POLYTECHNIQUE MONTRÉAL
UNIVERSITÉ D'INGÉNIERIE

PHS 6317 Nanoengineering of thin films

Course schedule – Winter 2024

12 January	Introduction – Scientific and technological challenges
19	Fabrication methods – Vacuum physics and vapor-phase techniques
26*	Fabrication methods – Plasma processes and process optimization
2 February	Fabrication methods - Plasma-surface interactions and diagnostics
9**	Fabrication methods – Thermal/Plasma spray technologies
16*	Optics of thin films 1, optical characterization, *Miniquiz1 (5%)*
23*	Optics of thin films 2, design of optical filters
1*** March	*Presentations – Emerging fabrication techniques (30%)*
	March 4-8 - Winter/Spring break
15**	Tribo-mechanical properties of films and coatings
22**	Electrochemical properties – corrosion and tribo-corrosion*(filter-20%)*
5 April	Functional films and coatings – Part 1, *Miniquiz 2 (5%)*
12	Functional films and coatings – Part 2
16	Life cycle analysis and environmental impact, **visits**
19* **	*Presentations – Emerging applications of nanostructured films (40%)*

Deadlines:

Project #1 – Fabrication technique:

Choice of the subject: **26 January**

Abstract and references: **9 February**

Report and presentation: **1st March**

Projet #2 – Design of an optical filter:

Choice of the subject: **23 February**

Report: **22 March**

Projet #3 – Application of nanostructured thin films:

Choice of the subject: **16 February**

Abstract and references: **15 March**

Presentation: **19 April p.m.**

Report: **22 April at 23:59**

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Project #3: Applications of nanostructured films and coatings
Thursday, April 19, B-530.2

8:30 Thomas Sicotte and Alexandre Gamache - Cellules photovoltaïques à pérovskite

8:48 Alexandre Carrière et Youssef Ben Mami - Électrodes transparentes pour ellules solaires

9:06 Veronika Cervenkova - Solar-thermal energy conversion - Transition metal nitrides

9:19 Alexandre Lussier - Fenêtres intelligentes thermochromiques

9:32 Alexandre Fall - Carbon nanotubes for sodium-ion batteries

9:45 Break

10:00 Luc Montpetit - Passivation of CdZnTe for x-ray detectors

10:13 Émilien Martel - Electrochromic, photochromic and gasochromic coatings-consumer optics

10:26 Étienne Tremblay et Nathan Sasseville - Couches minces pour l'él. organique – OLEDs

10:44 Christelle Abou Zeidan – Carbon nanotubes for flexible electronics

10:57 Thomas Lapointe - Photodétecteurs et leur conception/optimisation

11:10 Break

11:25 Alexandre Pinel - Couches minces d'hydroxyapatites pour les implants en biomedical

11:38 Bastien Izacard – Atomic oxygen barrier coatings for satellites

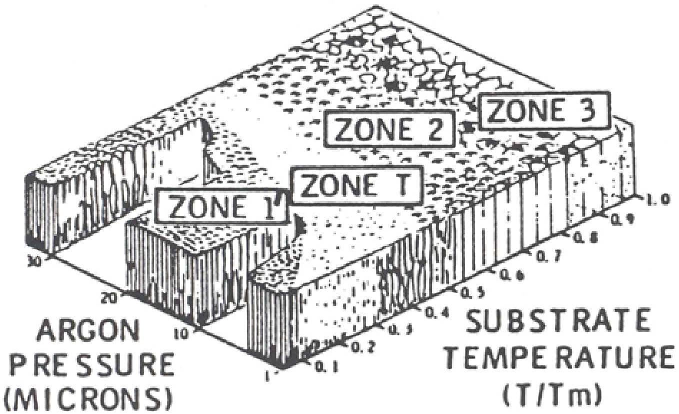
11:51 Arghavan Yazdanpanah Ardakani - Hudrophobic coatings for aircraft surfaces

12:04 Mathieu Bruzzese – Oxidation-resistance barrier coatings for aerospace applications

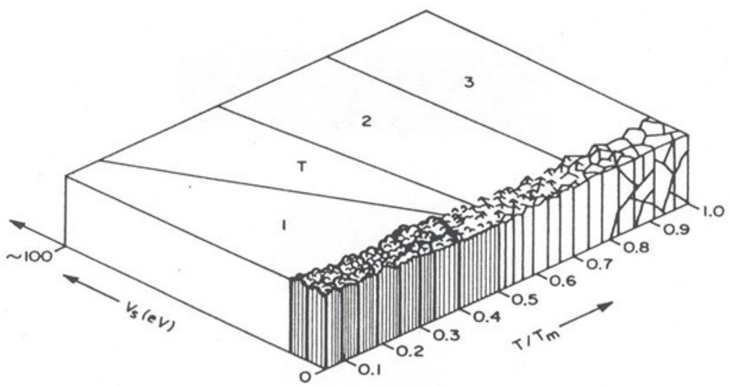
12:17 Mohamed Ammari - Thermal barrier coatings for aerospace gas turbine engine

12:30 End and course evaluation

Structural evolution and ion bombardment



J.A. Thornton, J. Vac. Sci. Technol., 11 (1974) 666.

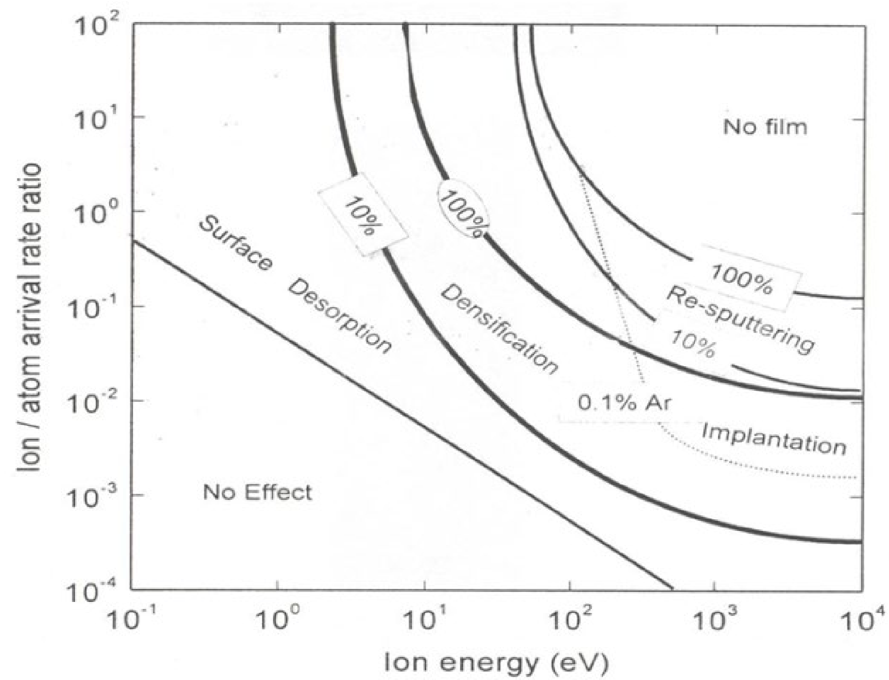


Messier, Giri and Roy, J. Vac. Sci Technol A, 2 (1984)

Control of the microstructure through surface effects (temperature, ion energy and ion flux: D*evelopments since 1960's.*

A. Anders, Thin Solid Films 518 (2010) 4087.
J.J. Colin et al, Acta Mater., 126 (2017) 481.

Ion bombardement effects *vs* relative ion flux and ion energy



Ion bombardment effects:

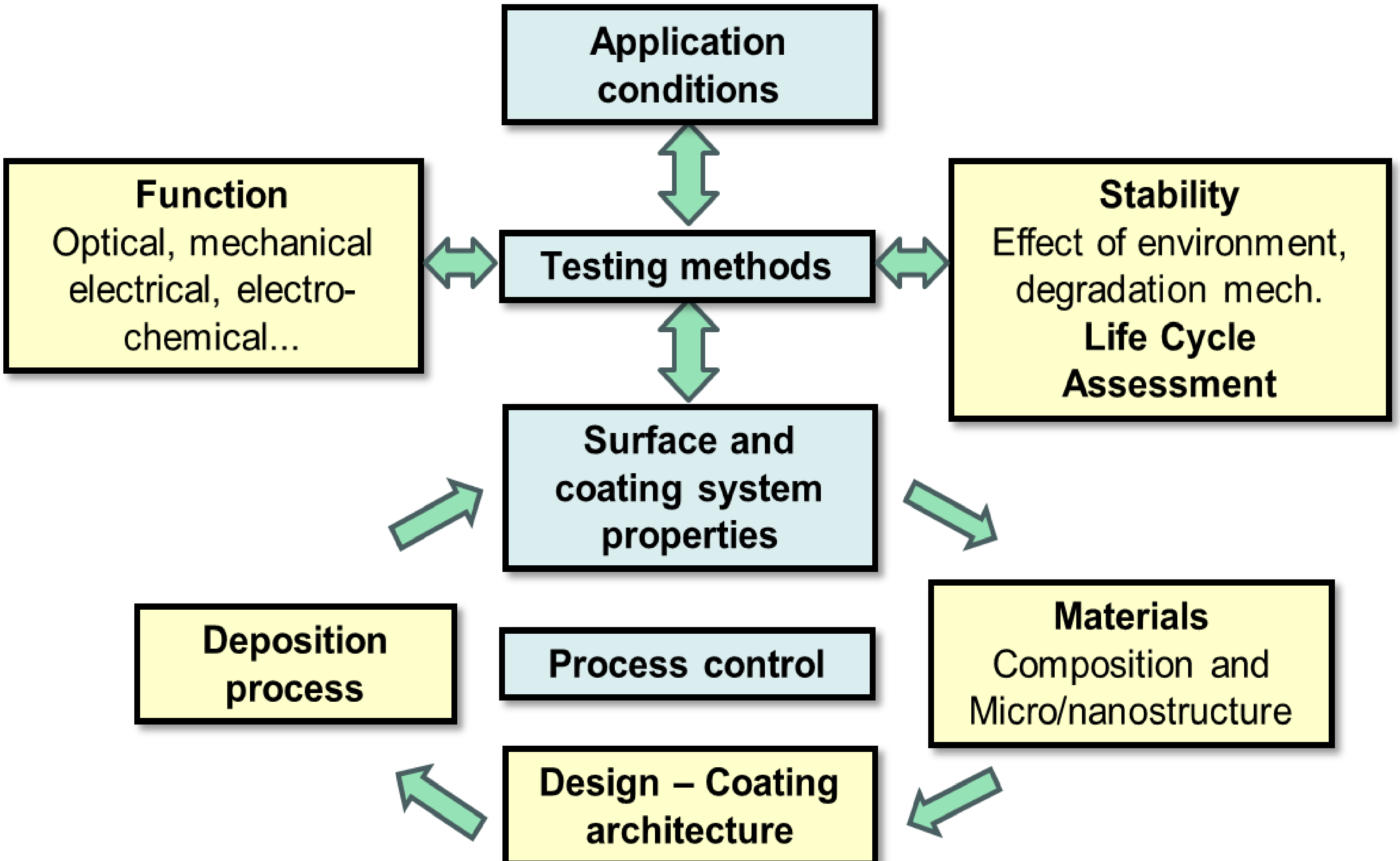
$$\boldsymbol{E_p \sim E_i \ . \ \Phi_i / \Phi_n}$$

$$\Phi_N = r_D \frac{\rho N_A}{m_A}$$

E_i < 1 keV, IEDF, Φ_i ion flux, Φ_n flux of cond.

Control of E_i and Φ_i / Φ_n : biasing, ionization, pulsing, …

The **holistic approach** to surface engineering



Development of functional thin film systems

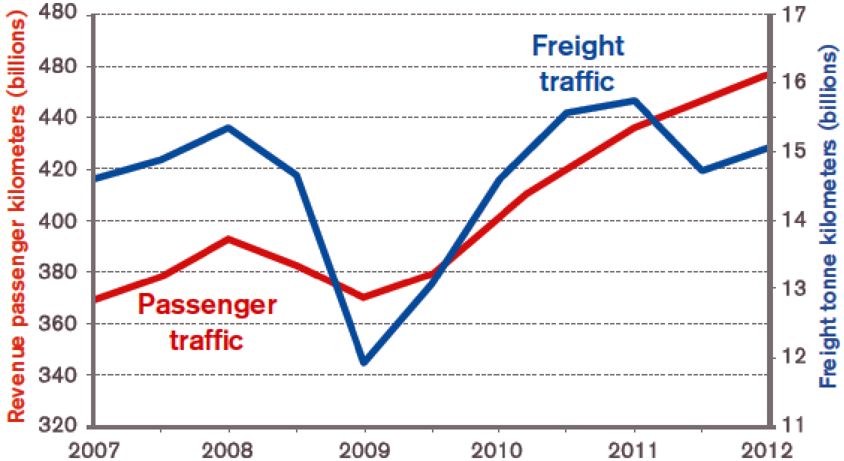
<u>Aerospace applications:</u>

- Erosion-resistant coatings
- Ice-phobic coatings

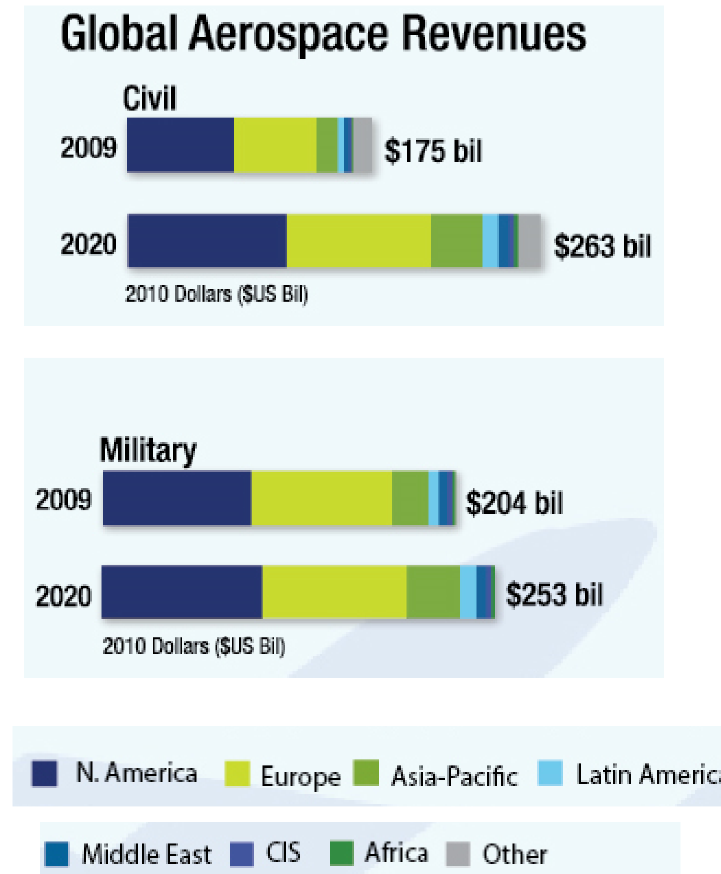
<u>Optical and energy applications:</u>

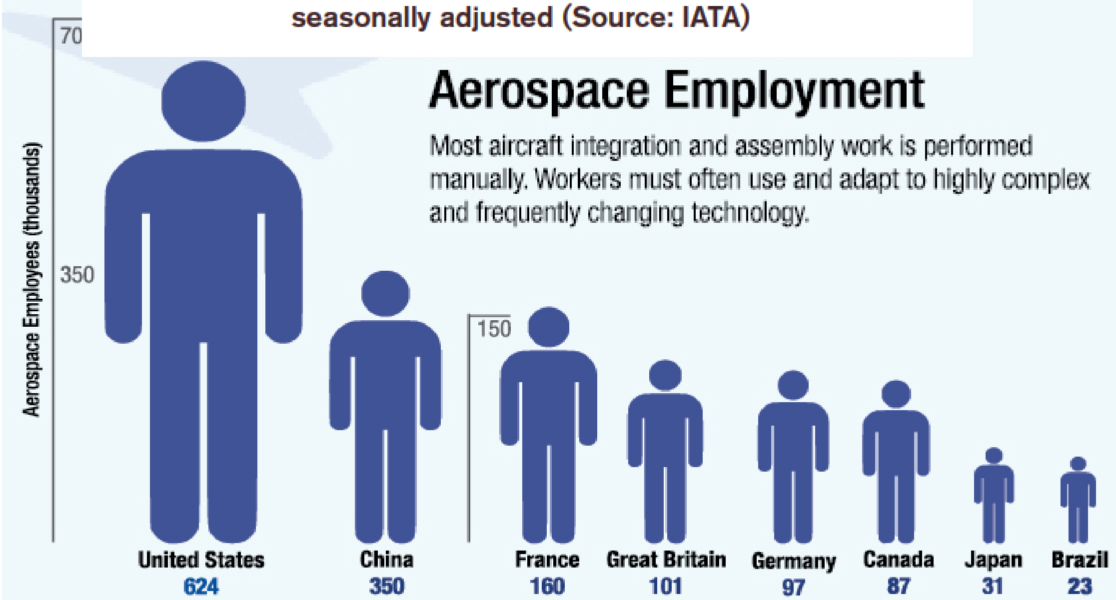
- Optical security devices
- Architectural glazings
  - Low-emissivity windows
  - Hard optical coatings
  - Smart (thermochromic) windows
  - New functions

World Aerospace Industry



Total passenger and air freight traffic, seasonally adjusted (Source: IATA)





Source: World Economic Forum
http://reports.weforum.org

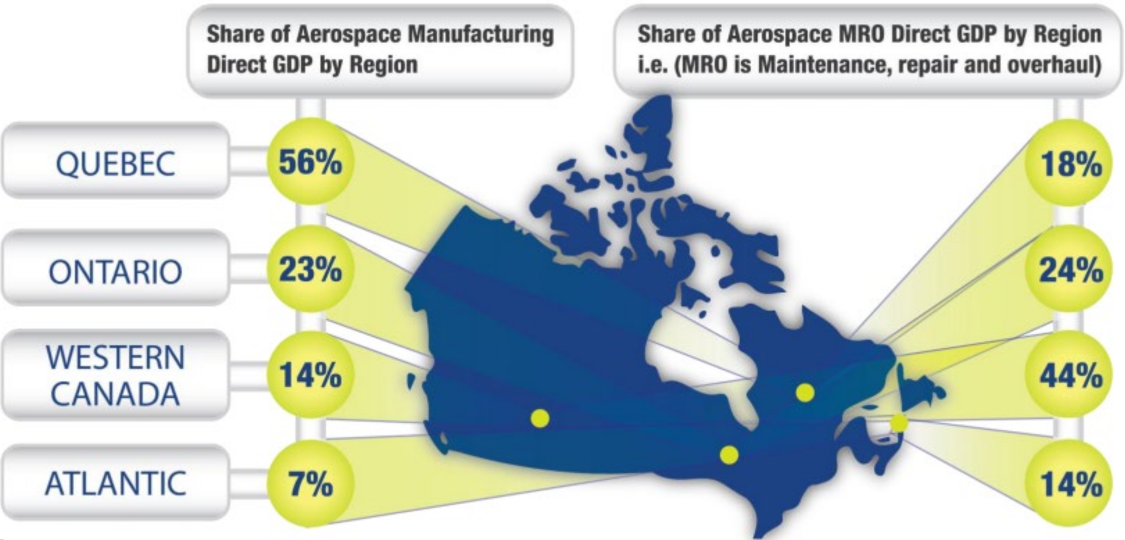
Canadian Aerospace Industry

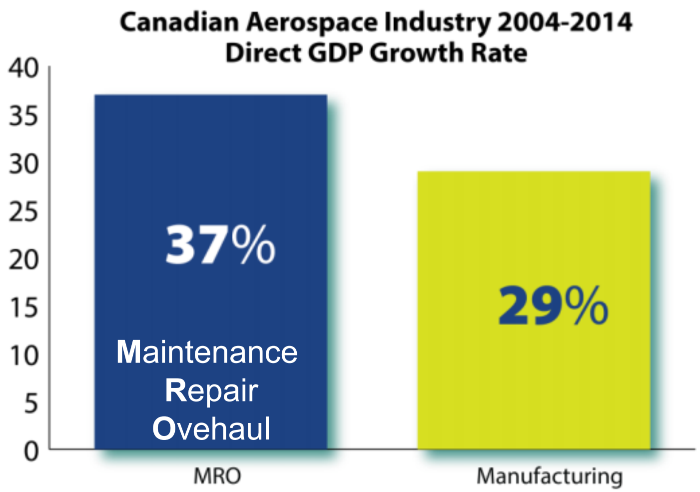
The Canadian aerospace industry contributed more than $29 B to GDP and 180,000 to employment in the Canadian economy in 2014

#1 In civil flight simulation
#3 In civil aircraft production
#3 In civil engine production

Complete tier coverage:
Regional aircraft; Business jets; Commercial helicopters; Landing gear; Space systems

A truly national industry

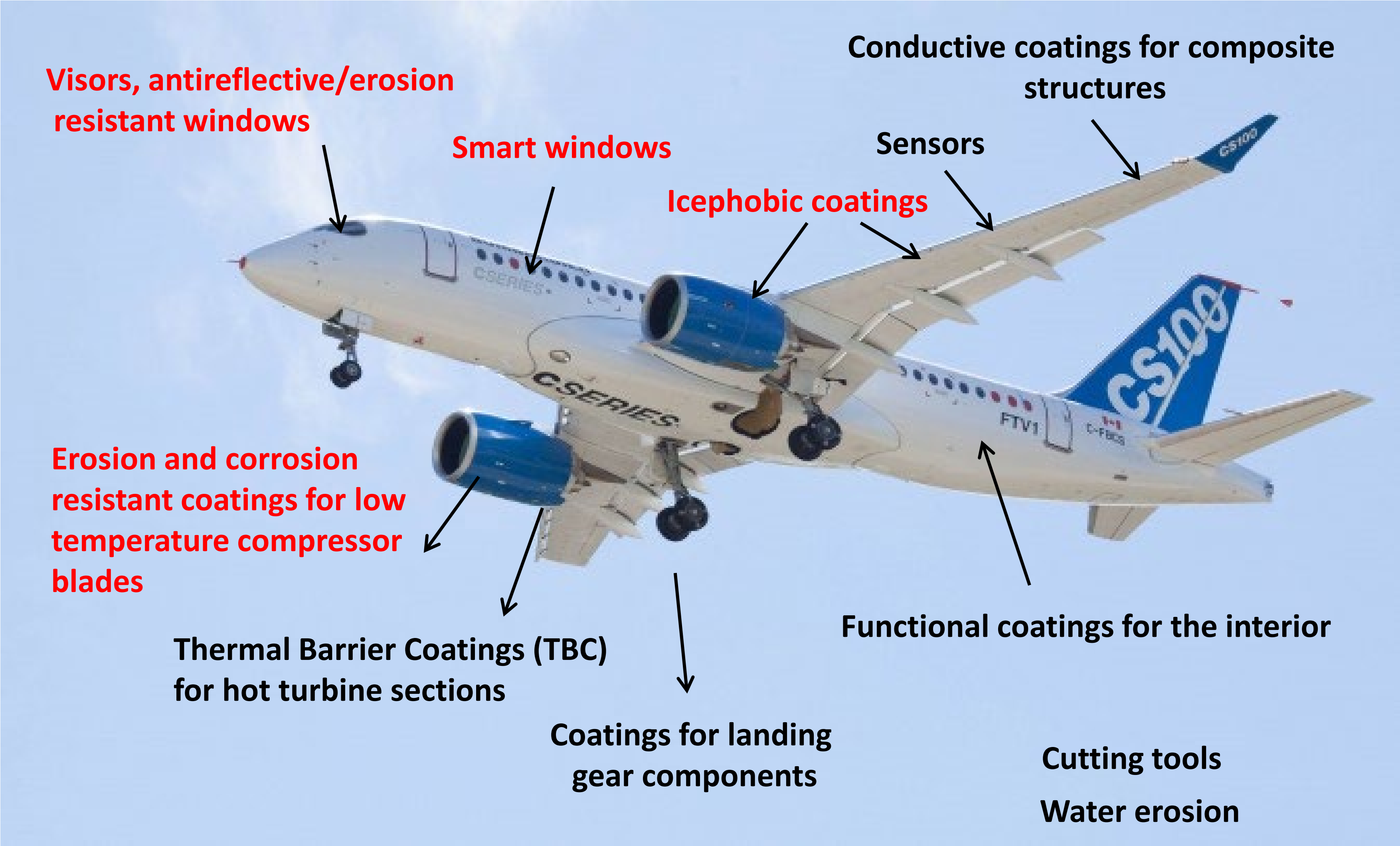




Source: Aerospace Industries Association of Canada, 2015

Source: http://commercialaircraft.bombardier.com/

Functional coatings for aircraft



Erosion-resistant coatings for aerospace

Military experience demonstrated that engine life could be shortened to a fraction of its designed service life in an erosive environment

