# Ellipsometry as a tool for identifying process issues in roll-to-roll sputter deposited metal-oxide coatings

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**Abstract**

Ellipsometry is an optical technique whereby the layer thickness, as well as optical properties such as the refractive index and absorption coefficient can be determined. The refractive index is sensitive to parameters such as the density, morphology and stochiometry of the layer being studied and so is a particularly useful indicator of process conditions and stability for metal-oxide layers. This presentation describes how ellipsometry has been used for optimisation of aluminium oxide and ITO roll-to-roll coating processes.

**Introduction**

The most commonly used techniques for measuring film thickness in the range of a few nanometres up to a few microns are profilometry (stylus and optical), reflectometry and ellipsometry. More sophisticated techniques might include SEM or TEM. The advantages of ellipsometry are that it can be used to accurately determine the film thickness and the optical constants: n (refractive index) and k (extinction coefficient). None of the other techniques mentioned can do this. Indeed, determination of film thickness via reflectometry requires the refractive index to be known already. Profilometry requires there to be a step-edge (profile) in the film in order to determine the thickness, which the creation of presents a non-trivial problem in itself. Optical profilometry can be problematic when trying to determine a step height between two optically different materials as it relies on the interference between light reflected from the surfaces at the top and bottom of the step. If only one of these is metallic then the phase change on reflection from that surface can lead to erroneous results.

The technique of ellipsometry relies on changes in the polarisation of light that is reflected from the surface and any relevant interfaces within a sample. The fundamental equation of ellipsometry is

$$\rho = \frac{R_p}{R_s} = \tan\Psi e^{i\Delta} \tag{1}$$

where ρ is the complex ratio of the complex reflection coefficients of p-polarised light, $R_p$ , to s-polarised light, $R_s$. The p and s subscripts refer to light that is polarised in the plane of incidence and light that is polarised perpendicular to the plane of incidence, respectively. Δ is the change in phase difference upon reflection from the sample and is given by

$$\Delta = \delta_1 - \delta_2 \tag{2}$$

$\delta_1$ is the phase difference between the p and s component for the incoming light wave and $\delta_2$ is the phase difference between the p and s component for the reflected wave. $\Psi$ is the angle whose tangent is the ratio of the magnitudes of the total reflection coefficients

$$\tan\Psi = \frac{|R_p|}{|R_S|} \tag{3}$$

$|R_P|$ and $|R_S|$ are the ratios of the outgoing wave amplitude to the incoming wave amplitude for the for the p and s components, respectively.

It is important to note that an ellipsometer measures $\Psi$ and $\Delta$. The subsequent determination of the thickness and optical constants is dependent on the use of a model. This model is the assumed structure of the sample. Calculations based on reference data for the assumed model are then compared to those for the measured sample data in order to obtain the refractive index and thickness of the sample in question.

**Ellipsometry Measurements and Data Analysis**

The ellipsometry measurements discussed in this paper were carried out using a Jobin Yvon MM16 spectroscopic ellipsometer. This is of a design known as phase modulated, which utilises 4 liquid crystal modulators to modulate and analyse the polarisation of the incident and reflected light beams. This ellipsometer employs a CCD detector which simultaneously collects data across the spectral range of 430-850nm. This enables fast measurement times, typically less than 20s for the types of samples discussed in this paper. All measurements were carried out at an angle of incidence of 70°, although the instrument has the capability to make measurements at angles of incidence between 55° and 90°.

The application being considered here, namely, inorganic thin film sputter deposition onto polymer substrates using a roll-to-roll coater, requires a small amount of sample preparation to be carried out before a successful ellipsometry measurement can be made. Firstly, the optical properties of the substrate itself need to be considered. In the case of PET, there are two important such properties to consider. These are: i) its transparency leading to unwanted reflections from the back surface of the substrate; ii) its birefringent nature whereby the refractive index is a maximum along a particular optical axis within the film and is a minimum along the perpendicularly opposed optical axis. In order to eliminate the problem of back surface reflections from the PET substrate, the back surface (uncoated side) of the PET is roughened, either mechanically or chemically. Light is then scattered from this surface and does not reach the detector of the ellipsometer. To overcome problems due to the birefringence of the substrate, it is necessary to ensure that any measurements of the bare substrate and the coated substrate are measured with the substrate in the same orientation. This can be achieved using a polariser to identify the optical axes or by, simply, ensuring all samples that are measured have the substrate orientation maintained as a constant.

