ENEA
Optical Coatings Group

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Thin Film Deposition and Characterization at Optical Coatings Lab, Reseach Center ENEA Casaccia

HeRe, ENEA Frascati, December 2-3, 2013

Casaccia Research Centre

ENEA
AGENZIA NAZIONALE PER LE NUOVE TECNOLOGIE, L'ENERGIA E LO SVILUPPO ECONOMICO SOSTENIBILE

ENEA

CASACCIA RESEARCH CENTRE

ITALIAN NATIONAL AGENCY FOR NEW TECHNOLOGIES, ENERGY AND SUSTAINABLE ECONOMIC DEVELOPMENT

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HISTORY

Construction of the Casaccia Research Centre began in 1959. It became the heart of applied nuclear research in Italy, the place where Italian technicians received European-level training. Other ENEA Centres were created in the following years, including those at Frascati, Saluggia and Trisaia.

Cattle shed at the "Casaccia" farm when it was converted (April 23, 1959).

Optical Coatings Laboratory (2010)

Optical Coatings Group (ENEA Casaccia) *Experience*

ENEA AGENZIA NAZIONALE PER LE NUOVE TECNOLOGIE, L'ENERGIA E LO SVILUPPO ECONOMICO SOSTENIBILE

Research and Development in the field of thin-film materials and optical coatings

- History

1980	Optical Coatings for Lasers (UV - NIR - IR) Other applications (architectural glasses, etc.) Thin Film Characterization Methods
1984	Optical Coating Design (in house software) Film Deposition Techniques (Optimization of PVD methods)
1982	National Network on Thin Films
1993-1996	High-quality Optical Thin Films (12 international partners)
1997-2002	UV coatings (7 partners / 5 countries)
2001-2005	European Free Electron Laser (7 partners / 4 countries)
2002-2010	Instrumentation for Environment protection and Art conservation Optical filters for Space (European Space Agency)

Optical Coatings Group:
Recent Research Projects

- ***Optical Filters for Space:***

2009-2011 Large-area Narrow-band Filters for Lightning Imager (ESA-ESTEC)

- ***Solar Cells:***

2010-2012 Si-based Solar Cells on Low-Cost Substrate (FP7)

- ***Plasmonics:***

2010-2012 Ultrathin metal oxides on conductors for miniaturisation of technological instruments (bilateral Italian-Chinese)

2013-2015 Plasmonics for Light Filtering (MAE Grande Rilevanza)

- ***Antarctica:***

2010-2014 Radiometric monitoring of harm UV level at South Pole (National Italian Antarctica Program)

Optical Coatings Group
Facilities

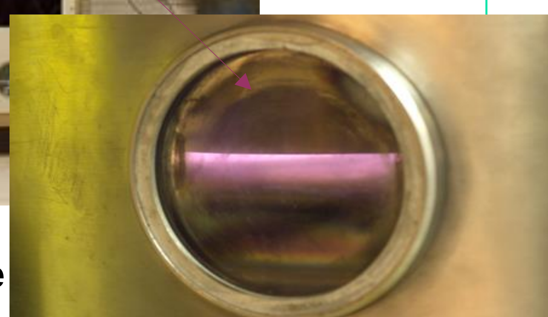
- ***Deposition systems*:**
  - radiofrequency sputtering
  - dual ion beam sputtering
  - e-beam evaporation (ion assistance)
  - thermal evaporation

Optical Coatings Group (ENEA Casaccia)
Facilities

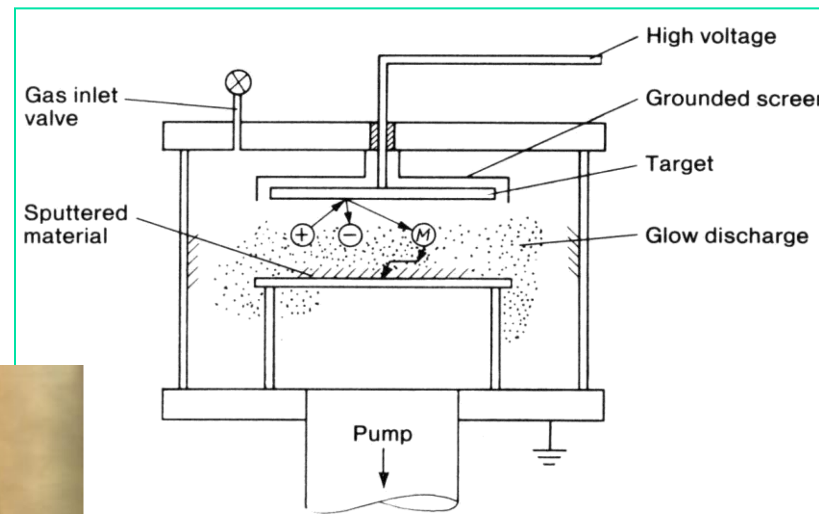
***Deposition systems**: radiofrequency sputtering*

- Three radiofrequency sputtering systems with 3 targets (target diameter 6.5 or 8 inches)
- One radiofrequency sputtering system with 2 targets (target diameter 6 inches)

With and without magnetron



Glow discharge



Typical working pressure ~10^{-3} mbar

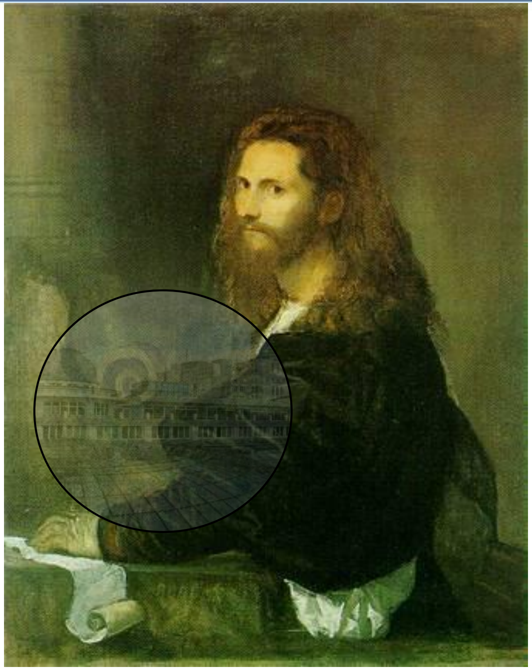
Deposition Facilities

Sputtering: comparison with other methods

- Materials with very high melting points are easily sputtered, both conducting (DC, RF and IBS) and insulating (RF and IBS)
- Sputtered films typically have a better adhesion on the substrate than evaporated films
- Sputtering sources contain no hot parts (to avoid heating they are water-cooled) hence are compatible with reactive gases and enables deposition on plastic substrates
- Advanced processes such as epitaxial growth are possible
- Possibility to cover uniformly large areas (depends on chamber geometry)
- DC and RF: conventional industrial techniques -> straightforward scalability

- Lower deposition rate compared to evaporation
- Film composition is close to that of the source material although not exact: light elements are deflected more easily by the working gas. However, this can be compensated by reactive gas insertion
- Inert sputtering gases are built into the growing film as impurities

Coated glass for artwork protection

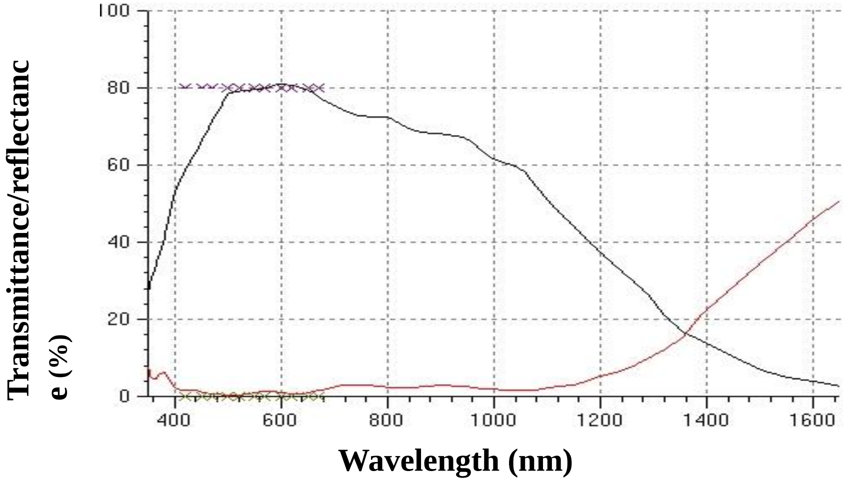


Objectives

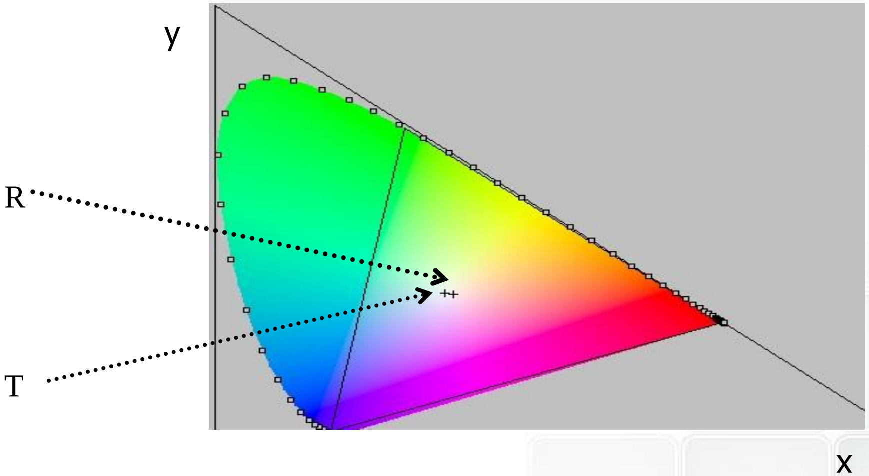
- Null transmission out of the visible (UV e NIR) to avoid radiation induced damage
- Low reflection in the visible (410-680 nm) and optimization of color rendering to improve the observer vision

Optical coating on glass

- antireflection coating in the visible
- materials with high absorption in the UV and infrared



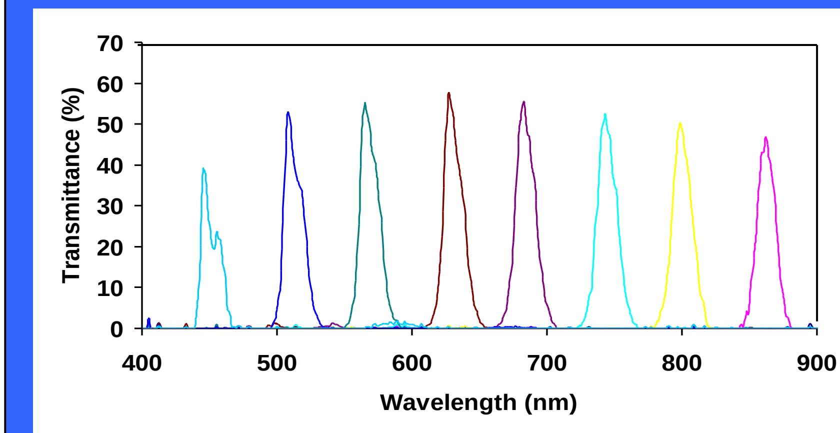
four-layer coating (ITO/SIO_2) on glass



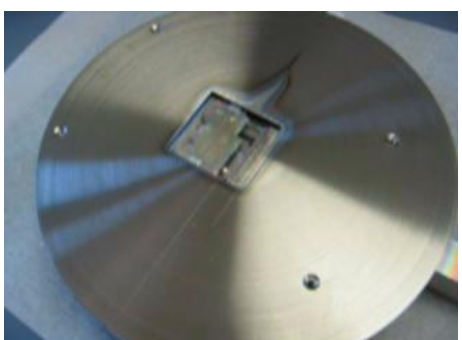
CIE color diagram (D65) for T and R

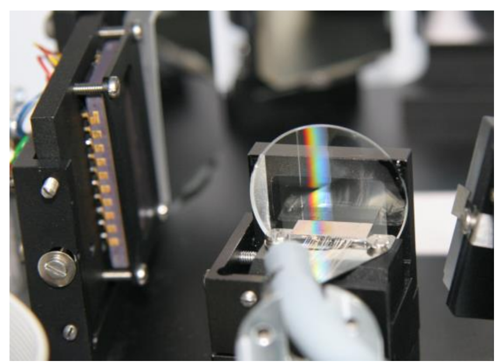
Optical Coatings Group (ENEA Casaccia)
Facilities

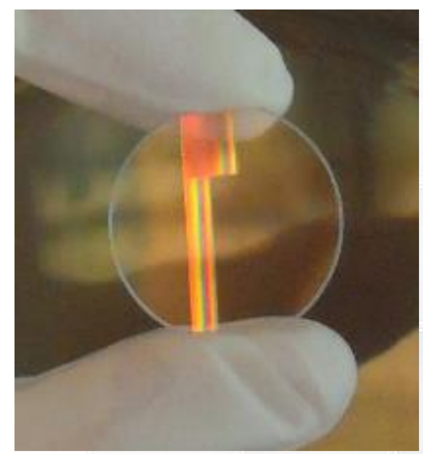
- ***Deposition systems**: radiofrequency sputtering*



