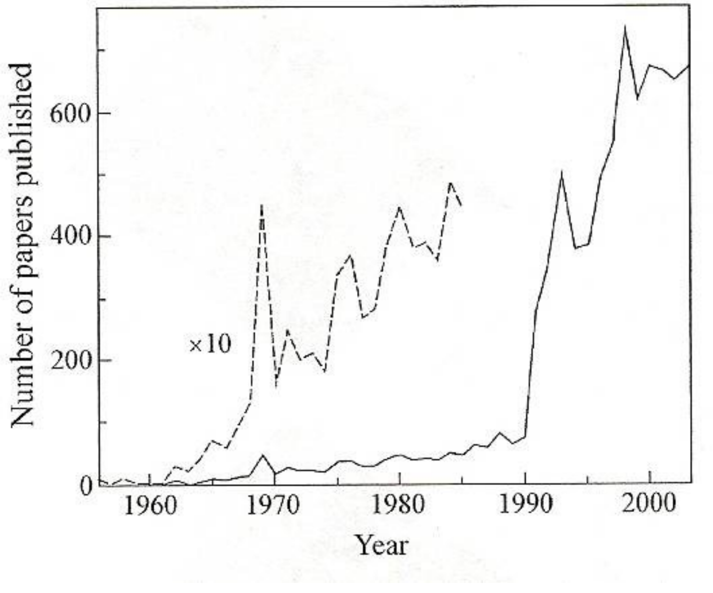
Summary of presentation

Characterisation of thin film solar cells using spectroscopic ellipsometry

Robert Greef, Southampton University

The growth of ellipsometry – papers published worldwide (1)



(1)Source:Hiroyuki Fujiwara:Spectroscopic Ellipsometry, Wiley 2007

- What is a solar cell?

Usually a multilayer device comprising e.g.

  - Semiconductors
  - Dyes
  - Metals
  - Rough and composite layers

- What is Ellipsometry?

  Reflectance spectroscopy at oblique incidence, measuring change in polarisation rather than just intensity

Ellipsometry is a rich data set: it responds to the materials and structural properties we are interested in i.e.

•optical properties,

•thickness of layers in multilayered structures

•interlayer roughness

and does so in a highly sensitive and easily-measured way.

Ellipsometry gets its name from the most general state of polarisation of light i.e. elliptical, the more familiar forms being linear and circular.

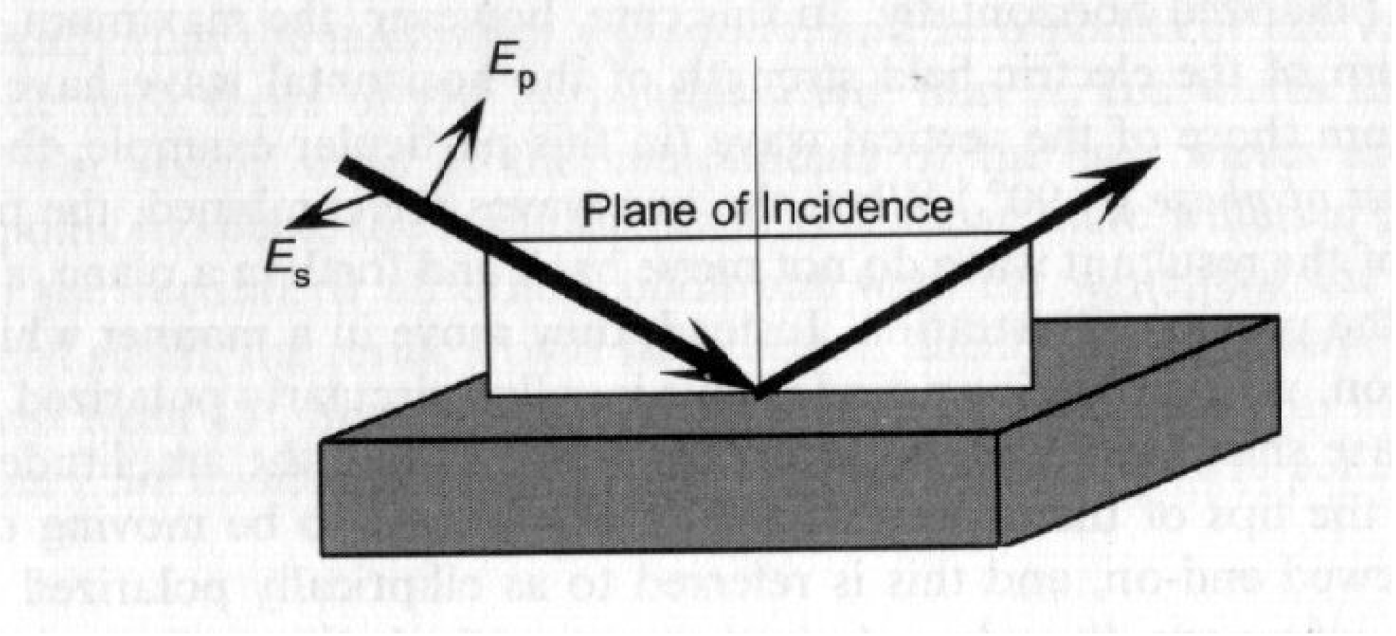
Polarised Light

- Characterised by the relative amplitude ψ and relative phase Δ of the orthogonal
- (*p* and *s*) electric vectors of the light ray after reflection from the target.
- The reflection coefficient is given by:

$$\rho = tan\ \psi .\ exp\ i\ \Delta$$

E_p and E_s are the parallel (to the plane of incidence) and perpendicular components of the electric field vectors.

They have a relative magnitude and can have a phase difference.



For bare surfaces the ψ range is 0 - 45° and Δ is 0° – 180°

For film-covered surfaces ψ is 0 – 90 ° and Δ is 0 – 360 °

Useful references to the basics of ellipsometry:

(1) Hiroyuki Fujiwara: “Spectroscopic Ellipsometry”, Wiley 2007

(Also covers more advanced topics and recent applications)

(2) Harland G. Tompkins and William A. McGahan:

“Spectroscopic Ellipsometry and Reflectometry”, Wiley 1999

(3) There is a lot of tutorial material on the internet. Try physics-animations.com for example, or Wikipedia and references therein.

(4) The websites of ellipsometer manufacurers (Woollam and Jobin-Yvon) have a lot of tutorial material.

The basics include:

The Fresnel equations for reflection from a 2-phse boundary, which define the polarising (Brewster) angle and the critical angle for internal reflection.

The Drude equations for reflection from a multilayer stack.

Optical Properties of Materials

- Complex refractive index

$$N = n + ik$$

- k is the extinction coefficient: = 0 for transparent materials
- $$\alpha = 4.\pi.k / \lambda$$

Fundamental relationship

- Δ and ψ **map 1 : 1** to n and k for reflection at a single interface e.g. a bare substrate

NB: It is not necessary to know even the basics of ellipsometry theory if you are using the technique as a routine tool, studying a system which is covered by the excellent instructions that come with modern ellipsometers. To get the most out of the technique with a new or complicated system, a more thorough knowledge is required.

Available instruments:

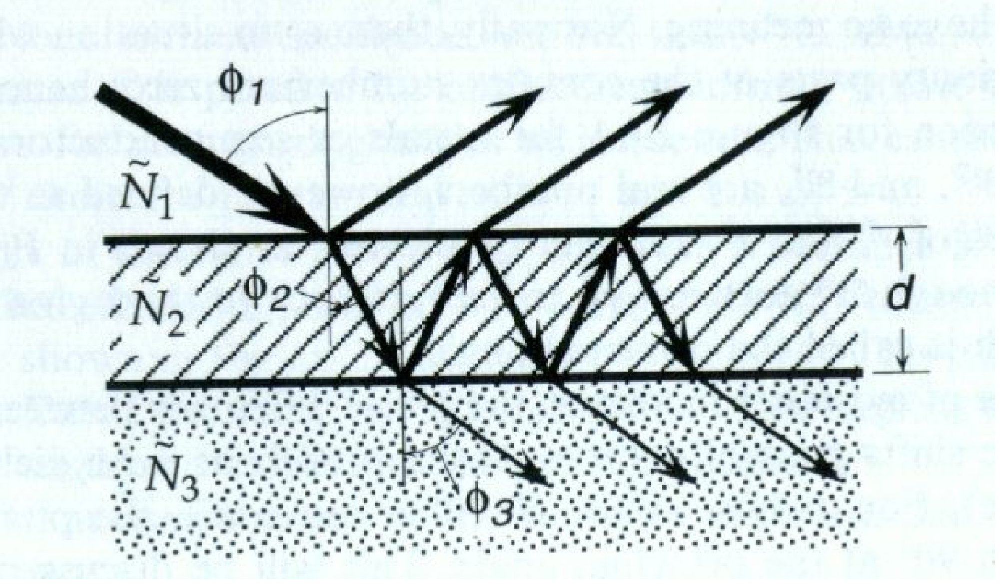
Woollam M2000 (ECS clean room)

Horiba Jobin-Yvon Uvisel (Engineering Materials)

Accurion(Nanofilm i-elli2000) microscopic imaging ellipsometer (Chemistry)

Woollam M2000 integrated with ALD chamber (available real soon now!)

For a film-covered surface, the detected signal is the vector sum of all the reflected and refracted rays, each one having its own contribution to Δ and ψ. Hence my term “rich data set.”