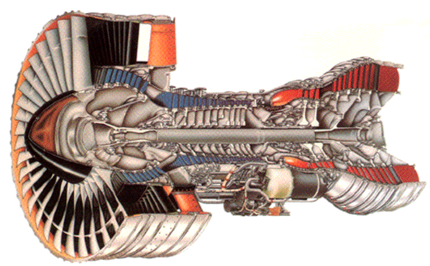
<u>Helicopter lifetime:</u>

- Vietnam = 100 hours
- Gulf War = 20 hours

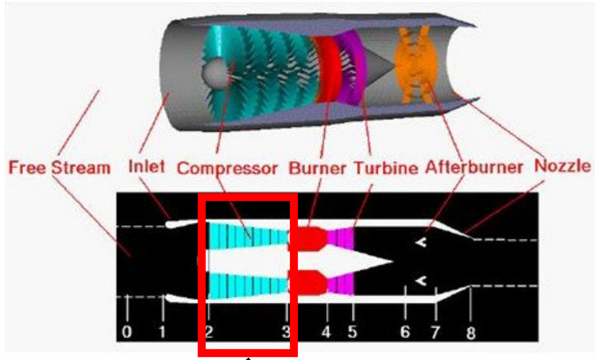
- Events of April 2010:

- Huge ash cloud spread from an Icelandic volcano toward Europe
- About 16,000 flights cancelled
- Costing to the airlines estimated at $200 million/day

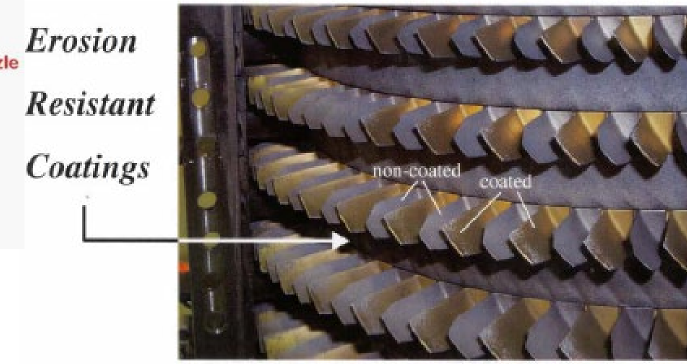
Problems in aircraft engine related to erosion



Example of a jet engine: Pratt&Whitney PW4000 turbofan (www.pratt-whitney.com)

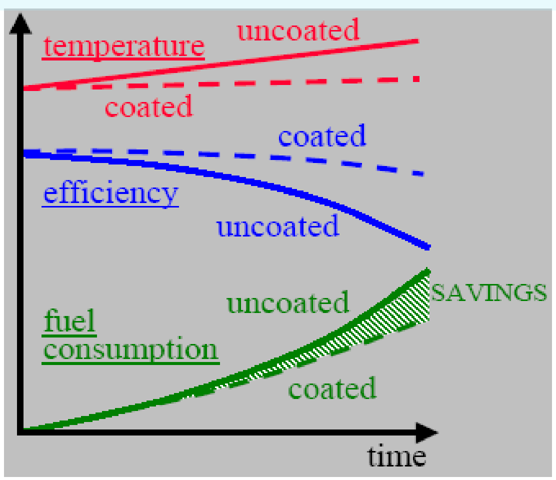


Compressor blades: Section 2-3
Temperature at 10 km vary
-14 ^{0}C is to 250 ^{0}C



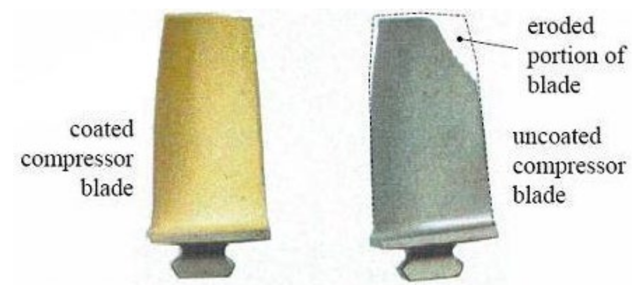
TiN - Erosion-resistant coating

- Sand, dust and other foreign objects are ingested into the engine mostly during take-off, landing, and in the case of helicopters during low level hovering



- Loss of aerodynamics
- Decrease in efficiency
- Increase in fuel consumption
- Increase in failure risk
- Increase in maintenance costs
- Reduces component/engine life

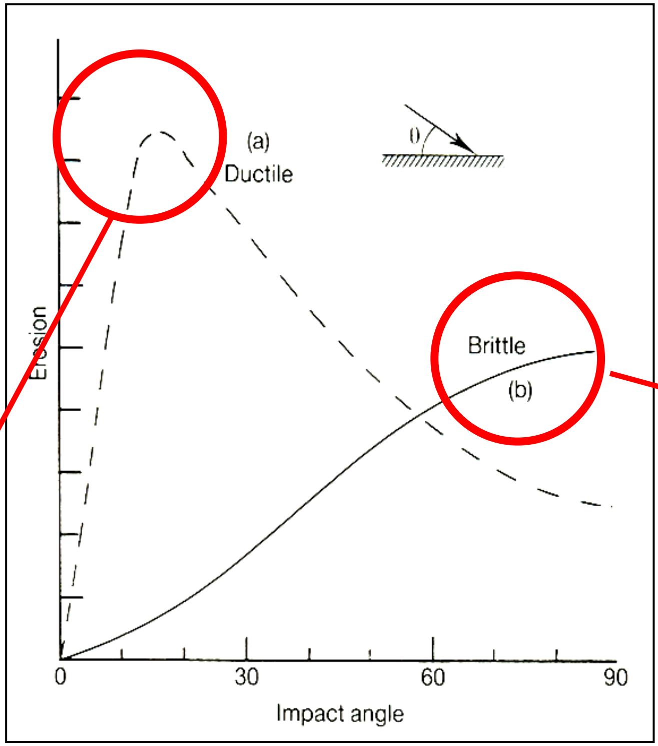
Hamed, A. et al. J. Propulsion and Power (2006). V22 350-360



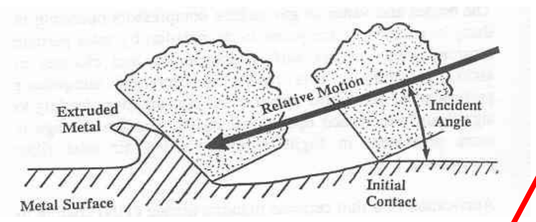
Results of T64 engine sand ingestion test conducted by GE and US Navy

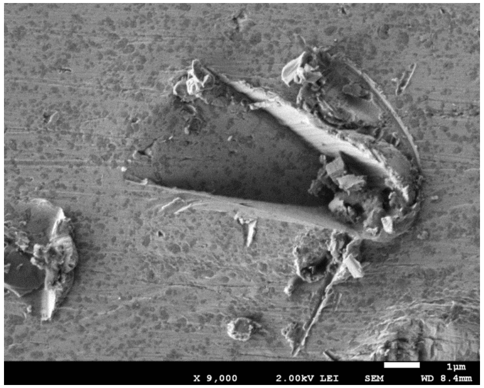
Courtesy of MDS Coating

Erosion behavior



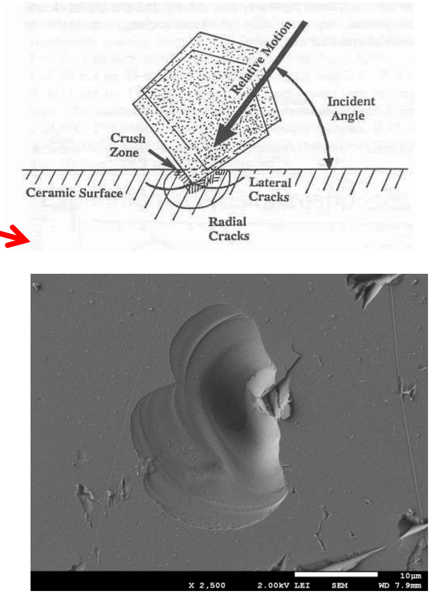
Ductile erosive response





- Micro-cutting
- Ploughing
- Work hardening
- Temperature effects
- etc.

Brittle erosive response



Fracture dominated mechanisms

I.M. Hutchings, Tribology, CRC Press, Boca Raton, 1992.

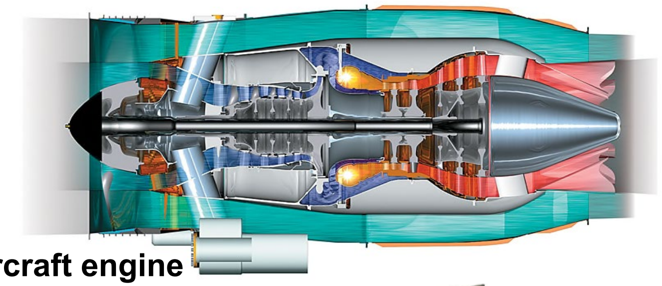
Protective coating requirements

Main concerns: performance; environmentally friendly processes; economics

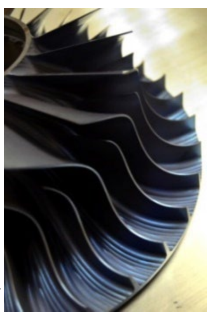
Multi-scale and life cycle considerations

Protective coating design and fabrication

macroscale

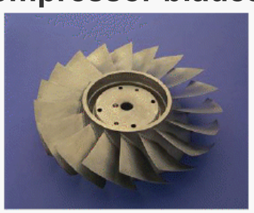


Aircraft engine



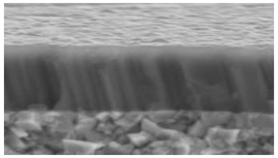
Diffuser

Compressor blades



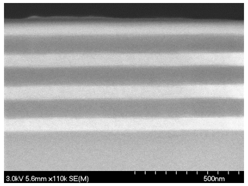
Single Rotor

microscale



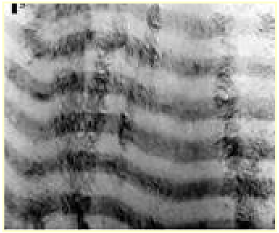
single layer coating

gradient coating



multilayer coating

nanoscale



nanolaminates

nanocomposites

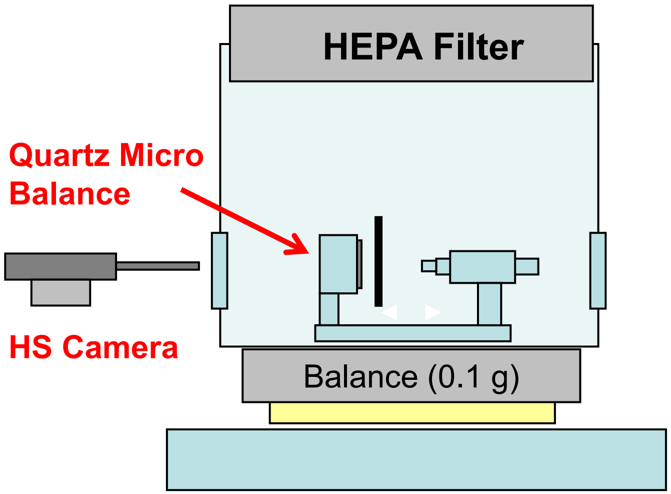
fatigue

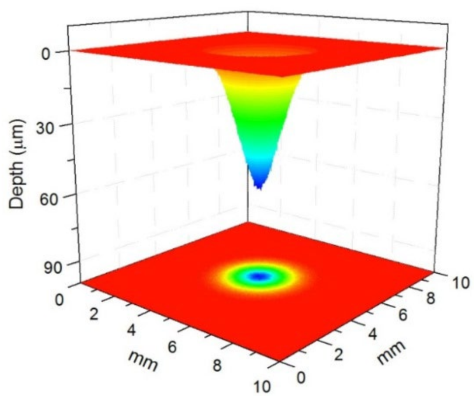
Protective coating removal (re-manufacturing)

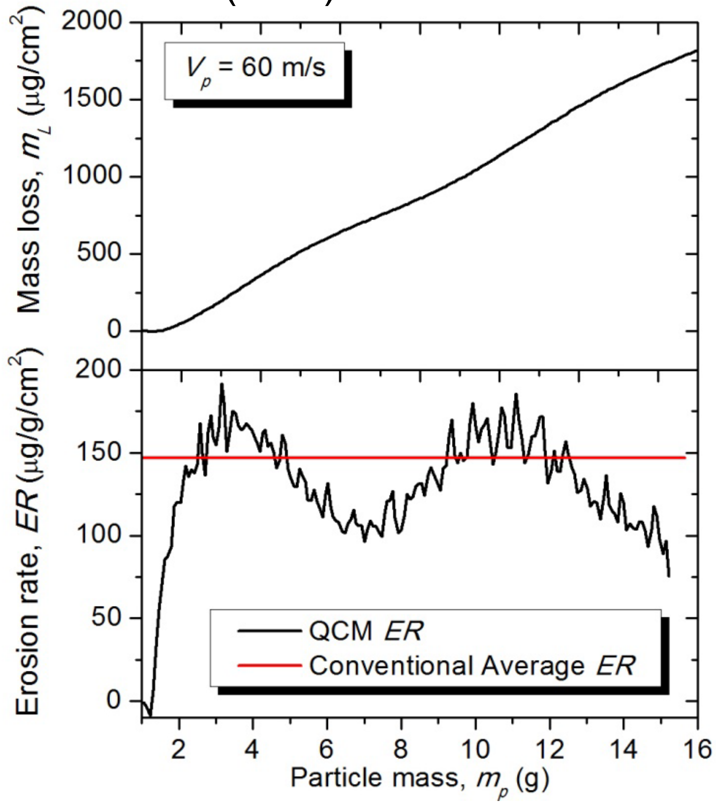
Aircraft engine (cold part) – multiple requirements: Erosion resistance, ice-phobicity, complex shapes (non-line-of-sight deposition), no fatigue debit

Erosion testing methodology

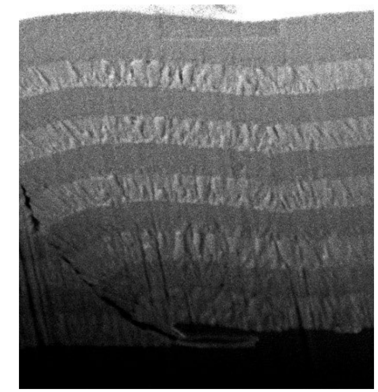
Based on ASTM G76 – Solid particle erosion (SPE)



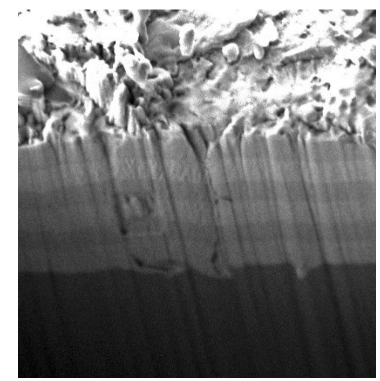




Cross-sections prepared by Focused Ion Beam



10 layers before erosion

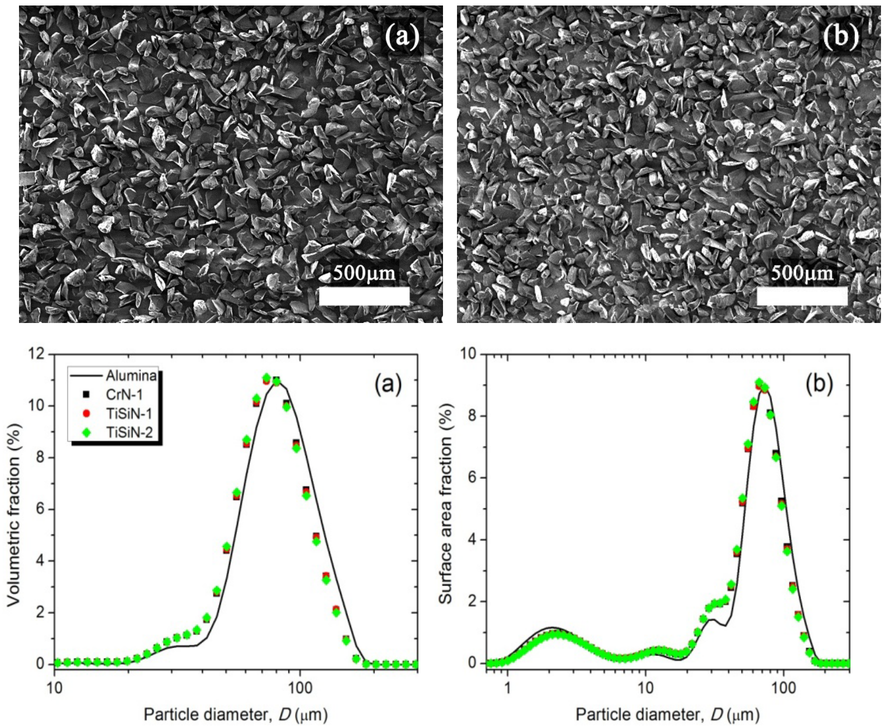


6 layers after erosion

<u>Ex.:</u> Mass loss and erosion rate of a Cr/CrN multilayer coating as a function of particle mass. The QCM enables one to see the variation of erosion rate of each layer – in real time !

E. Bousser et al, Surf. Coat. Technol. 237 (2013) 313-319

Realistic particle impact

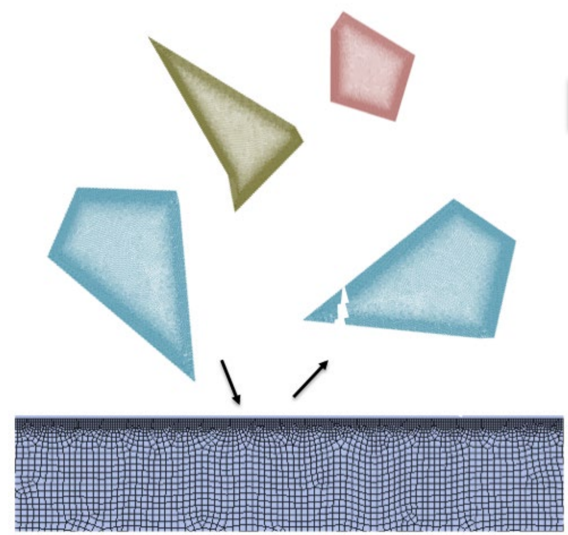


Micrographs of Al_2O_3 particle size distributions measured by Laser Diffraction Spectroscopy before and after erosion testing

E. Bousser et al, J. Mat. Sci. 48 (2013) 5543 - 5558

Realistic erodent shape, size and mechanical properties:

- Generation of random polygonal objects
- Fracture of erodent particles
- Energy dissipation



Finite element meshing of randomly generated erodent powder particles

Key parameter: $H_{particle}$ / H_{target}

Surface Material Response

The tribological behaviour of a system is intimately related to the surface response to loading and deformation. These can be described by the main material's parameters.

Elastic Modulus (E)

Hardness (H)

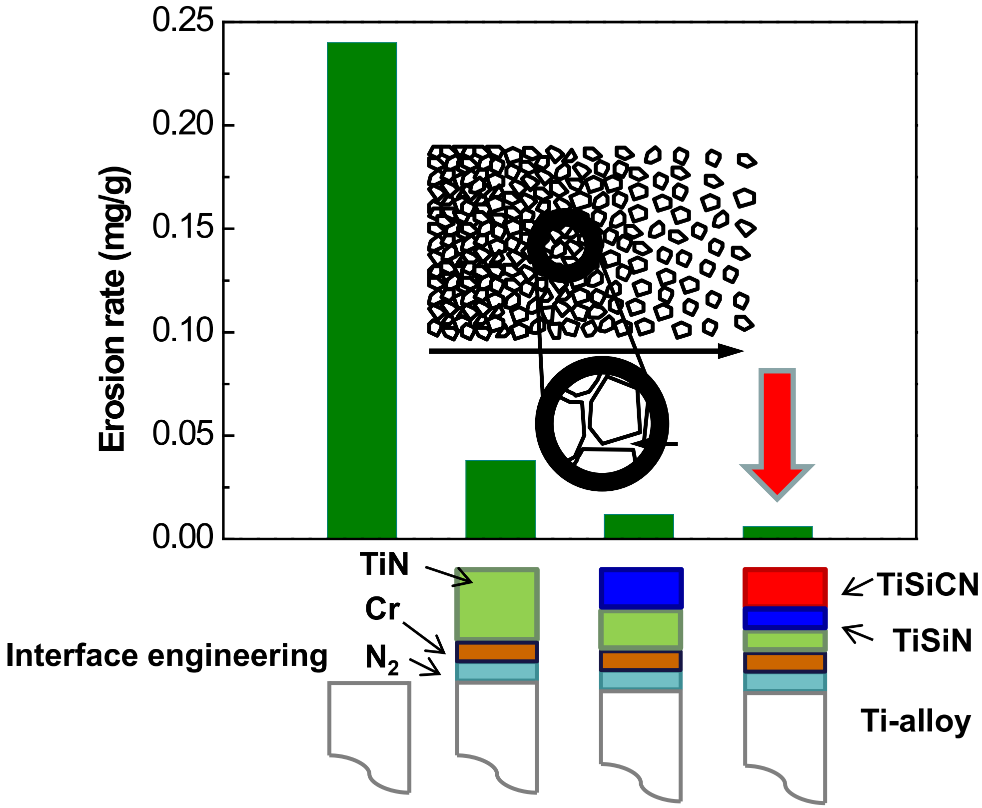
Toughness (K_c)

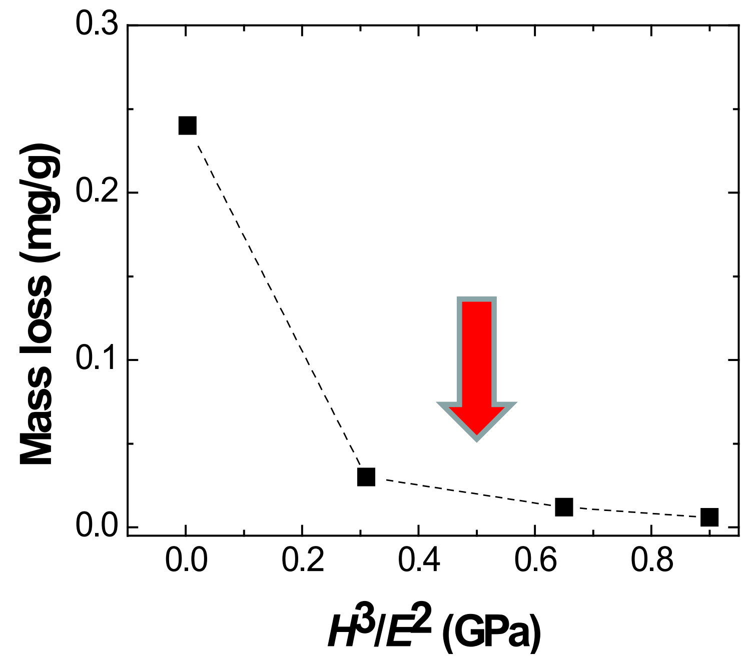
Tribological response of coated systems :