Transmittance at different positions of an LVF

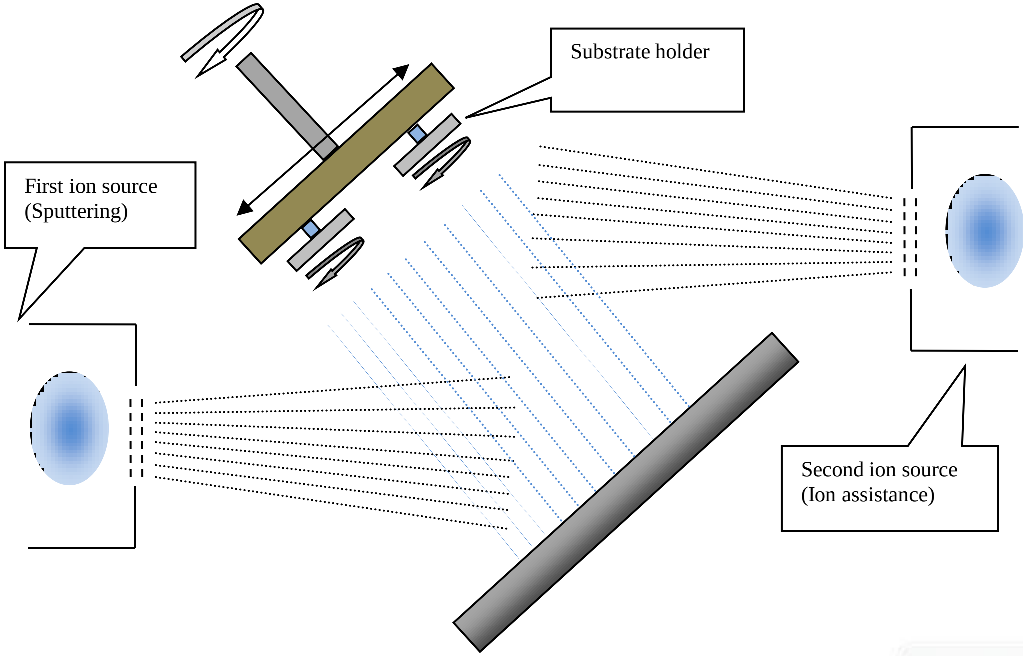






Optical Coatings Group (ENEA Casaccia)
Facilities

- **Deposition systems**: ***dual ion beam sputtering***



In the target is external to the ion source. Ion source can work without any magnetic field like in a hot filament ionization gauge.

In a Kaufman source ions are generated by collisions with electrons that are confined by a magnetic field as in a magnetron. They are then accelerated by the electric field emanating from a grid toward a target.

As the ions leave the source they are neutralized by electrons from a second external filament.

IBS Sputtering: advantages and disadvantages

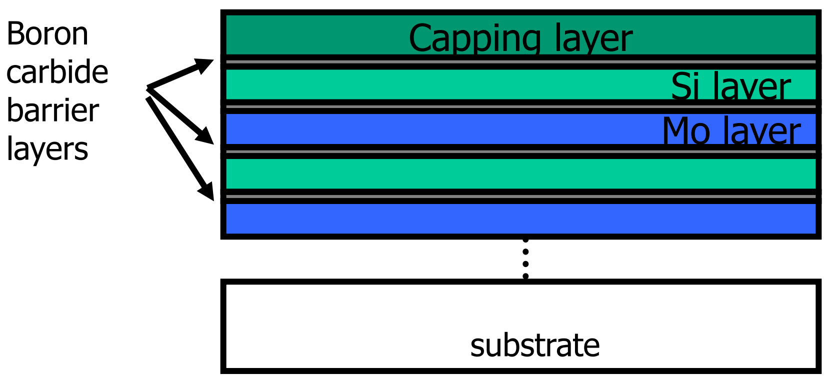
- The energy and flux of ions can be controlled independently
- Operates at lower pressure (typically ~10^{-4} mbar) -> clean process
- In ion-assisted deposition (DIBS), the substrate is exposed to a secondary ion beam operating at a lower power than the sputter gun -> even denser films (e.g. diamond-like carbon)

- Even lower deposition rate
- The principal drawback of IBS is the large amount of maintenance required to keep the ion source
- “Almost bulk films” often means very high mechanical stress -> delamination. Awareness of stress compensation.
- Large areas coating is more challenging

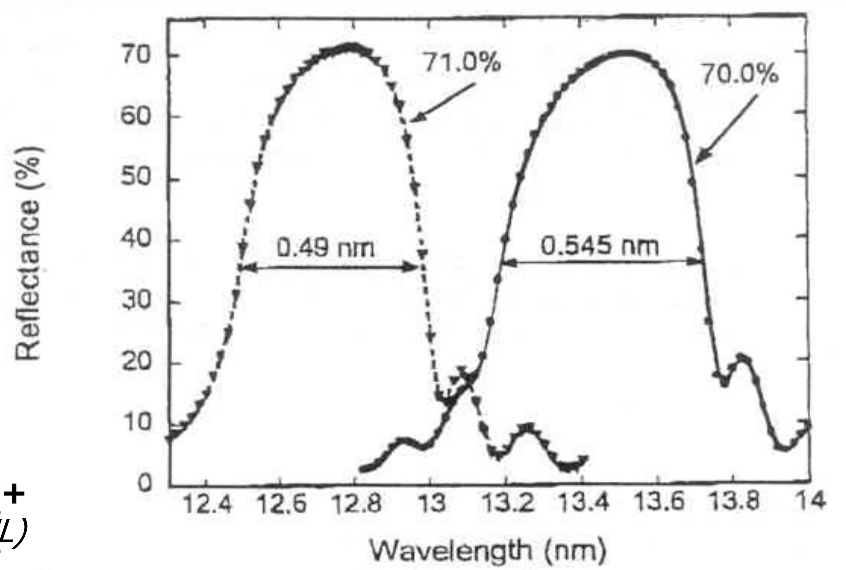
Mirrors for EUV lithography

- **Objective**:
Realization of two radiation sources with high brightness for EUV micro-lithography and preliminary tests on lithographic mask reproduction silicon wafer
- **Multilayer coatings**:
  - high reflectance (half-band width >2%) centered at 13-14 nm
  - reproducibility of the central wavelength should be better than 1%.

>100 layers

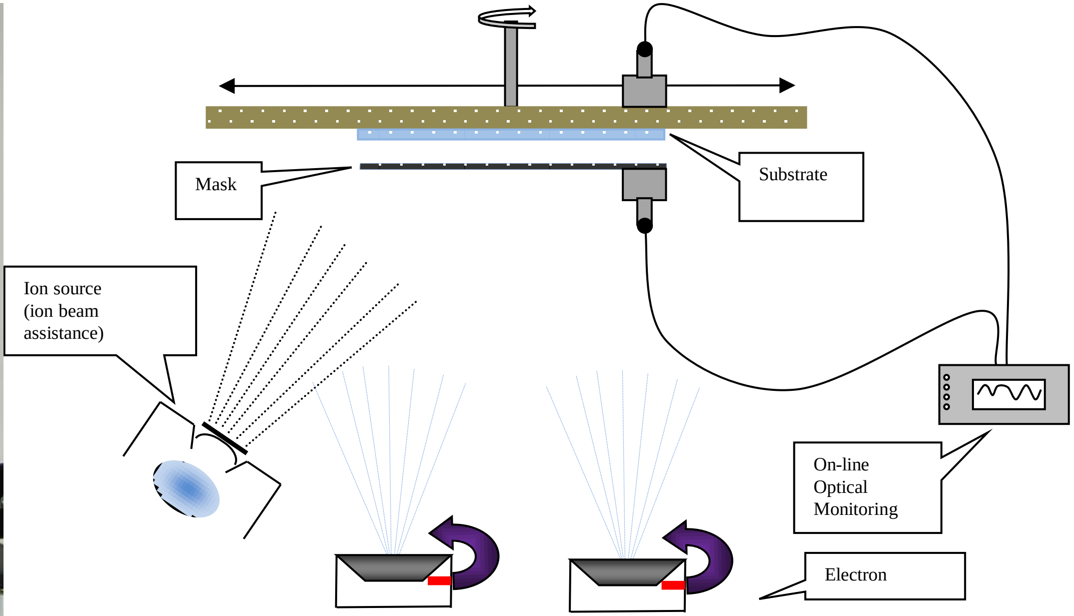


[Si(4.37nm)/B_4C(0.4nm)/Mo(2.25nm)/B_4C(0.25nm)]^{50}+ Si(4.2nm) from *Lawrence Livermore National Laboratory(LLNL)*



Optical Coatings Group (ENEA Casaccia)
Facilities

Deposition systems: *ion-assisted e-beam evaporator*

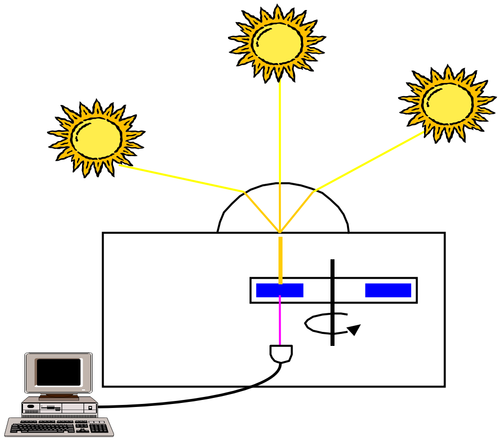


- **In ion-assisted deposition (IAD), the substrate is exposed to a secondary ion (Kr+ or Xe+). A Kaufman source, similar to that used in IBS, supplies the secondary beam.**
- **Operates at lower pressure (typically ~10^{-5} mbar) -> very clean process**
- **High deposition rate**
- **Film composition maybe adjusted by injection of reactive gases**
- **Low-density films (low-energy process if without IAD) -> low stress**

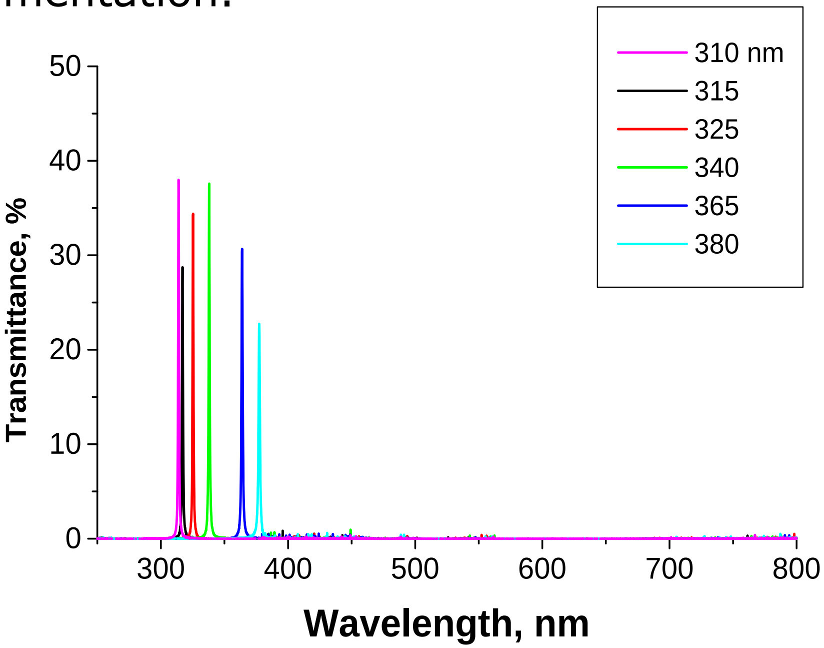
Narrow-band transmission filters (Antarctica)

▪**Objective**

Measurements of the increased flux density of solar radiation reaching the ground (ozone depletion), in the range 280 to 380 nm, to estimate the genetic damage to living organisms. Measurements need to be performed continuously at remote sites using standalone instrumentation.