The Drude equations, sometimes called the Fresnel analysis, enable Δ and ψ to be calculated for any number and combination of films, given their optical constants and thicknesses.

Important characteristics of the ellipsometric method

•Method is self-referential – 2 properties of the same beam are measured, giving high immunity to source noise.

•Extreme sensitivity – in a favourable case this means sensitive to less than a monolayer surface coverage.

•Will measure thicknesses up to ≈10μm.

•For a transparent film on a substrate of known n and k, a single measurement gives n & thickness of the film.

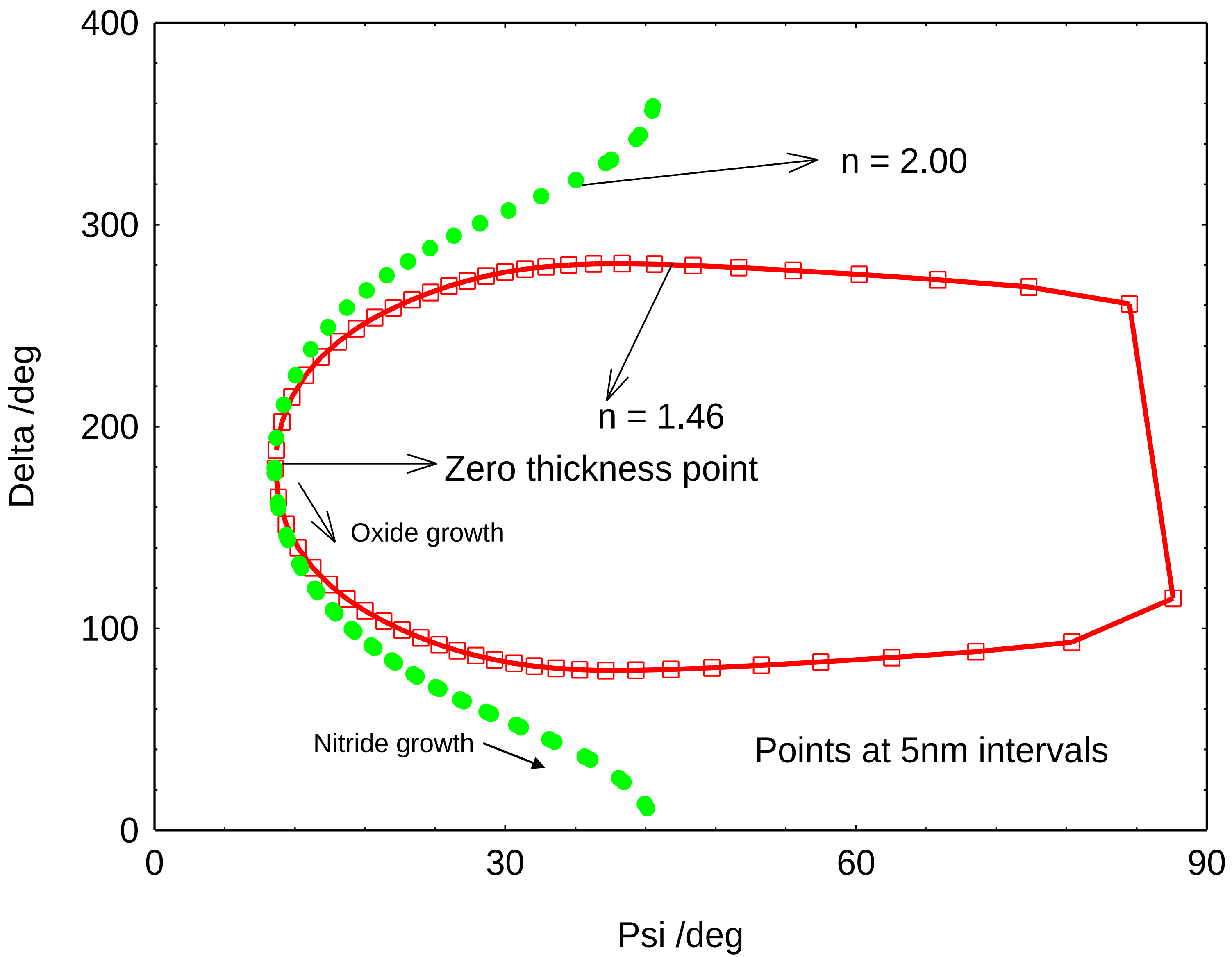
Delta Psi trajectories for film growth at constant wavelength

Though the most familiar displays in working with the Woollam and Horiba ellipsometers are delta psi plots vs wavelength, plots of delta and psi for a single wavelength with varying thicknesses illustrate some of the important features of the technique to bear in mind when analysing ellipsograms of whatever kind.

Next is a slide illustrating two trajectories for common materials, SiO_2 on Si, and Si_3N_4 on Si

- All trajectories go through the zero-thickness point, this point being characteristic of the substrate material.
- For high film indices, the trajectory can wrap on the 0 /360 boundary
- The thickness sensitivity varies widely, being a minimum at the zero-thickness point.
- The closed figure overlaps exactly at multiples of the periodic thickness

Film thickness trajectories on Si at φ = 70° and λ = 633nm

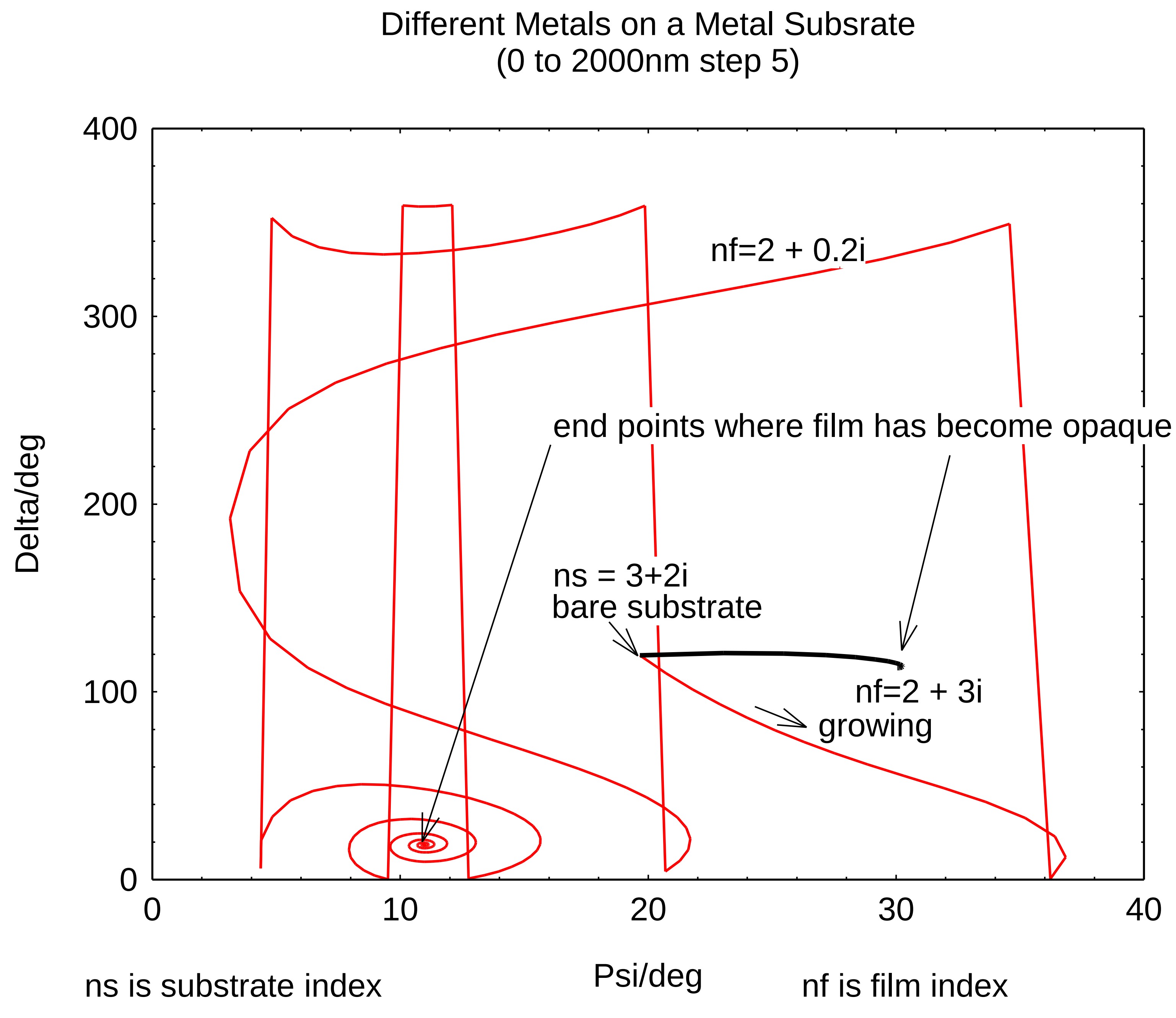


Absorbing Films

The next slide shows how, when the growing film is absorbing, the trajectory does not repeat, but moves to an end point where the light no longer penetrates the film i.e it appears as a new substrate on top of the first one.

The start points and end points are characteristic of the pure materials, so the end points can be used to obtain the optical constants of the film material.

