510	

Table 1. Results of large-area measurement of reflectance spectra. These results can be compared with the localised measurements below.

3.2 Micro-spot spectral reflectance:

Light deleivery and collection was via a 50x objective, giving a 10 micron spot on the sample. The laser-processed areas acted as location marks on the samples, as the measurement of film thickness was carried out with the surface profiler and the micro-reflectance spot positioned at distances of 40, 80, and 120 microns from the edge of the laser- ablated area (points marked a, b, c in figure 5). Gold coating of the samples was not necessary, as the coating thickness was large enough to enable positioning of the profiler objective with sufficient accuracy that the ghost reflection could be excluded.

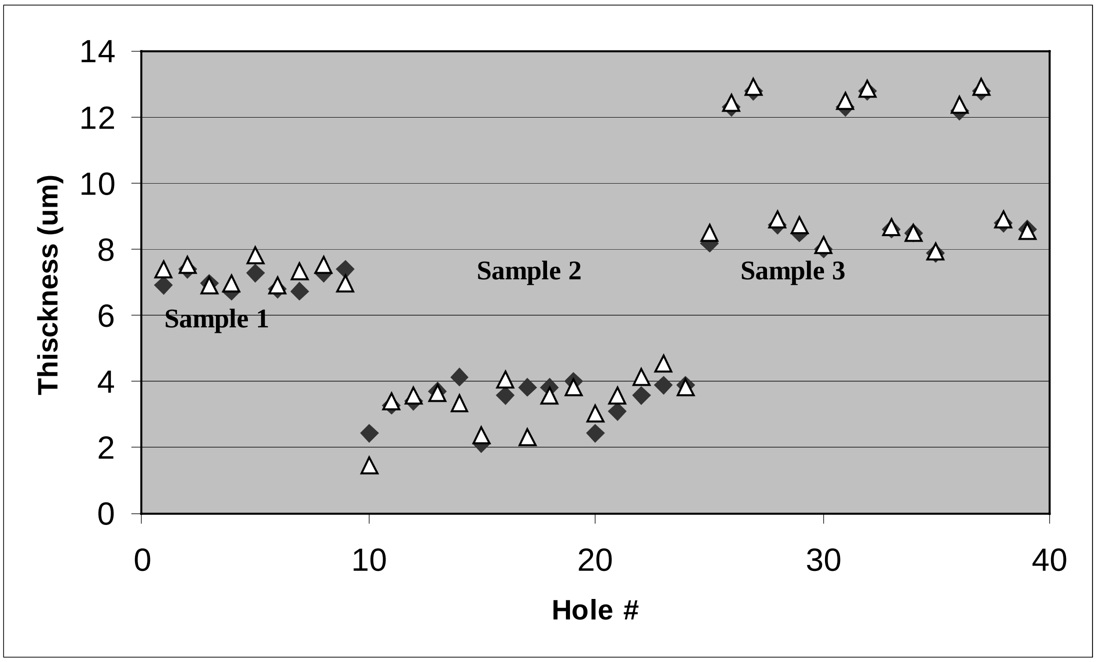

Figure 6 shows the recorded thickness as measured by the surface profiler (diamonds) at distances of 40, 80 and 120 µm from the laser drilled hole and the thickness calculated from the reflected spectra at the same locations (triangles).

The pigment in samples 1 and 2 has a significant effect on the reflectance spectrum and this affects the spectral range over which a good fit to the model can be made. As a consequence, the fitting error (rms deviation between measured and predicted spectra) for the data for samples 1 and 2 is larger and may explain the variation between the thickness measurements carried out on the same samples using the surface profilometer and the spectral reflectance probe. In addition, while the predicted spectrum could be fit to the measured spectrum for sample three over the full wavelength range (500 to 750 nm), the selected range had to be reduced to 630 to 750 nm for the pigmented samples (note the excellent correlation for points on sample 3 in figure 6).