- **H/E**
  Elastic strain to failure (Leyland and Matthews, 2000)
- **H^3/E^2**
  Onset of plastic deformation (Tsui et al., 1995)
- **H/K_c**
  Index of brittleness of a surface

Erosion resistance of nc-TiSiCN coatings

<u>Test:</u> 50 μm alumina particles; Normal incidence
Erodent speed: 90 m/s; Coating thickness ~10 μm



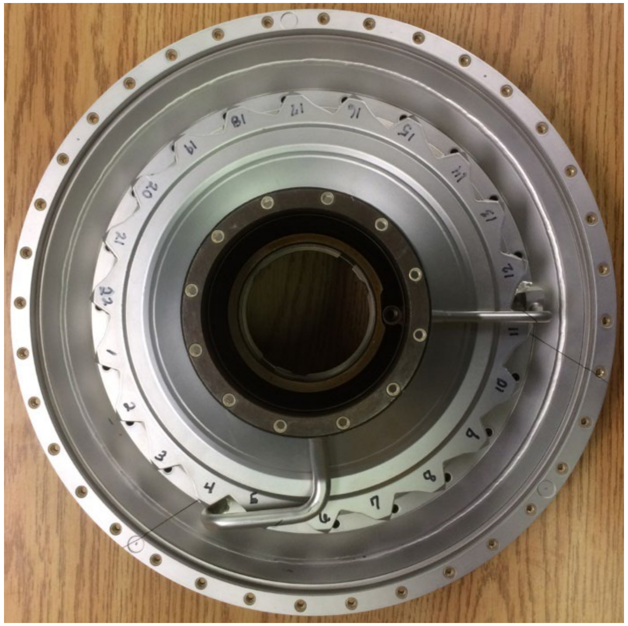


Improvement of the erosion resistance ~50x

Review of Functional Coatings: L. Martinu, O. Zabeida, J.E. Klemberg-Sapieha, in "Handbook on Thin Film Deposition Technologies", P.M. Martin, ed., Elsevier, 2010, pp. 394-467

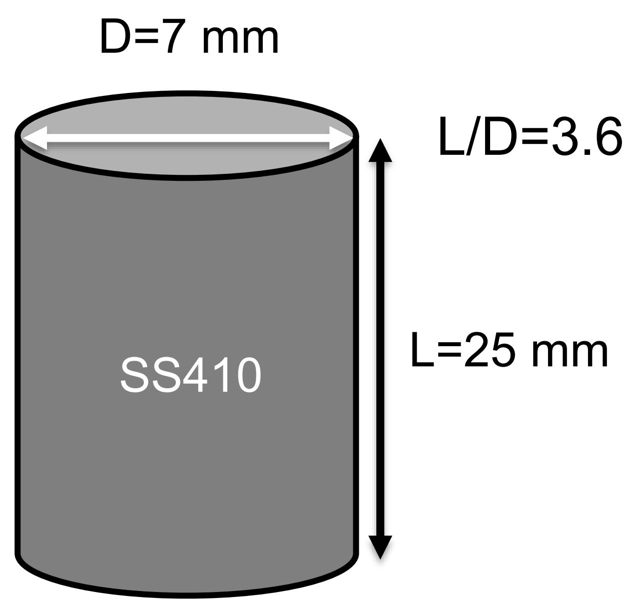
Coating complex shape engine components

Top view



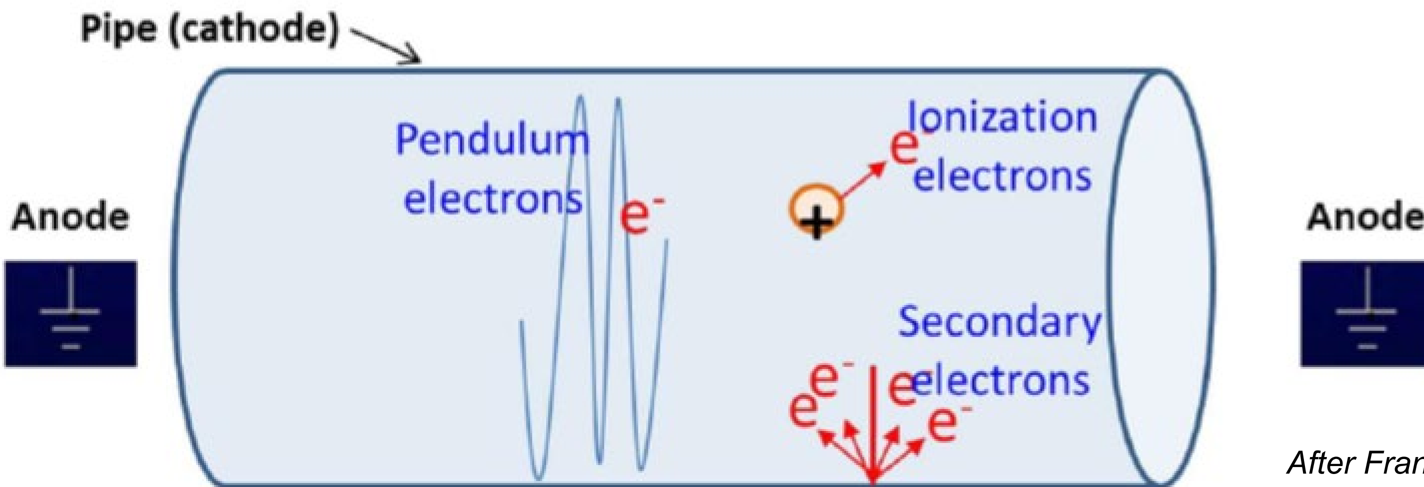
Internal cavities and narrow tubes: e.g. diffuser

The diffuser conducts the air to the combustion chamber by means of numerous narrow gas inlets (cavities) which are similar to tubes.



Hollow cathode discharge

Hollow cathode (HC) discharge mechanism:
Electron pendulum effect



After Frank Papa, Duralar
SVC TechCon, April-May 2019

The cathode geometry confines the plasma leading to an oscillatory mouvement of the electrons – pendulum effect – increased probability of ionization.

Plasma density can attain up to $\mathbf{n_e=10^{12}\ cm^{-3}}$, compared to the usual $n_e=10^9 - 10^{10}\ cm^{-3}$

In PECVD, this can potentially lead to high dissociation and deposition rates

See, for example, S. Muhl, A. Pérez, "The use of hollow cathodes in deposition processes: A critical review", Thin Solid Films 579 (2015) 174.

HC PECVD System at Polytechnique

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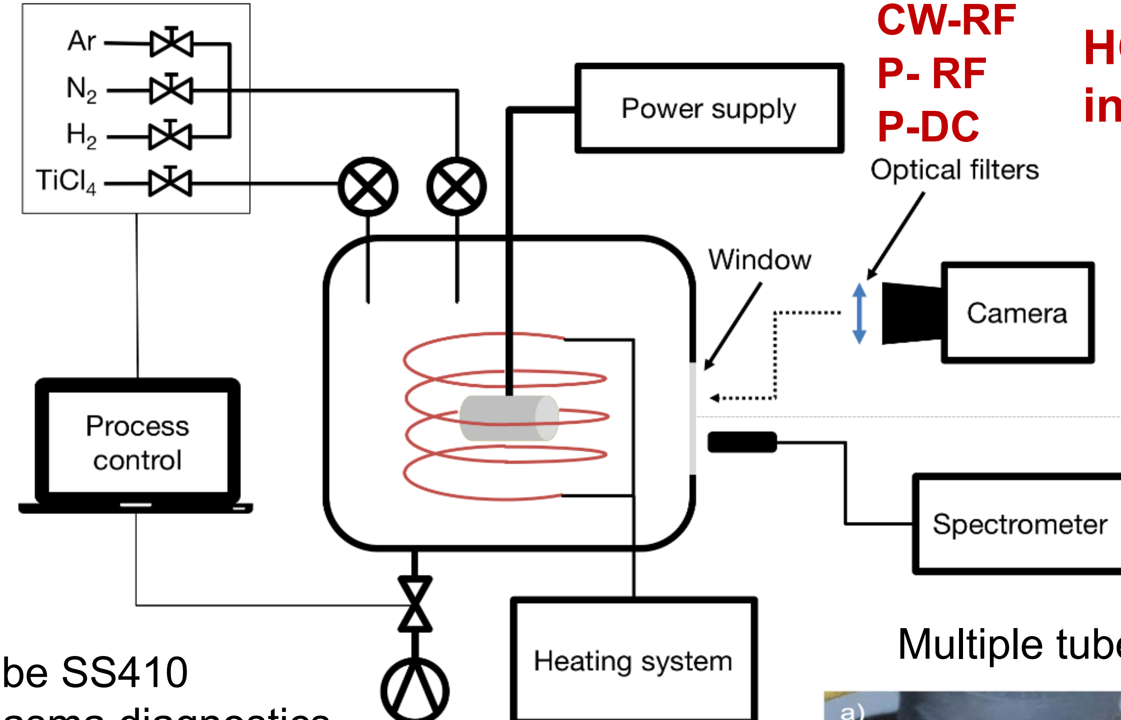
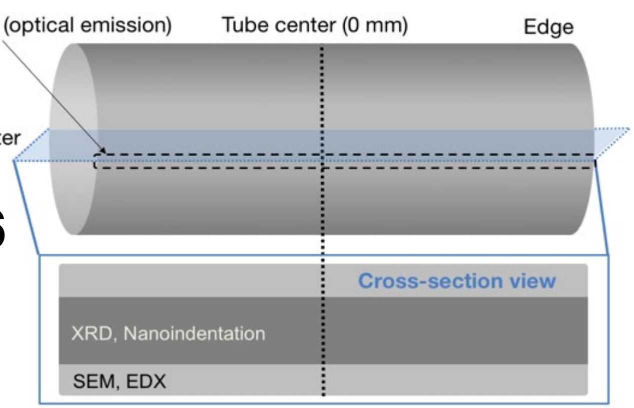
CW-RF
P- RF
P-DC

HC PECVD process in immersed tubes



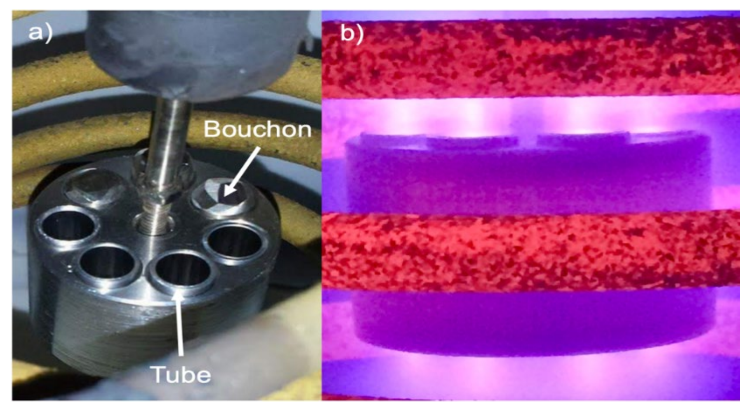
Single tube SS410
Slit for plasma diagnostics

L/D=3.6



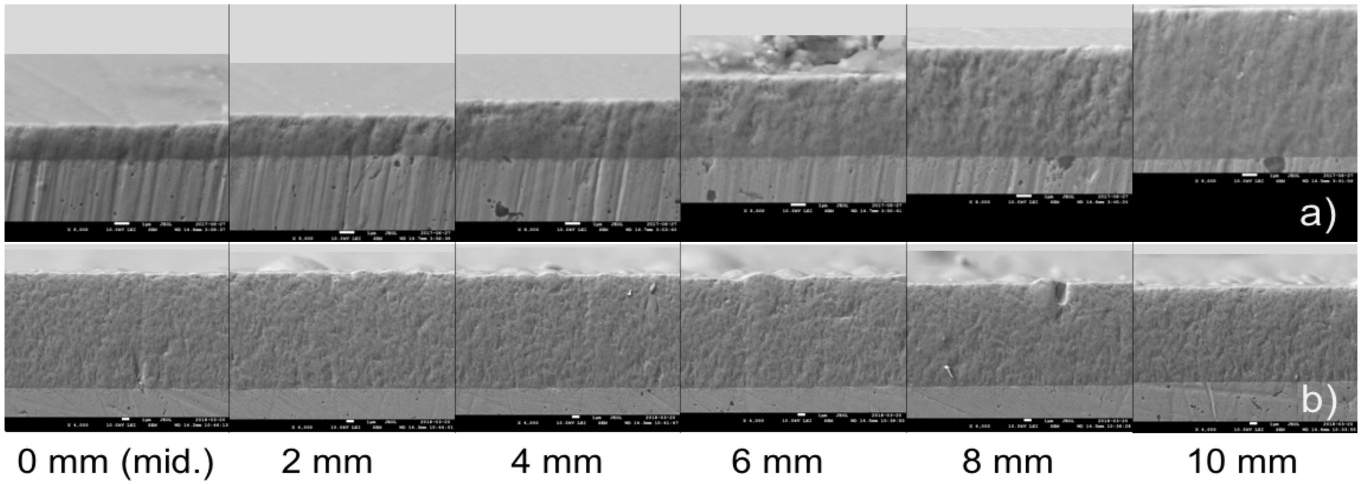
b)

Multiple tube deposition system



A. Kilicaslan et al., Surf. Coat. Technol., 377 (2019) 124894

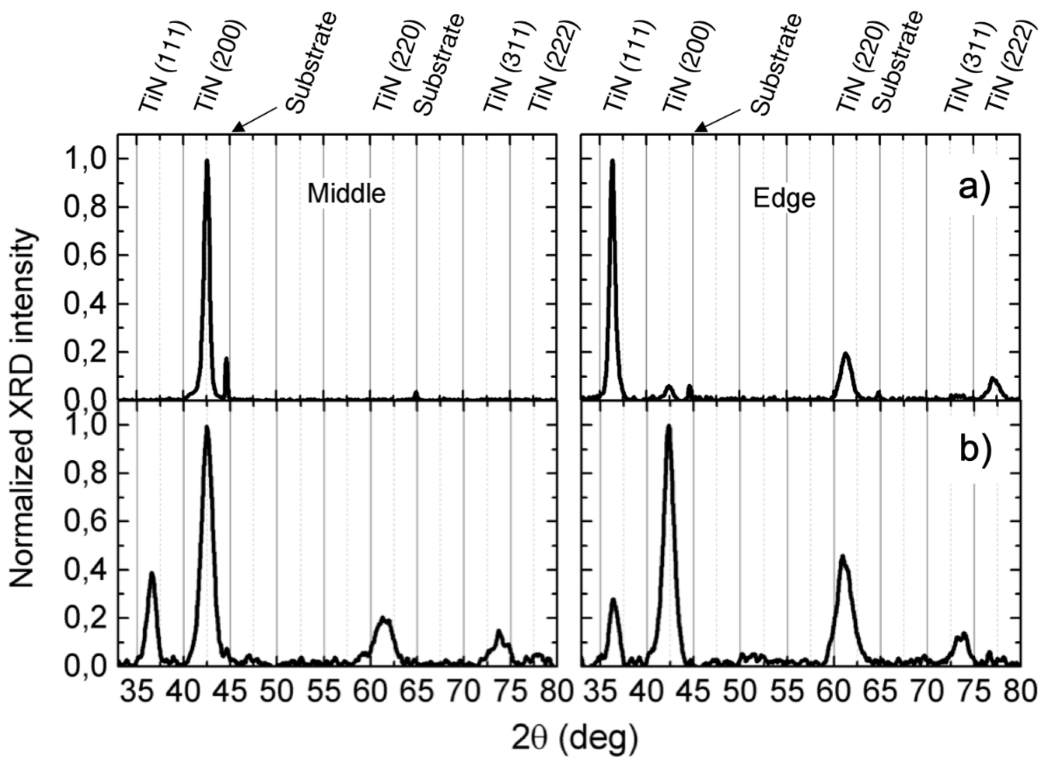
TiN coating microstructure along the tube axis



CW RF

SEM cross-sections

Pulsed-DC



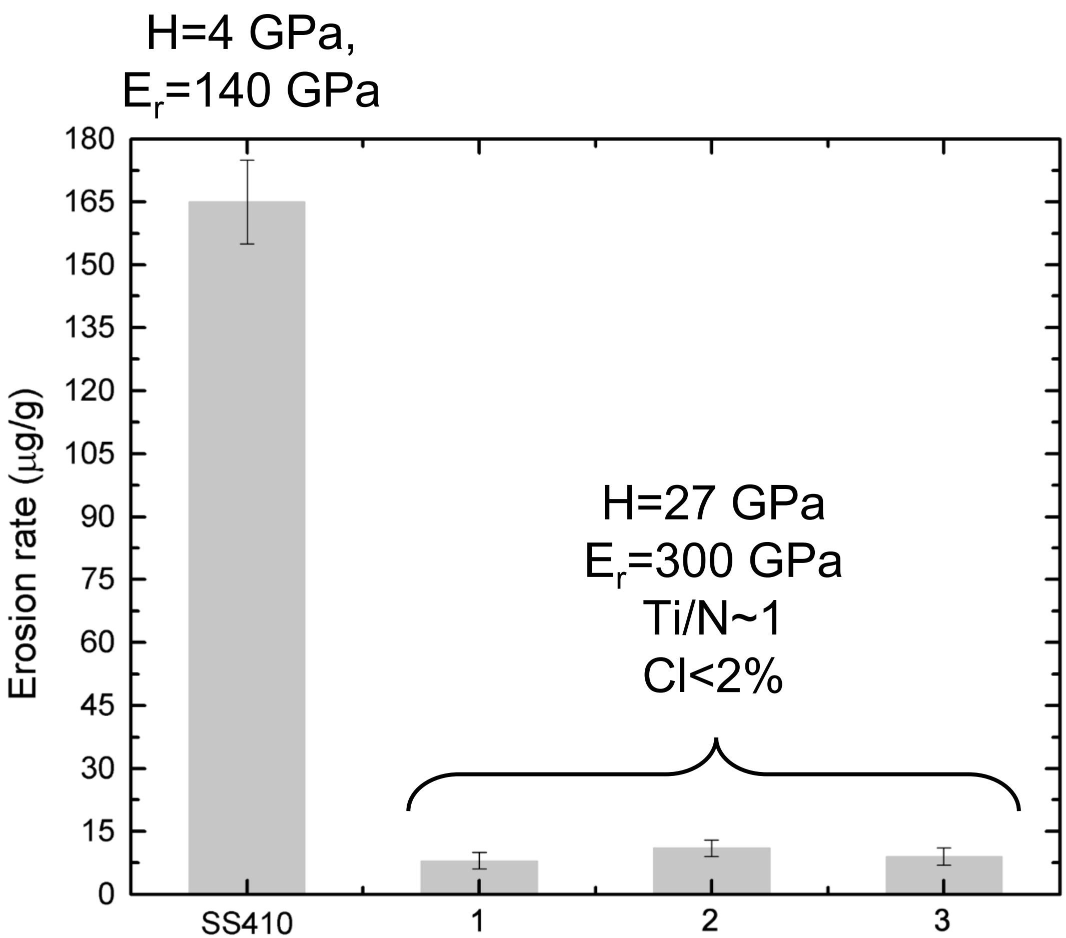
CW RF

XRD

Pulsed-DC

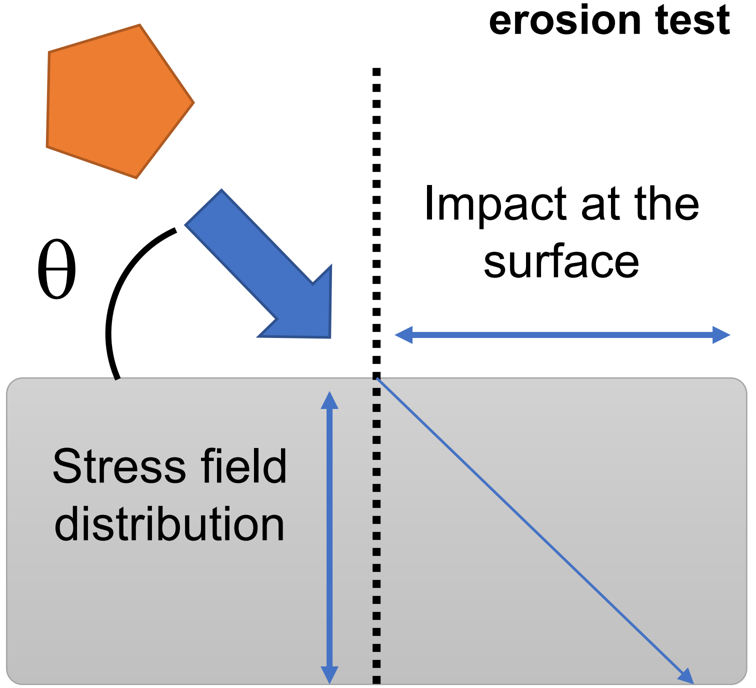
A. Kilicaslan et al., Surf. Coat. Technol., 377 (2019) 124894

Inside-tube erosion test results



Improvement of erosion resistance of TiN coated tube by a factor of 15-20 compared to SS410.

Grazing incidence solid particle erosion test

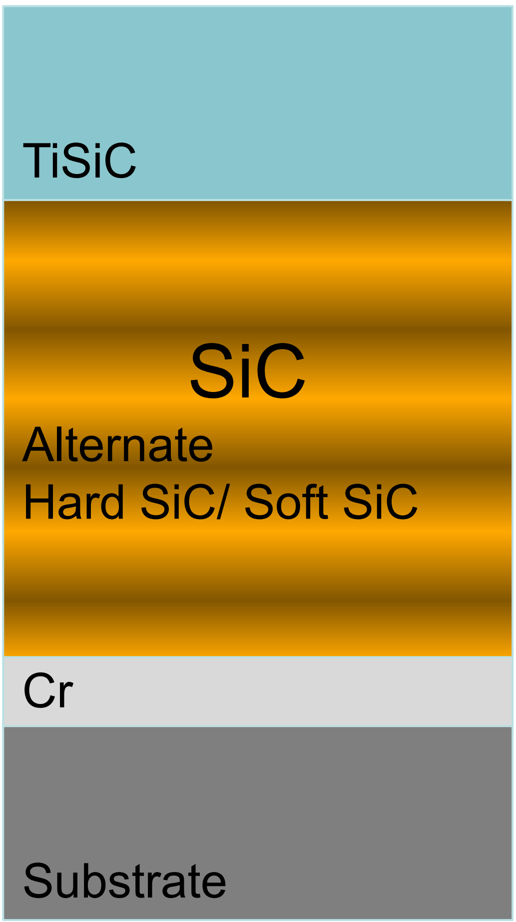


Low particle impact angle reduces the stress depth during impact.
The coating thickness to protect the substrate can be lower.