When the film is weakly absorbing, the path to the new substrate is long (red curve), when it is strongly absorbing the path is short (black curve)


Different Metals on a Metal Subsrate
(0 to 2000nm step 5)
400
300
200
100
0
0
10
20
30
40
Delta/deg
Psi/deg
nf=2 + 0.2i
end points where film has become opaque
ns = 3+2i
bare substrate
nf=2 + 3i
growing
ns is substrate index
nf is film index

Steps to analysing ellipsometry results

Construct a model of the target, in terms of the materials, if known.

Known materials will have a **dispersion equation (dsp)** to represent n & k as a function of wavelength, of which there are many types.

If there are similar materials or models in the manufacturers data base, or the wider literature, use these as starting points in the fitting process.

If a good fit is obtained, examine the results for feasibilty. Are the thicknesses as expected? Plot the dsp's for the materials. Are they physically meaningful?

The following case histories are from the work of the Solar Energy Laboratory in Engineering Sciences at Southampton University.

Analyses by Robert Greef and Lefteris Danos

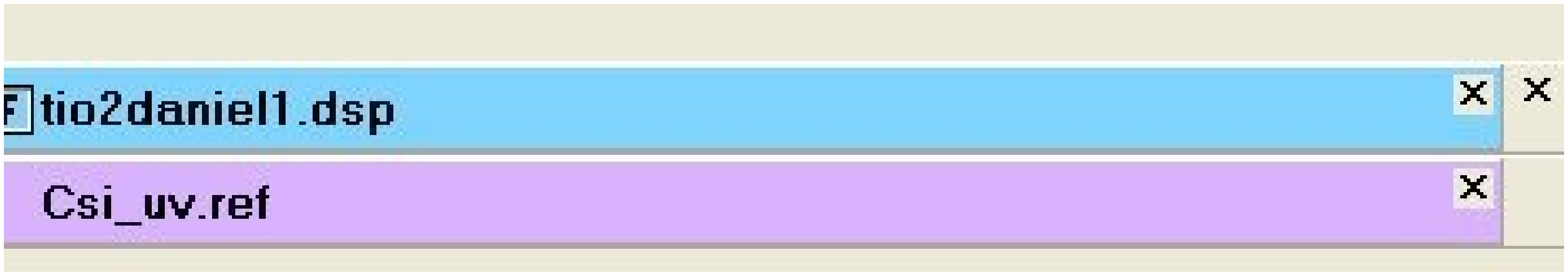
Case History – TiO2 on Si – by Daniel Ng

A TiO2 coating on Si was required as an anti-reflection coating. This was attempted using sol-gel methodolgy. Making a coating is not difficult, but getting it to be uniform, homogeneous and of the right thickness is. Ellipsometry provided a tool to check all these properties, offline, by looking at a series of finished samples. The film could then be compared with literature values of the properties of TiO2 made by other methods.

Test samples were made and examined by ellipsometry with the results on the next slide.

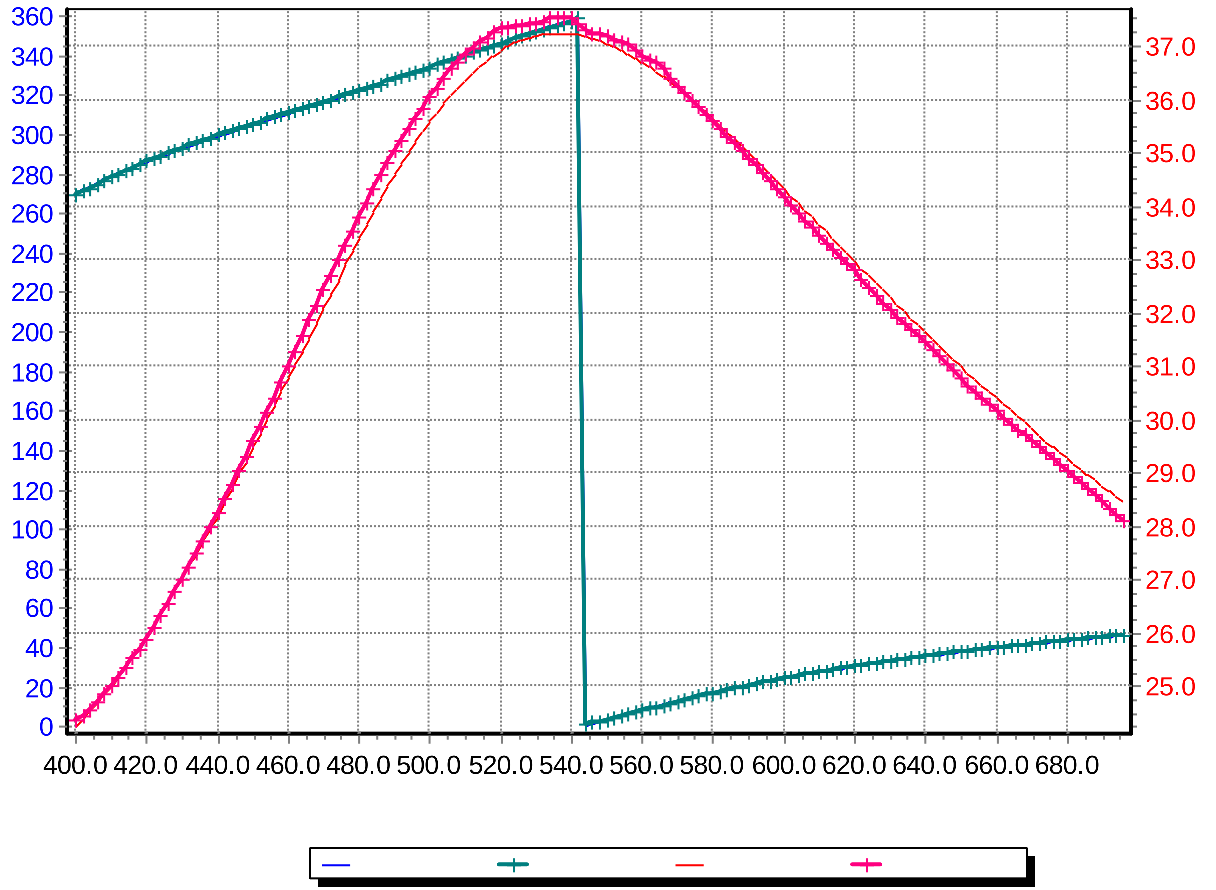
To interpret the data, the results must be compared with a model of the substrate + film structure

TiO2 on Si – a simple? structure



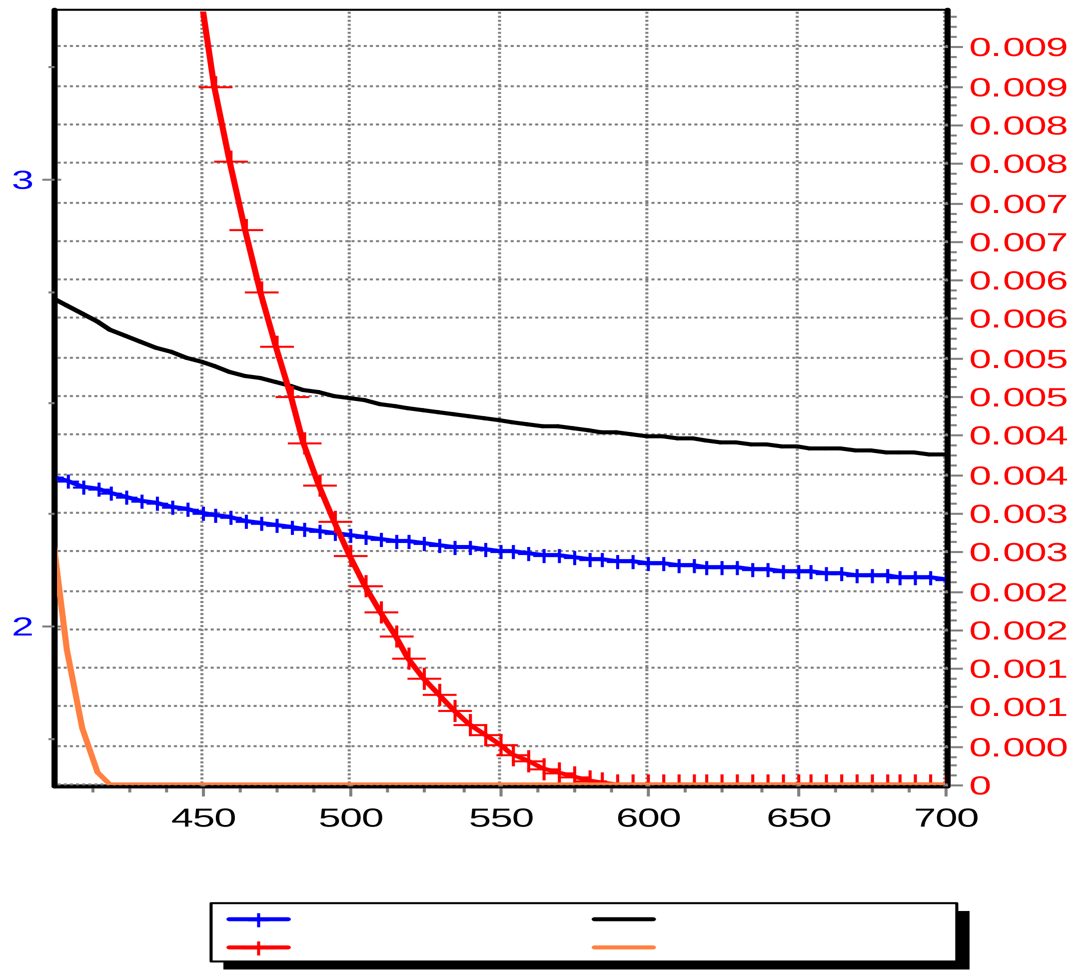
This is the simplest possible structure. It gives a good fit to the “New Amorphous” model of the literature data. But are the parameters obtained meaningful? (next 2 slides)

TiO2 on Si – a simple? structure



A good fit is obtained using the literature dsp for TiO2 as starting point.

