Optical Characterization of Organic Semiconductors by Spectroscopic Ellipsometry

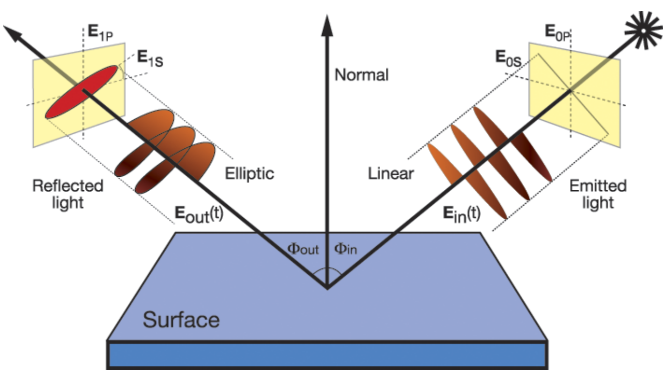
Spectroscopic Ellipsometry Solution

Spectroscopic Ellipsometers are optical thin film measurement tools for determining film thickness and optical constants (n,k) of thin film structures.
They are widely used in the microelectronics, display, photonics, photovoltaics, lighting, optical and functional coatings, biotechnology industries.

Advantages of Ellipsometry

- Non destructive technique
- No sample preparation
- Rapid measurement and simple to operate
- No reference measurement needed
- Very sensitive for ultra-thin film measurement down to 1Å
- Single and multi layer thin film measurement
- Information rich for layer stack description (interface, roughness, film gradient, film anisotropy etc…)
- Direct and accurate determination of optical constants (n,k)

When compared with other optical metrology instruments the unique strengths of spectroscopic ellipsometers are based on their highly precise and simple experimental measurements plus physical and material information derived from optical constants characterization.



$$\rho = \tan(\Psi) e^{i\Delta} = \frac{\tilde{E}_p^{out} / \tilde{E}_p^{in}}{\tilde{E}_s^{out} / \tilde{E}_s^{in}} = \frac{|\tilde{r}_p|}{|\tilde{r}_s|} e^{i(\delta_p - \delta_s)}$$

Measured data: Ψ and Δ

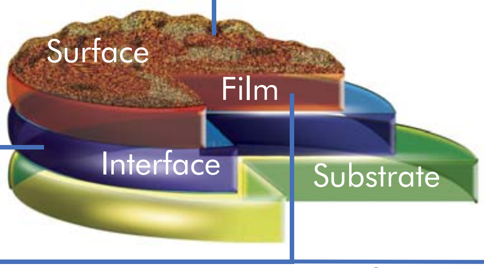
Thin Film Measurement Capabilities

Interfacial Behaviour

- Interface thickness
- Composition of mixed materials forming interface
- Monitor interface thickness in real-time: film growth, adsorption
- Monitor real-time changes at interfaces

Surface Measurement

- Roughness thickness
- Native oxide thickness
- Any surface film thickness
- Depolarization coefficient



Thickness Measurement

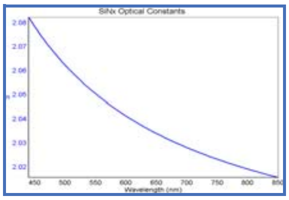
- From a few Å to ~30 μm
- Single and multi layers

Optical Properties

- Optical constants (n,k) and α
- Optical bandgap Eg
- Transmittance, Reflectance

Material Properties

- Gradient, anisotropy, composition, crystallinity, microstructure information provided by the optical constants characterization
- Film porosity

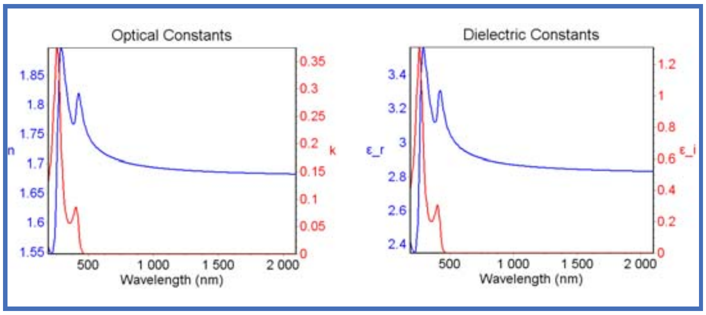


Thin Films & Materials Range

- Substrate materials: Silicon, GaAs, glass, sapphire, plastic, metals…
- Film materials
  - Dielectrics: Al_2O_3, SiO_2, TiO_2,…
  - Semiconductors: Silicon, SiGe, compound alloys
  - Thin metal films: Ag, Al, Cr, Cu
  - Transparent conductors: ITO, ZnO, SnO_2
  - Polymers, organic materials