Layout of the solar radiometer



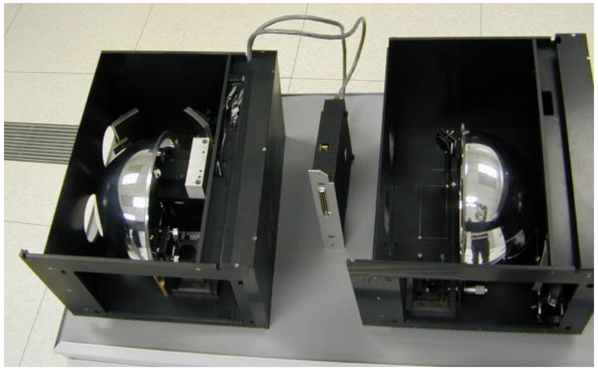
Instrument development

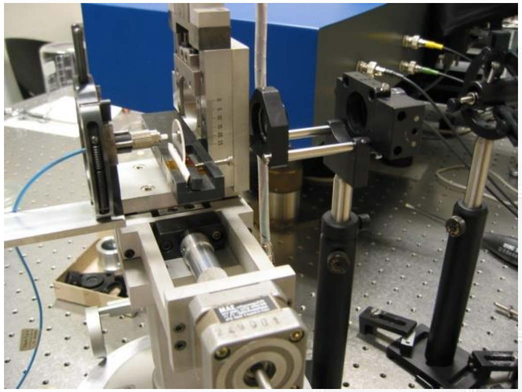
- optical entrance system, consisting of quartz elements, designed to condense the total sky radiation and the direct solar radiation into a well collimated parallel beam
- set of 12 interference filters with peak-wavelengths at 285, 287, 290.5, 292, 295, 298, 305, 310, 320, 340, 360, 380 nm (0.5÷0.8 nm FWHM)

Optical Coatings Group (ENEA Casaccia)
Facilities

Optical Measurement Tools

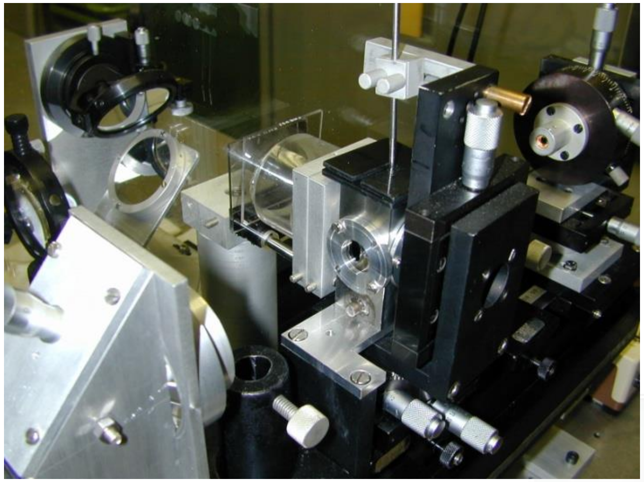
- UV-VIS-NIR PE Lambda-19/ Lambda-950 spectrophotometers
- FT-IR PE GX spectrophotometer (double-detector: down to 100 cm^{-1})
- Ellipsometers/polarimeters (250-1000 nm) + VASE (down to 2500 nm)
- Set-up for localized transmittance/reflectance measurements (UV-NIR, spatial resolution ~20μm)
- Coblentz spheres for low level scattered light spectral measurement





Optical Coatings Group (ENEA Casaccia)
Facilities

- ***More Instrumentation***
  - Laser deflection calorimeter (230-1000 nm)
  - Stylus profilometers
  - Set-up for transmittance/reflectance measurements at different temperatures (8K – 350K, UV-NIR)
  - WYCO Interferometer
  - HeNe, Argon, CO_2 laser sources
  - Mechanical tests



Optical Coatings Group:
Face Technological Challenges

•***Optical Filters for Space:***

-Large-area Narrow-band Filters for Lightning Imager (ESA-ESTEC)

• ***Solar Cells:***

- TCO film profiling using ellipsometry

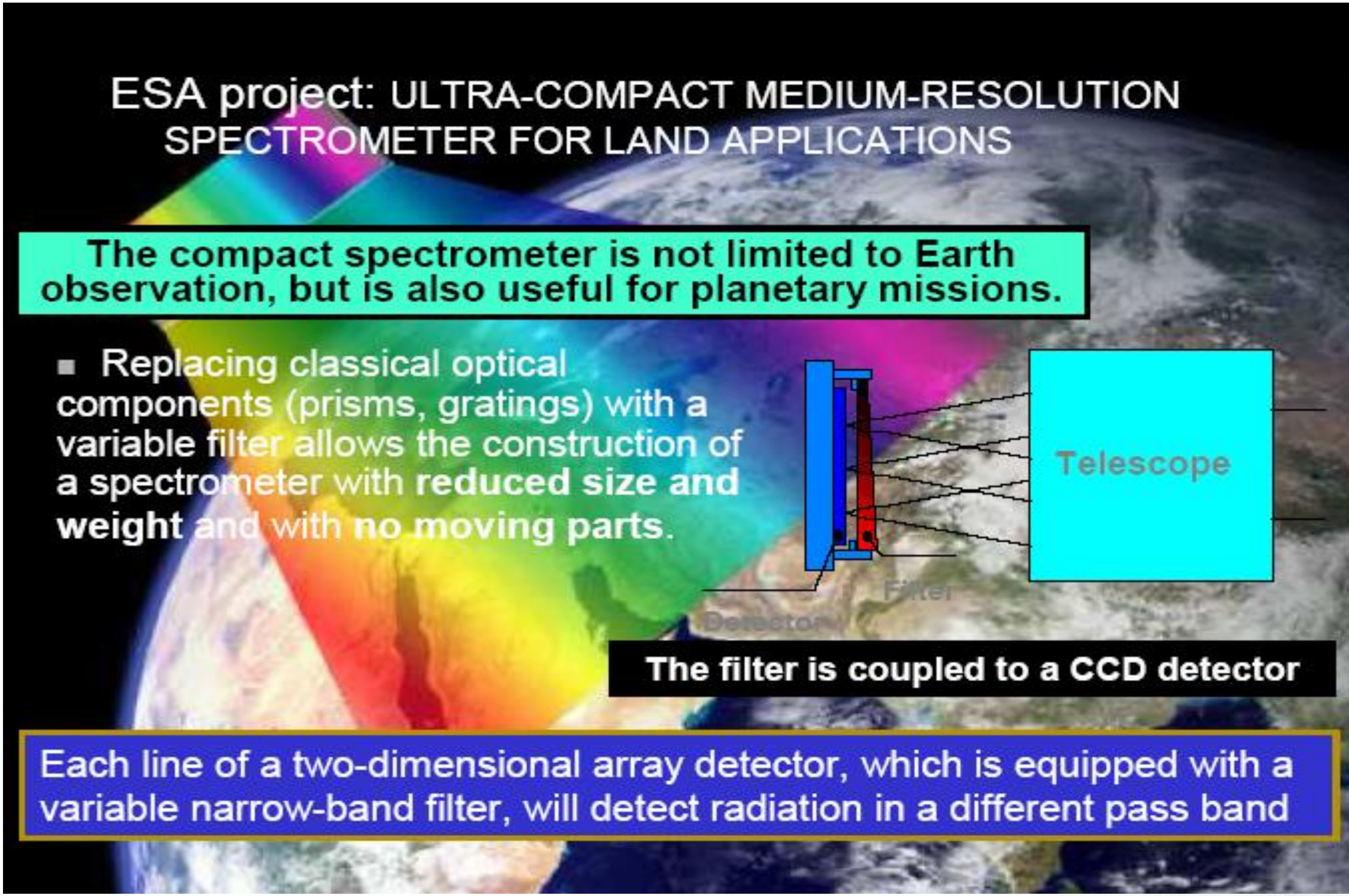
• ***Plasmonics:***

- ATR-enhanced ellipsometry for characterization of ultrathin metal oxides on conductors

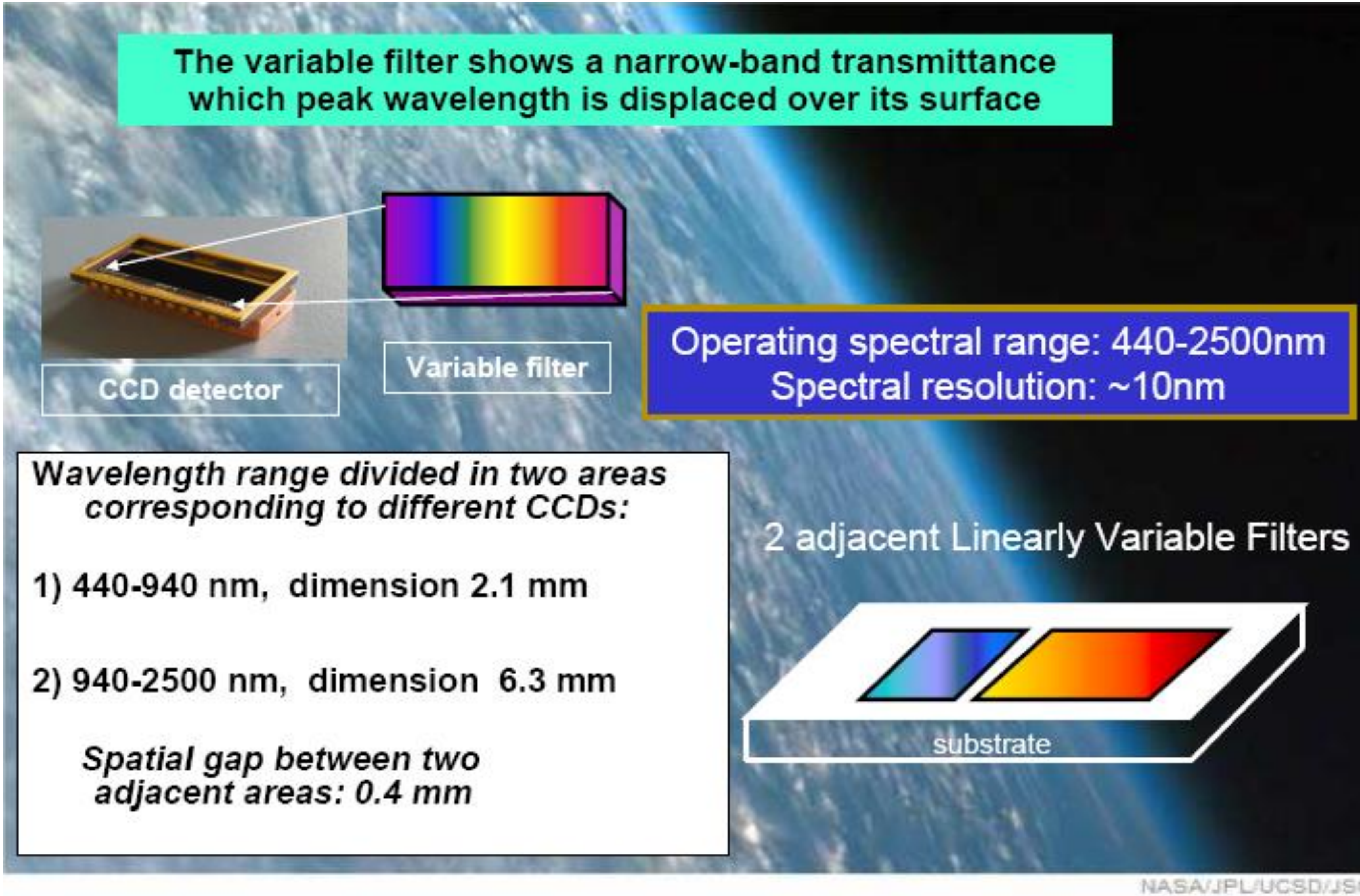
• ***Antarctica:***

- Radiometric monitoring of harm UV level at South Pole (National Italian Antarctica Program)

Mini-spectrometer for Earth imaging



Filter specifications (variable filters)

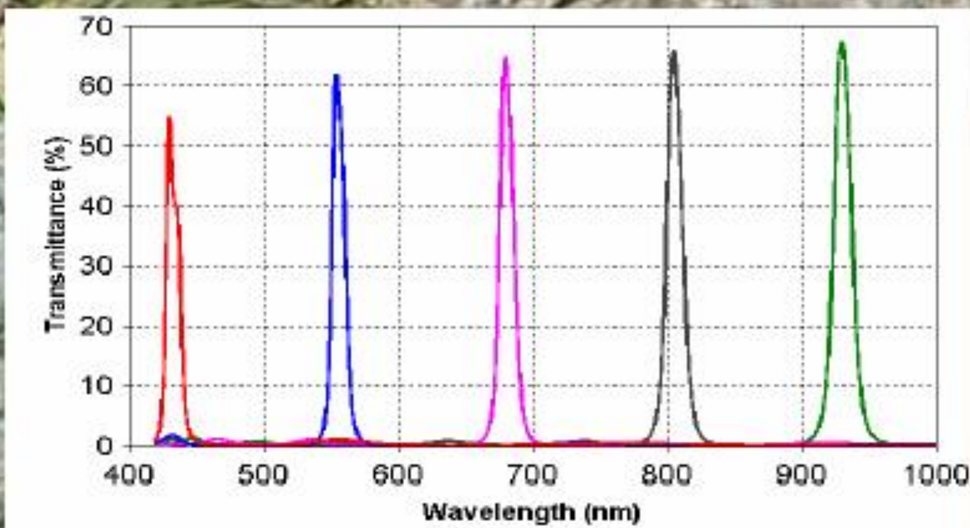


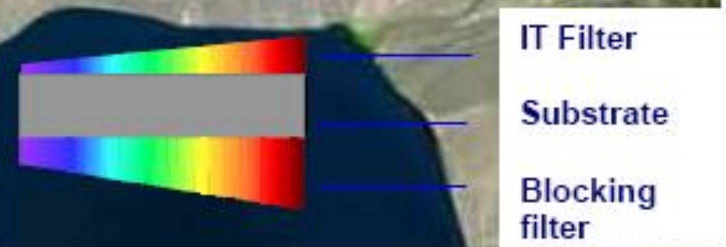
A.Piegari, J.Bulir, and A. Krasilnikova Sytchkova, “Variable narrow-band transmission filters for spectrometry from space. 2. Fabrication process”, Appl. Opt. 47 (2008), Issue 13, pp.C151-C156