Another approach is to use silicon witness samples which are taped to the web using polyimide adhesive tape prior to deposition of the coating. The latter technique makes use of the fact that the silicon substrate is absorbing and hence there are no back surface reflections to consider. In addition, the use of silicon witness samples also avoids the problem with the birefringent nature of the PET substrate.

So far, only off-line measurements have been discussed as that is the only experience of the author. It is also possible to use ellipsometry in-line on vacuum web coaters. In this case, the movement of the web would be an important consideration.

Samples of alumina, silica and ITO were deposited onto the raw PET side of ST504™ substrates and at the same time onto silicon witness samples as described above. The alumina and silica samples were deposited using a dual cylindrical magnetron with a target voltage control feedback loop controlling the flow of oxygen. The ITO was deposited from a planar ceramic target using a pulsed DC power supply and a constant flow of ~2% oxygen. Conditions were varied as indicated in the results section that follows.

The data obtained was analysed using the DeltaPsi software package supplied with Jobin Yvon ellipsometers. Once the data has been measured, a model that best represents the actual sample is created and simulations based on this supposed model are run in order to compare the results to the measured data for the sample of interest. The software includes a library of reference data for the most commonly encountered materials, but it is also possible to create reference files for new materials. For the silicon witness samples, ellipsometry measurements were carried out for the bare substrate and the sample model then consisted of this measured data for the substrate with the relevant reference data file as a coating on top of this. Simulations were carried out using a range of nominal thicknesses to gain an idea of the robustness of the model.

## Results and Discussion

### Alumina:

The results of ellipsometry measurements for a series of aluminium oxide samples made at different target voltages and at two different web speeds are shown in Table 1. The top 3 rows show the results for samples taken at one edge of the coating (labelled as the back), the centre 3 rows are for samples taken from the centre of the web and the bottom 3 rows are the results of measurements made on samples taken from the other edge of the web, (front of the web). The coating width is ~350mm. In each case the aluminium oxide thickness, refractive index and the "goodness of fit" parameter, $\chi^2$ are given. In all cases it can be seen that $\chi^2$ is very small, indicating a good fit of the values calculated from the measured data to the calculated values from the assumed model reference data. This gives us confidence that the model is a good model and that the sample is indeed what we thought it was. The thickness values decrease with decreasing target voltage, which is as it should be; as the target voltage is decreased, more oxygen is

| Web speed | 0.2m/min | | | | | 0.4m/min | |
|---|---|---|---|---|---|---|---|
| Control voltage | 428V | 420V | 413V | 403V | | 428V | 413V |
| Thickness (nm) | | 74.0 | 68.2 | 64.2 | | 43.5 | 38.1 |
| Refractive Index | | 1.771 | 1.764 | 1.732 | Back | 1.769 | 1.733 |
| $\chi^2$ | | 0.167 | 0.110 | 0.080 | | 0.067 | 0.059 |
| Thickness (nm) | 74.6 | 67.6 | 66.8 | 56.5 | | 38.5 | 34.1 |
| Refractive Index | 1.769 | 1.742 | 1.712 | 1.710 | Centre | 1.744 | 1.698 |
| $\chi^2$ | 0.214 | 0.122 | 0.102 | 0.070 | | 0.053 | 0.059 |
| Thickness (nm) | 77.7 | 71.1 | | 60.2 | | 41.4 | 35.5 |
| Refractive Index | 1.784 | 1.764 | | 1.714 | Front | 1.761 | 1.717 |
| $\chi^2$ | 0.191 | 0.146 | | 0.069 | | 0.061 | 0.058 |