A. Kilicaslan et al., Surf. Coat. Technol., 377 (2019) 124894

Super-elastic erosion resistant coatings
Trampoline effect

25 µm thick SiC/TiSiC multilayer



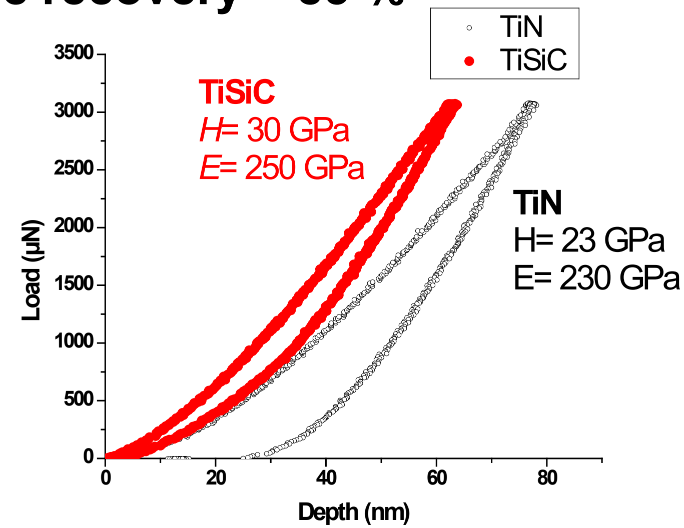
Hardness
Wear resistance
Elasticity/plasticity

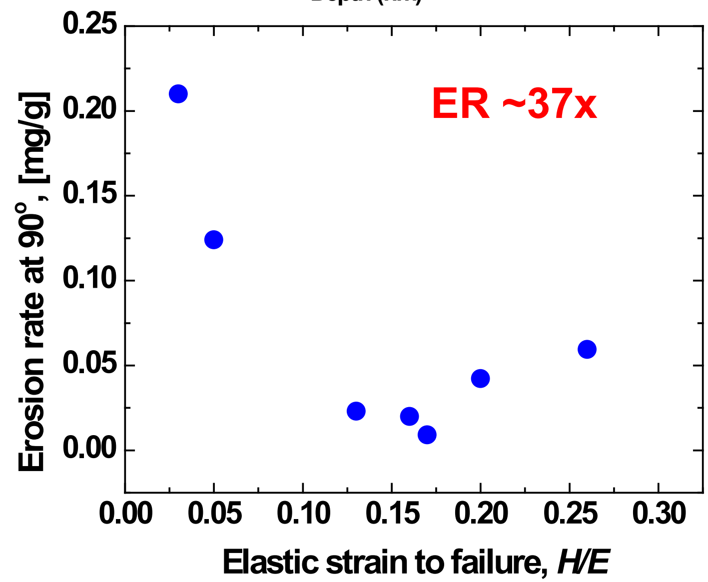
Thickness
Adhesion
Corrosion resistance
Damping

Adhesion

50 µm
Alumina
particles

Elastic recovery ~ 85 %

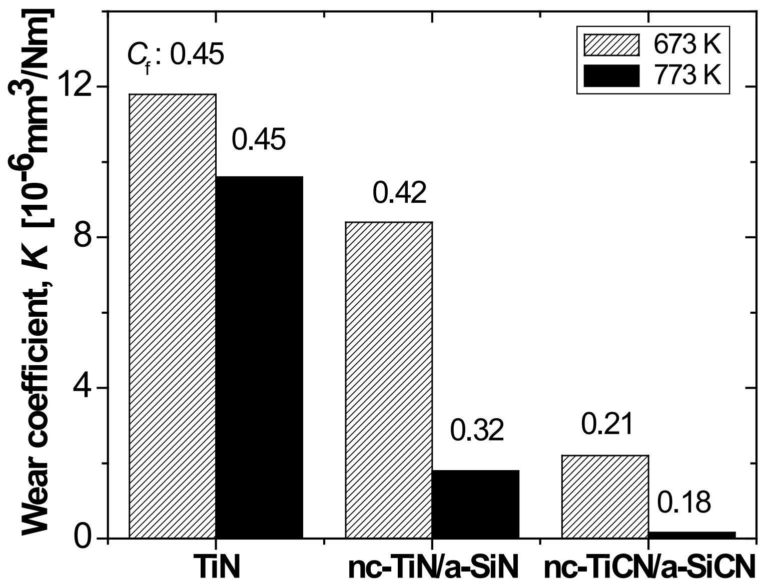


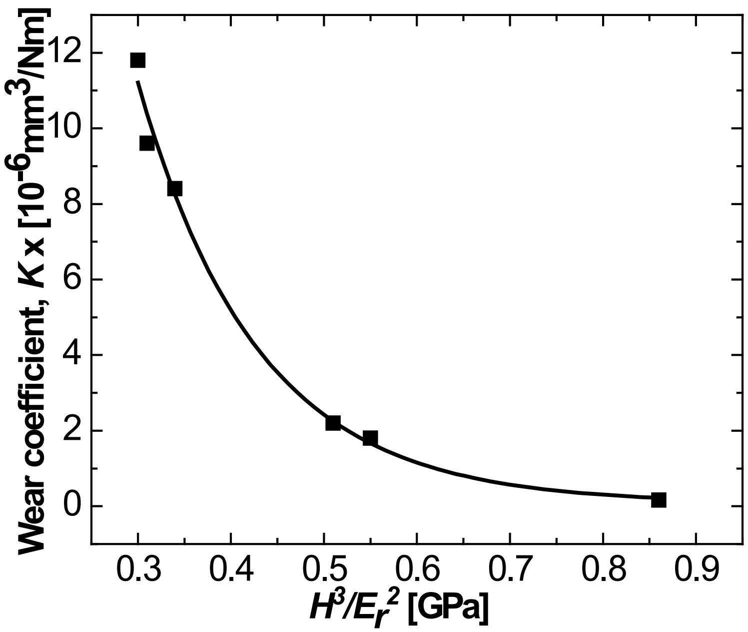


S. Hassani, et al., Surf. Coat. Technol., 205 (2010) 1426

Wear rate vs. H^3/E^2 : experiment

Wear conditions (pin on disk):
Alumina ball (6 mm dia), sliding speed 1.8 m/min, load 2 N





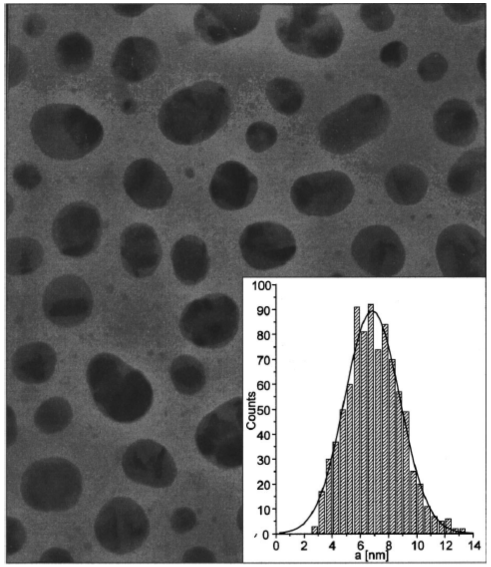
S. Guruvenket et al., Surf. Coat. Technol. 2009

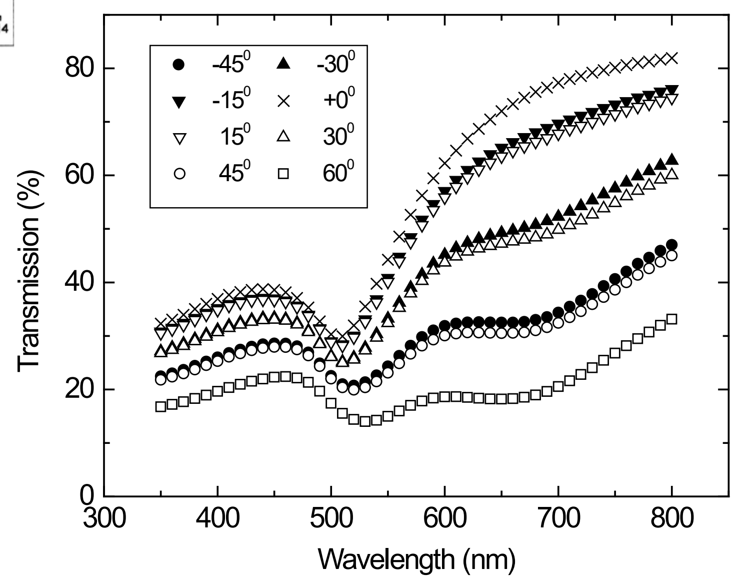
Wear and corrosion protection – C-based films

Courtesy of Ali Erdemir, Argonne National Laboratory

Quest for the red color: Au/SiO_2 nanocomposites

Spherical particles





<u>Ellipsometry:</u>

D. Dalacu et al., JAP 2000

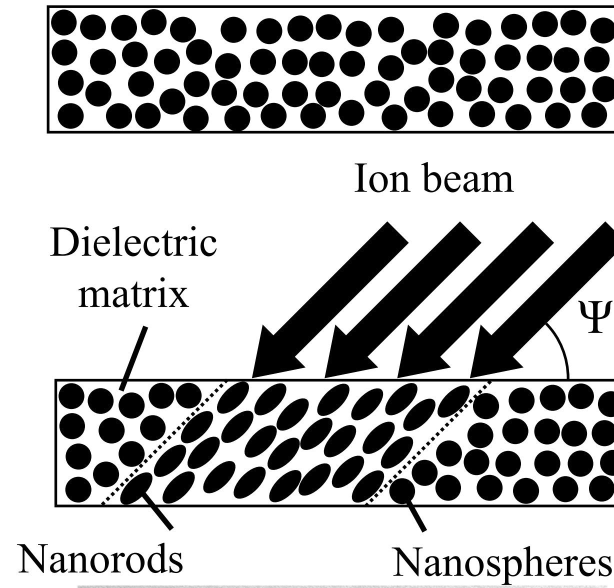
<u>Nanorods:</u>

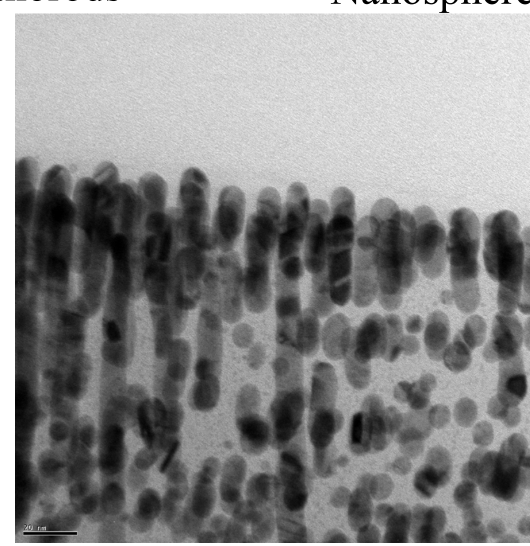
J.-M. Lamarre et al., TSF 2004

<u>NLO properties:</u>

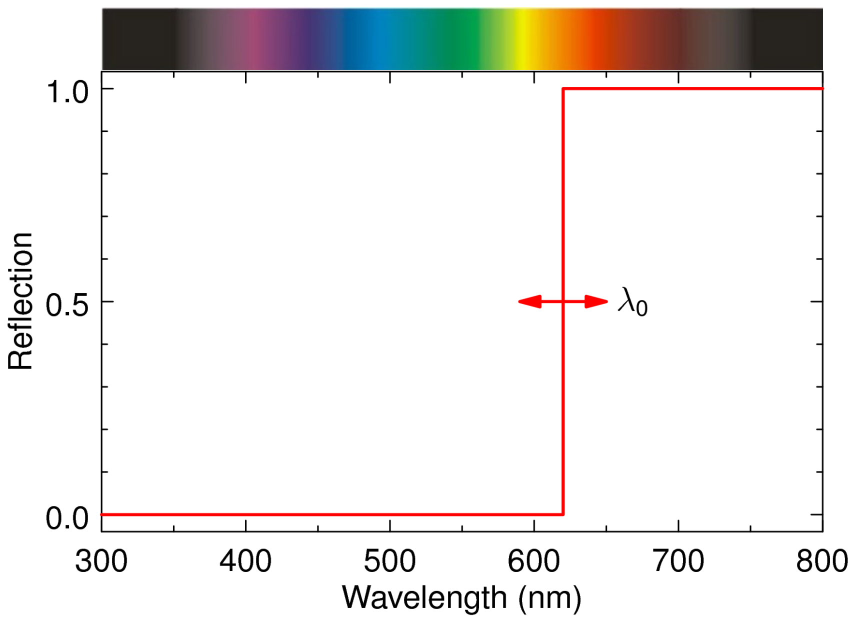
J.-M. Lamarre et al., Opt. Comm. 2008

Nanorods





Definition of the target red color



Requirements:

- Attractive color
- Color doesn't depend on viewing angle
- Unexpensive and non-toxic materials
- High scratch, wear and corrosion resistance

3 layer design

Ideal reflection spectrum

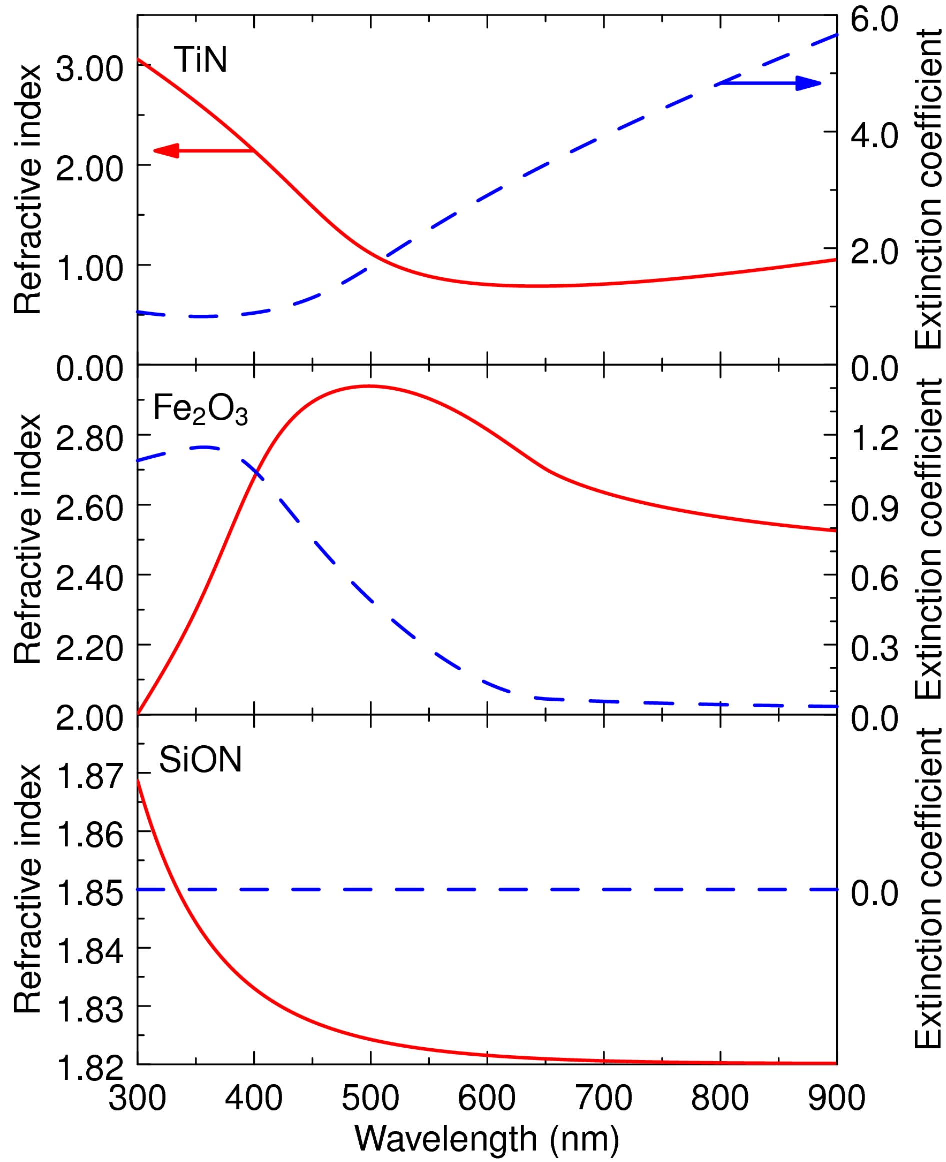
Target color coordinates

Layer 3	SiON	Antireflective layer Protective layer
Layer 2	Fe_2O_3	Absorbing layer
Layer 1	TiN	Reflective layer Hard layer Adhesion layer
Substrate	Stainless Steel	

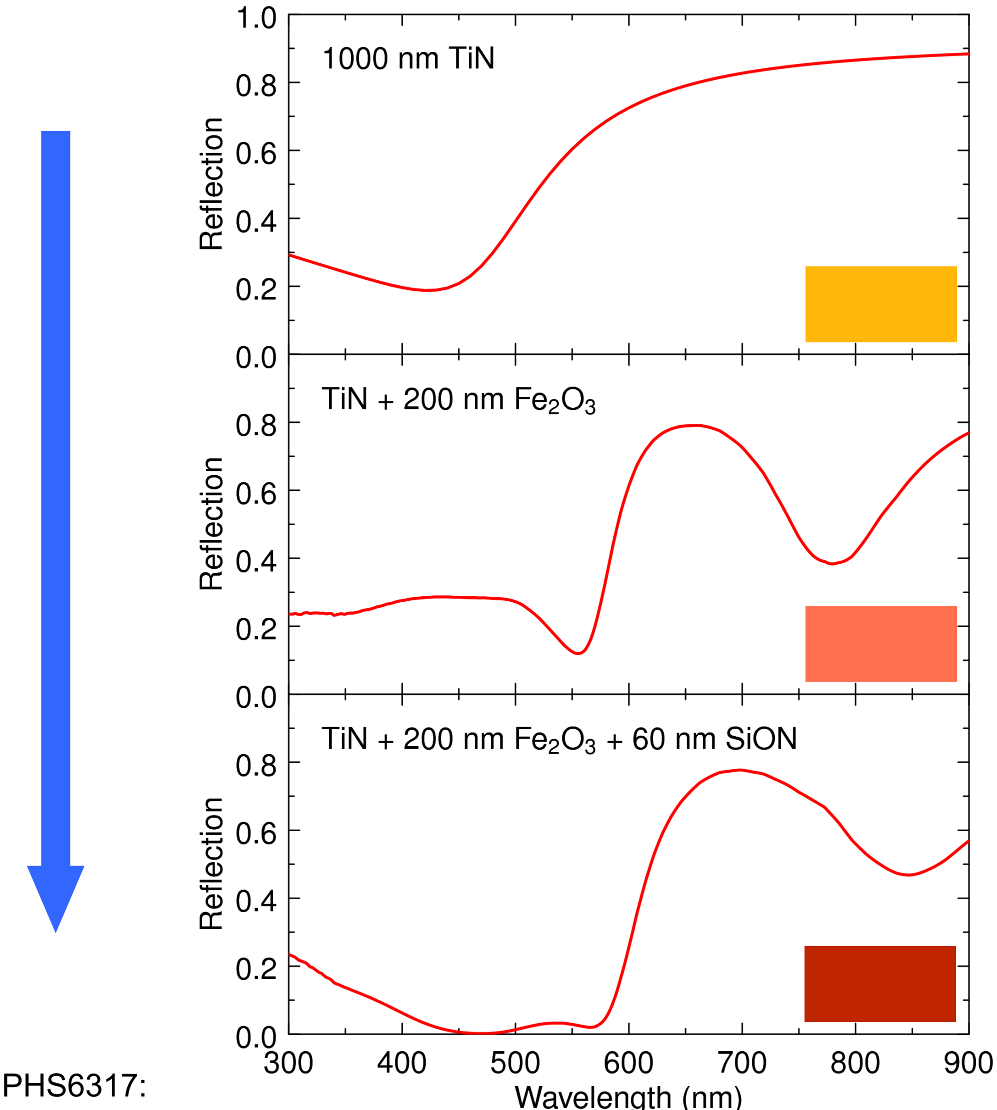
R. Vernhes et al., Proc. SVC, 2010

Dispersion curves of single coatings

Single films measured by ellipsometry



Color maps simulations



Deposition of single films of TiN, Fe_2O_3 and SiON

Evaluation of *n*,*k* by ellipsometry

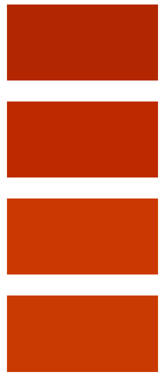
Generation of series of reflection spectra

Calculation of color coordinates

Generation of color maps in RGB color space

Reflection spectra of deposited coatings

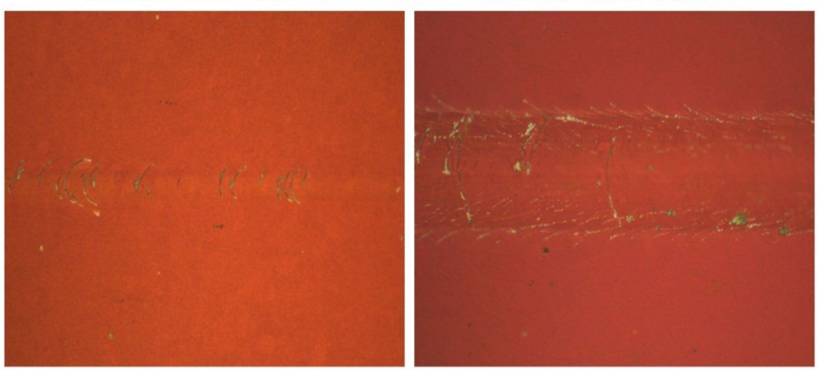
Sample 1
Sample 2
Sample 3
Sample 4



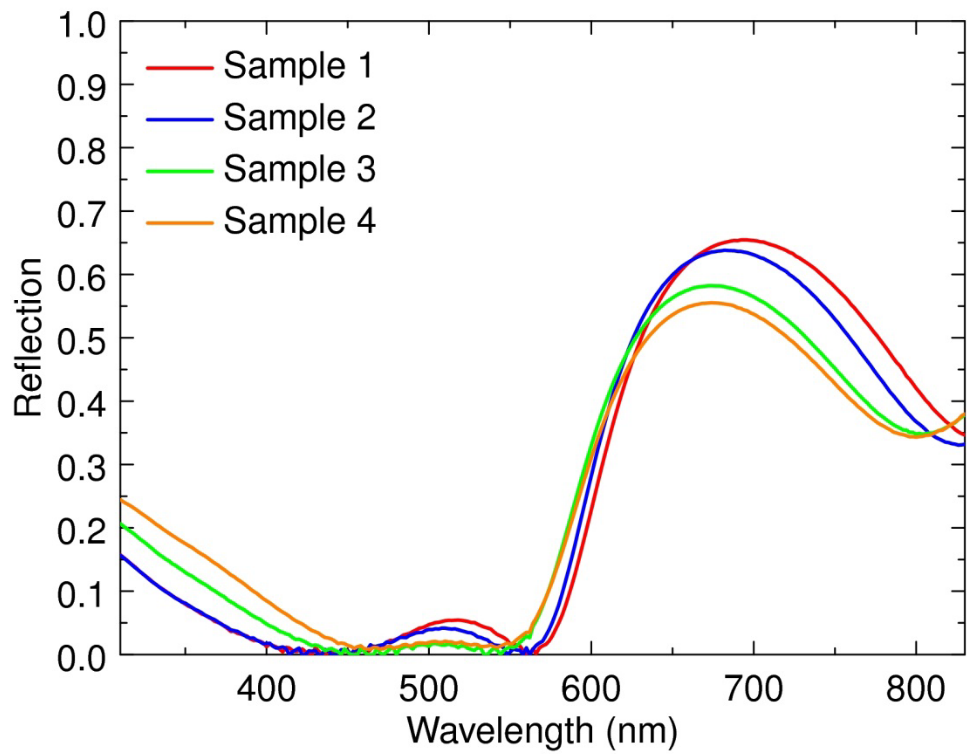
Enhancement of the scratch resistance

Fe_2O_3/SiON coating
Critical load: 0.34 N

TiN/Fe_2O_3/SiON coating
Critical load: 5.65 N

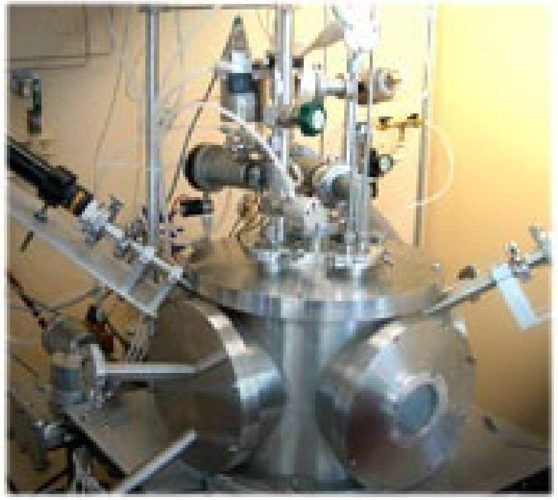


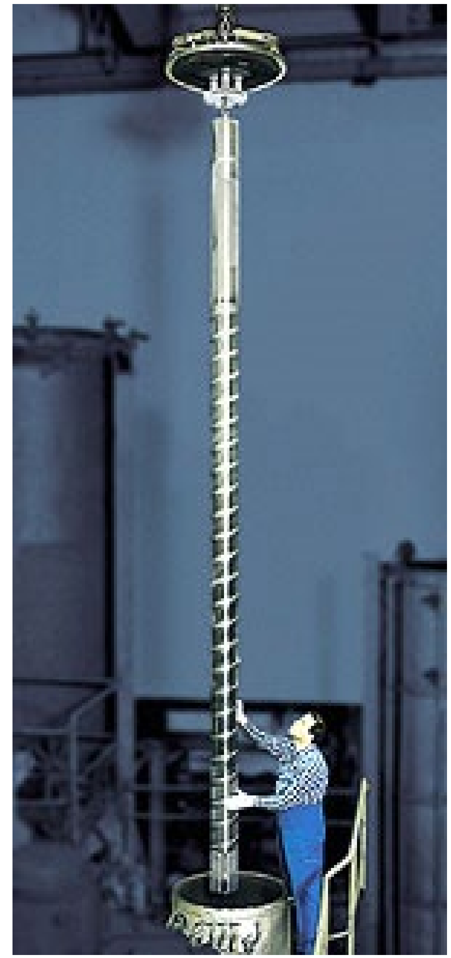
Reflection spectra of red coatings measured by spectrophotometry