Linearly Variable Filter design

- Induced Transmission filter: Ag - SiO_2 – Ta_2O_5, 21 layers
- Back-side blocking filter: SiO_2 – Ta_2O_5, 38 layers

Operating range 440-940 nm (first area)





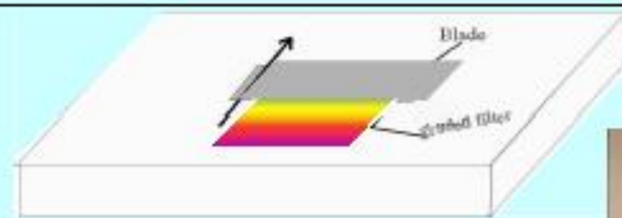
Bandwidth: 10-20 nm
Spectral gradient: 250nm/mm

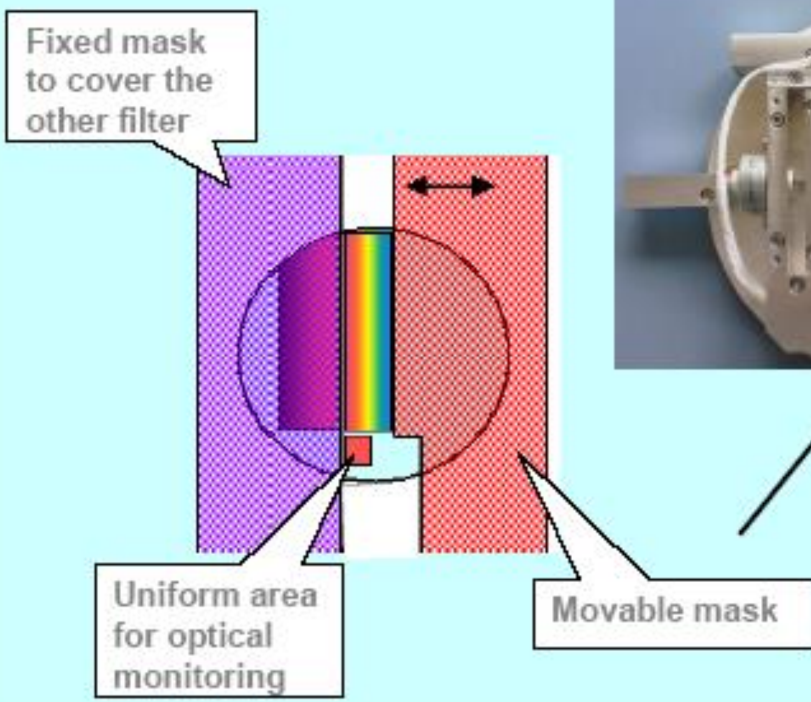
The transmittance curve is displaced over the filter surface, by a variation of the coating thickness with a linear gradient
(**IT filter in the VIS-NIR: min thickness ~ 1000nm, max 2500nm**)

NASA/GSFC/METI/ERSDAC/JAROS, and the U.S./Japan ASTER Science Team and Jesse Allen

Masking apparatus for graded coatings

- Masking blade moved during film deposition
- The coating profile controlled by mask speed





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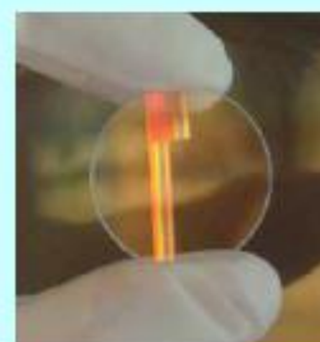
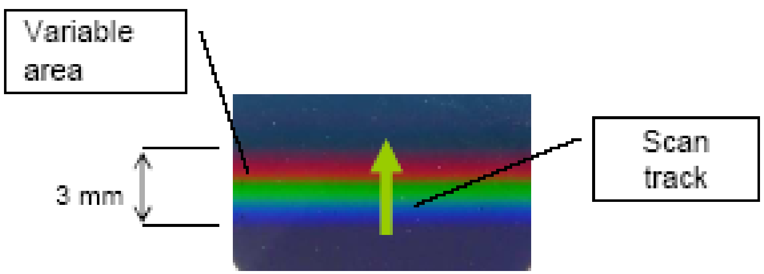
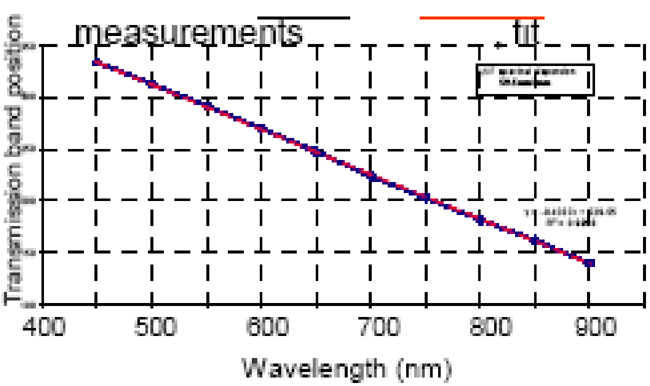


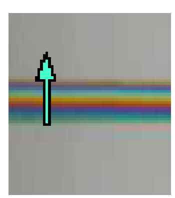
Localized Transmittance measurements

- Measurements are carried out by a dedicated set-up

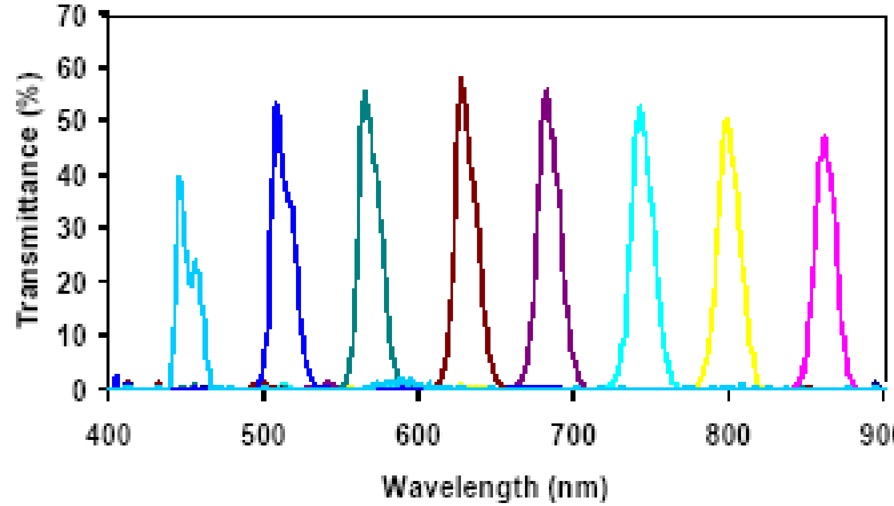
- Characterization range: 400 ÷ 1000nm
- 2-D translation micrometric system: min step 0.25 μm
- Spectral resolution: < 2 nm
- Spatial resolution: < 20 μm

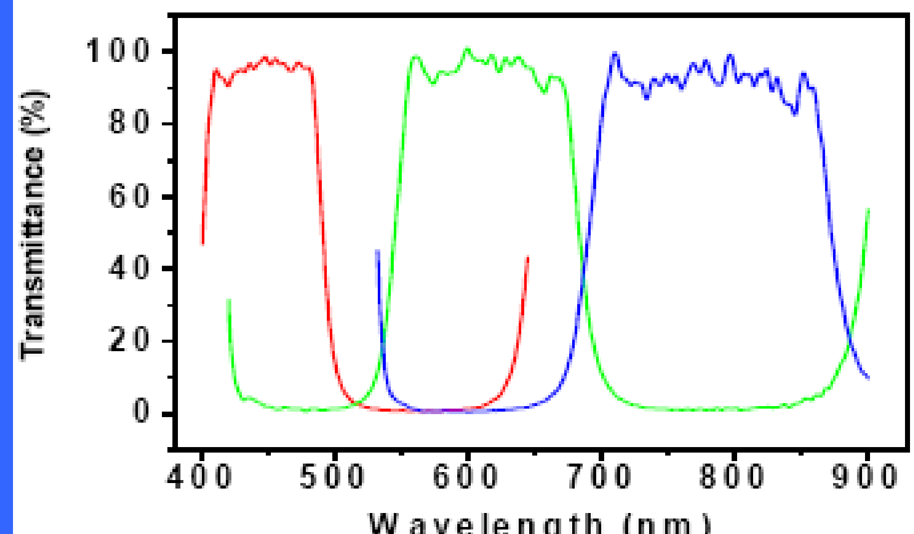






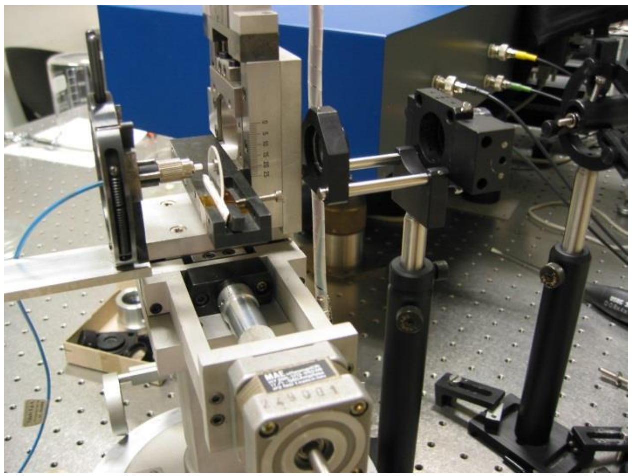
Blocking filter

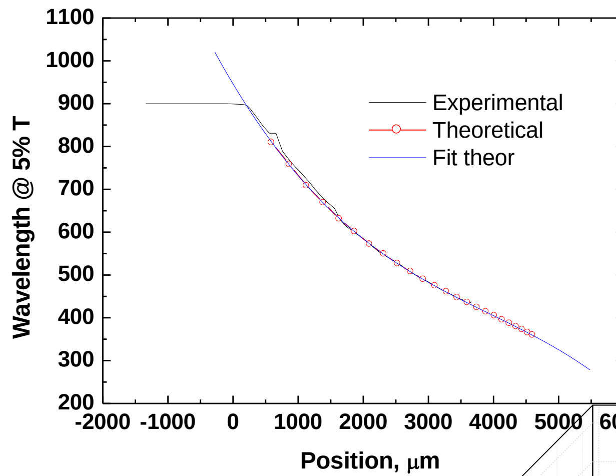


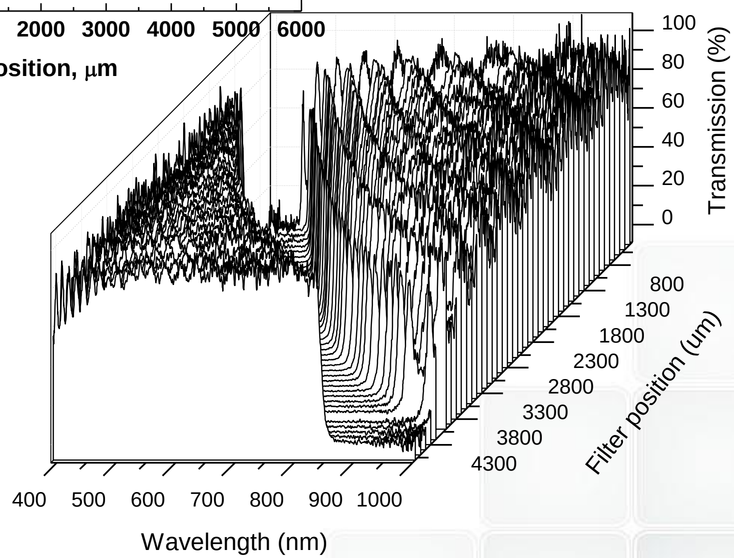


Measurement Examples

All-dielectric (59 layers) low band-pass filter with nonlinear spatial profile







Spectrometer: OO USB2000

Wavelength range: 400 – 1100 nm

Spectral resolution: 2.5 nm

Spatial resolution: 25 μm

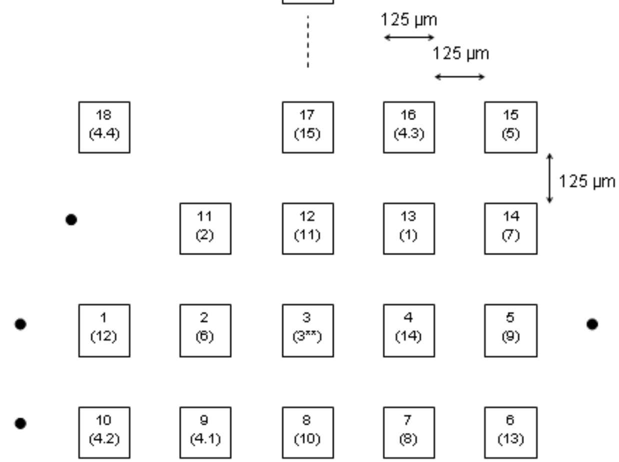
Spatial step: 50-100 μm

A.K. Sytchkova et al "Transmittance measurements on variable coatings with enhanced spatial resolution", *Chin Opt Lett* **8** (2010), pp.103-104.