Comparing the fitted (+ markers) and literature optical constants for TiO2 on Si



Fit parameters for the TiO2 on Si sample

Parameters

1)	L1 Thickness [nm]		=	69.120	± 0.058
2)	tio2daniel1	n∞	=	1.7435310	± 0.0321036
3)	tio2daniel1	ωg	=	2.0699380	± 0.0763415
4)	tio2daniel1	fj	=	0.1428441	± 0.0147048
5)	tio2daniel1	ωj	=	5.0955250	± 0.1856096
6)	tio2daniel1	Γj	=	1.0857810	± 0.0826035

Correlation matrix

=1=	=2=	=3=	=4=	=5=	=6=
1.000	-0.265	-0.479	-0.389	0.234	-0.260
	1.000	0.857	0.183	-0.993	-0.074
		1.000	0.595	-0.857	0.342
			1.000	-0.228	0.956
				1.000	0.023
					1.000

This is a typical statistics output for a fit to a model – New Amorphous in this case. The number and type of the fit parameters varies with the type of dsp

Conclusions from the TiO_2 fit:

The fit is well-behaved, with small error limits, and (mostly) low parameter correlations.

The optical constants of the TiO_2 layer deviate substantially from the literature values. The k values are higher, suggesting that the surface may be rough, and the n values are lower suggesting a lower density than the literature values i.e. void content.

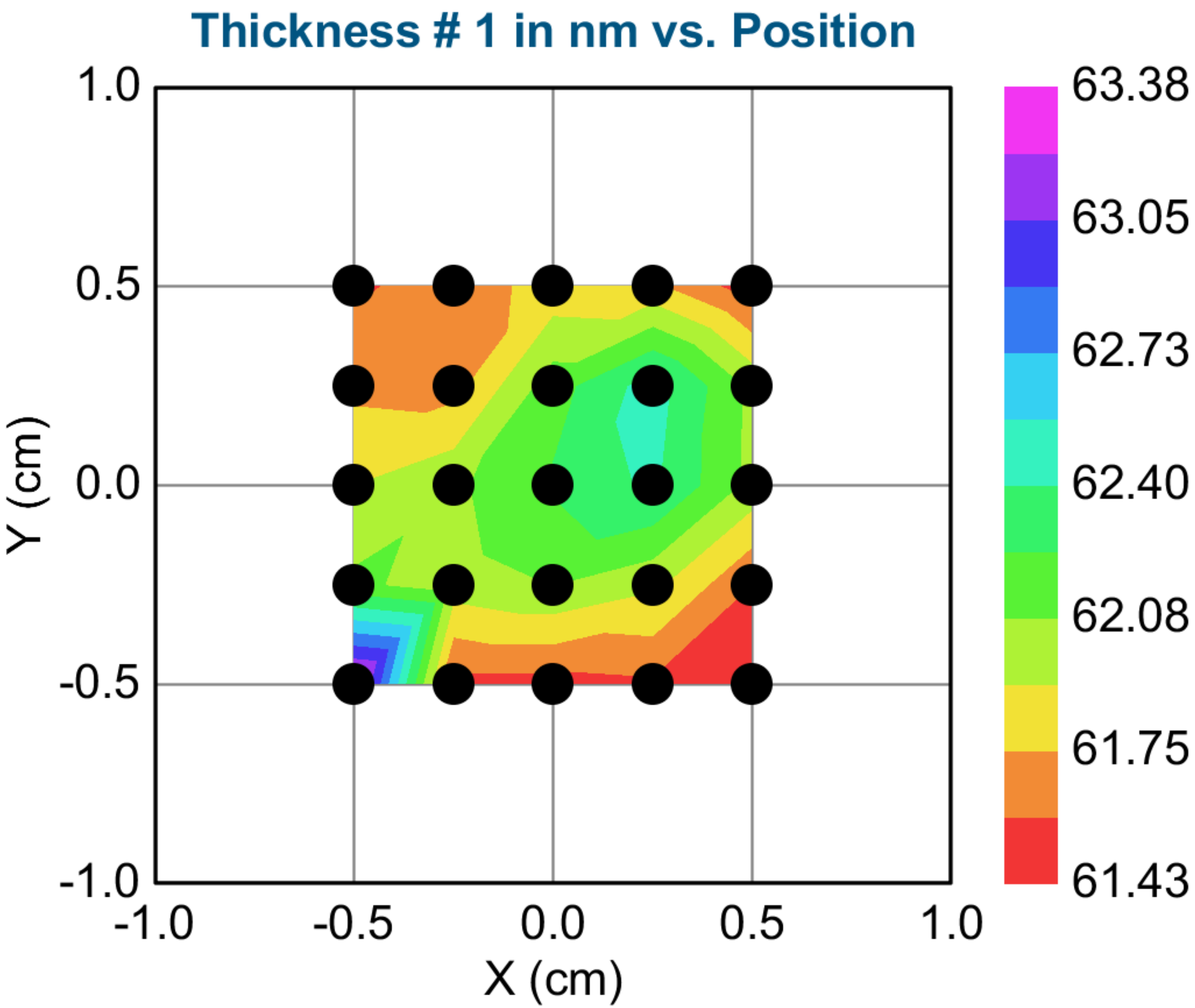
Both of these effects can be modelled in favourable cases by using a more complex model.

Map of TiO_2 and TiN films on Si

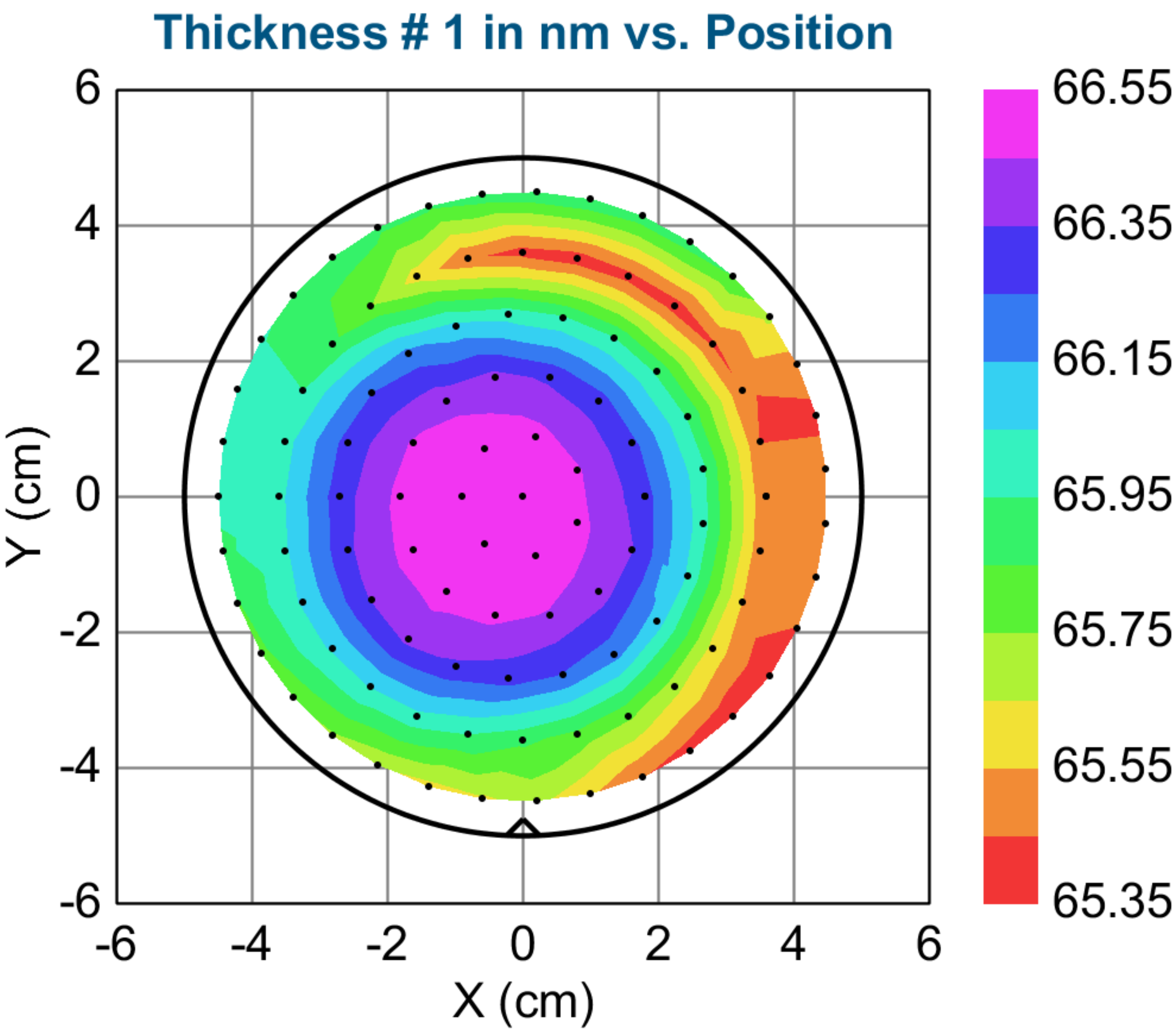
The following 2 slides show how the ellipsometric parameters and hence the film thickness can be mapped across the surface of a sample.