R. Vernhes et al., Proc. SVC, 2010

From laboratory to industrial scale

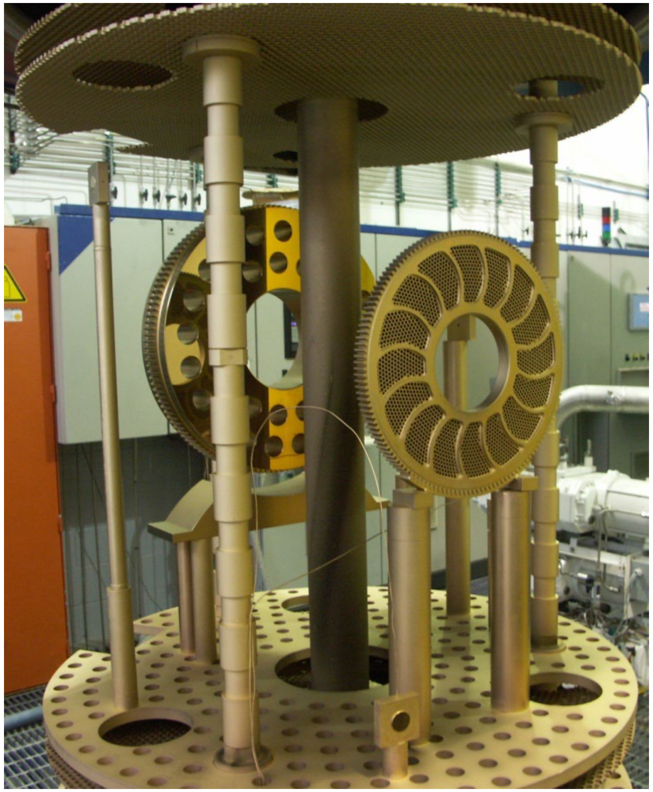




Multi-zone PECVD-PVD system

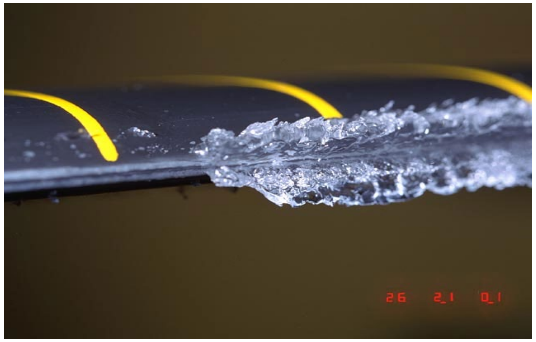
Industrial deposition system for the fabrication of DLC coatings for automotive parts and other applications. Each chamber contains six 1.6 m long electrodes. **(Courtesy of Hauzer Techno Coatings)**

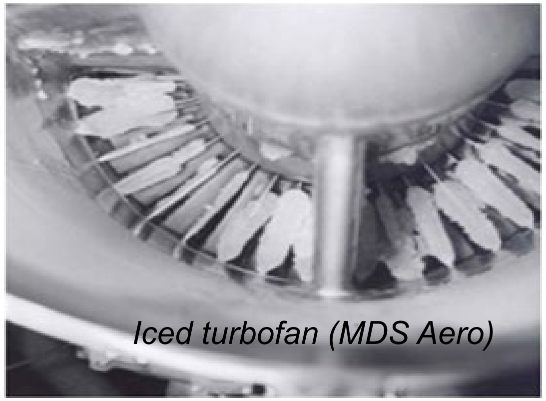
PECVD system for hard protective coatings



Example of a commercial system for the deposition of hard protective coatings: 1.6 m^3 volume chambers, metal carbides, nitrides and borides from halide precursors, 1,600 kg of parts coated in one run in high power medium frequency pulsed plasmas (Rubig power supplies) **(Courtesy of PATT Technologies Inc., Canada)**

Aircraft engine: Ice accretion





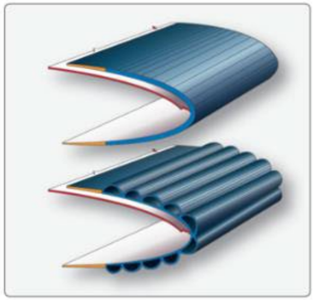
Iced turbofan (MDS Aero)

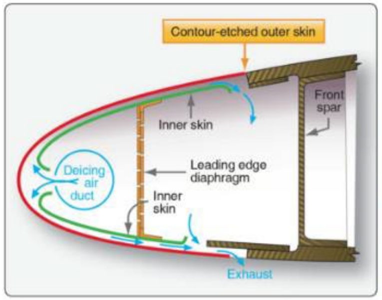
Ice accretion on aircraft caused several severe accidents, which killed crews and passengers and destroyed aircrafts

In flight, ice forms from **supercooled water droplets** with a diameter ranging from **10 µm to 250 µm** at 0 to -20°C

3 main problems:
- Liquid water freezing
- Frost formation
- Snow adhesion

Current Solutions – Active systems





Pneumatic Boots

- Add weight
- Only apply to wings

Heating systems

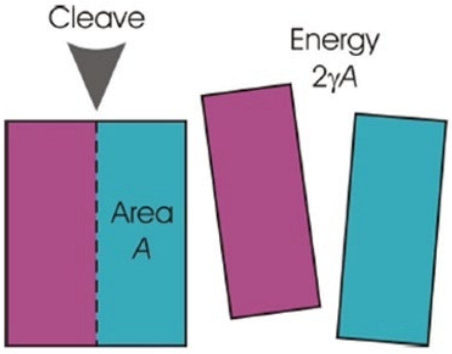
- Add weight
- Increase fuel consumption

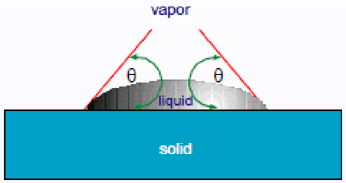
Glycol spraying

- Must be applied on ground
- Not environmentally friendly

POLYTECHNIQUE MONTRÉAL
UNIVERSITÉ D'INGÉNIERIE

Surface energy forces





Forces within liquids and solids and across their interfaces include:

Polar Interactions:

- Ion-ion (+ -)
- Ion-dipole (H-bond)
- Dipole-dipole
- Dipole-induced dipole

Non-Polar interactions:

- Hydrophobic (dispersion forces)

Polar — Higher energy — stronger

weaker — Non-polar — Lower energy

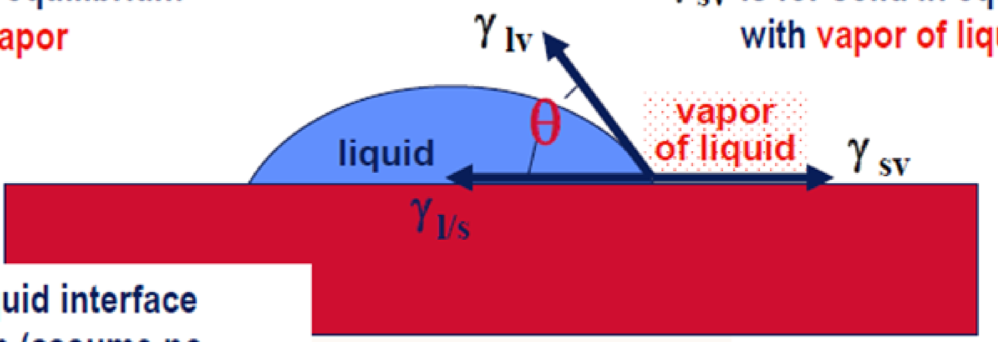
These forces exist between individual molecules

Aircraft engine: Ice accretion

Force Balance at the Contact Angle (θ)

γ_{lv} is for liquid in equilibrium with its own vapor

γ_{sv} is for solid in equilibrium with vapor of liquid



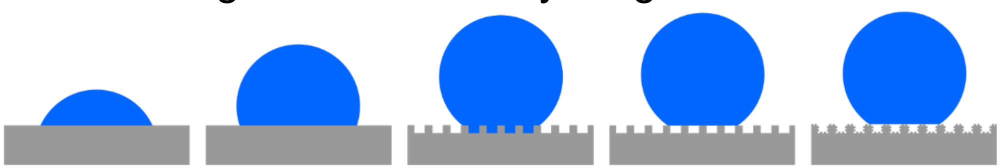
$\gamma_{l/s}$ is for solid-liquid interface at equilibrium (assume no swelling of solid by liquid)

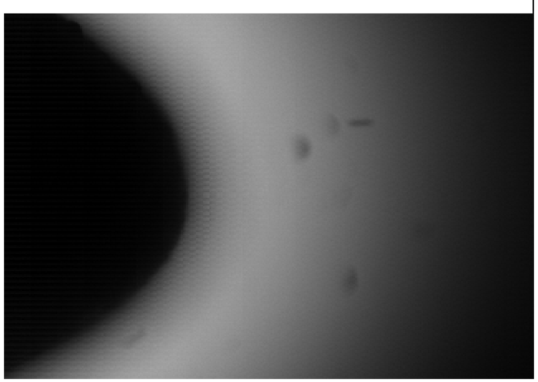
At equilibrium: $\gamma_{sv} = \gamma_{l/s} + \gamma_{lv}\cos\theta$ (Young-Dupré Eqn)

Ice accretion assessment

Superhydrophobic surfaces and icephobicity - Solution:

- Most extreme case of Cassie-Baxter wetting
- Inspired by lotus leaf
- Combine micro- and nano-scale features for hierarchical roughness
- Very high contact angle and water mobility
- Common fabrication: deposit hydrophobic coating on hierarchically rough surface





Durability assessment

- Expose sample to numerous icing/deicing cycles
- Observe sample degradation
- Droplets impacting on the surfaces rebound without freezing.
- Ice-phobic surfaces delay ice formation.

Wind-tunnel testing (Concordia U.)

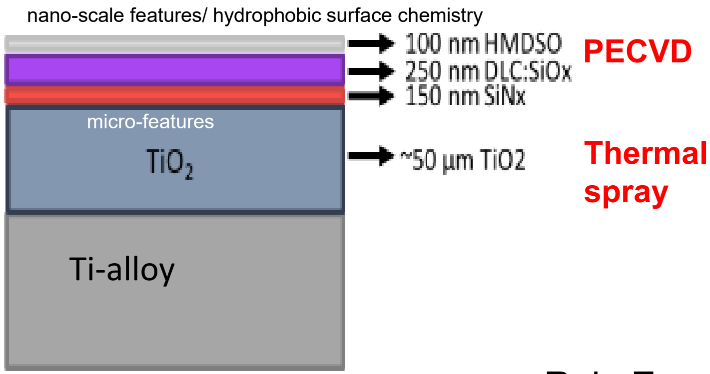
Real-time measurements of droplet/surface interactions via High speed (HS) camera monitoring

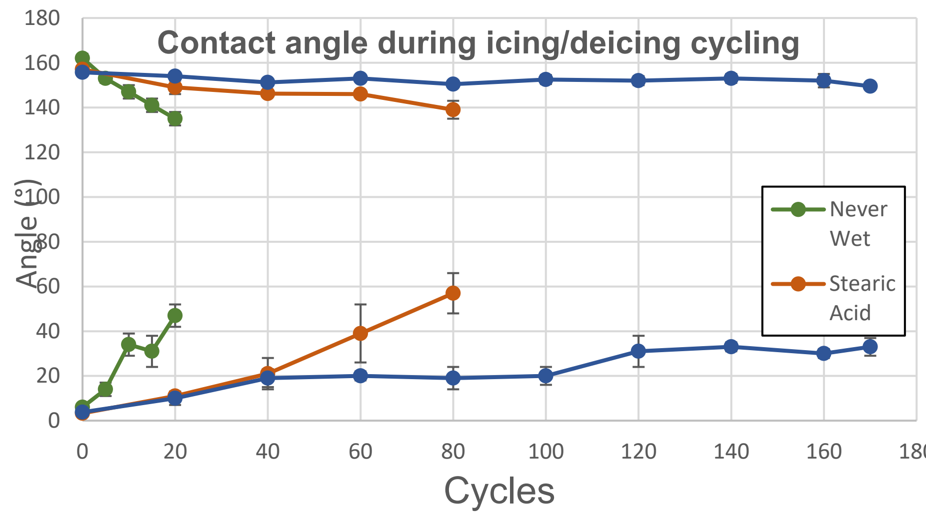
Conditions:

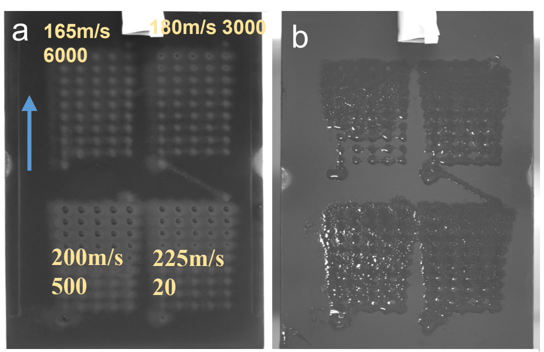
- Droplet size: 20 μm to ~1 mm
- Droplet T°: Room T° to -20°C
- Droplet speed: up to 50 m/s
- Holder T°: Room T°

Durable Icephobic Duplex Coating System

Thin-on-thick coating system
"hierarchical roughness"







Rain erosion of a) plasma-deposited DLC-based coating vs. b) stearic acid coating

Rain Erosion

- Tested number of impacts required for change in surface wettability
- No change after 6000 impacts at 165 m/s for DLC-SiO_x-based sample
- Droplet spreading is well-contained even after failure

- Durability - Icing/Deicing cycling
- Icephobicity - Ice Adhesion
- Durability - Rain Erosion

DLC-SiO_x -based top-coating

- Superior durability
- Maintained surface micro- and nano-structure
- Maintained droplet mobility even after 170 cycles
- Coating neither pierced nor removed
- Only chemical changes observed

*S. Brown, et al., Surface and Coatings Technology, **401** (2020) 126249.*

Development of functional thin film systems

Aerospace applications:

- Erosion-resistant coatings
- Ice-phobic coatings

Optical and energy applications:

- Optical security devices
- Architectural glazings
  - Low-emissivity windows
  - Hard optical coatings
  - Smart (thermochromic) windows
  - New functions

Need for advanced security devices

Counterfeiting causes significant issues worldwide

Economic impact

Loss of revenue, company image, etc.

$ 1,770,000,000,000 US/year in 2015[1]

Social impact

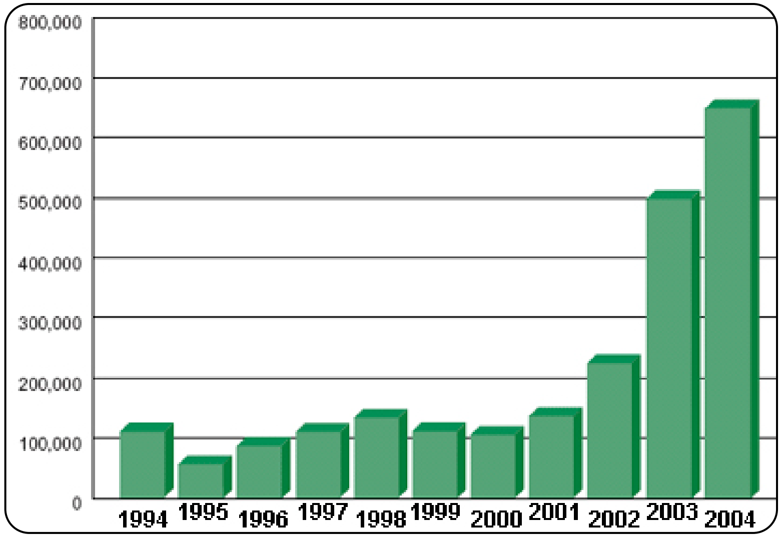
Public's safety, health hazards, etc.

For example, up to 70% of pharmaceutical products in developing countries such as Nigeria are counterfeit[2]

1. Business Action to Stop Counterfeiting and Piracy
2. World Health Organization

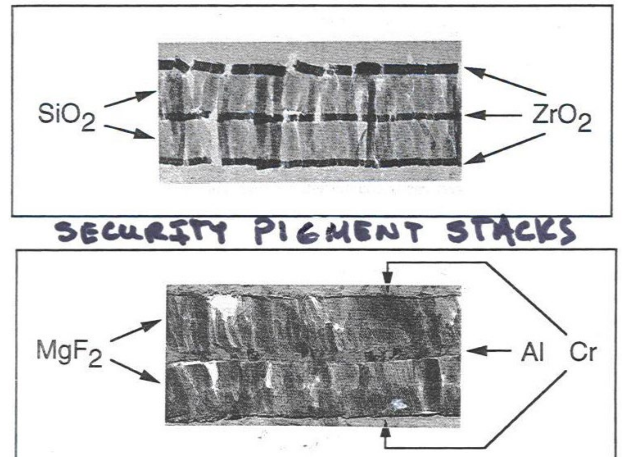
B. Baloukas and L. Martinu, in: Optical thin films and coatings, edited by A. Piegari, and F. Flory, Woodhead Publishing, 2013, Elsevier 2018 (2nd edition).

Interference security image structures



Total number of Canadian banknotes passed and seized

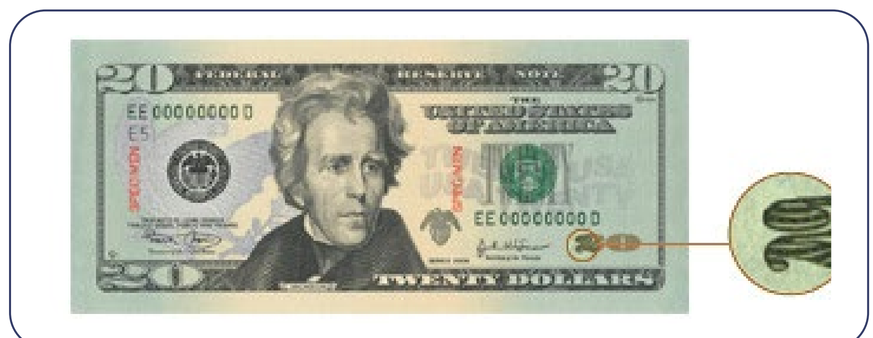
http://www.rcmp.ca/scams/counter_e.htm



Optically variable devices - OVDs

Canadian banknote

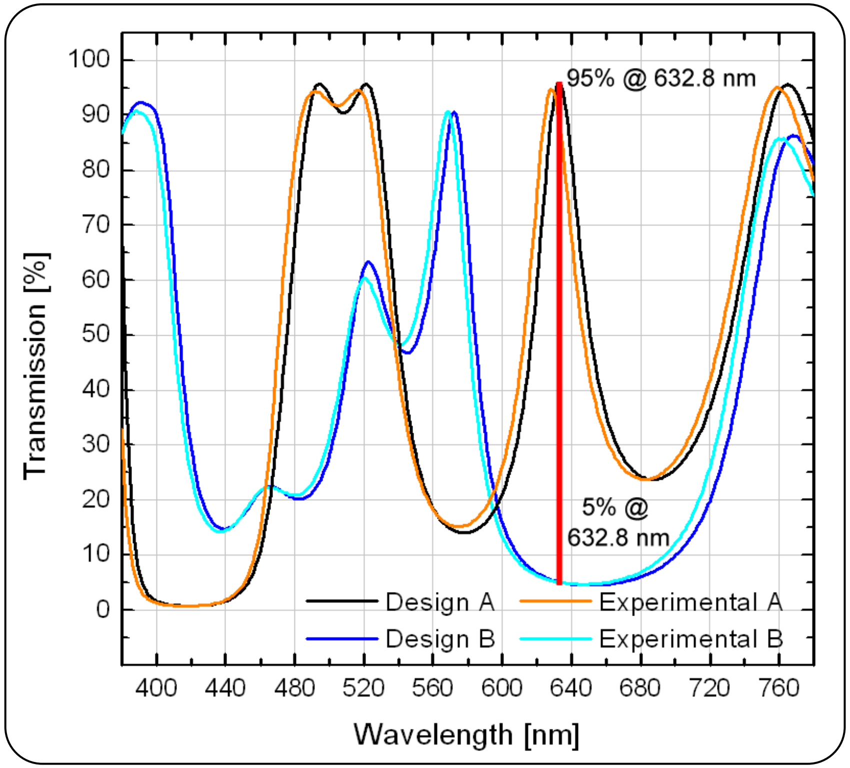
Optically variable ink



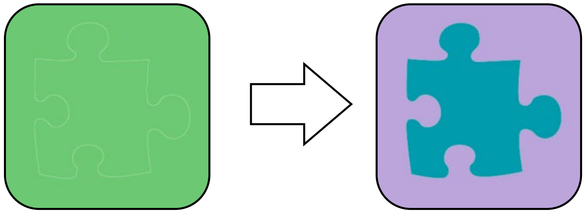
Metameric interference filters

Metamerism: Two objects with different reflection or transmission spectra present the same color under a specific light source and for a specific human observer.