Measurement Examples

Ion-damaged diamond

Measurement at each damaged point determined as having minimum transmission within vicinity (min translation step 25 μm)

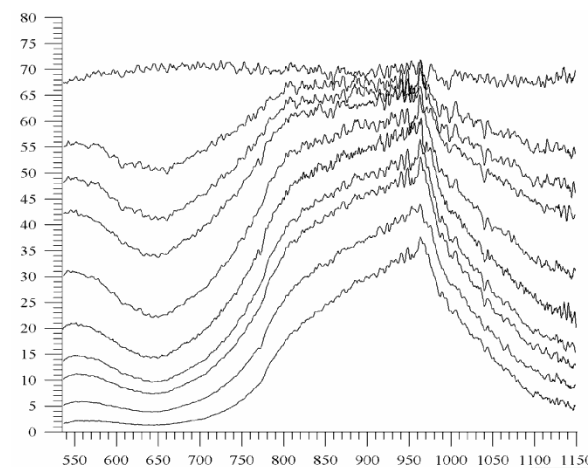


Spectrometer: OO SQ2000

Wavelength range: 200 – 1200 nm

Spectral resolution: 0.8 nm

Spatial resolution: 50 µm

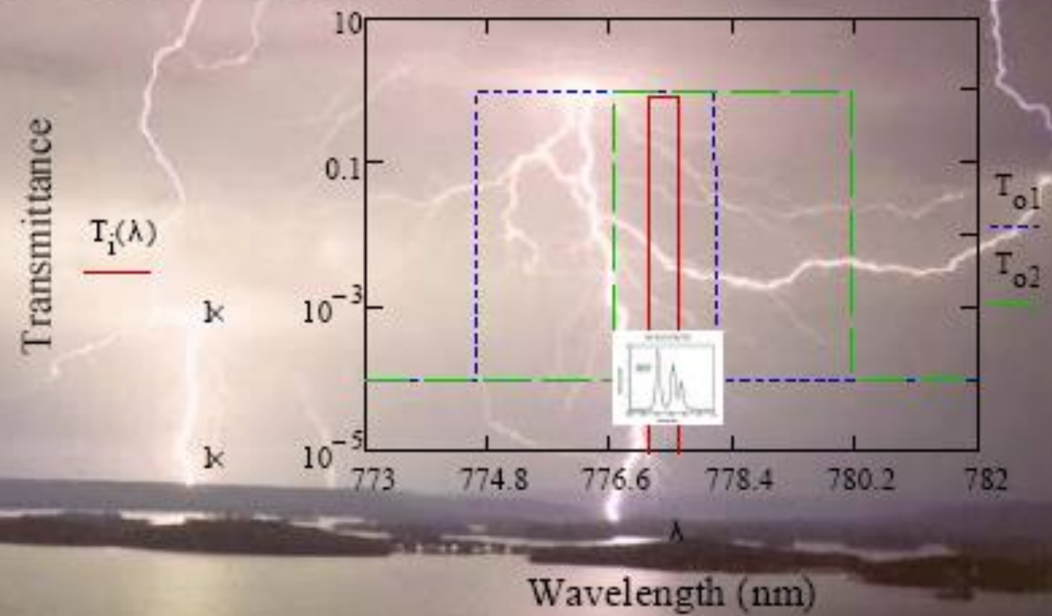


A. Battiato et al, “Spectroscopic measurement of the refractive index of ion-implanted diamond”, Opt Lett 37 (2012) pp. 671-673
S. Lagomarsino et al “Complex refractive index variation in proton-damaged diamond”, Opt Express 20 (2012), pp. 19382-19394

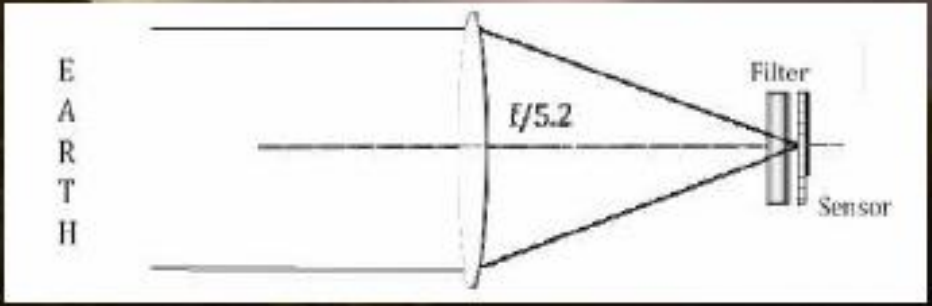
Filters for the Lightning Imager

ESA project: METEOSAT THIRD GENERATION

- Filter must discriminate light generated by lightning (from background)
- Detection of Oxygen I Triplet (strongest line) located between 777.15 and 777.6 nm
- Operating range 300-1500nm



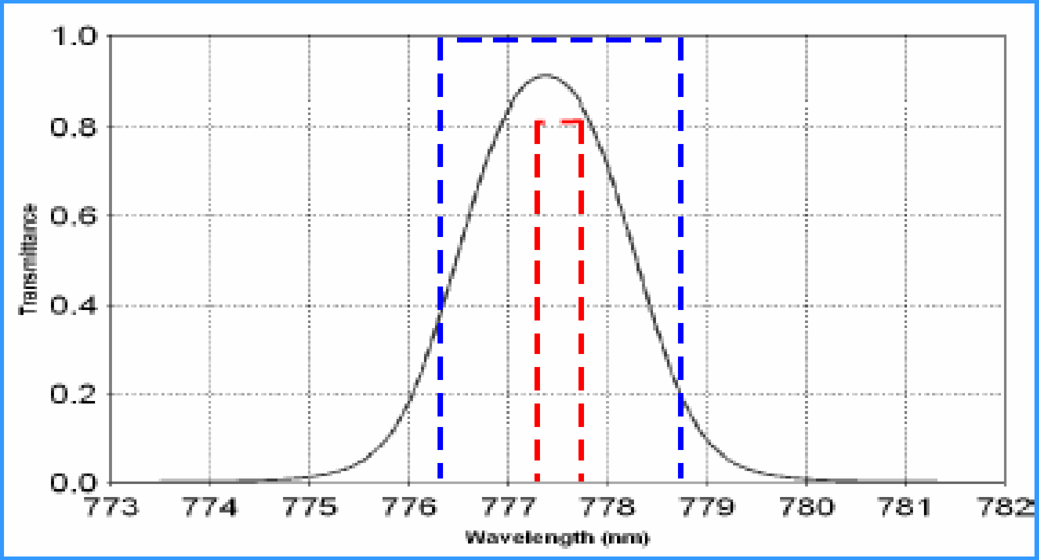
The wavelengths of interest must be transmitted for all incidence angles in a range of +/- 5.5° or in a cone angle of +/- 5.5°



Large-area narrow-band filter

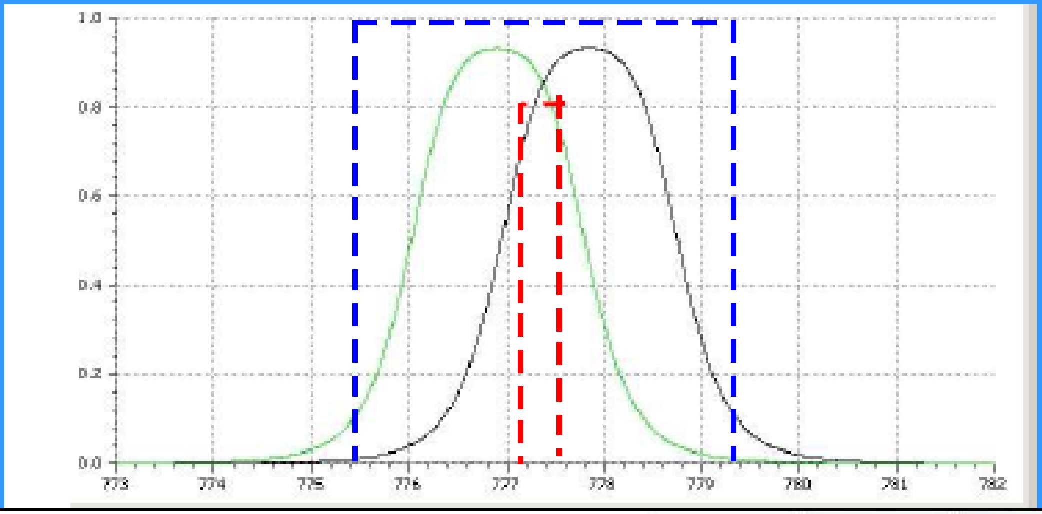
- Narrow band filter
  Fabry-Perot triple cavity
  58 layers (SiO_2 - TiO_2)

  transmission bandwidth
  2.5 nm



- Convergent beam
- Collimated beam

  $\pm$ 5.5°



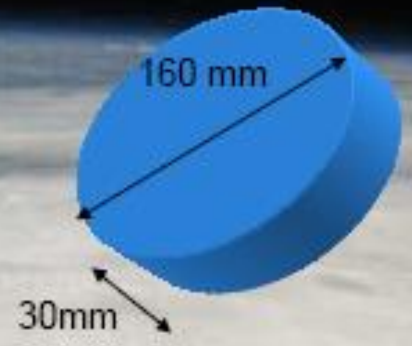
- A sun-blocking filter is needed for the required outband rejection ($<10^{-4}$)

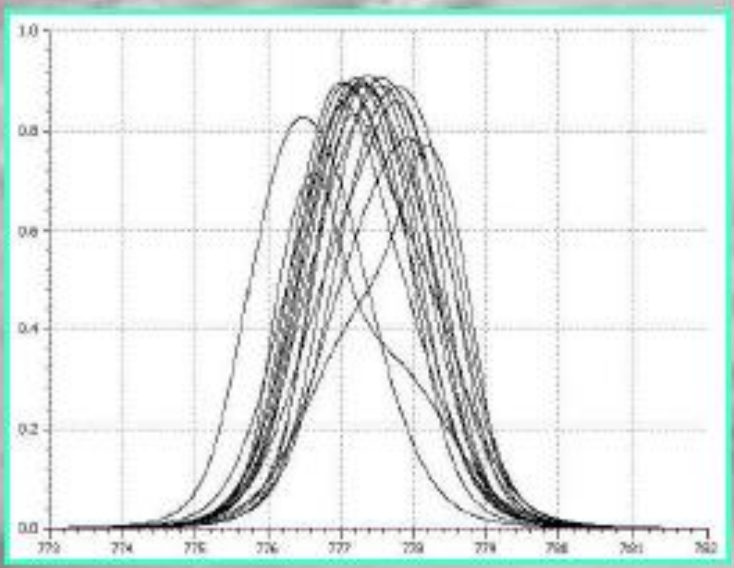
A. Piegari et al "Optical transmission filters for observation of lightning phenomena in the Earth atmosphere", *Appl.Opt.* **50** (2011), pp.C100-C105