At the Heart of Optical Constants Capabilities

Spectroscopic Ellipsometers are the tool of choice for measuring optical constants (n,k) (also called complex dielectric constants) of materials.
The precision of optical constants are in the range of 10^{-3}.

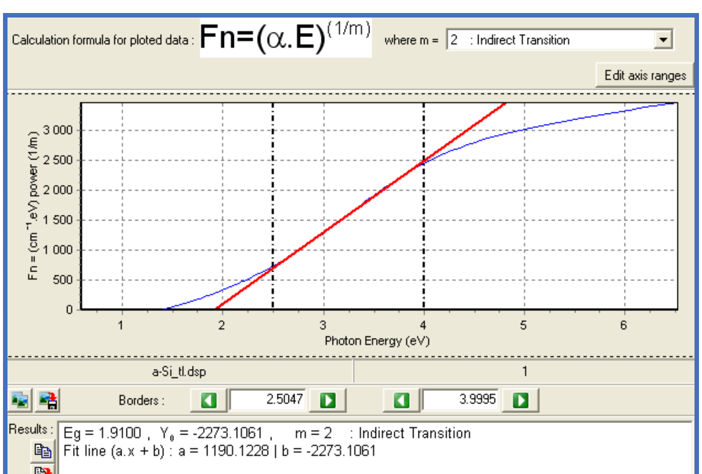


Through measurement of optical constants, SE can provide detailed knowledge of :

• Electronic properties of material such as band gap Eg

Three methods are implemented in the software to calculate the optical bandgap value, including:

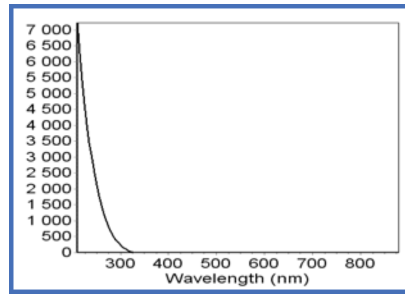
- Tauc model based on the relation: $\alpha h\nu = A(h\nu - E_g)^n$ where $h\nu$ is the photon energy, α the absorption coefficient, Eg the band gap and A is a constant.
The extrapolation of straight line to $(\alpha h\nu)^n = 0$ axis gives the value of the band gap. For a direct transition, n=0.5, and an indirect one n=2.
- E_{04} value defined as the energy for which $\alpha = 10^4$ cm^{-1}.
- A directly calculated Eg parameter from a dispersion formula (Tauc Lorentz, Adachi-New Forouhi, Afromovitz, New amorphous, Tanguy)



• Absorption coefficient α

The absorption coefficient (α) is simply given by the relation:

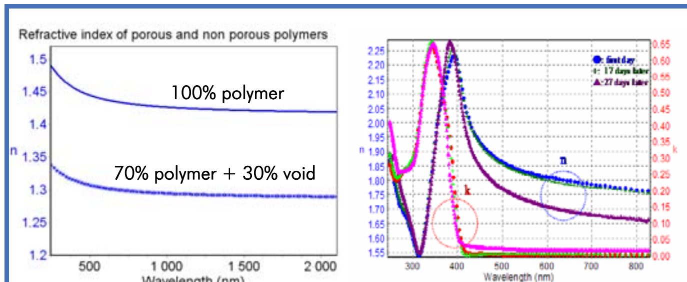
$$\alpha = \frac{4\pi k}{\lambda} \quad \text{in } cm^{-1}$$



It provides an **insight into material properties** such as:

- Composition,
- Degree of ordering or crystallinity,
- Hydrogen content,
- Conductivity,
- Porosity,
- Aging,

And any other variables that affect the optical constants of materials.