Note the sensitivity of the thickness (vertical) scale.

TiO2 on Si


Thickness # 1 in nm vs. Position
Y (cm)
X (cm)
1.0
0.5
0.0
-0.5
-1.0
-1.0
-0.5
0.0
0.5
1.0
63.38
63.05
62.73
62.40
62.08
61.75
61.43

Si3N4 on Si



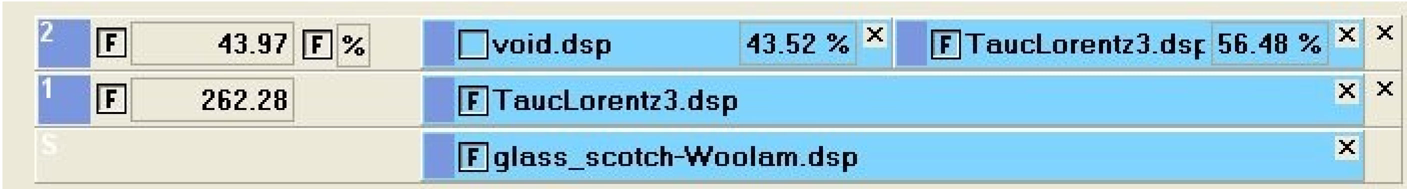
Thickness # 1 in nm vs. Position
6
4
2
0
-2
-4
-6
Y (cm)
-6
-4
-2
0
2
4
6
X (cm)
66.55
66.35
66.15
65.95
65.75
65.55
65.35

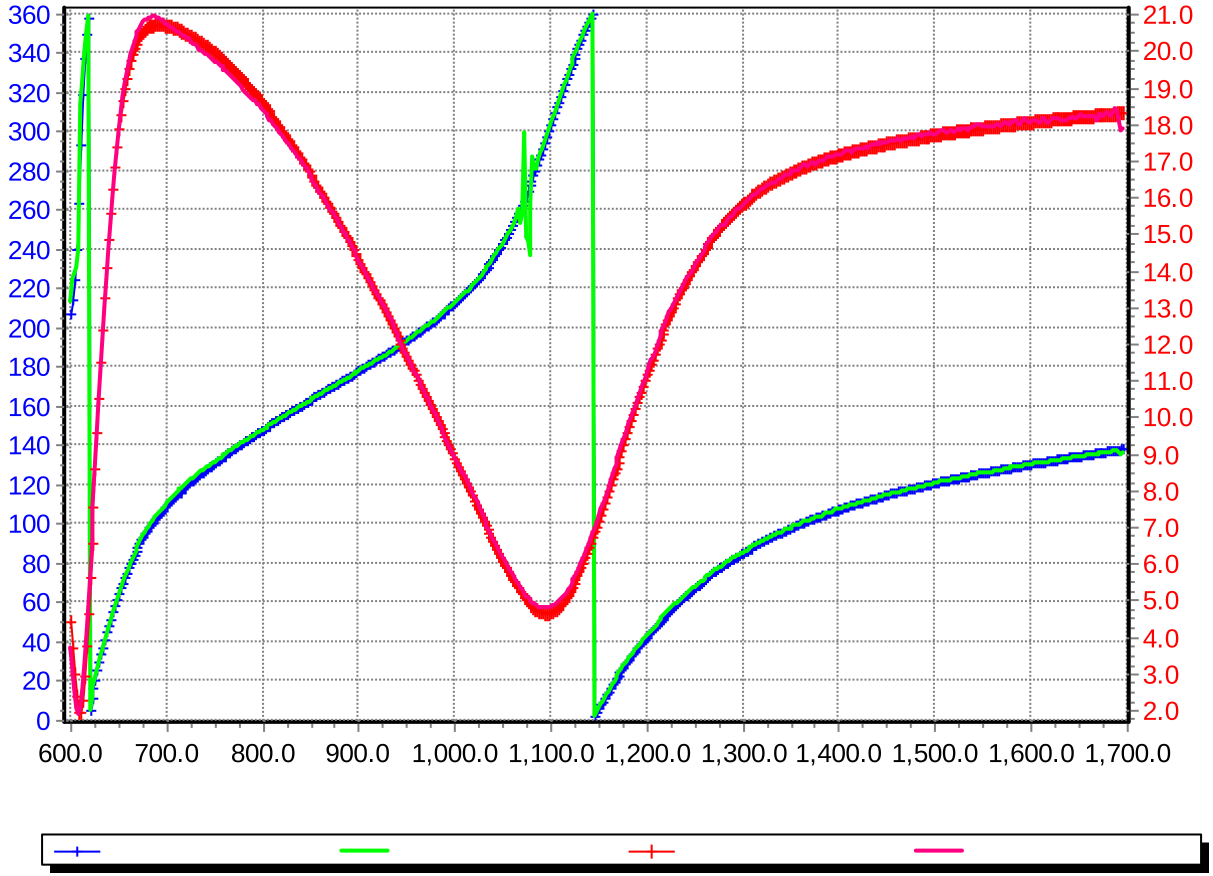
CdS on glass (next slide)

This is an investigation of the growth habit of CdS on a glass substrate. Care has to be taken when using a thin glass substrate such as a microscope slide to suppress the unwanted reflection from the back surface of the glass. In this case this is done by using sticky tape on the back surface.

The example also shows how a rough surface can be modelled as a non-uniform surface by the inclusion of voids.

The fit obtained to the model is very good, but the long-wavelength n value for CdS is about 0.2 below the literature value, suggesting that CdS may grow in different habits with different growth conditions.





Parameters

1)	L1 Thickness [nm]	=	262.308	±	0.618
2)	L2 Thickness [nm]	=	43.905	±	0.211
3)	L2 % void.dsp	=	43.50	±	0.38

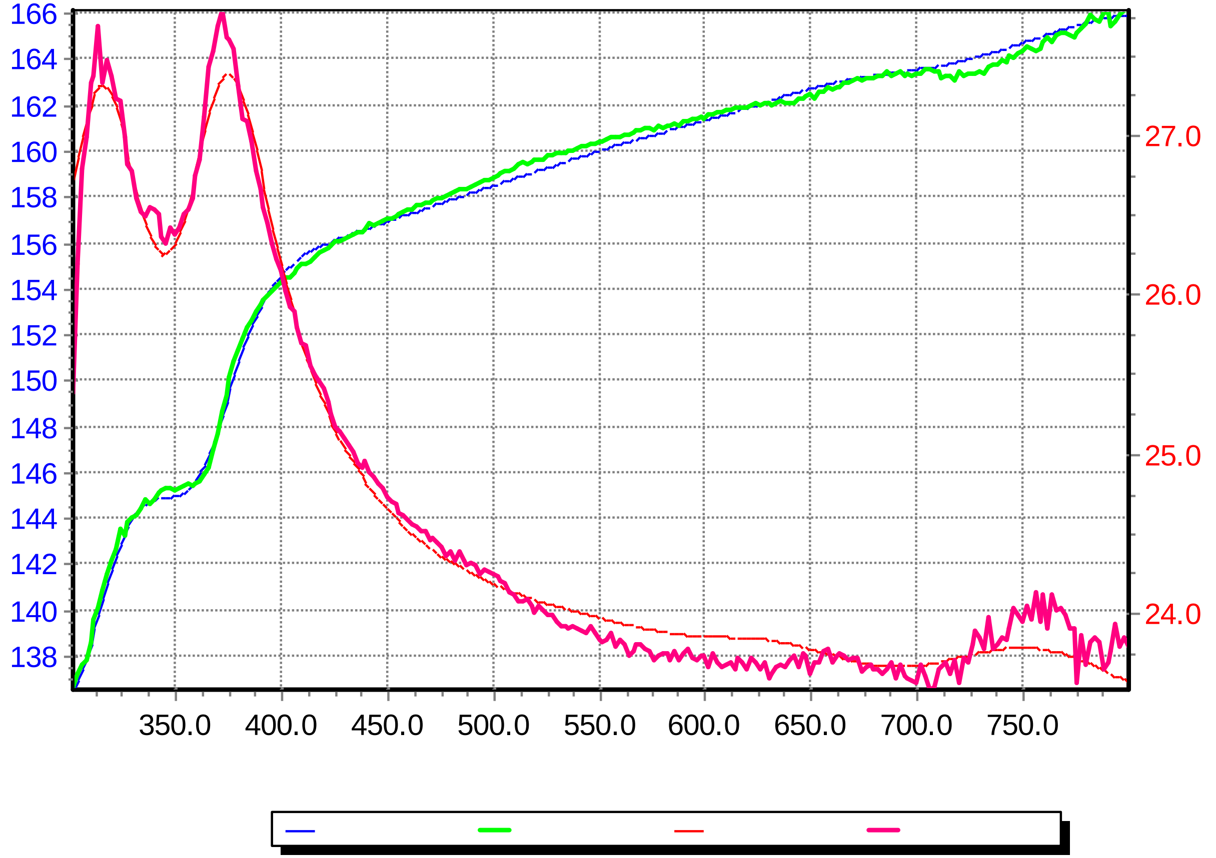
CdTe on Si (next slide)

This material needs a more complex model, as it has two peaks in ψ in the visible spectrum range. Therefore a 2-oscillator dsp is selected from a general multiple-Lorentzian dsp.