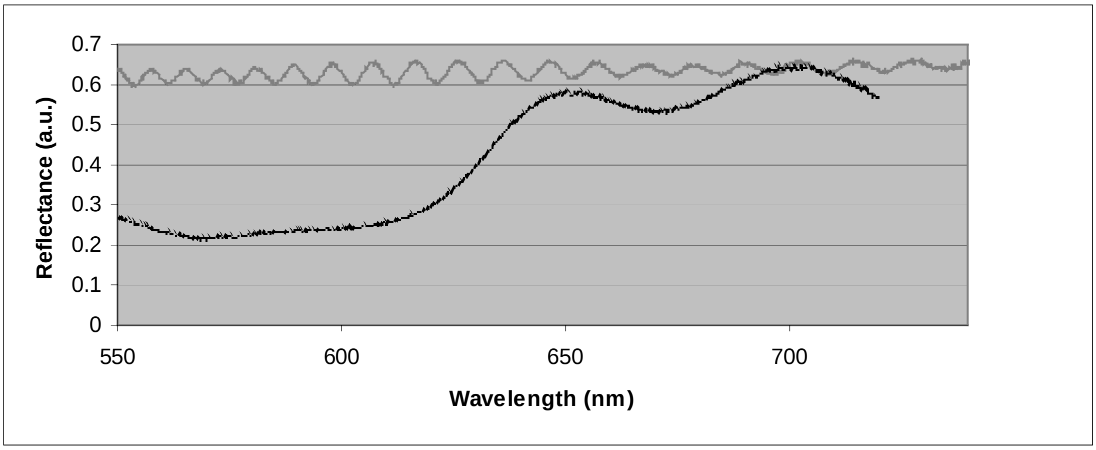

Figure 7. Reflected spectra for clear (grey spectrum, top) and pigmented films, samples 3 and 1, respectively.

Despite this difficulty, the correlation between the measurements with the two techniques remains very good.

The second set of samples comprised nine polymer-coated stents. The coatings were noticeably rougher for these samples, most likely due to the difficult geometry of the samples. Similar laser ablation and measurements were made on this set, however, these samples required gold coating to ensure accurate surface profile measurements. Gold was deposited in a vacuum sputterer.

The measured spectra were again analysed and modelled using the film thickness software. In this case, one laser-drilled hole on each stent was chosen and three evenly spaced measurements were recorded adjacent to that hole. It was not possible to get ‘reasonable’ fits between measured and predicted spectra for a number of recorded spectra. In these cases, there were no modulations apparent in the spectrum and it is assumed that this was due to local roughness on the samples (note the variation in thickness at the three measurement points on a given sample, table 2, below.). The tables below summarise the results of the reflectance modelling analysis and the profilometer step height measurements of coating thickness.

Surface profilometry

Sample	40 µm	80 µm	120 µm
Sample 4	2.8	1.8	1.5
Sample 5	3.6	4.0	2.9
Sample 6	2.1	2.7	4.5
Sample 8	1.5	2.5	3.4
Sample 9	3.2	2.5	1.8
Sample 10	4.3	5.1	4.5
Sample 11	3.8	3.8	4.5
Sample 12	2.8	1.8	1.5
Sample 13	3.6	4.0	2.9

Spectral reflectance

Sample	40 µm	80 µm	120 µm
Sample 4	2.4		
Sample 5	1.8	2.4	3.0
Sample 6	2.0	1.8	1.5
Sample 8	2.6	2.1	2.6
Sample 9	2.9	2.2	2.7
Sample 10	3.9	4.1	
Sample 11	3.9	3.7	
Sample 12	2.2	1.9	1.4
Sample 13	3.0	2.9	2.8

Table 2. Comparison of the thicknesses measured on the coated samples using reflectometry and profilometer analysis. The gaps in table 2b are where it was not possible to make a reasonable fit to the data.

The analysis above also tallies with observations made during initial laser etching, where the thicker coatings above (samples 5, 10, 11 and 13) required fifteen thousand shots to remove the coating, compared to ten thousand for the thinner ones.