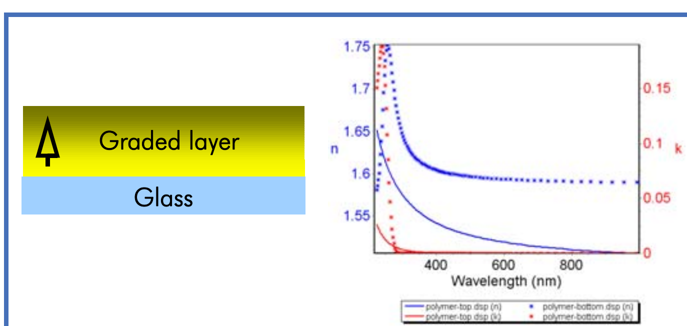


Refractive index decreases with porous films

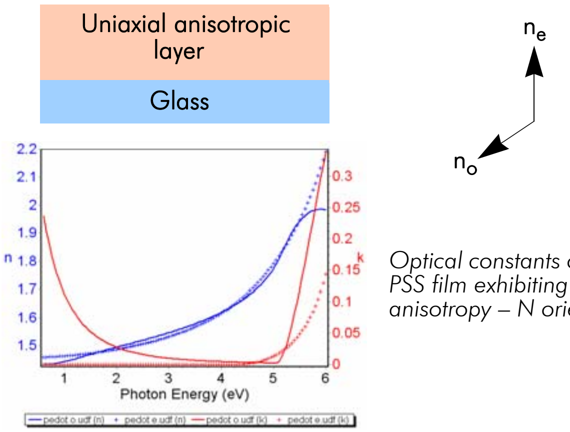
Optical constants change due to effect of aging on a-NPD layers

• Optical gradient and anisotropy of materials

A **graded film** exhibits a change to its optical constants through the layer. It specifies one value of (n,k) at the bottom and another one for the layer top.

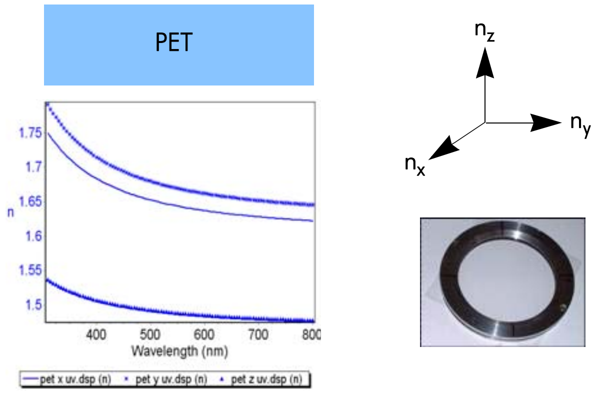


A **uniaxial anisotropic** film exhibits two different sets of optical constants, commonly called n_e (for extraordinary ray) and n_o (for ordinary ray).



Optical constants of PEDOT-PSS film exhibiting uniaxial anisotropy – N oriented

For **biaxially anisotropic films** 3 different sets of optical constants are measured, n_x, n_y, n_z and k_x, k_y, k_z.



Large Range of Spectroscopic Ellipsometers

HORIBA Jobin Yvon spectroscopic ellipsometers are available for research and manufacturing metrology covering spectral ranges from vacuum UV to near-IR. Models include:

- Table-top for R&D and QC with UVISEL and Auto SE

UVISEL

Auto SE

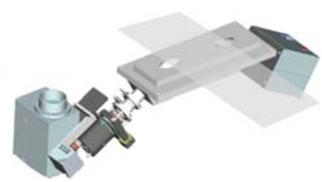
Fully automatic for fabs with FF-1000* and UT-300*

FF-1000

UT-300

**FF-1000 and UT-300 integrates UVISEL or Auto SE ellipsometers*

- In situ for thin film process monitoring and In line for roll to roll processing with adapted configurations of UVISEL or Auto SE



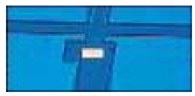
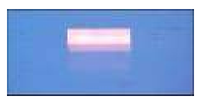
Main Features