Manufacturing challenges

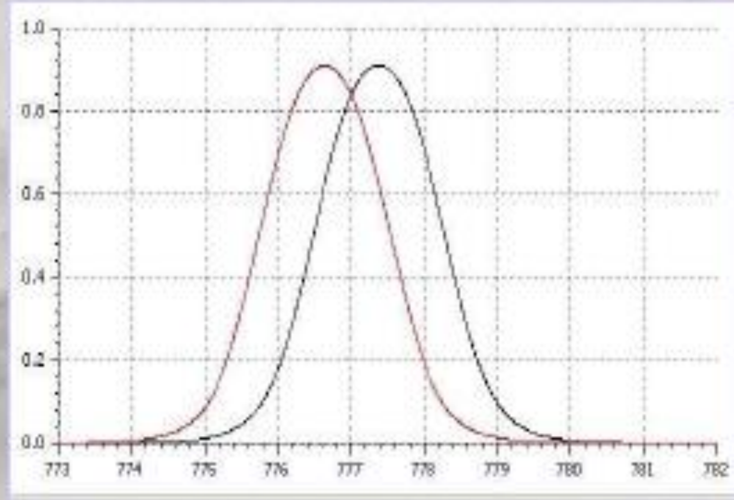
Uniformity and reproducibility

- Filter diameter 100 -160mm
- Manufacturing errors < 0.1% on layer thickness





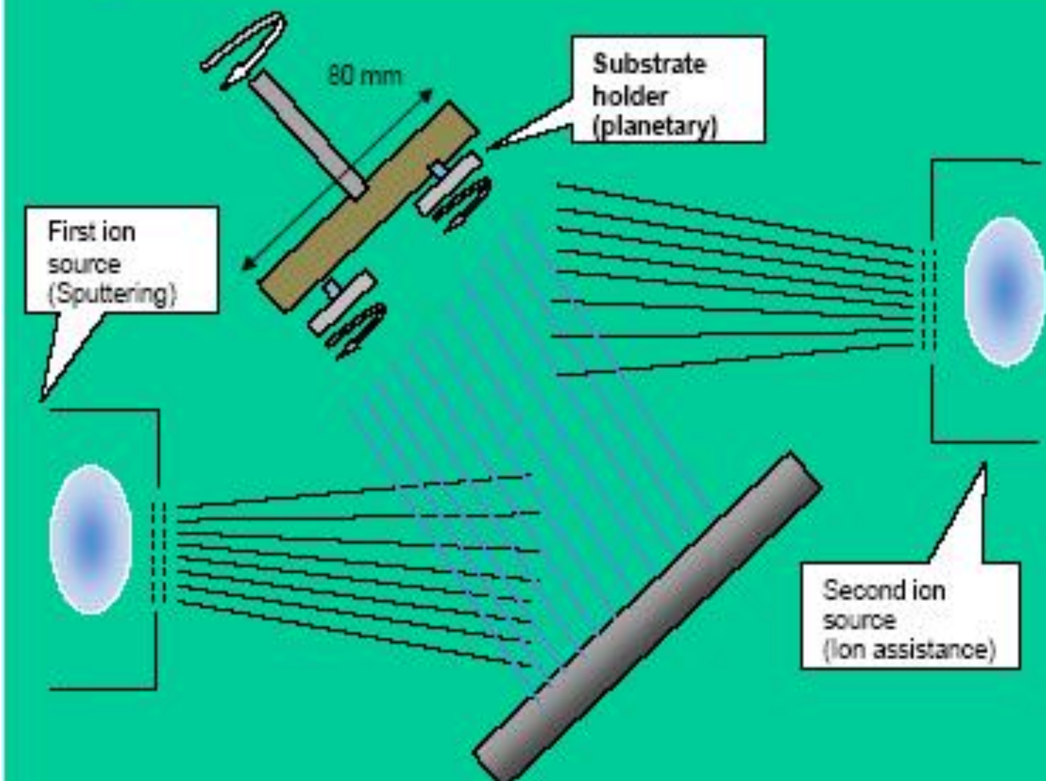
Effect of random errors of 0.1%

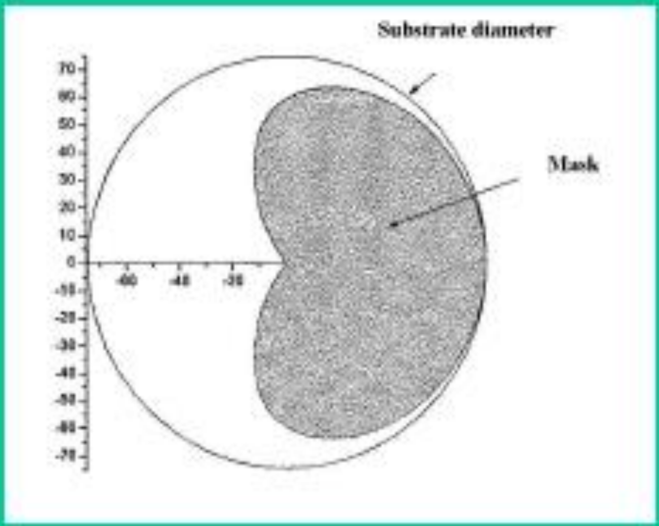


Effect of systematic deviation of 0.1%

Masking apparatus for large area coatings

- **Ion beam sputtering deposition or electron beam evaporation**
- **Profiled mask to improve uniformity designed by software**





Environmental testing

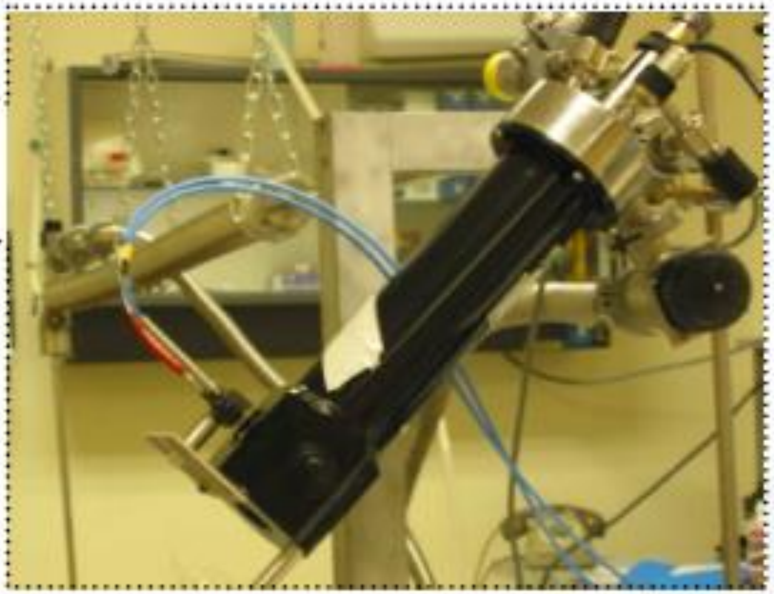
Challenging requirements:
- Precise spectral positioning
- Bandwidth accuracy
- Control of thickness profile

- Environmental durability
  - ✓ Mechanical resistance
  - ✓ Adhesion, abrasion, humidity....
  - ✓ Thermal cycling (cryogenic temperature)
  - ✓ Exposure to ionizing radiation

Coatings must be spectrally stable and mechanically robust

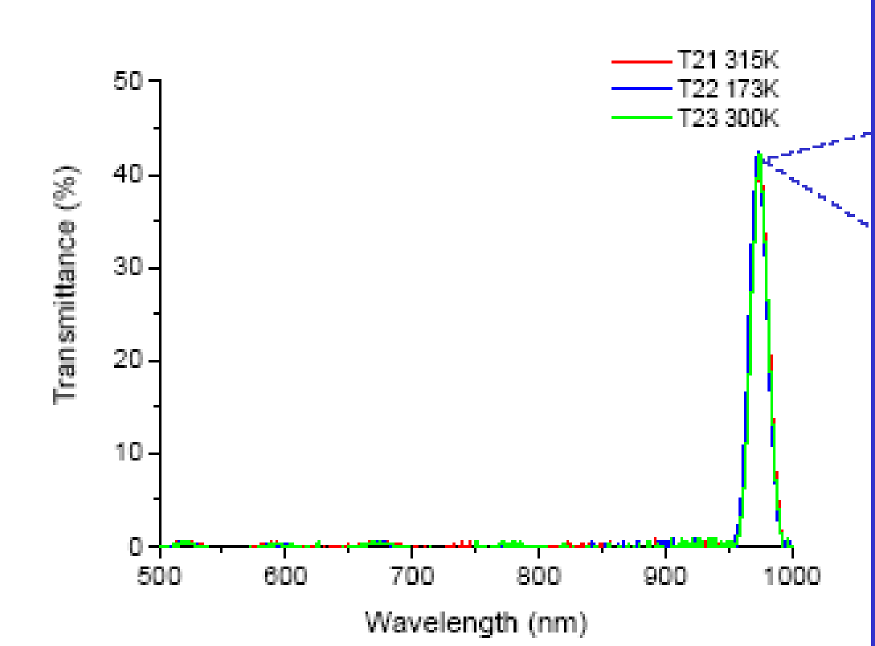
Cryogenic temperature measurements

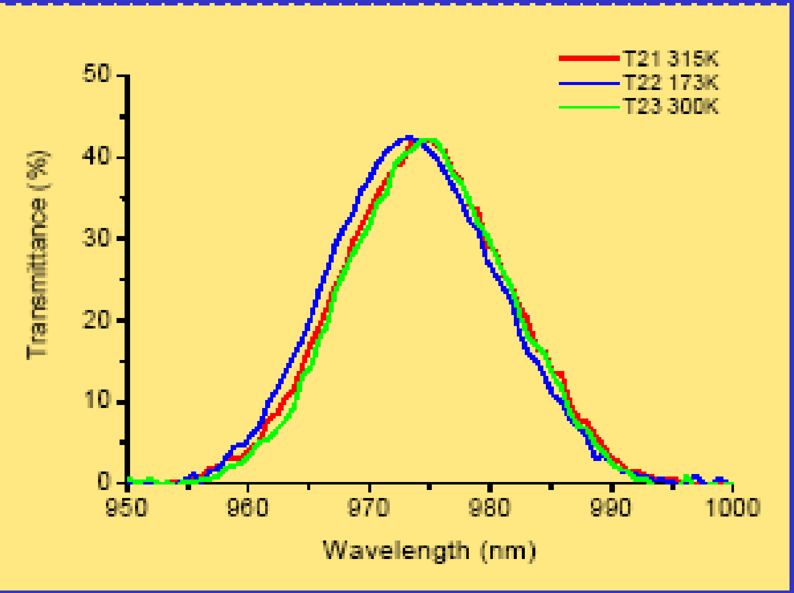
- Transmittance and reflectance measurements
- Wavelength range 400-1000 nm
- Temperature range 8-315K (cryostat) and 315 - 350K (heated vacuum chamber)
- Internal pressure 10^{-4} Pa



Cryostat

Thermal cycling test on filters



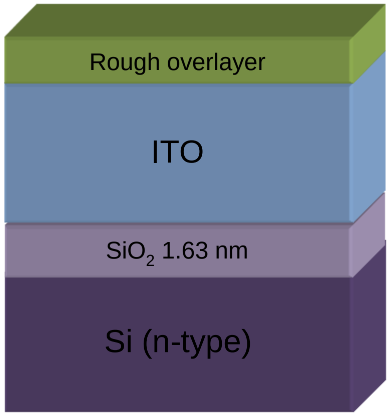


Metal-dielectric filter transmittance during the 8° thermal cycle

No visual changes. The filter functionality has not been compromised.
Blue shift at cryogenic temperature (max shift during cycling is less than 2 nm)