A reasonably good fit is obtained from a simple one-layer model with thickness 2498nm, but the resultant n and k values for the film are much lower than the literature values. A better model could be fitted by incorporating voids in the CdTe layer.

Such a refinement might be a useful guide to changing the growth conditions to produce a more perfect layer.

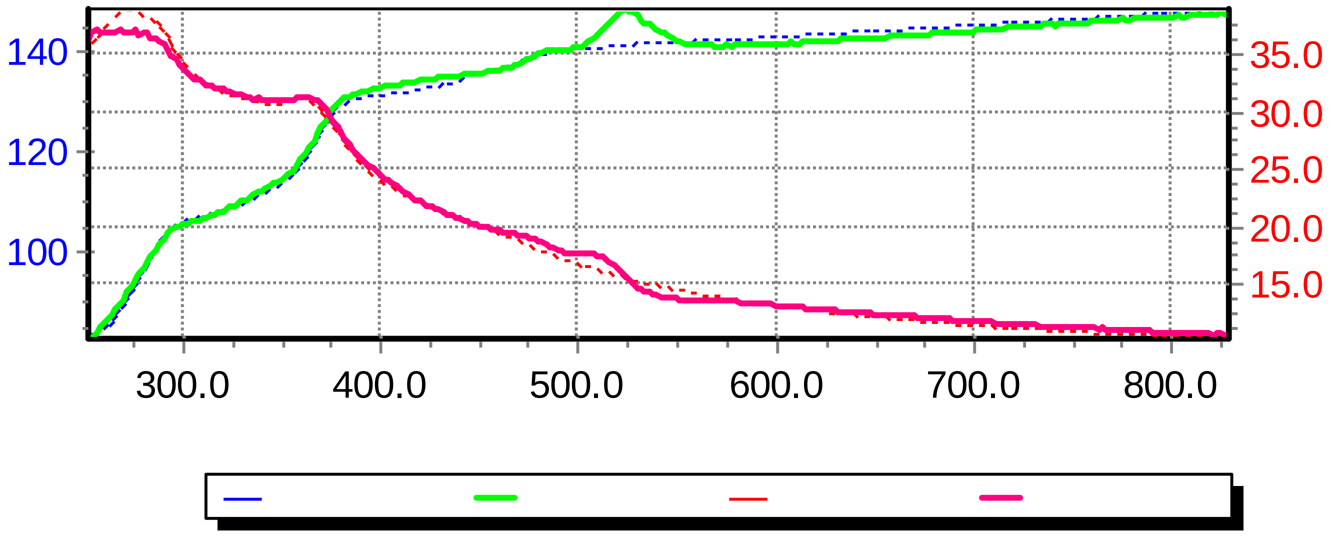
Technium Optic CdTe on Si

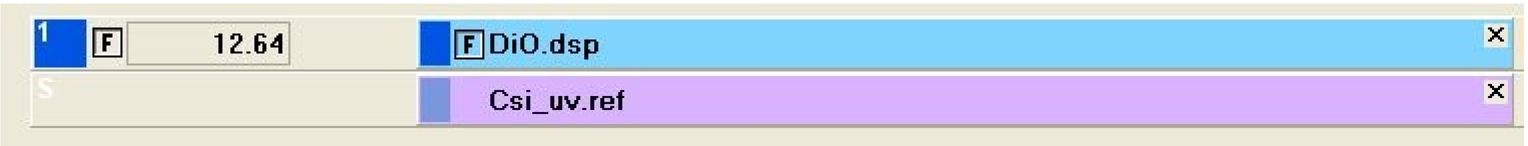


DiO on Si
(next slide)

This is an example of a very thin organic layer on Si. DiO is a dye consisting of a long straight chain molecule with large dye molecule at the end. It is designed to be amphiphilic i.e It will form a monolayer on water with the dye head submerged while the straight chains line up out of the water. This is a Langmuir-Blodgett layer. These layers are being used to investigate energy transfer to Si solar cells.

12.64nm DiO on Si





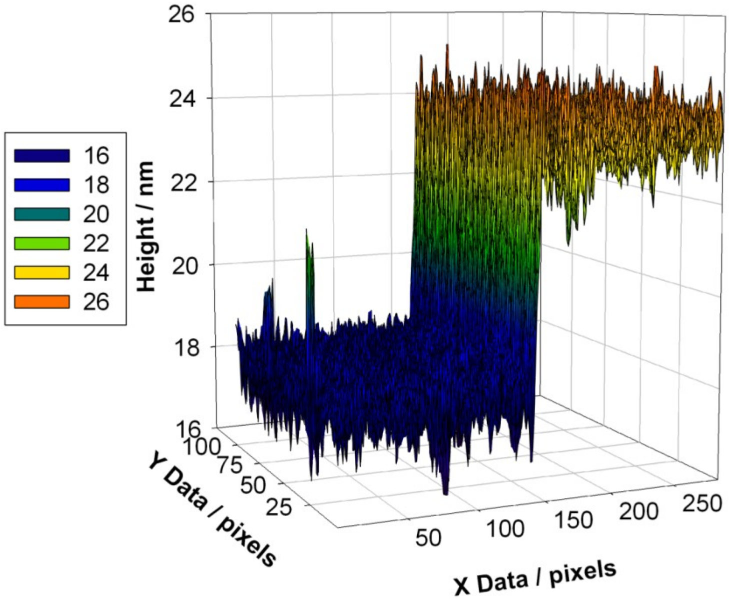
This uses a very simple model and a classical dsp with 2 Lorentzian oscillators. The fit could be improved by adding an oscillator centred on 530nm. This would not improve the thickness estimate, which is the main parameter of interest.

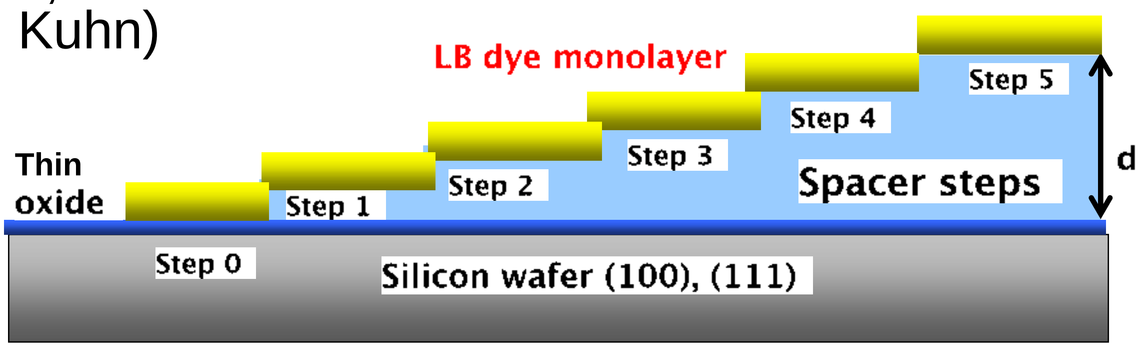
Imaging ellipsometry of thin organic layers using the Nanofilm microscopic ellipsometer (next slide)

The image shows how organic Langmuir-Blodget dye films of progressive thickness can be assembled and measured. The step height is 8nm.

Spacer structures on Silicon

- LB Films allows to build steps on Si and control the distance to Si Surface
- A dye monolayer deposited on top and monitor fluorescence as a function of distance
- Distance measured accurately using Spectroscopic Ellipsometry
- Treat as dipole emission near interface using classical theory for a single mirror (Chance, Prock and Silbey (CPS) , Kuhn)





L. Danos et al Thin Solid Films *516* *(2008) 7251*

In-Situ Process Monitoring by Ellipsometry

In-situ monitoring can often provide great advantages in shortening the development cycle in film growth engineering. An example follows, in which single-wavelength ellipsometry was used in the production of ZnO layers to be used as piezo-electric sensors.