	UVISEL	Auto SE
Technology	Phase modulation	Liquid crystal modulation
Spectral range	142-2100 nm*	440-850 nm
Detection system	Monochromator with PMT + InGaAs detectors Multiwavelengths with PMT detectors	CCD
Microspot optics At 70°	Down to 60x180µm	Down to 25x60µm
Vision	External CCD camera	Integrated

**5 models with different spectral ranges are available*

Unique Integrated Vision System

The Auto SE ellipsometer integrates the unique MyAutoView vision system. It allows the user to view the measurement spot on the sample and to choose the optimum position and spot size accordingly.

Sample Type	Advantages of MyAutoView	Examples
Patterned sample	Direct visualization of the measurement spot on the pattern area	
Sample with inhomogeneous surface (stripe, strain)	Optimization of the position of the measurement spot	
Transparent substrate: glass & plastic	Visualization and selection of front reflection	

Innovative Technologies for High Performance Ellipsometers

HORIBA Jobin Yvon spectroscopic ellipsometers integrate innovative modulation technologies, including phase modulation and liquid crystal modulation.
Both designs have no moving parts and in combination with advanced optical design and detection systems, HORIBA Jobin Yvon ellipsometers provide highly accurate and sensitive measurements for any types of samples under any conditions.

Versatile Optical Measurement Capabilities

HORIBA Jobin Yvon ellipsometers provide a large range of optical measurement capabilities.

Optical measurement	For what ?
Ellipsometric data	Film thickness, optical constants, and many other parameters for layer stacks
Kinetic ellipsometric data	To control the growth process of thin films – in terms of film thickness, optical constants, composition, …
Mueller matrix (polarimetric data)	Complete description of anisotropic films or substrates
Polarized/unpolarized reflectance/transmittance	Additional optical information measured by ellipsometer, that can also be used in addition to ellipsometric data for better accuracy
Scatterometry	Optical dimension of structure (patterned periodic sample)

Ellipsometry Power for Organic Semiconductor Applications

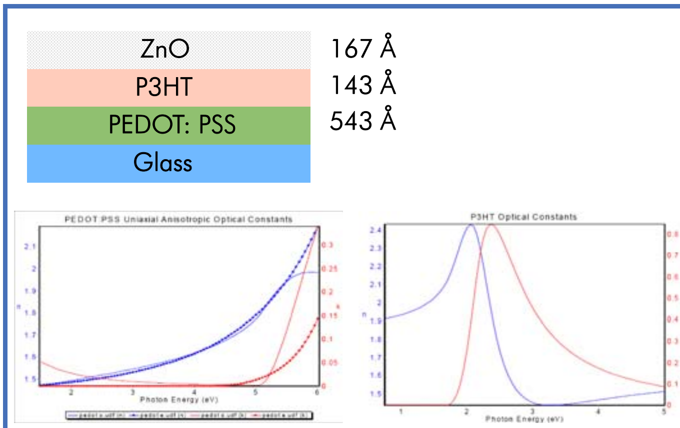
HORIBA Jobin Yvon Expertise

Materials	(n,k) @ 633 nm*
P3HT	n=2.374 – k=0.171
PEDOT:PSS	n_o =1.492 – k_o=0.029 n_e=1.484 – k_e=0
PPV	n_o =1.81 – k_o=0.011 n_e=1.55 – k_e=0
Alq_3	1.715<n<1.791 – k=0
NPD	1.763<n<1.822 – k=0
CuPC	n=1.855 – k=0.47
ZnPc	n=1.626 – k=0.01
PMMA	n=1.485 – k=0
Pentacene	n=1.447 – k=0.381
α4T	n_o =1.602 – k_o=0 n_e=1.548 – k_e=0
Photoresist	1.592<n<1.665 – k=0
PC	1.530<n<1.595 – k=0
PP	n=1.491 – k=0
PET	n_x=1.634 – n_y=1.658 – n_z=1.483
PEN	n_x=1.881 – n_y=1.729 – n_z=1.677
TAC	n=1.462 – k=0
PTFE	n=1.308 – k=0