Creation of a hidden image effect by combining two metameric interference filters:



Hidden image concept (0 and 50 degrees)



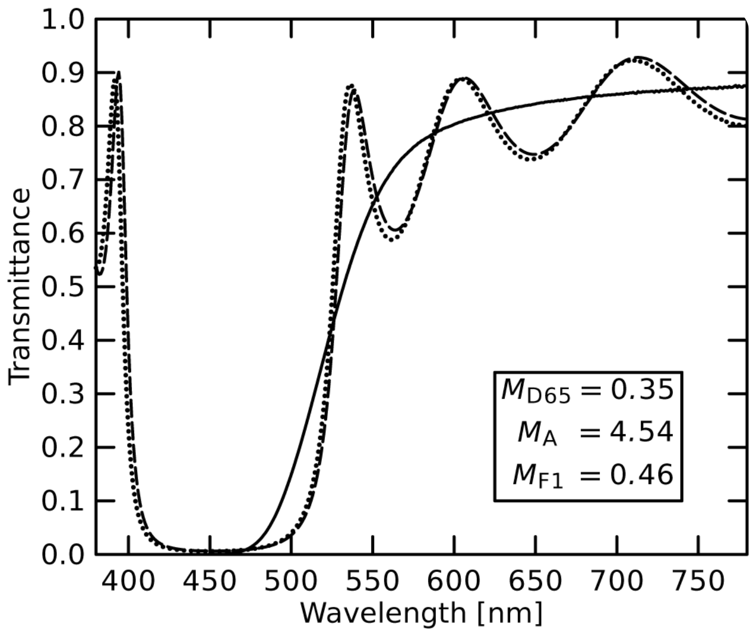
- Pairs of complex metameric filters are **highly sensitive to deposition errors**.

B. Baloukas, L. Martinu, Appl. Opt. 2008

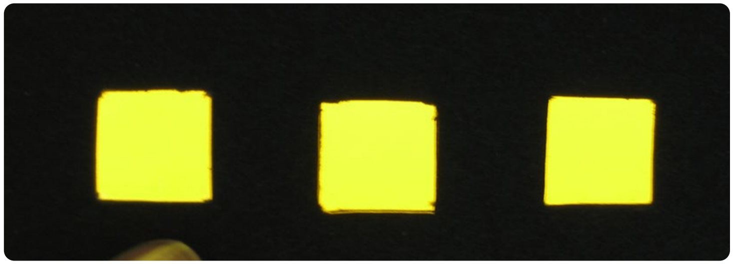
Metamerism in transmission: Polymer film and interference filters

One of the filters is replaced by a **simple non-iridescent material** (NIM):

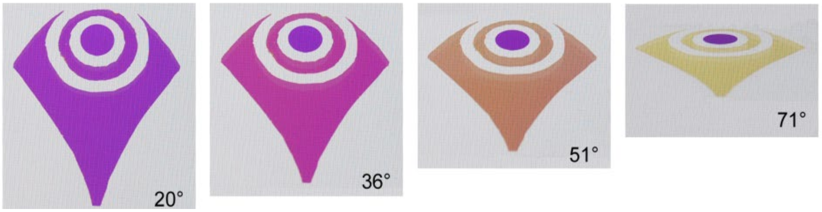
Benefits: Presence of a color reference;
Easy to authenticate by light in transmission;
Automatic authentication by laser scanning.



Spectra for Kapton® film (continuous line), metameric filter design (dashed line) and deposited filter (dotted line).



Device based on a filter and two Kapton® windows.

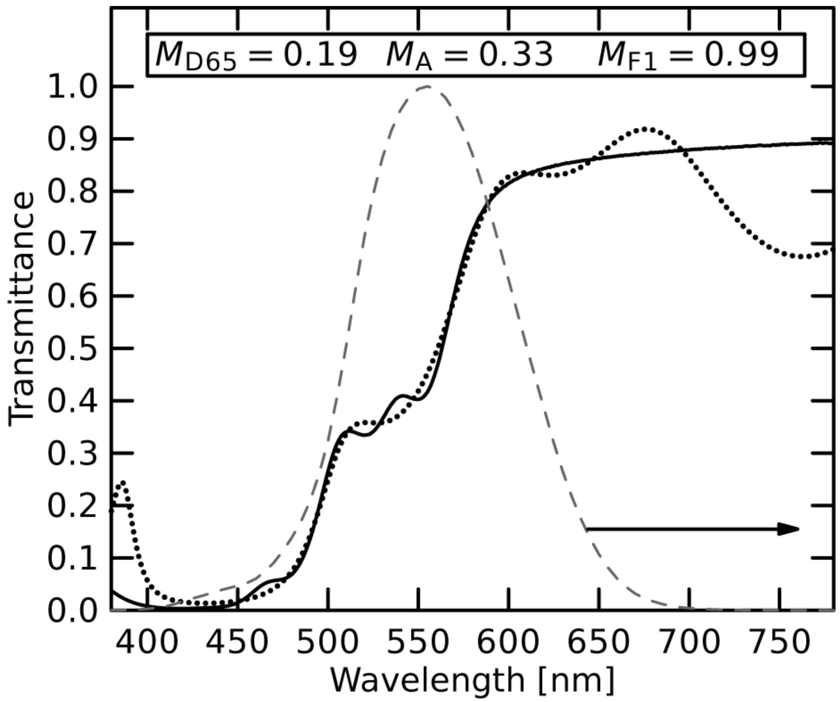


Transmission metameric device combining a transparent coloured paint and an interference filter.

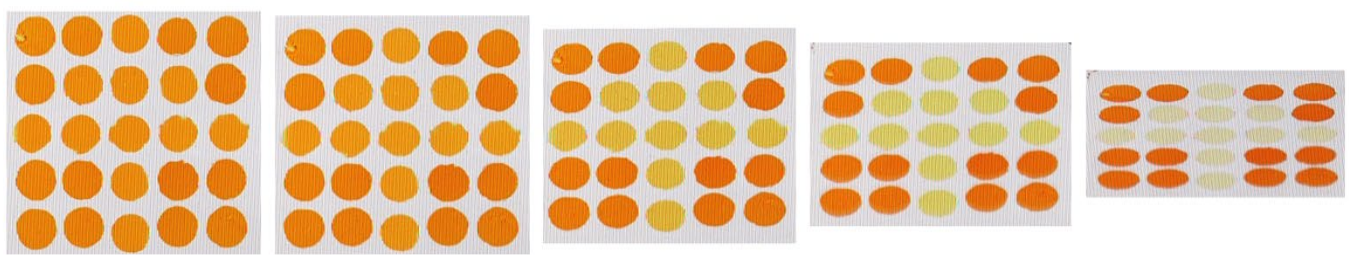
B. Baloukas, Appl. Opt. 2008
B. Baloukas et al., Appl. Opt. 2010
B. Baloukas et al., SolMat, 2011

Design strategy for metameric filters

Color tolerances are inversely proportional to the luminous efficiency curve of the human eye (dashed line): Decrease of the number of layers



Transmission spectra: orange Pébéo transparent paint.



B. Baloukas, Appl. Opt. 2008

E. Cetinorgu-Goldenberg et al., Applied Optics, 50 (2011) 3351-3359

Current electrochromic devices

- Variable reflectivity mirrors for the automotive industry (glare control);
- Smart windows for energy control and comfort.

Smart window by SageGlass

Rear view mirror by Gentex

Boeing 787 Dreamliner
www.aerodefensetech.com

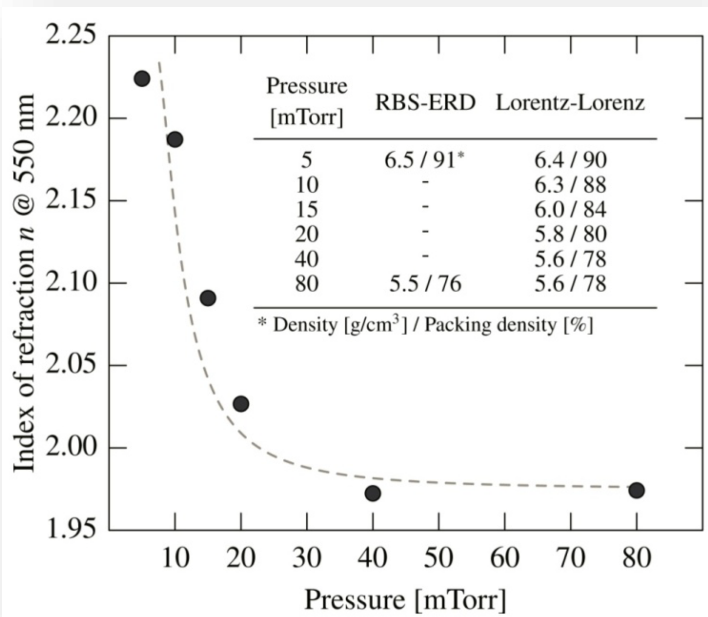
C. G. Granqvist, “Progress toward roll-to-roll processing of inorganic monolithic electrochromic devices on polymeric substrates,” *Sol. Energ. Mat. Sol. C.,* **92** (2) 2008.

C. G. Granqvist, *et al.*, “Progress in chromogenics: New results for electrochromic and thermochromic materials and devices,” *Sol. Energ. Mat. Sol. C., vol.* **93** (12) 2009.

Electrochromic coatings

Chromogenic materials:
C.G. Granqvist, Sol. En. Mater.
Solar Cells, 2007

Sputtered dense/porous WO_3

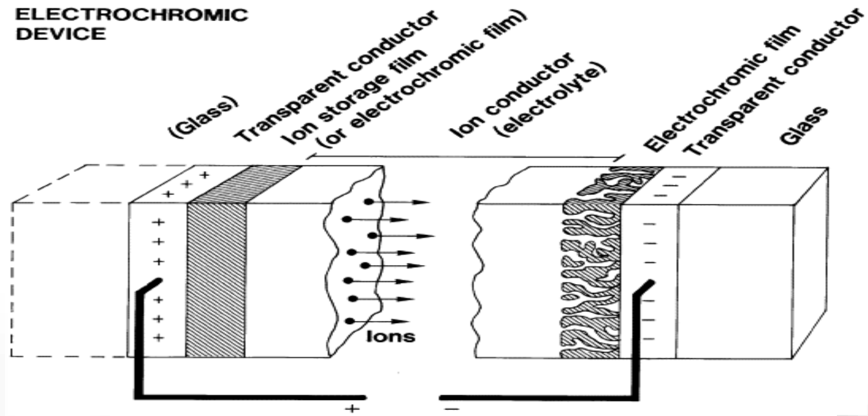


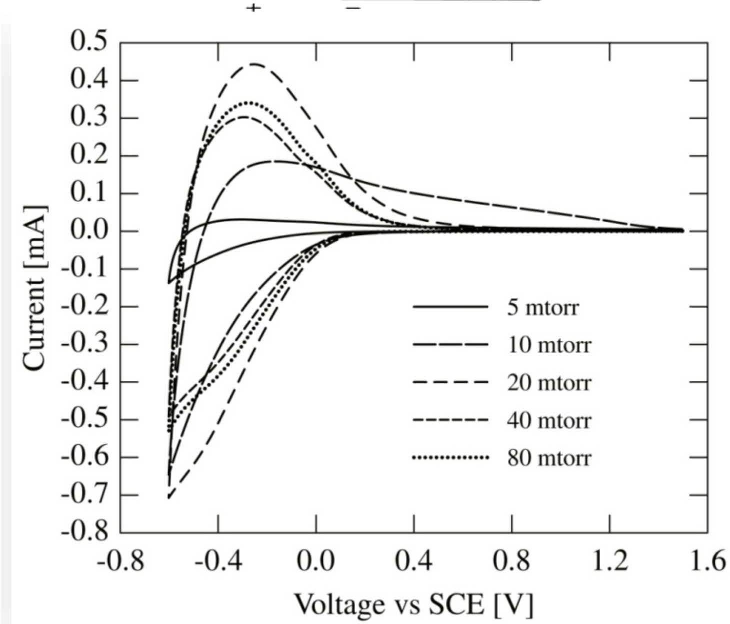
Pressure [mTorr]	RBS-ERD	Lorentz-Lorenz
5	6.5 / 91*	6.4 / 90
10	-	6.3 / 88
15	-	6.0 / 84
20	-	5.8 / 80
40	-	5.6 / 78
80	5.5 / 76	5.6 / 78

* Density [g/cm^3] / Packing density [%]

Refractive Index as a function of pressure.

B. Baloukas et al., Appl. Opt. 50 (2011) C41-C49

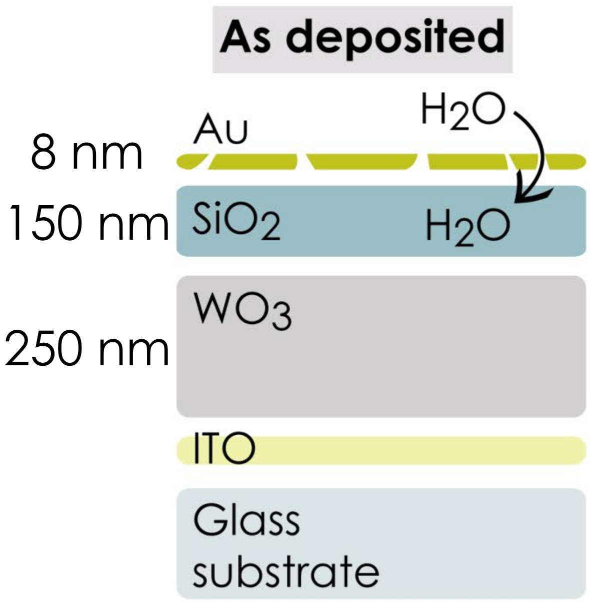




Cyclic voltammograms for WO_3 films prepared at different pressures.

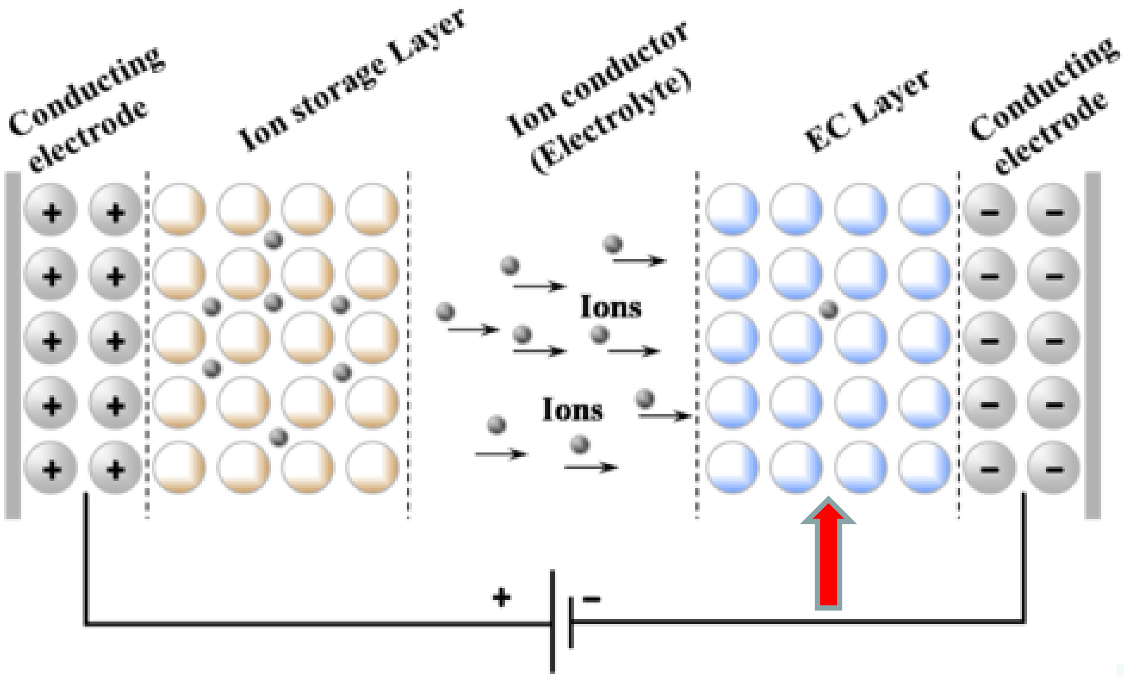
Deb devices

Simple all-solid state electrochromic devices (4 layers):



B. Baloukas et al., Appl. Opt.,50 (9) 2011

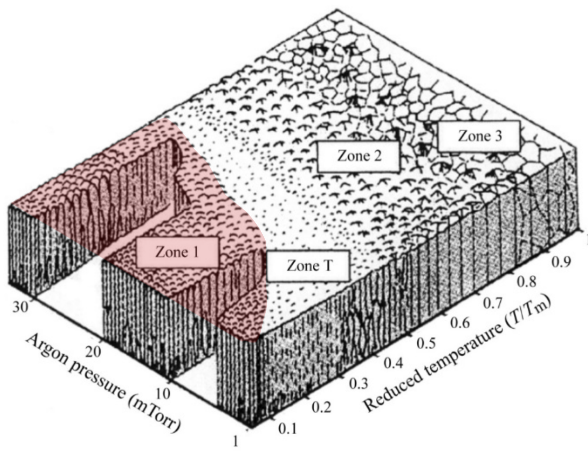
Electrochromic devices



Typical configuration of an electrochromic device.

Interference filter

Sputtered dense/porous WO_3



Structure zone model

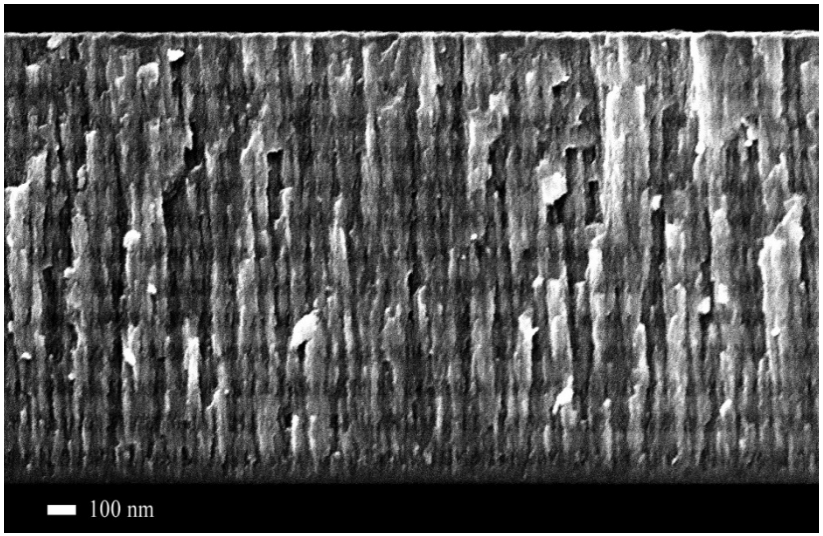
Variation of the refractive index by changing the deposition pressure.

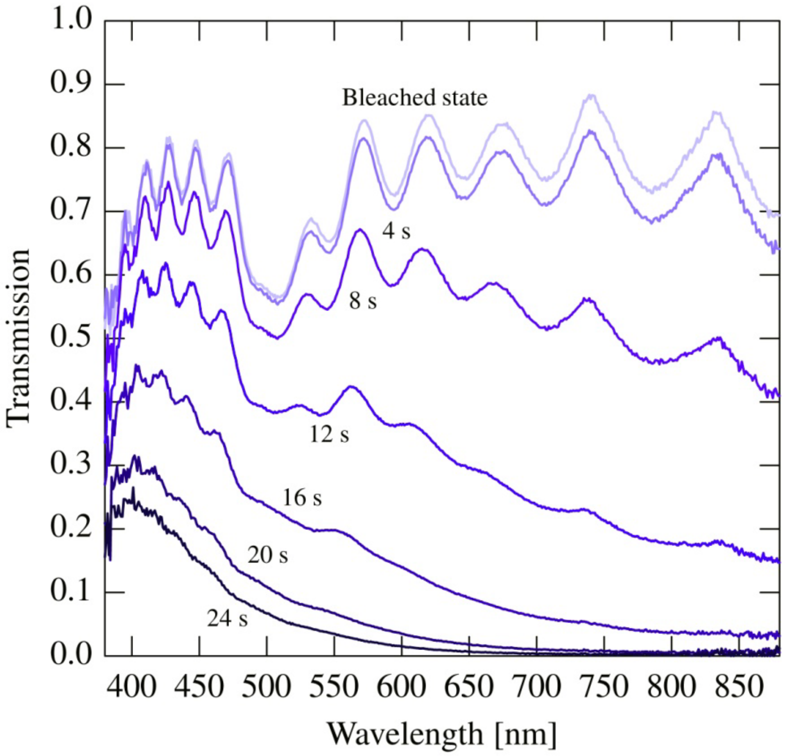
WO_3 is a transition metal oxide which has been extensively studied for its **electrochromic properties**.

The coloration process requires electron and **ion insertion**. Previous work has shown that sputtering WO_3 at a pressure of **10-20 mTorr** leads to optimal results.

Dense/porous WO_3 electrochromic interference filters - EIF

p-WO_3 / d-WO_3 : Δn = 0.2 (27 layers)



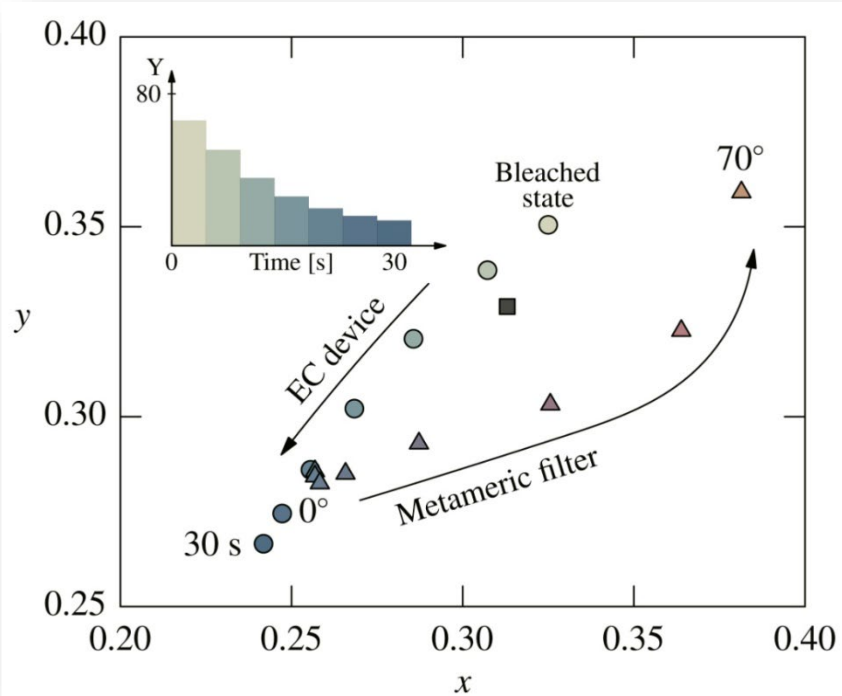


Transmission variation during a coloration cycle of the 27-layer porous/dense WO_3 filter.

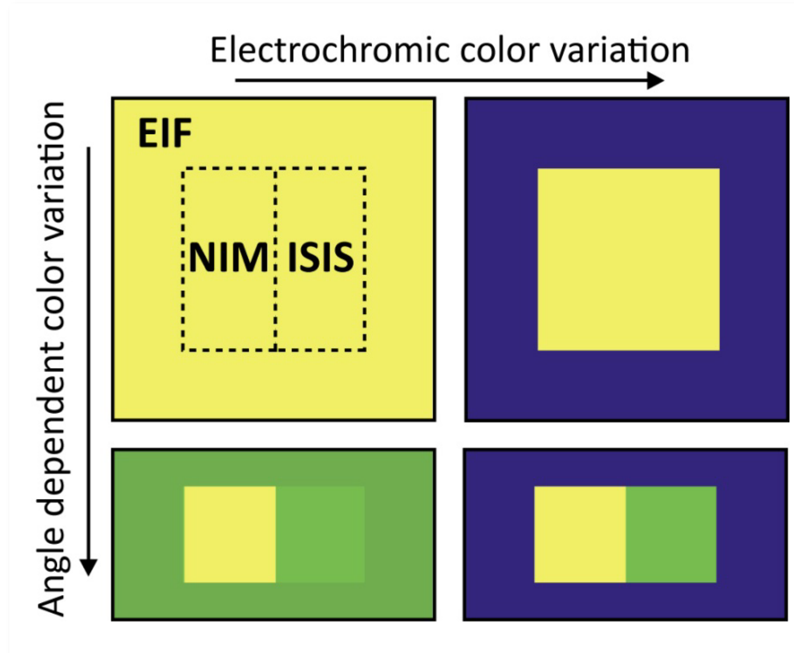
B. Baloukas et al., Appl. Opt. ***50*** *(2011) C41-C49.*
B. Baloukas et al., Sol. En. Mat. Sol. Cells ***95*** *(2011) 807.*
B. Baloukas et al., Appl. Opt. ***51*** *(2012) 3346.*

Nanocomposite p-WO_3 - SiO_2 / d-WO_3 : Δn = 0.6 (11 layers)

EIF's color variation



Color variation of the EIF during coloration (circles) and of the metameric interference filter as a function of the observation angle (triangles). Square - reference white, D65 illuminant.