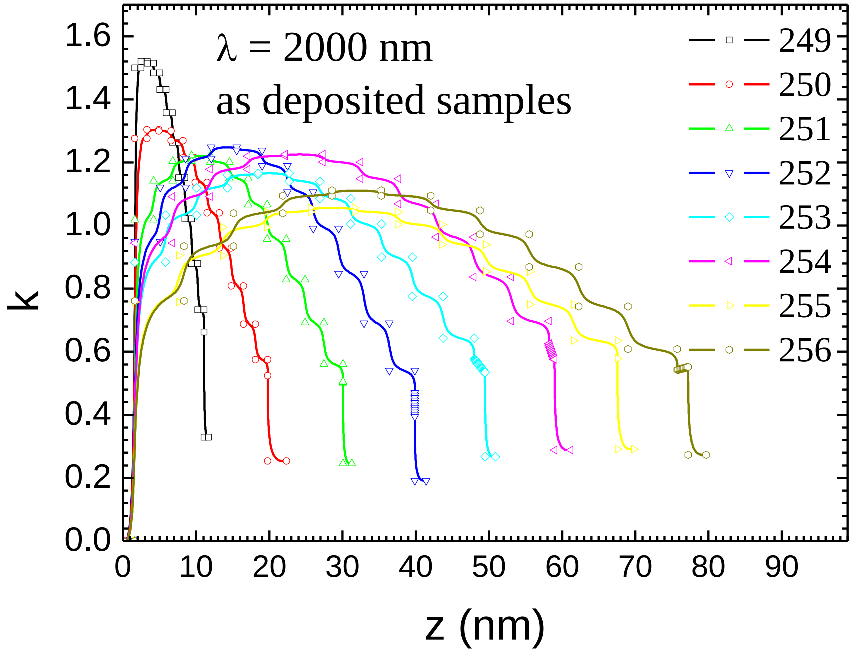
ITO optical conductivity

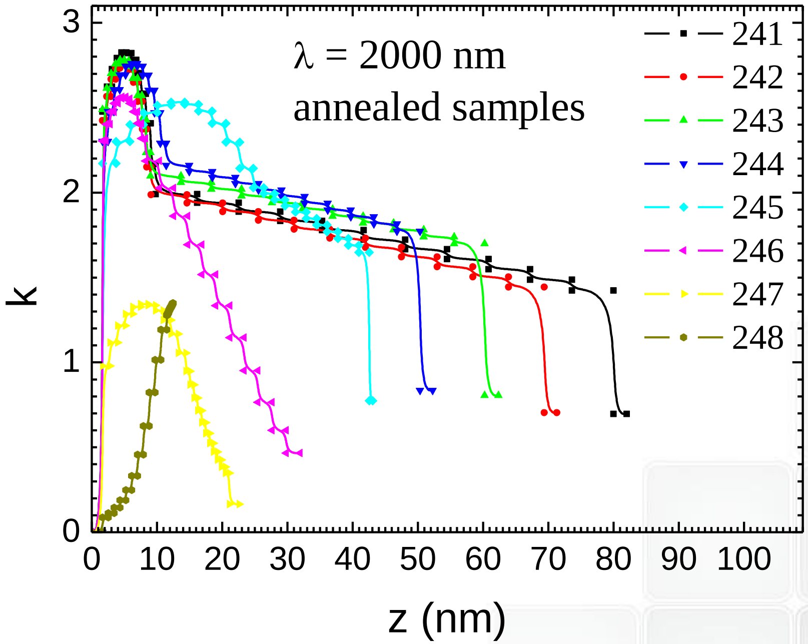
Model



λ = 300-2500 nm ; θ = 55°-75°

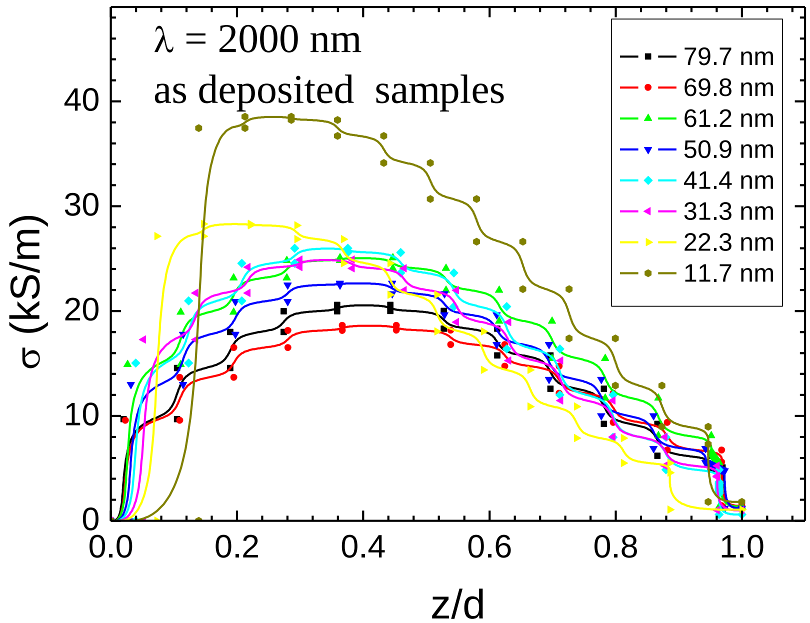
$$\left\{ \begin{array}{l} \Psi(\lambda,\theta) \\ \\ \Delta(\lambda,\theta) \end{array} \right. \Rightarrow \left\{ \begin{array}{l} n(\lambda,z)=n(\lambda)q(z) \\ \\ k(\lambda,z)=n(\lambda)q(z) \end{array} \right.$$

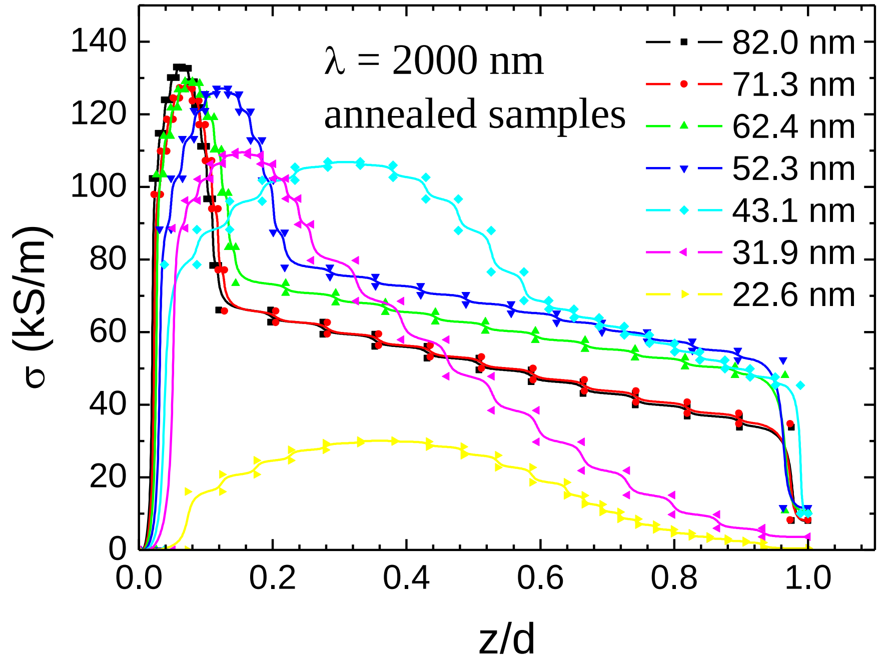




A. Sytchkova, et al, "Depth dependent properties of ITO thin films grown by pulsed DC sputtering", Materials Science & Engineering B 178 (2013), pp. 586-592

ITO optical conductivity





The majority of carriers in *as-deposited* ultra-thin ITO films is concentrated at sample half-depth, while carrier distribution becomes asymmetric for the thinne films, with a maximum located at 40% of the thickness.

Upon *annealing, a* carriers redistribution occurs, and their higher concentration is located in first 10% of the film thickness.

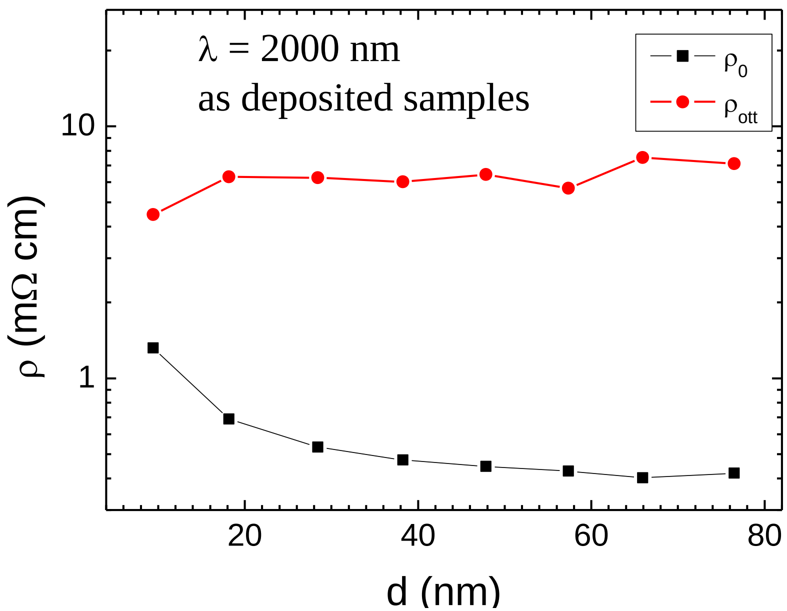
ITO resistivity comparison

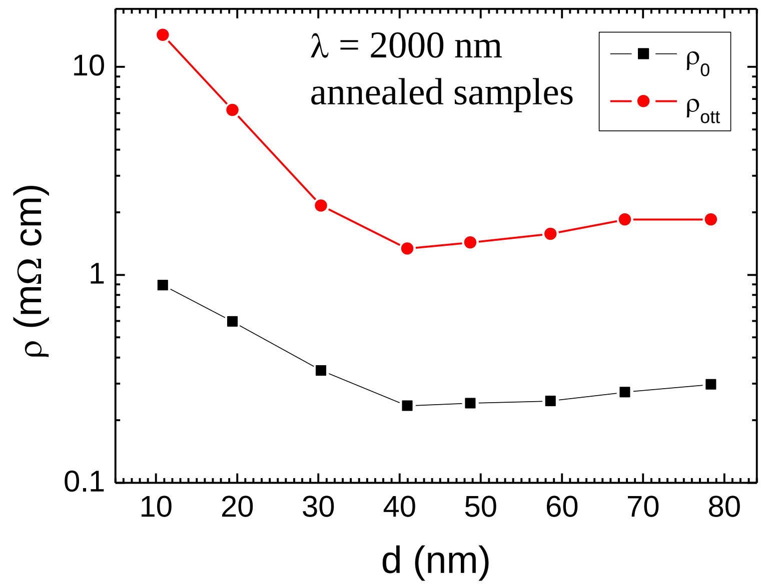
From $\sigma(z)$, the optical conductivity σ_{ott} has been estimated :

$$\sigma_{ott} = \frac{1}{d}\int_0^d \sigma(z)dz$$

d is film thickness.

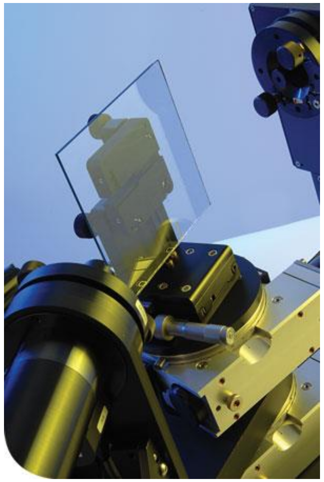
$\rho_{ott} = 1/\sigma_{ott}$ has been compared with the DC resistivity (ρ_0) (4-points probe measurements)

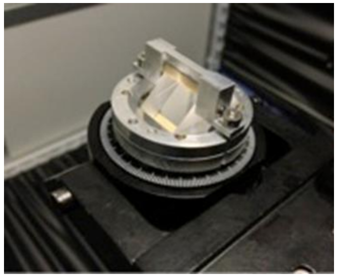


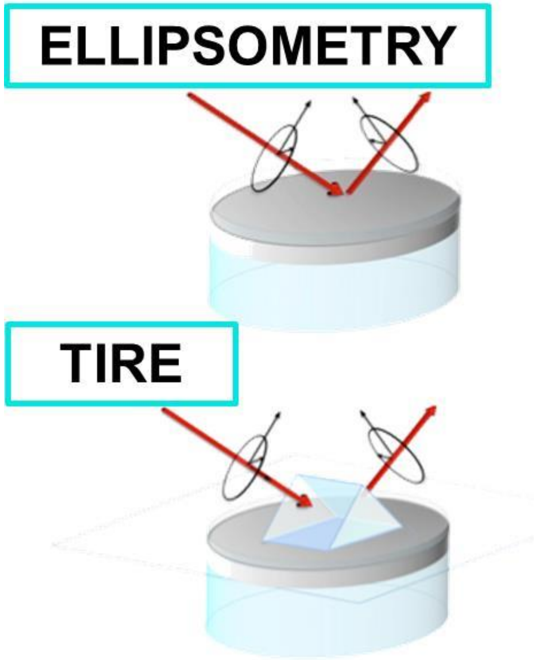


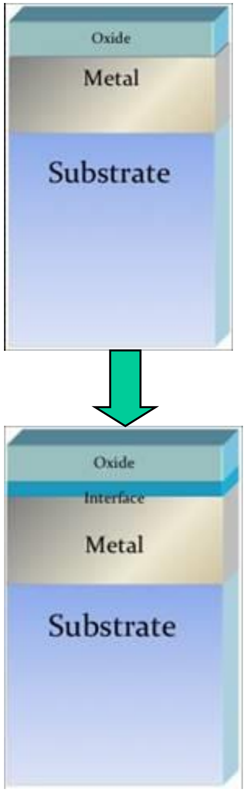
- The two types of resistivity have similar behaviour for both samples' set
- Minimum value of resistivity is obtained for the annealed ~40 nm thick sample (sample named 245) using these two independent measurement techniques.