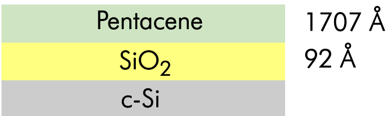
*depending on manufacturing process and conditions

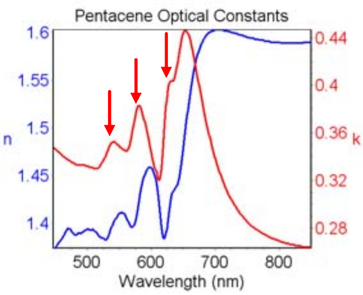
Organic Semiconductor Applications

- Organic Photovoltaic Device



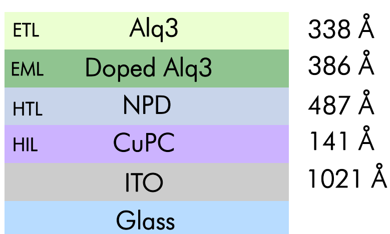
- Organic Thin Film Transistor

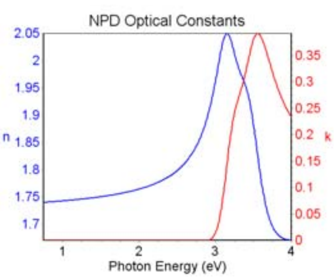


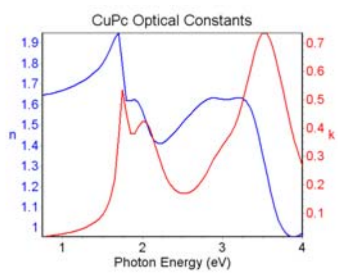


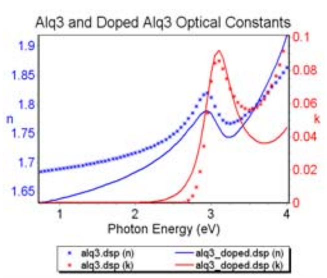
Note the accurate characterization of optical constants of pentacene exhibiting 4 absorption peaks at 654, 630, 580 and 540 nm.

- Small Molecule OLED Device





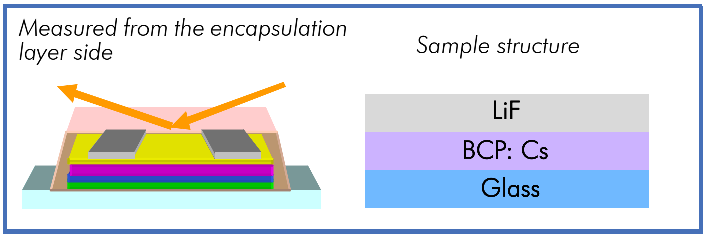




- Encapsulated OLED Devices

Usually, organic materials are encapsulated to avoid environmental aging due to oxygen and water absorption. Ellipsometric analysis can be performed on such samples. The two examples below show accurate characterization of OLED device encapsulated either by a thin dielectric layer or a glass cap.

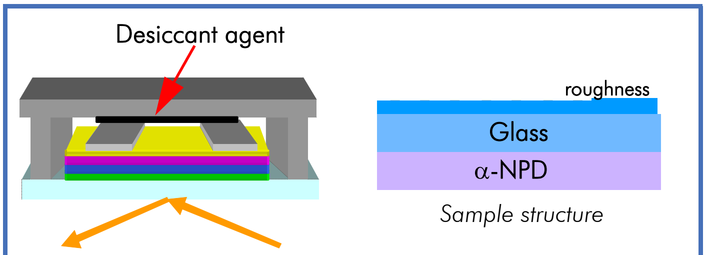
Encapsulation by dielectric layer



	Thickness (nm)	n@633nm
BCP:Cs	63.6	1.661
LiF	74.4	1.327
Total thickness by ellipsometry	138	

Excellent correlation was obtained with a stylus profilometer where a total thickness of 135 nm was measured.