*Table 1: Ellipsometry results for aluminium oxide coatings sputter deposited onto silicon witness samples positioned at three positions across the PET web width. The columns represent samples made using deposition conditions with various target voltages and web speeds.*

added and the process is heading towards the poisoned target mode where the deposition rate is at its lowest. The aluminium oxide thicknesses for the samples made at 0.4m/min are ~half the value of the samples made at 0.2m/min at the same target voltages, as is to be expected. The most interesting feature of this dataset, however, is the non-uniformity of the coating across the web width. In all cases the central sample position shows a diminished thickness compared to the outer edges, with the back edge having a heavier deposition than the front edge. The refractive index follows the same pattern. Higher values of the refractive index indicate a metal-rich coating and lower values indicate an oxygen rich coating. This effect can be explained if there is a higher deposition rate at the edges of the coating window, or, if the oxygen delivery is reduced at the edges. This therefore indicates a problem with the oxygen delivery system, the pumping, or the magnetron design. No such uniformity problems have been observed when depositing metallic coatings, although it is noted that the measured parameter, namely sheet resistance, may not be as sensitive a measure as the refractive index. It was therefore concluded that the most likely cause of the problem was either the oxygen delivery system or an asymmetry with the pumping system

**ITO:**

Figure 2 shows the resistivity minimum for ITO deposited from a planar ceramic target and Table 2 gives the corresponding results of ellipsometry measurements for each of the data points in the graph. The oxygen flow is increasing from left to right across the table. It can be seen that neither the thickness nor refractive index varies significantly across the range of oxygen concentrations considered here. For ITO, the refractive index is rather insensitive to changes in the oxygen concentration around the minimum of resistivity. It is, however, useful to determine the thickness accurately using ellipsometry in order to obtain a value for the resistivity of an ITO sample, together with the measured sheet resistance.

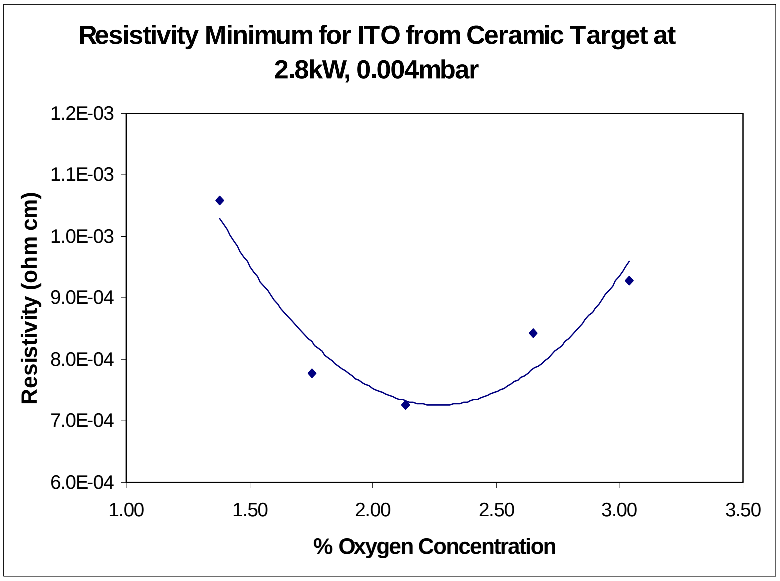


*Figure 1: Resistivity minimum curve for ITO deposited from a planar ceramic target onto silicon witness samples taped to a web of PET film. Resistivity of the samples is plotted as a function of oxygen gas flow concentration.*

| | A | B | C | D | E |
|---|---|---|---|---|---|
| Thickness (nm) | 99.9 | 96.0 | 96.8 | 97.9 | 97.8 |
| Refractive index (@633nm) | 1.986 | 2.019 | 2.006 | 1.991 | 1.976 |

*Table 2: Ellipsometry results for thickness and refractive index of ITO samples as indicated in figure 1 above.*

## Conclusions

This work shows that ellipsometry is a powerful tool for the non-destructive analysis of thin film coatings produced in a roll to roll coater. As a turn-key instrument, it can be used to easily and accurately determine the thickness and refractive index of a wide range of coatings on polymer substrates, as long as the coating is reasonably transparent (thickness limitation for metals is up to ~50nm). It is also useful tool in helping to identify process issues that might otherwise go undetected. For example, the refractive index of oxides of silicon and aluminium is very sensitive to the oxygen stochiometry. This fact has been used here to identify uniformity problems due to either gas delivery, pumping or magnetron issues.