TIRE sensitivity







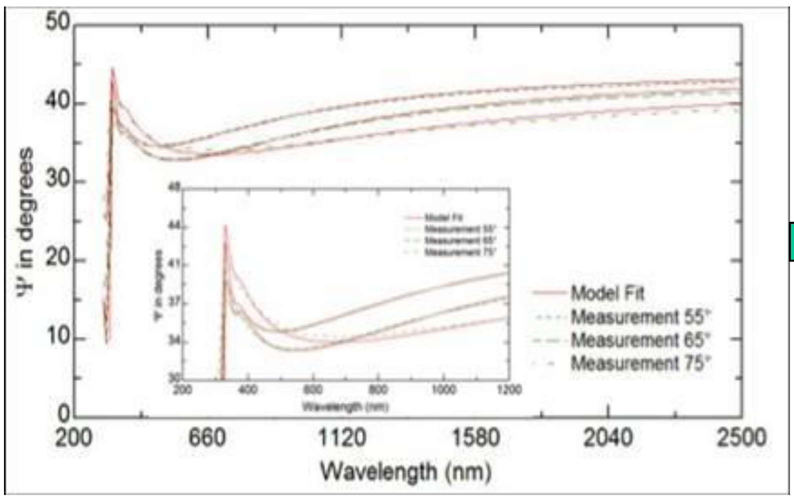


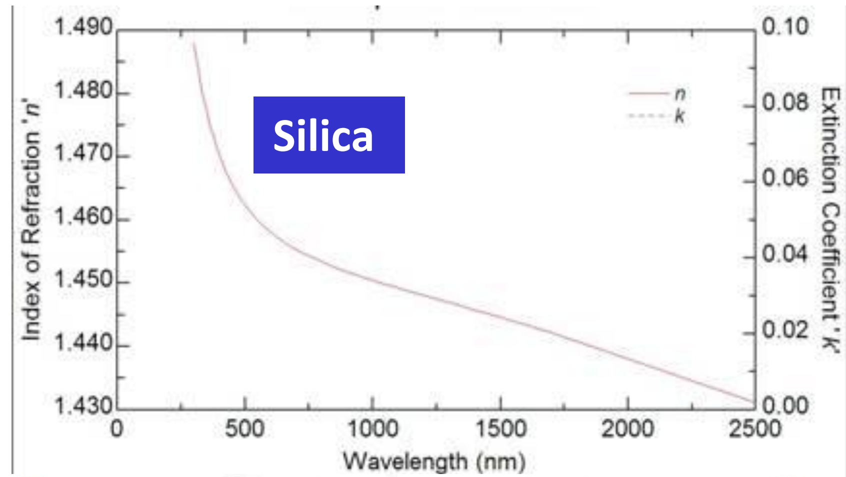
Total Internal Reflection Ellipsometry (TIRE) is ellipsometry under ATR conditions which gains from the Surface Plasmon Resonance (SPR) phenomenon.

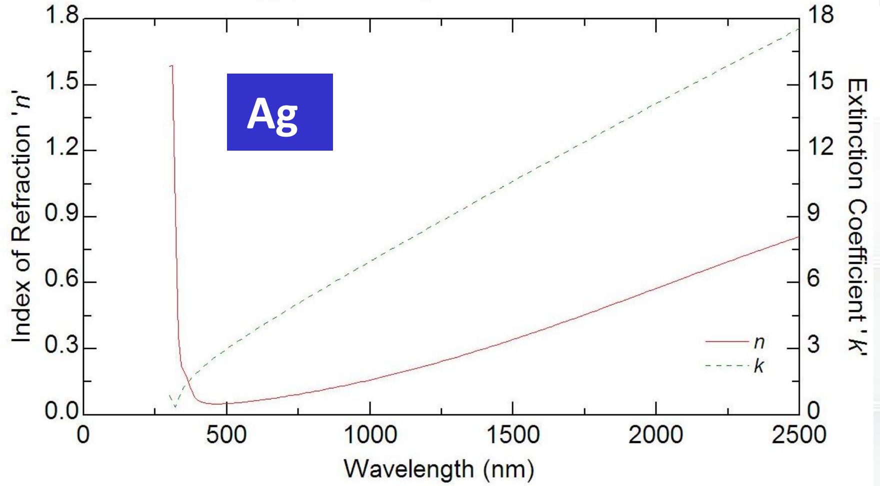
Computations have found that TIRE can detect the optical properties of the interface even if the interface is thinner than 0.5 nm.

TIRE sensitivity to the interface

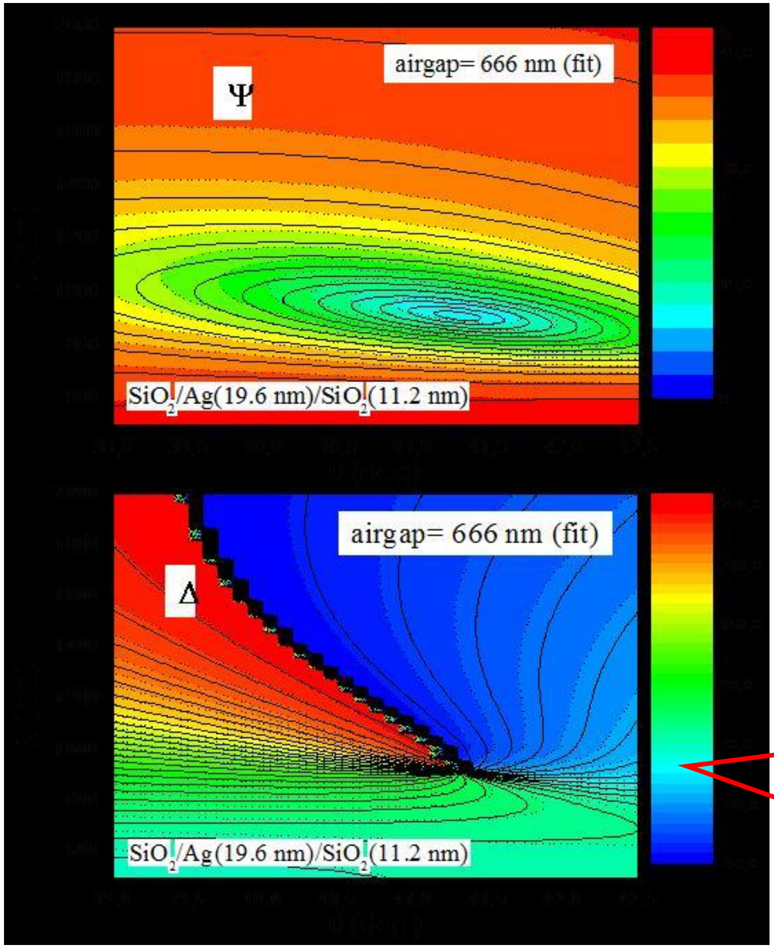
Fitting of the **VASE** data has a satisfactory quality if the **model without interface** is considered, and the model complication by the interface insertion does not improve the fit.







TIRE sensitivity to the interface



Material optical constants and layer thickness are from VASE modeling.

The air-gap value has been determined by fitting procedure.

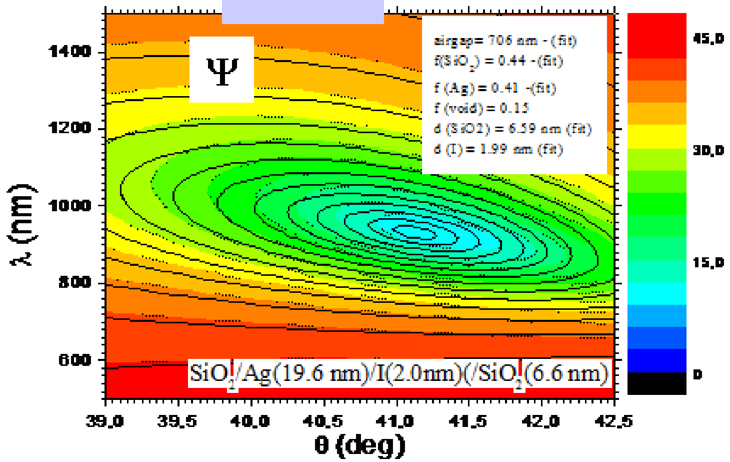
TIRE provides a room for the model improvement

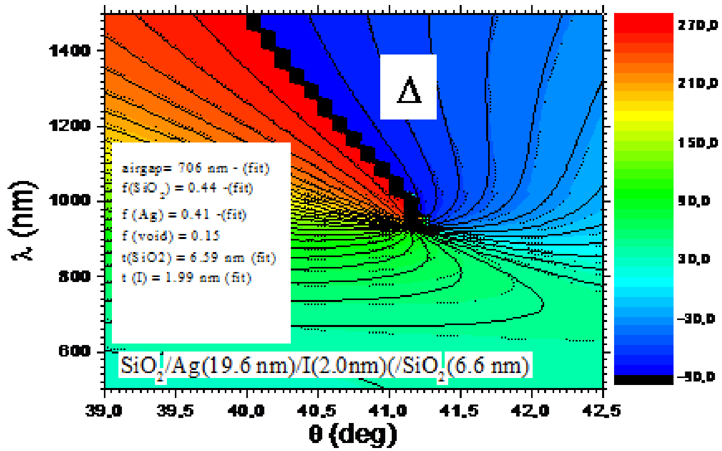
D. Zola, et al "Ellipsometric Modeling of Ultrathin Silver-Silica Heterostructures", Proc OIC 2013 TA7

Interface modelling

The optical response of the sample may be modeled considering different hypothesis on the interface formation

EMA

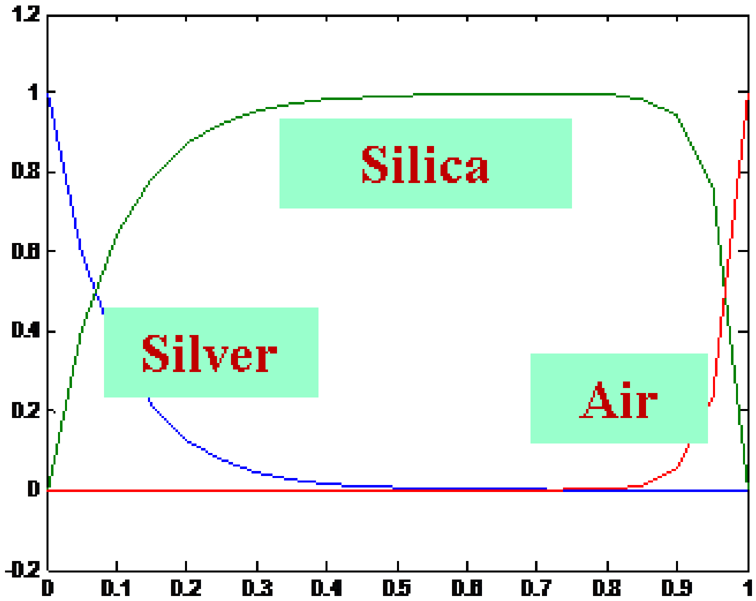


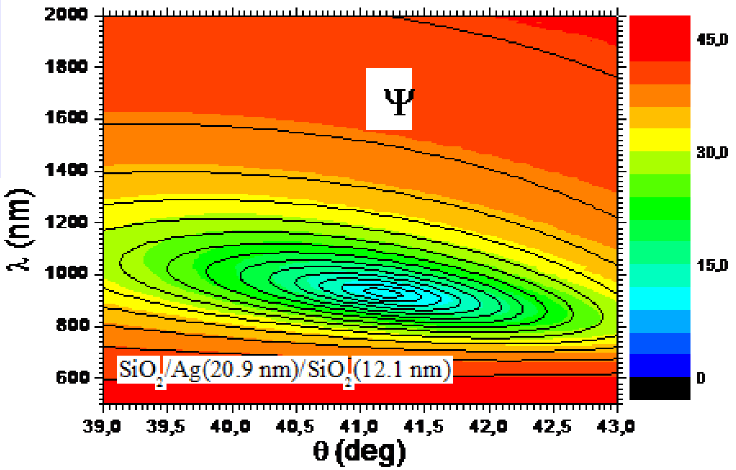


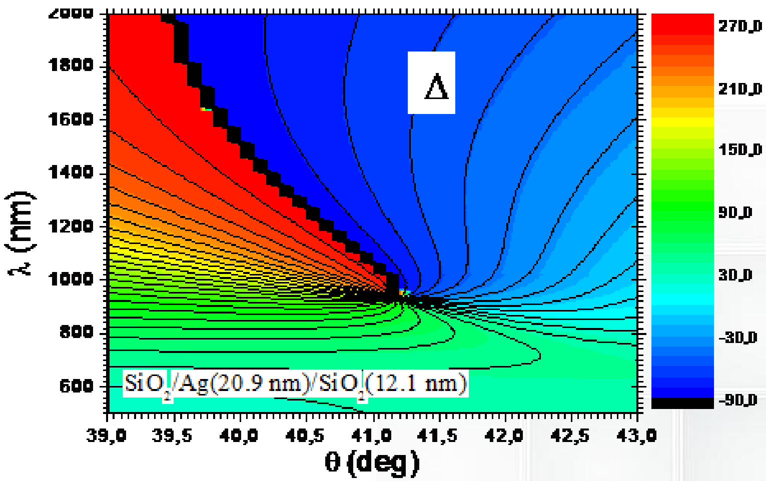
Interface modelling

The optical response of the sample may be modeled considering different hypothesis on the interface formation

An alternative is represented by the refractive index profiling based on the assumptions on the film growth type.







Optical Coatings Group: Outlook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Thank you for your attention!