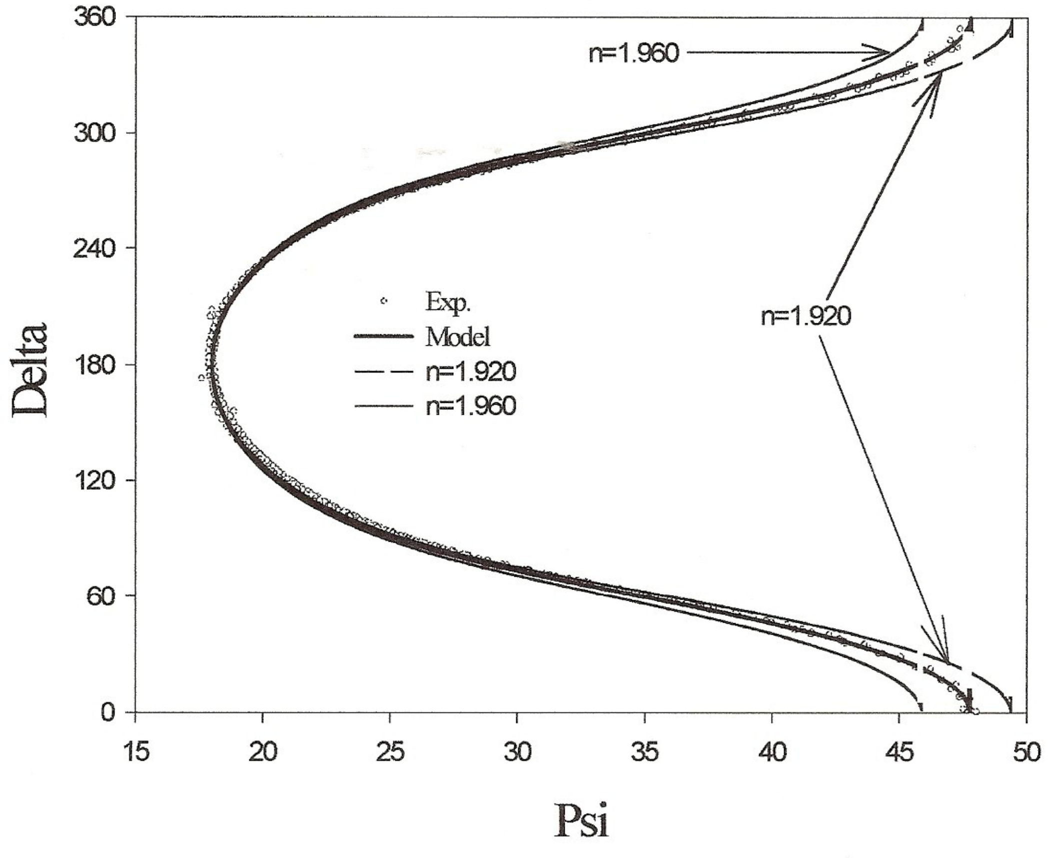
A real-time display of the delta-psi trajectory is a useful diagnostic tool, as the ideal response can be used as a template to report film growth habit, giving an opportunity to correct growth conditions on-the-fly.

ZnO is weakly anisotropic. Previous calculations had shown that this effect would be negligible for the layers of interest.

The target n value is 1.94

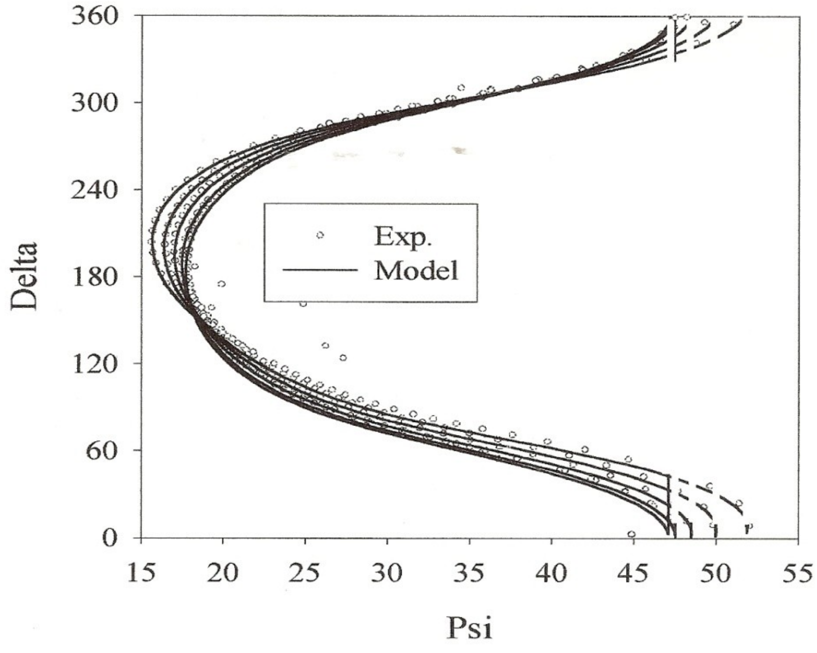
Simulated response – wide range of n

See slides 16-19 for more theoretical plot shapes



What is actually observed during growth

The lack of overlap of the trajectories shows that the growth is not ideal.

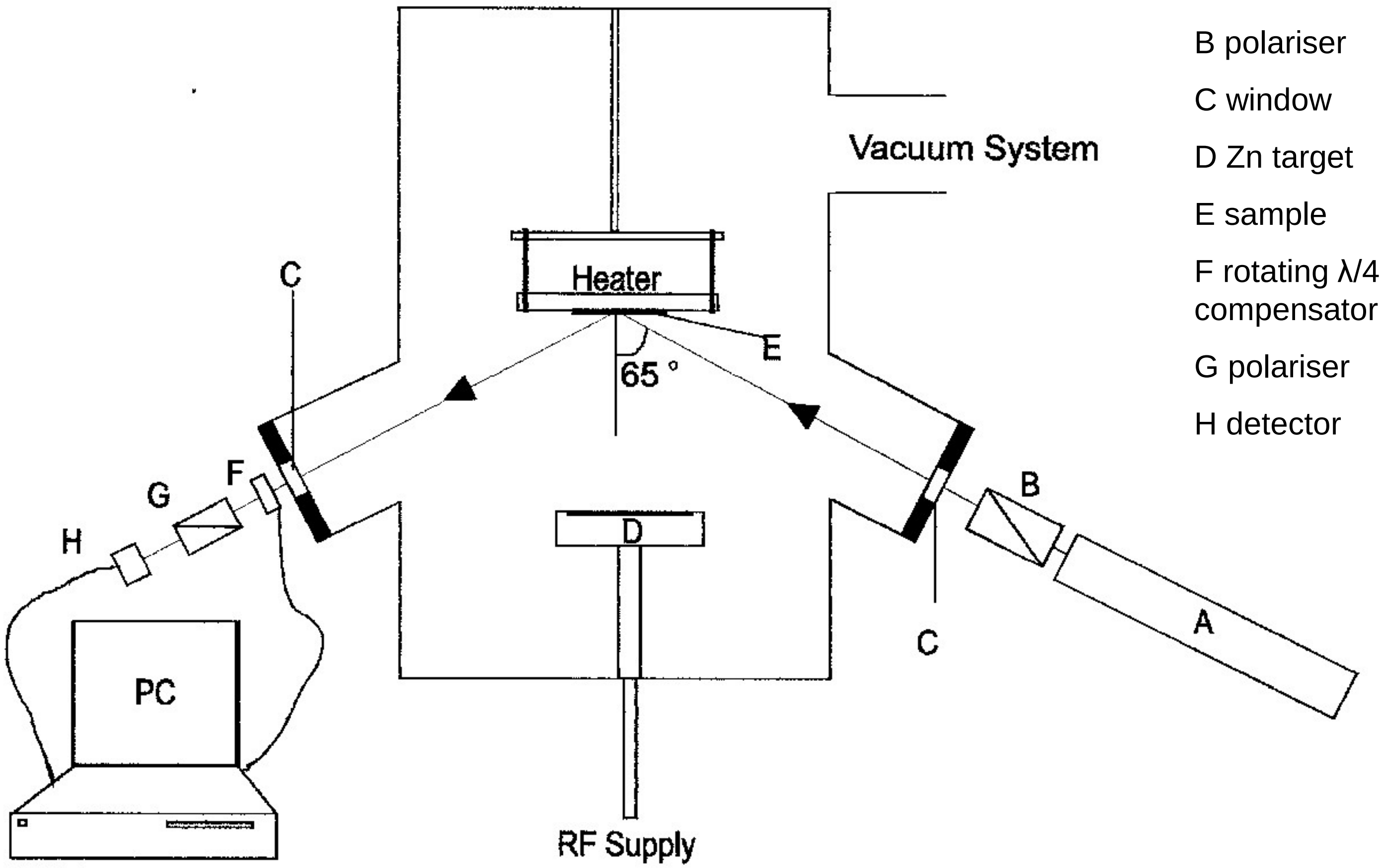


The growth parameters – total gas pressure, gas mix, sample temperature, magnetron power, can all be varied during the growth cycle, the result appearing as a delta-psi trajectory for comparison with the ideal response.

When this was done, the critical factor was found to be the sample temperature. With these settings, films were prepared, and after a number of cycles the growth rate was found by off-line calculation.

With the more modern commercial ellipsometers, the growth rate calculations can also be done in real time.