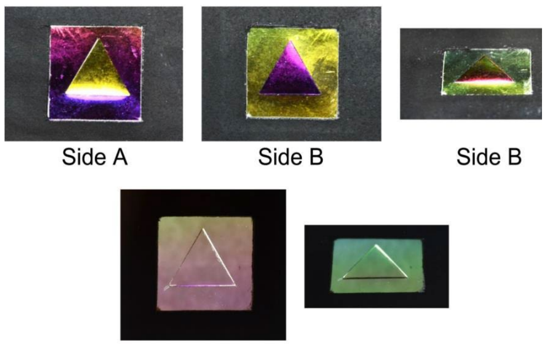


Possible active optical security devices.
Outer square – EIF
Center square - Non-iridescent material or an interference security image structure.

B. Baloukas et al., Solar En. Mat. Sol. Cells, 95 (2011) 807-815

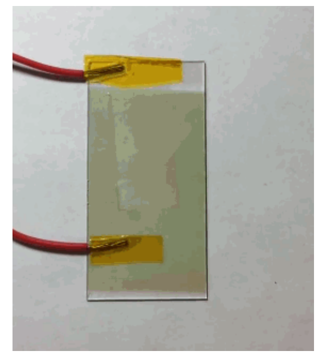
Toward smart multifunctional meta-surfaces

All-dielectric or Metal-dielectric interference filters



+

Electrochromism



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Combination

<u>Future generation of devices</u>

- More complexity (new effects and materials – more difficult to reproduce - security)
- Interactive and « smart »
- More durable
- Suitable for energy- and vision-related applications (architectural glass, glasses…)
- Opportunities of nanostructuring for new complementary functions

Banque du Canada

B. Baloukas and L. Martinu, in: Ch. 17 "<u>Optical thin films and coatings</u>", 2nd edition, A. Piegari, F. Flory, eds., Elsevier, 2018.

Saving energy for a sustainable future

"…a large fraction of the **energy delivered to buildings is wasted because of inefficient building technologies**." DOE: 30% of the energy is lost (42 G$).

"Open question — 70 percent of energy needs to be saved by 2030 in new buildings…"

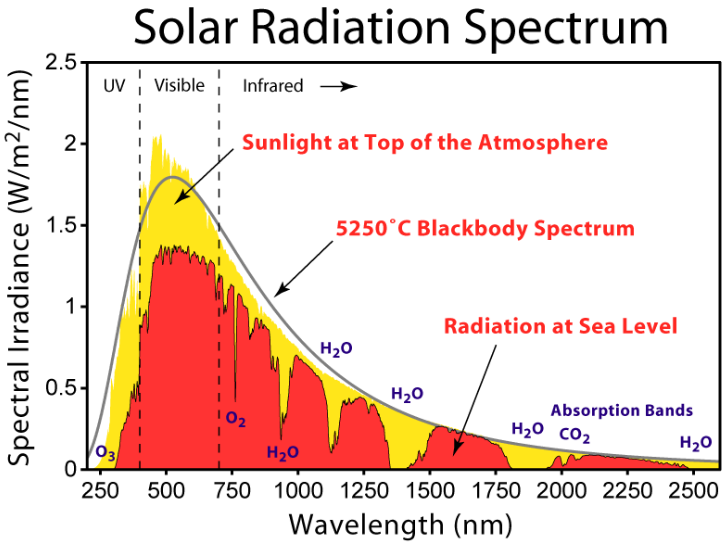
"**These energy savings can be made not by reducing the standard of living, but by utilizing more efficient technologies…**" [1]

vs.

[1] *B. Richter, et al., How America can look within to achieve energy security and reduce global warming, Rev. Mod. Phys. 80 (2008) S1-S109.*

Windows and low-E coatings

Windows:
- User comfort, natural indoor lighting, architectural style.
- Thermal weak point (high emissivity, $\varepsilon = 1\text{-}R$).



Low-E windows:

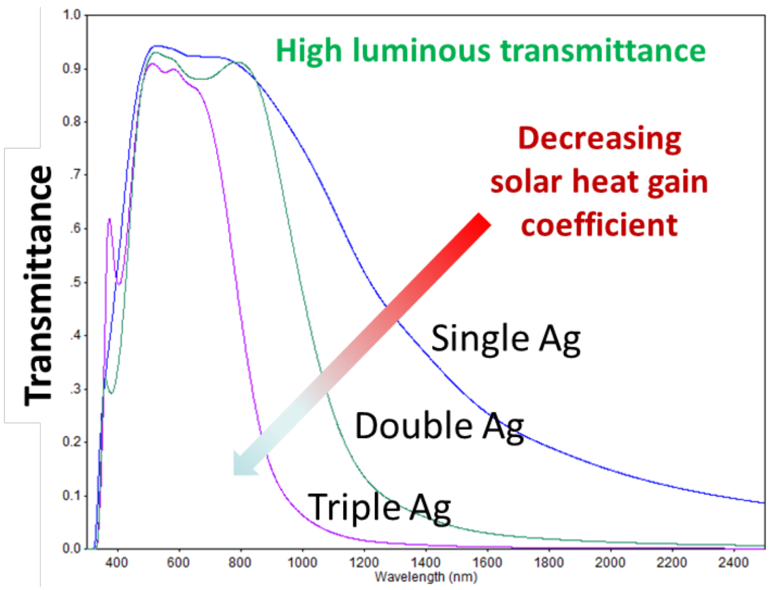
Silver-based low-emissivity coatings **passively** control the heat flux:
- Allow visible light through;
- Reflect a defined % of the near-IR [solar heat gain: 780 nm to 2500 nm];
- Reflect the IR.

→ **Results in cooling and heating cost reductions**

[1] Smith, G.B. & Granqvist, C.G., Green nanotechnology, CRC Press, 2011
[2] Wikimedia.org

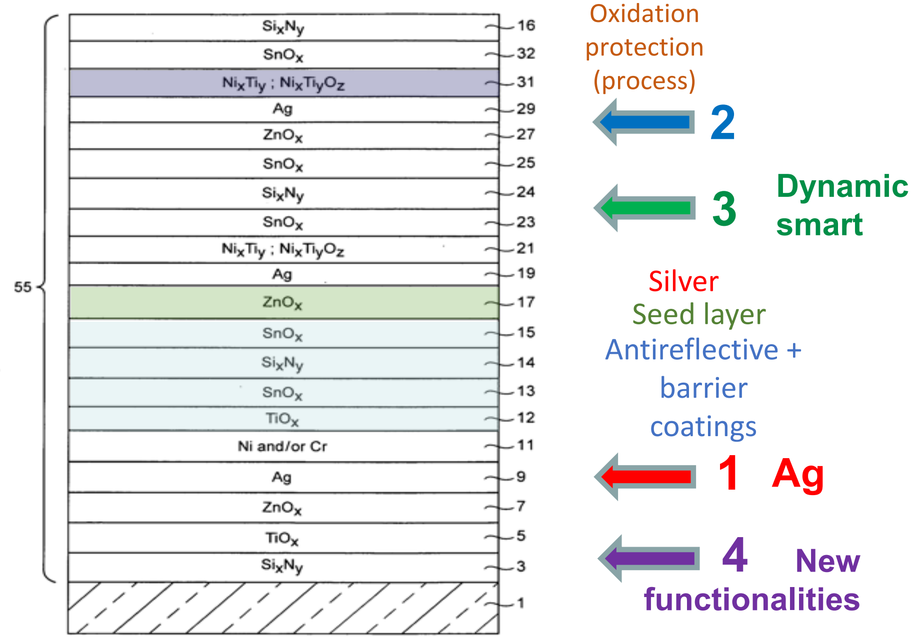
Low-E silver-based coatings

Modeling by *OpenFilters* at FCSEL



Single: TiO_2|Ag [10 nm]|TiO_2
Double: TiO_2|Ag [10 nm]|TiO_2|Ag [10 nm]|TiO_2
Triple: TiO_2|Ag [10 nm]|TiO_2|Ag [10 nm]|TiO_2|Ag [10 nm]|TiO_2

OpenFilters open-source software:
S. Larouche and L. Martinu, Applied Optics, 47 (2008) C219



[2]

Example of a triple silver low-e coatings taken from the patent literature:

R. Blacker et al., Guardian Industries, US Patent: US20120225224A1

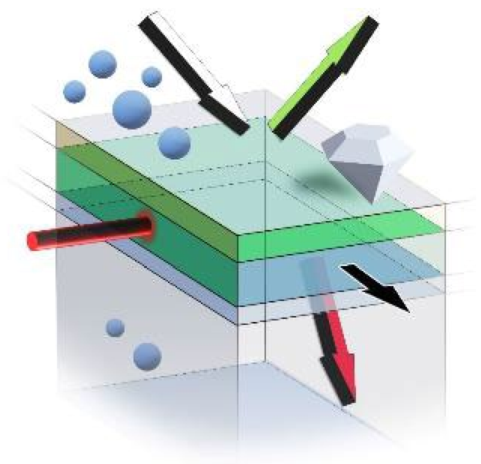
Challenge / Solution 1:

Decrease the thickness of Ag – from 12 to 6 nm! – lower cost

Tailoring initial film growth: *S. Hafezian, et al., Appl. Phys. Lett., 109 (2016) 121603.*

Optical protective coatings

- **Anti-reflective coatings**
- **Architectural glass**
- **Displays**
- **Touch screens**
- **Solar cells …**

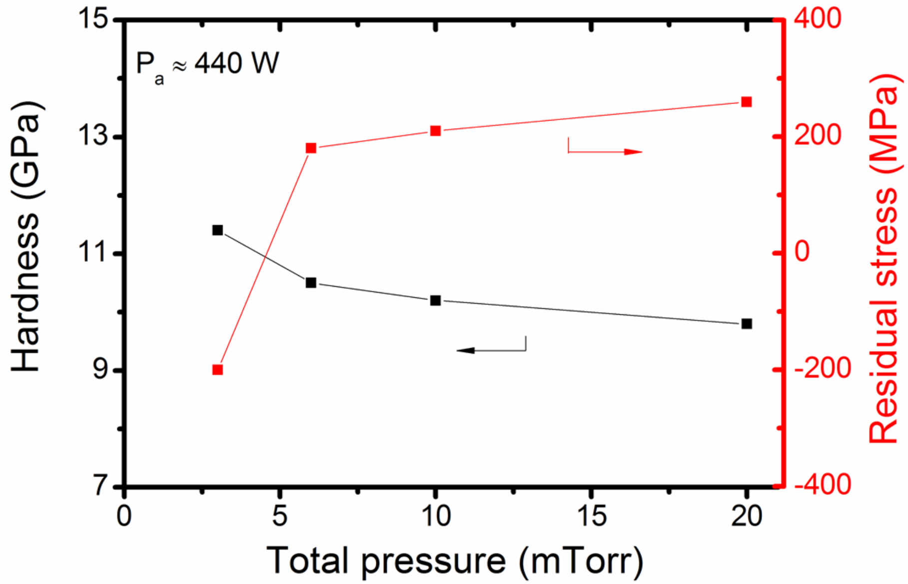


https://www.hcvacuum.com/

- **High hardness and high toughness coatings** can enhance the scratch and damage resistance of glass substrates in multiple applications.
- Toughness can have important effects on multiple failure modes, such as tensile cracking and flexural strength of the coatings.

Hard optical coatings by low duty cycle pulsed DC

Hard transparent Al_2O_3 films

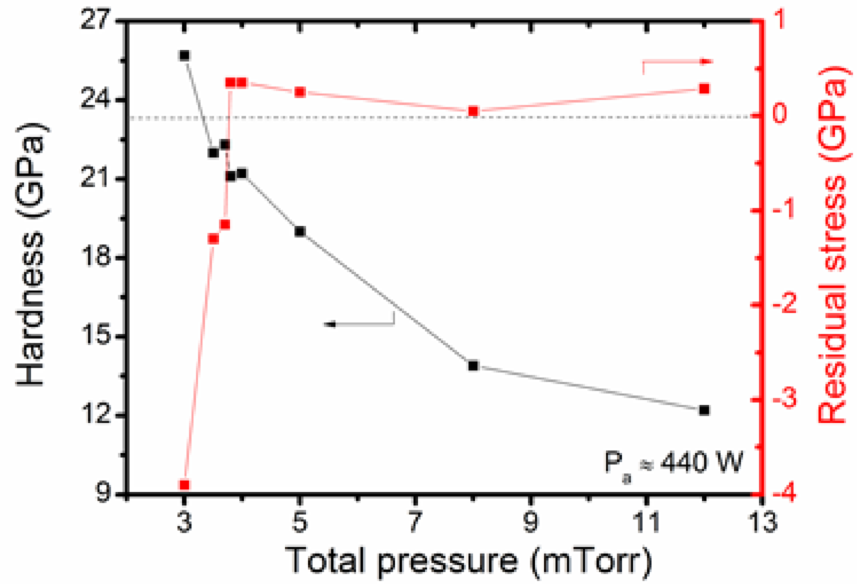


After optimization: *H* = 11 GPa, near zero stress, medium refractive index

***n* = 1.66 @ 550 nm | Frequency: 10 kHz, pulse length: 10 μe**

J. Kohout et al., J. Vac Sci. Technol. A, ***35*** *(2017) 061505.*

Hard transparent AlN films



After optimization: *H* = 23 GPa, near zero stress, high refractive index

***n* = 2.08 @ 550 nm | Frequency: 10 kHz, pulse length: 10 μs**

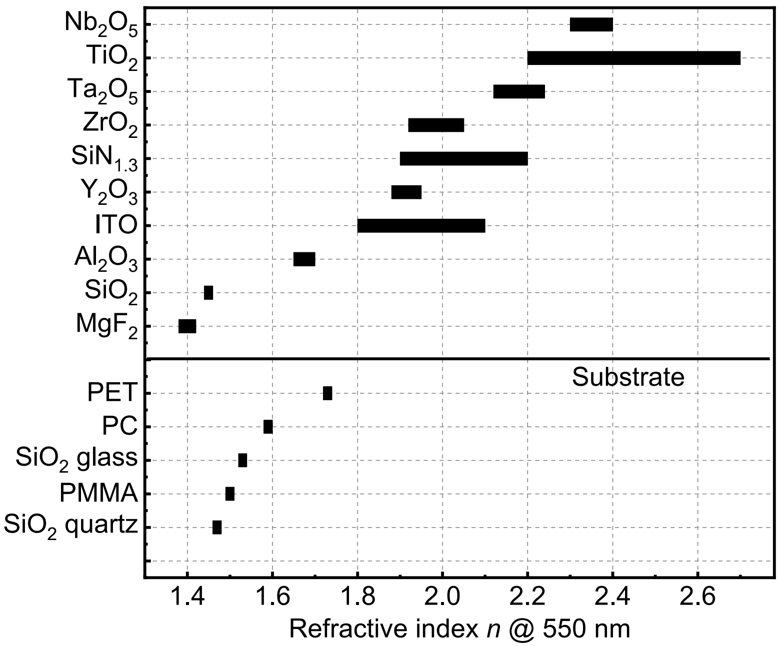
J. Kohout et al., Vacuum ***124*** *(2016) 96.*

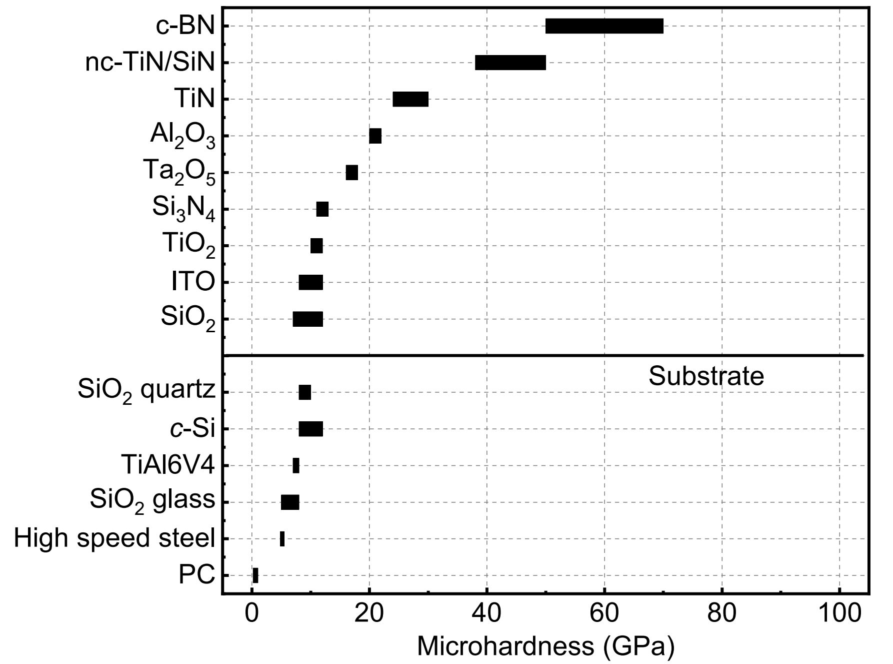
Mechanical properties of optical coatings

Refractive index

Toughness?

Hardness





Tough optical material – ZrO_2:

- High refractive index;
- Low absorption;
- High hardness;
- High toughness.

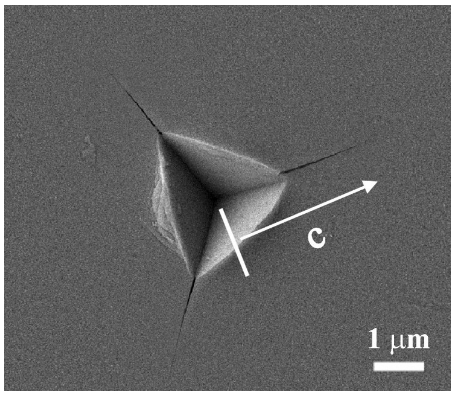
L. Martinu et al., Plasma-Enhanced Chemical Vapor Deposition of Functional Coatings, 2010, 362-465

*C. Hübsch et al., Acta Biomaterialia **11** (2015) 488–493.*

*Richard H. J. Hannink, J. Am. Ceram. Soc. **83** (2000) 461–487.*

Toughness testing

- **Indentation methods**

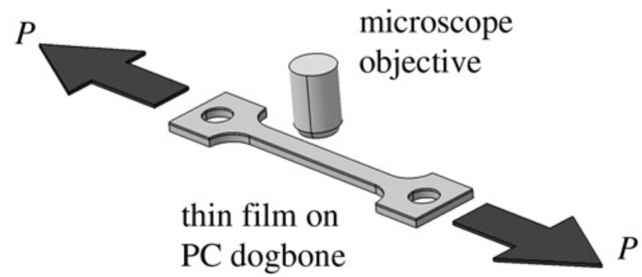


Lawn-Evans-Marshall model

$$K_c = \alpha \cdot \sqrt{\frac{E}{H}} \cdot \frac{P_{max}}{c^{3/2}}$$

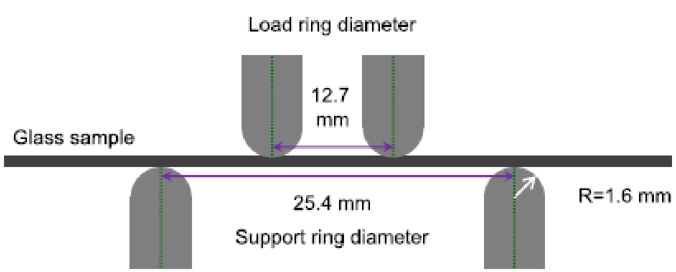
α = 0.016 for a Vickers pyramidal indenter;
α = 0.0535 for a cube corner indenter.
(Jang and Pharr, 2008)

- **Tensile methods**

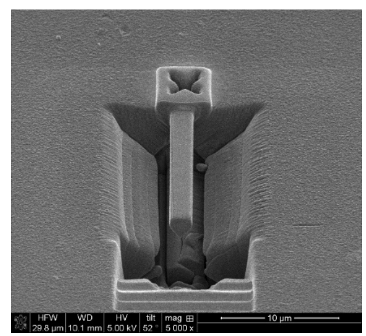


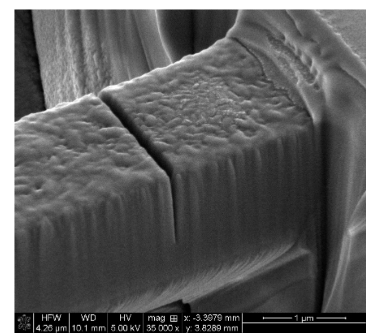
B.A. Latella et al., Surf. & Coat. Tech. ***201*** *(2007) 6325–6331.*

- **Bending methods**



- **Micro-mechanical methods**



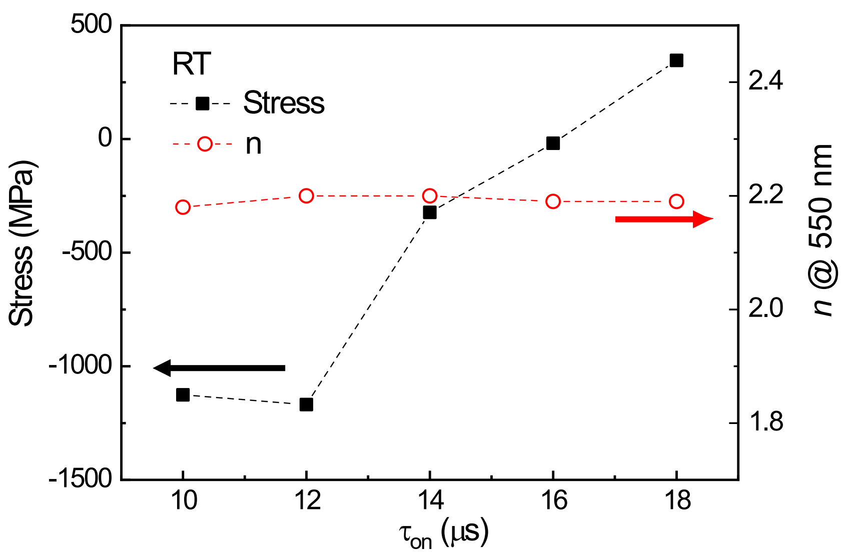


E. Bousser et al., J. Mater. Sci. ***48*** *(2013) 5543–5558.*
G. Hu et al., J Non Cryst Solids ***405*** *(2014) 153–158.*

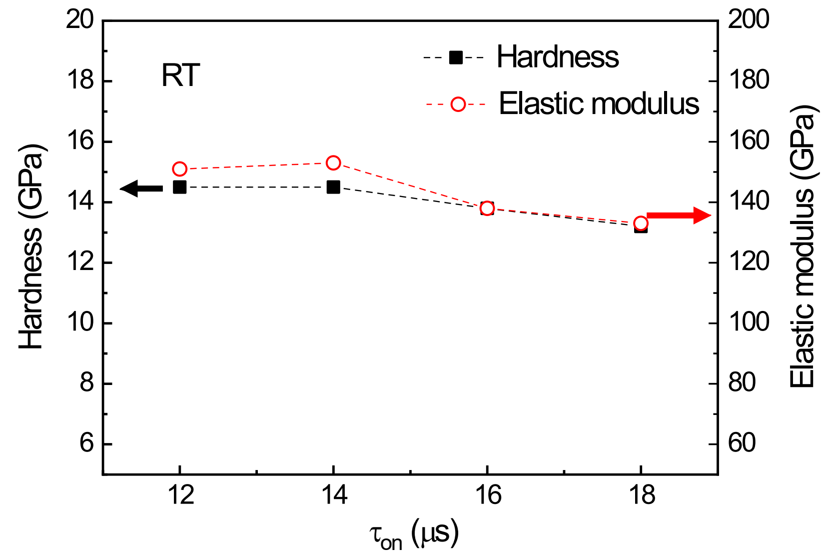
POLYTECHNIQUE MONTRÉAL
UNIVERSITÉ D'INGÉNIERIE

Effect of pulse length on the optical and mechanical properties of ZrO_2 films

Stress and refractive index



Mechanical properties



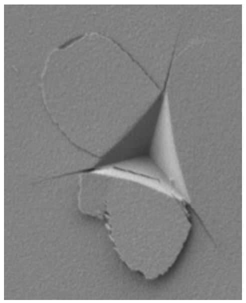
By increasing the pulse length and maintaining the same average power:

- The stress changes from a high compressive stress level (~1200 MPa) to a low tensile stress level.
- The refractive indices are ~2.2; it slightly decreases with the pulse length.
- The hardness of the coating at low stress level is ~14 GPa.