The graph below presents these measurements and shows that although there is a spread in the measured thicknesses for each sample, there is a significant variation in the centre value from sample-to-sample. Also of significance is the fact that there is no systematic variation between the measurement techniques. Also note that in general, the spread in values of the three Zygo measurements on the gold-coated samples (i.e. the measurements over an area of 120 µm) is as large in a number of cases as the spread in measurements in going from the Zygo to spectral measurement technique, i.e local variations in thickness account for a significant proportion of the scatter in the graph below.

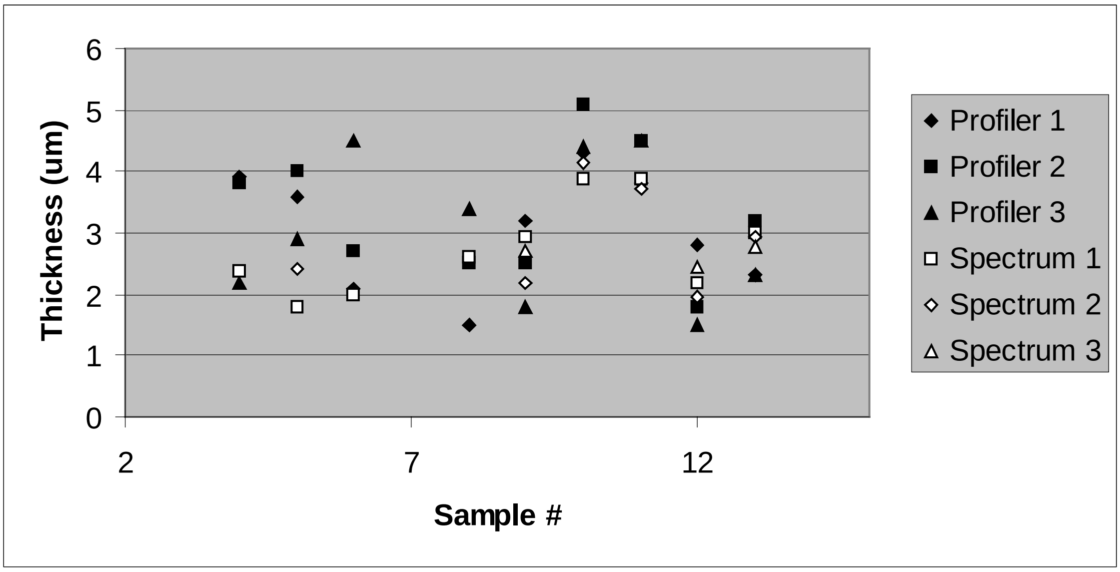

Figure 8. Plot of measured thickness for holes drilled on the stents as measured by the surface profiler (dark marks) and the spectral technique.

4. Conclusion

The application of the spectral reflectance technique to the measurement of polymer coatings has been demonstrated. This application has been extended to the micro-spot range and has allowed measurements to be made on curved, localised features, with a spot-size of ten microns. The spectral measurements have been correlated with step-height measurements made using a scanning white-light interferometer. This correlation required that the analysis of the interferometer data be extended to allow for the measurement of transparent films. The correlation between the techniques was very good and indeed is shown to be robust even to the addition of pigments. Based on this work, it is apparent that the spectral reflectance technique provides a useful option as a non-contact probe for the localised measurement of coating thickness, even on devices with a challenging geometry.

5. Acknowledgement

The authors would like to acknowledge Mr. Finbarr Dolan and Mr. Ronan Thornton of Medtronic-AVE Ltd. for technical and financial assistance in the execution of this work.

6. References

1. Hecht & Zajac, *Optics*, Addison Wesley 1974, p 294.
2. L. Deck and P. de Groot, *High-speed non-contact profiler based on scanning white light interferometry, ASPE Proceedings,* 1993, p. 424-426.