In-situ monitoring of sputtered ZnO films for piezoelectric transducers



A: HeNe laser

B polariser

C window

D Zn target

E sample

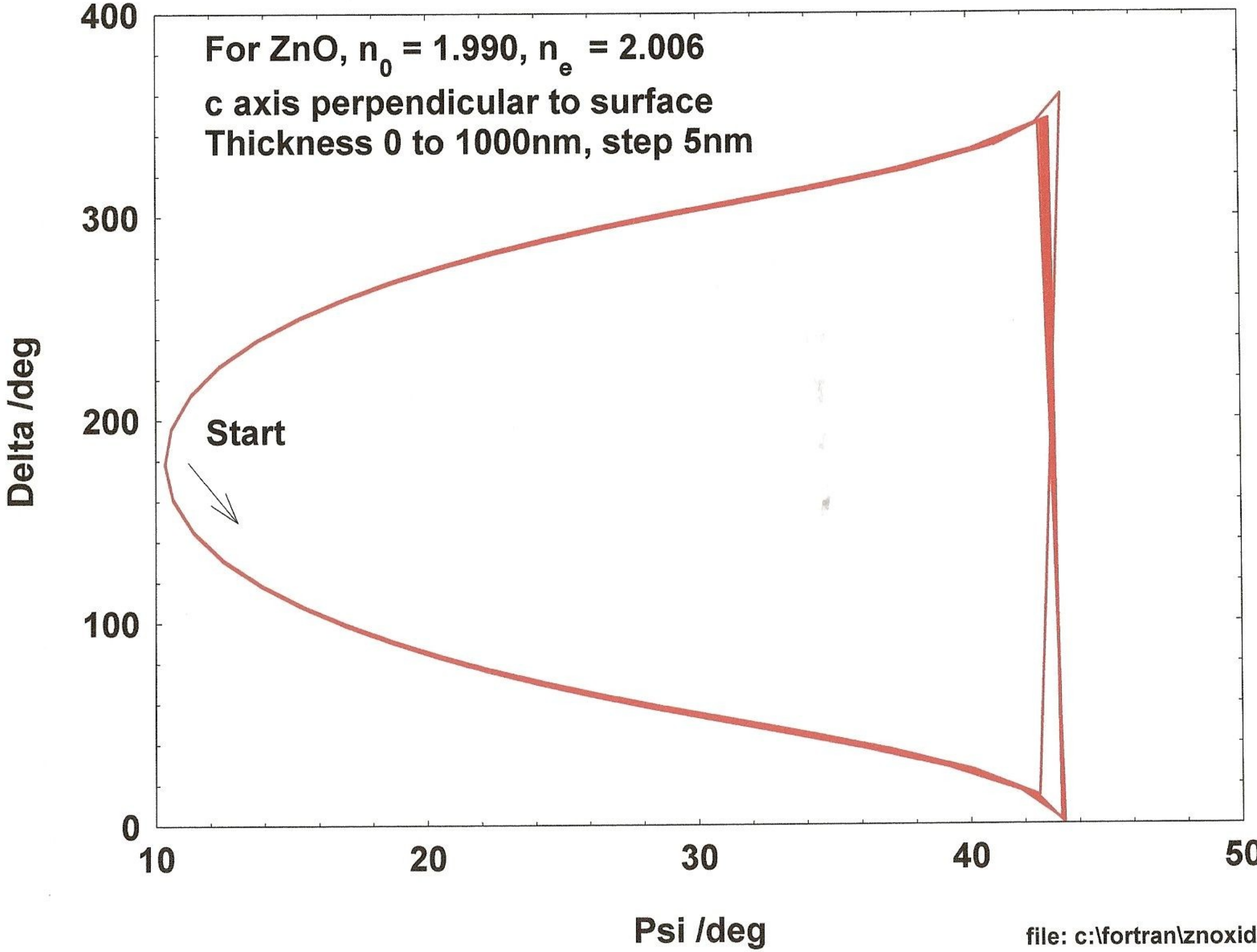
F rotating λ/4 compensator

G polariser

H detector

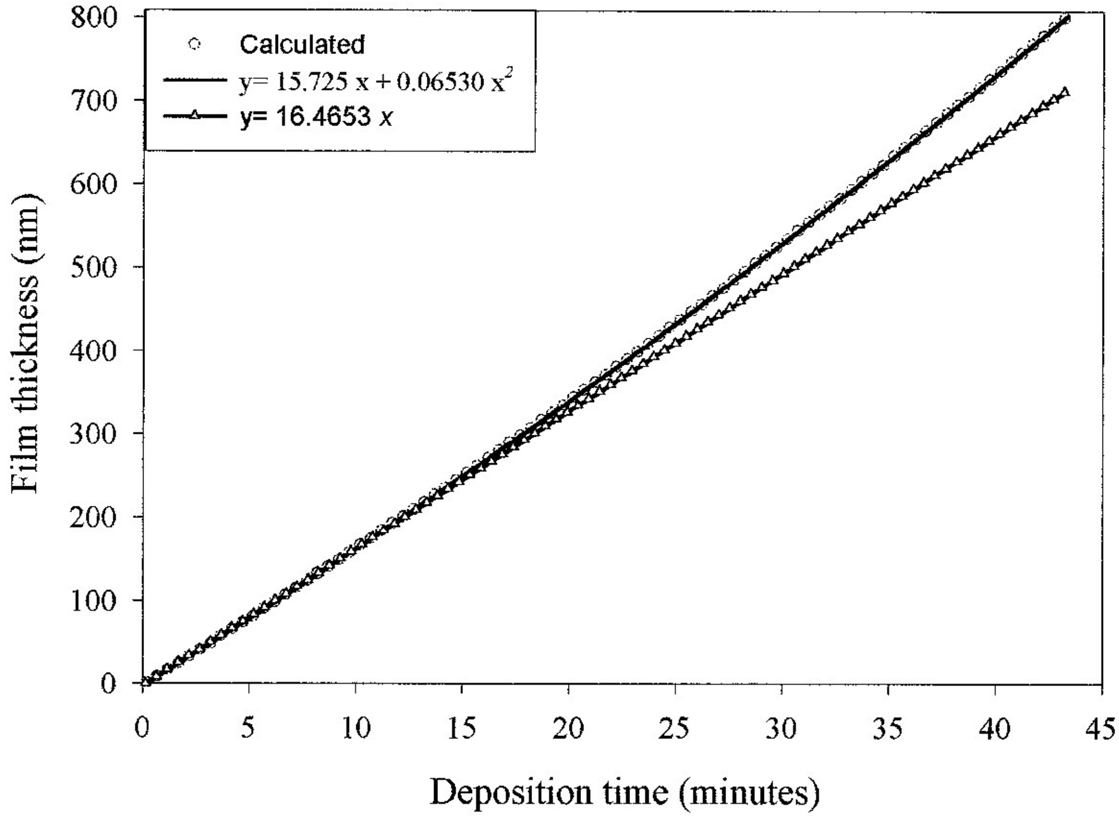
N.K Zayer, R. Greef, K. Rogers, AJC Grellier, C.N Pannell Thin Solid Films 352 (1999) 179-184 file: c:\fortran\znoxide.dat

Growth of anisotropic ZnO on Si at φ = 65°



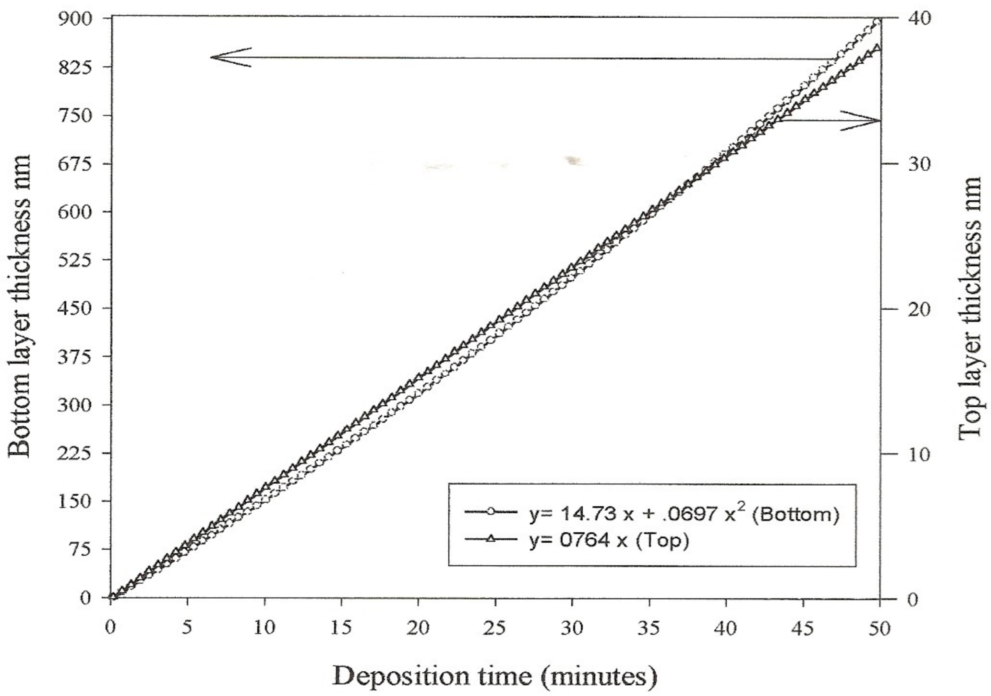
file: c:\fortran\znoxide.dat

N.K. Zayer, et. al.



After 15min the growth rate begins to deviate from the linear growth rate and settles to a weakly parabolic rate.

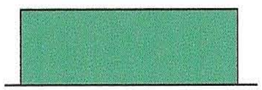
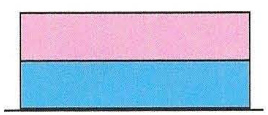
Fig.(6)
N.K. Zayer, et.al.



This is modelled by a two-layer film, the lower having a non-linear growth rate.

In-situ ellipsometric modelling of ZnO growth by magnetron plasma sputtering

Results at 3 temperatures

	n	Growth Law	Total d/nm	Dektak/nm	Insertion Loss/dB
100 deg C 	1.5 1.94	d = at d = at + bt^2	638	622 +/-10	15.4
200 degC 	1.94	d = at + bt^2	804	787 +/-nm	4.9
300 degC 	1.93 to 1.51 1.942	d = at d = at + bt^2	940	913 +/-10	19.25

Summary of the model results: 200degC produces a uniform layer with an n value close to the ideal for ZnO. The thicknesses agree closely with the stylus measurements, and the ultrasound power insertion losses are minimised.

Conclusions

Ellipsometry is a powerful and versatile technique for characterising the layer structure of solar cells.

Analysis can be done offline on simple and complex structures.

In-situ analysis in real time during film growth adds another dimension of knowledge that can expedite and greatly shorten development time.