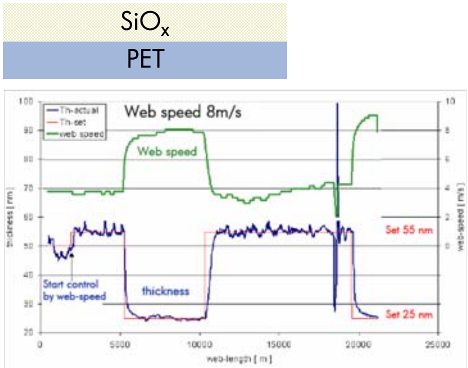
Encapsulation by glass cap



Impossible to measure from the layer side due to the desiccant which fully absorbs ellipsometric incoming light ⇒ Measured from the glass side

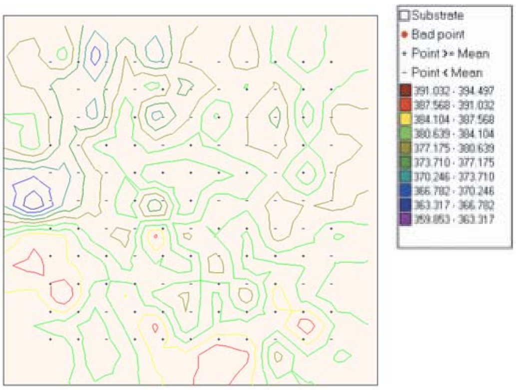
	Thickness (nm)	n@633nm
α-NPD	54.1	1.793

- Roll to Roll Thin Film Process



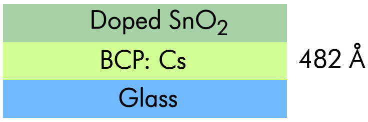
In line thickness control of SiO_x barrier layer on PET film

Electrical Conductivity* Mapping

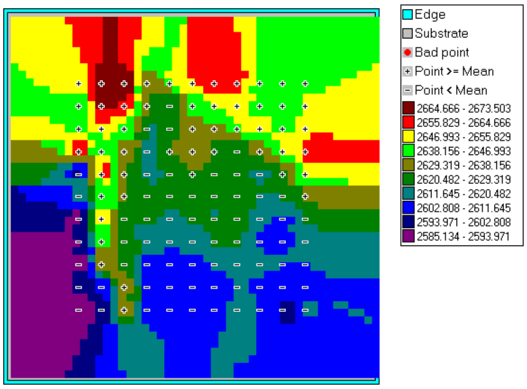


*Derived from Drude dispersion fitting

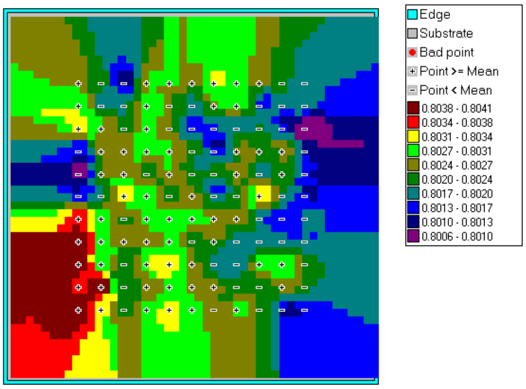
- Transparent Conducting Oxides



Thickness Mapping of layer 2



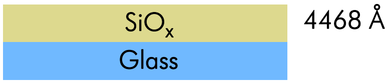
Optical Transmission Mapping*

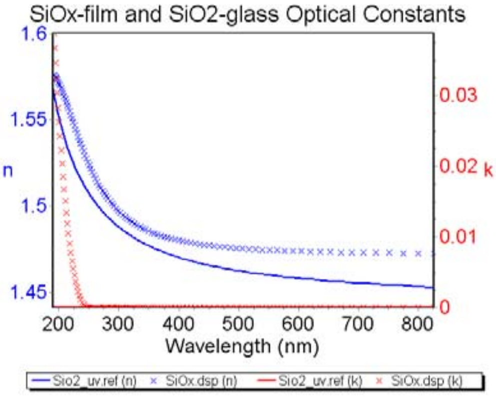


*T at 633 nm

- Films with Low Index Contrast

Phase Modulated Spectroscopic Ellipsometry makes possible the characterization of films with low index contrast such as a SiO_x layer deposited on glass substrate. Thickness and optical constants of the layer were determined.





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