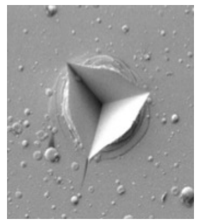
Perspectives of protective optical coatings

Toughness comparison of different materials:

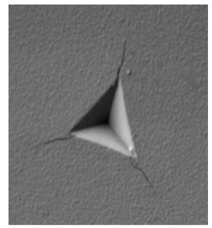
indents performed at 120 mN (coating thickness of ~2 μm)



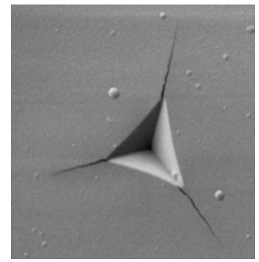
SiO_2



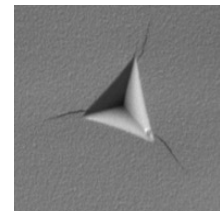
Al_2O_3



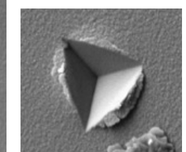
SiON



AlON



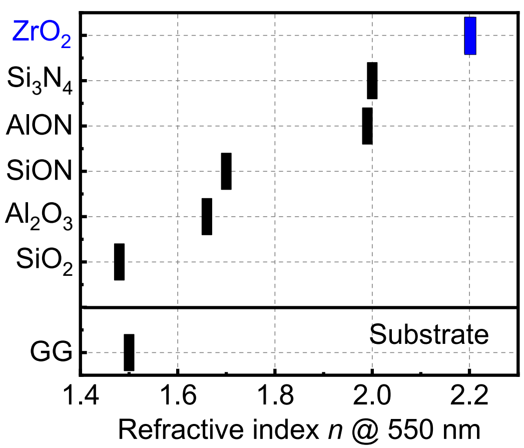
Si_3N_4



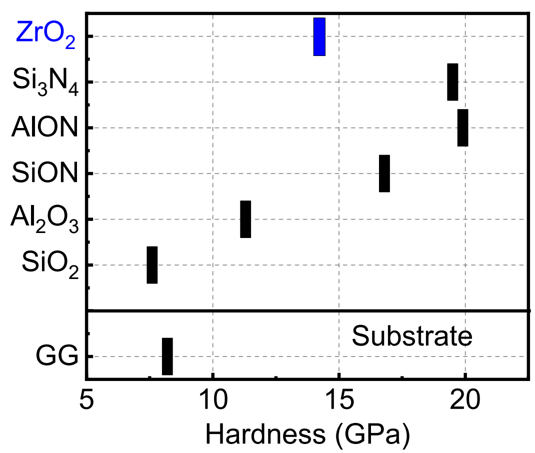
ZrO_2

Optical and mechanical properties of different coatings

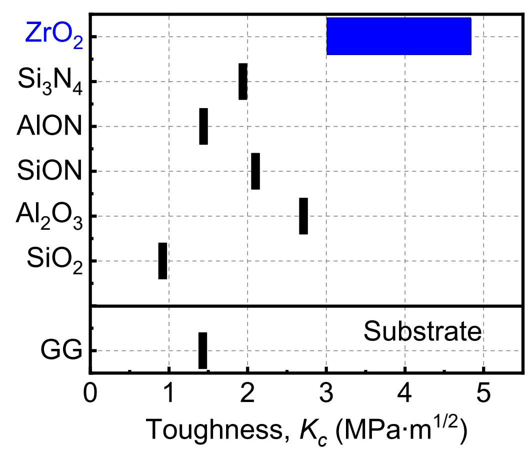
- **Refractive index *n***



- **Hardness**



- **Effective toughness**



Towards smart windows

Courtesy of Guardian Industries

Type of smart window glazing	Low-E	Photochromic	Electrochromic	Thermochromic
1) General optical behavior	*1) Passive*	*1) Active*	*1) Active*	*1) Active*
2) Most notable optical variation	*2) No optical variation*	*2) Changing visible transparency*	*2) Changing visible transparency*	*2) Changing infra-red transparency*
3) Energy source	*3) None*	*3) Light activated*	*3) Electrically activated*	*3) Heat activated*

Chromogenic windows are proving to be an effective means to control building solar heat gain.

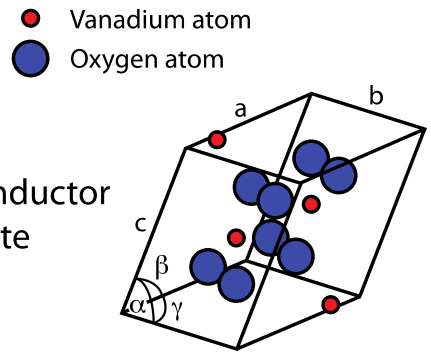
Dynamic and adjustable spectral selectivity

Angular selectivity, color and aesthetics, …

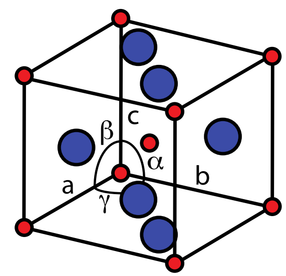
VO_2 basic properties

Atomic structure

Semiconductor state



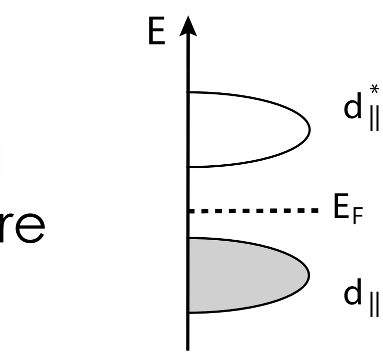
Monoclinic structure
$a \neq b \neq c$
$\alpha = \gamma = 90° \neq \beta$

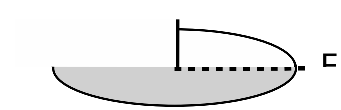


Metallic state

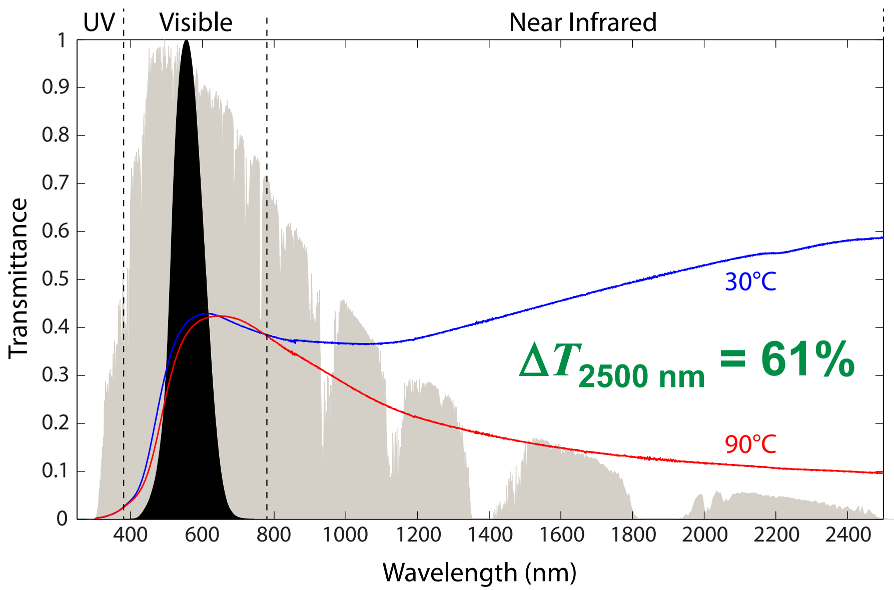
Tetragonal structure
$a = b \neq c$
$\alpha = \gamma = \beta = 90°$

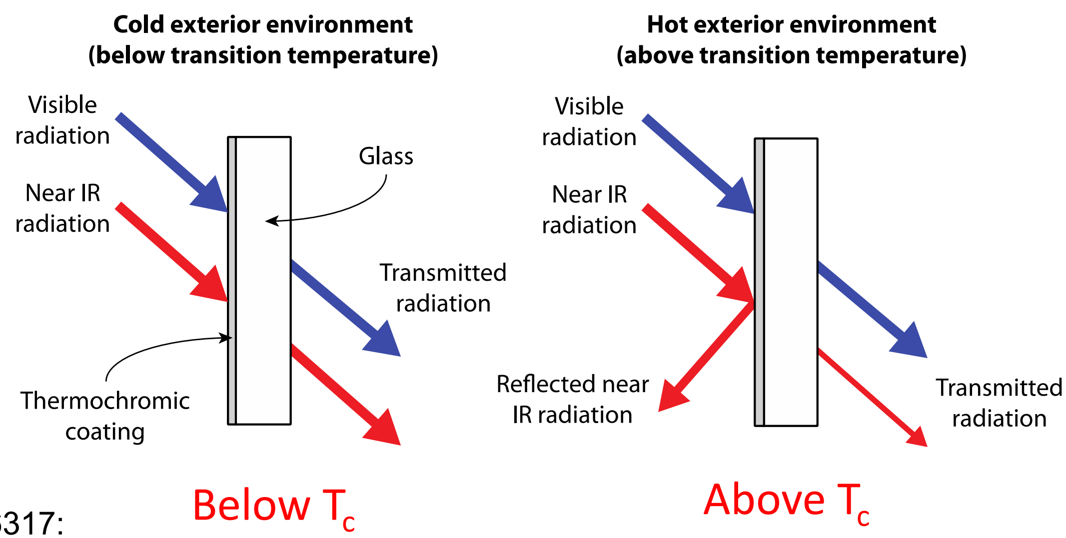
Band structure





Thermochromic (VO_2) smart window coatings





Challenges and solutions

High transition temperature - T_C
(T_c: 68°C) – doping (W, Mo,…)

Unattractive color

Filters or plasmonic particles (10 nm)

Low visible transmittance
Antireflective coatings,
Nanoparticles (10-30 nm) - nanothermochromics

High deposition temperatures
(> 400°C)

What about HiPIMS?

Active materials for smart coating systems

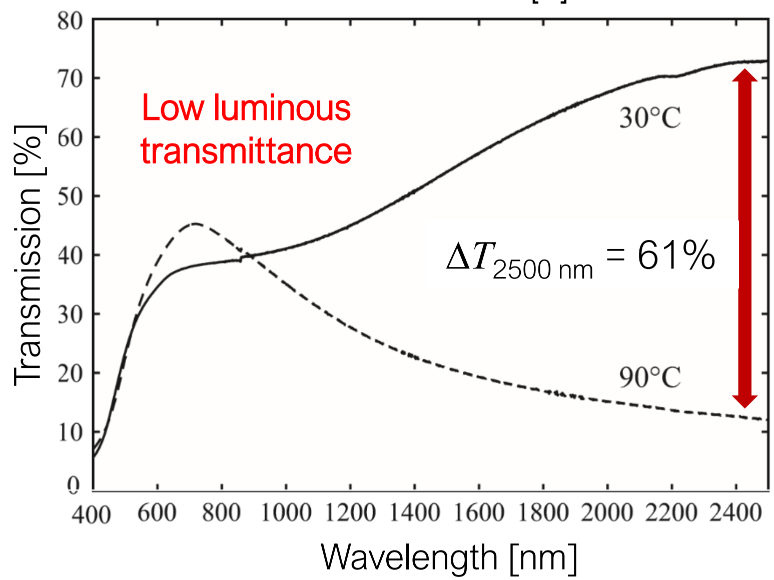
Actively modulate the transmission in the visible / NIR / IR:

■ Electrochromic ■ Gasochromic ■ Photochromic ■ **Thermochromic**

Thermochromic VO_2

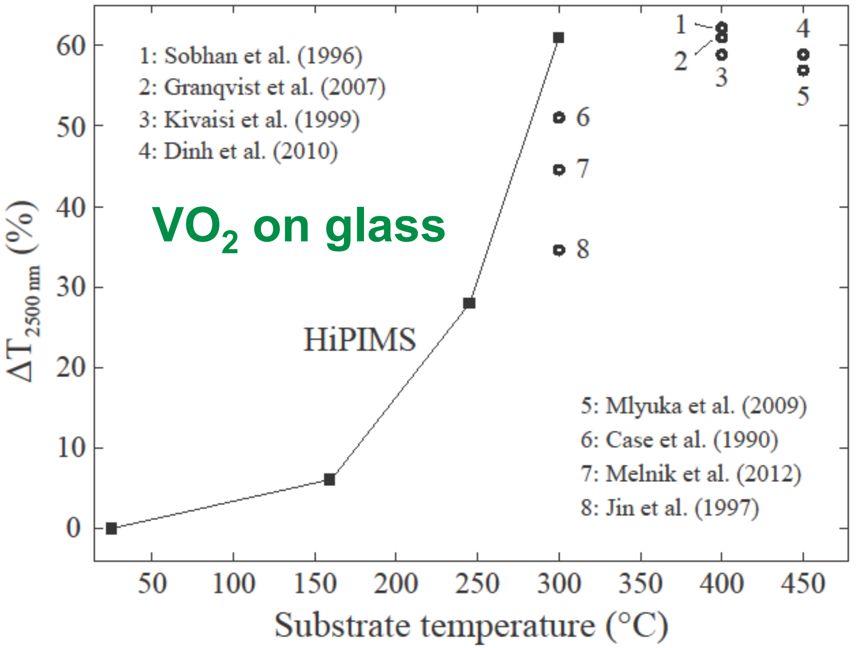
< 68°C	Monoclinic Semiconductor
> 68°C	Tetragonal Metallic

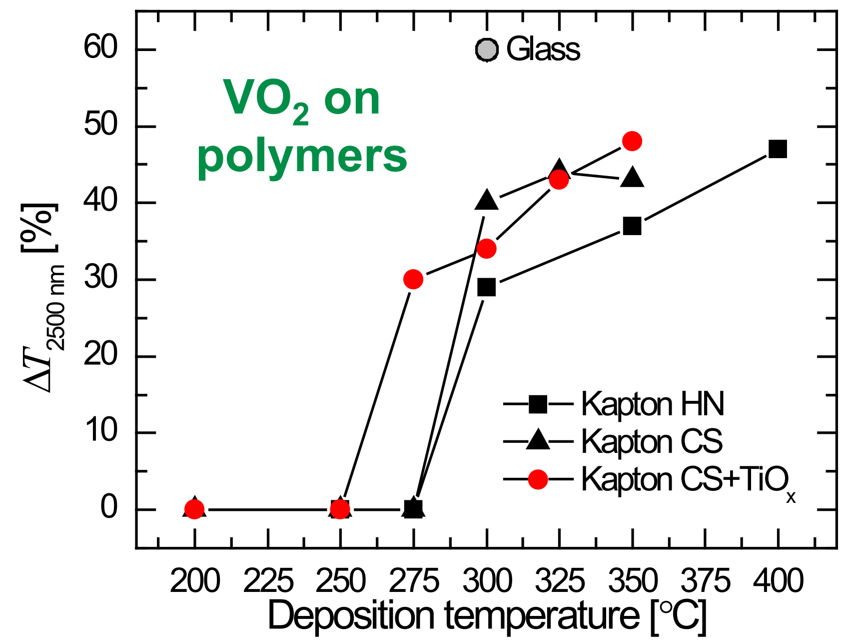
Transmission of a 75-nm-thick **HiPIMS-deposited VO_2** film at 30°C and 90°C [1].



J.-P. Fortier, et al. "Thermochromic VO_2 thin films deposited by HiPIMS," Sol. Energ. Mat. Sol. C. ***125*** *(2014) 291–296.*

Thermochromic VO_2 films by HiPIMS





Temperature-induced optical transmission difference at 2500 nm: $\Delta T_{2500\text{ nm}}$ = 61%.

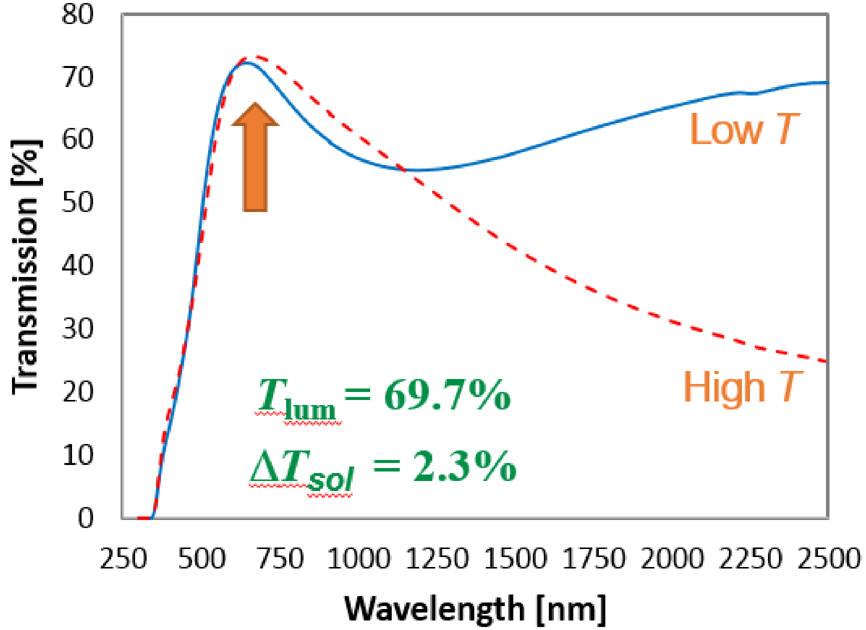
$\Delta T_{2500\text{ nm}}$ vs. substrate temperature T_s = 300°C, lower than in other studies

J.-P. Fortier et al., Sol. Energy Mat. Sol. Cells ***125*** *(2014) 291.*
S. Loquai et al., Sol. Energy Mat. Sol. Cells ***155*** *(2016) 60.*

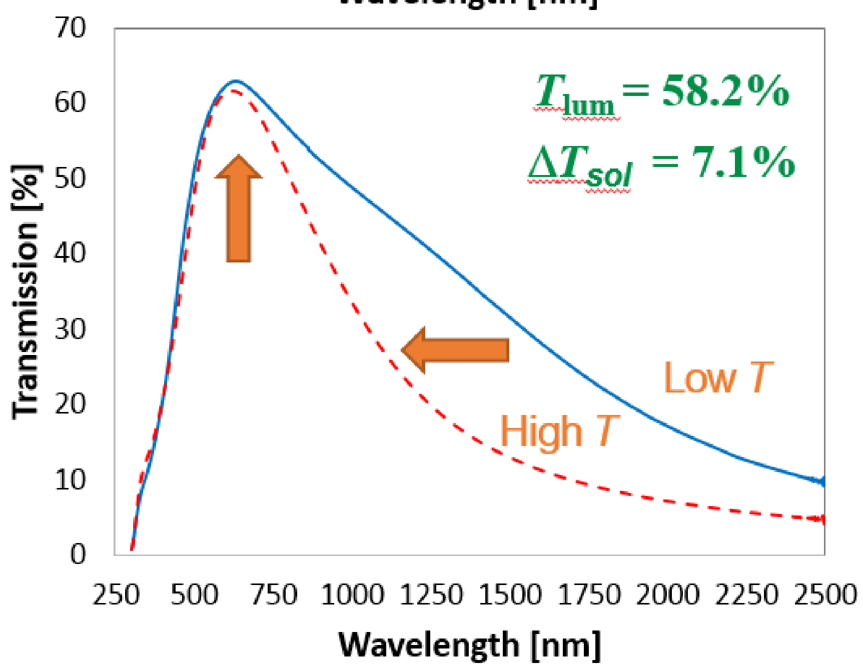
Smart thermochromic low-E window

Experiment

AR - Si_3N_4
VO_2 [**26 nm**]
AR - Si_3N_4
B270



AR - Si_3N_4
Ag [11 nm]
VO_2 [**27 nm**]
AR - Si_3N_4
B270



B. Baloukas et al., Sol. En. Mat. Sol. Cells ***183*** *(2018) 25-33*

Impact of Ag:

- Increase in T_{lum}.
- Increase in ΔT_{sol} due to increase in variation in the 800 nm to 1500 nm range.
- Low-E:

	ε [%] LT | HT
No Ag	87.6 | 67.5
Ag	10.0 | 10.5

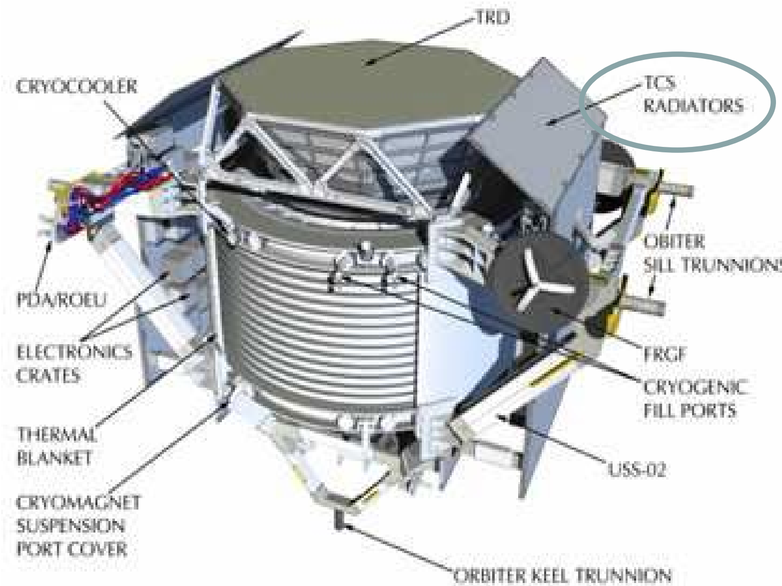
Emissivity calculated as 1 - *R* (5 - 25 μm)

Energy management in satellites – smart radiator

Space environment heat load:

Sun side 1300 W/m^2
Dark side 5 W/m^2

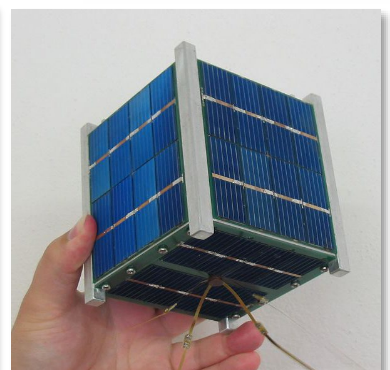
Thermal Control System (TCS):
Thermostatically controlled resistive electric heaters, louvers.



Micro- and Nano-Satellites

Defined by a mass between 1 and 100 kg

Spaceworks, 2019



http://www.radioamateurs.news.sciencesfrance.fr/?p=86304

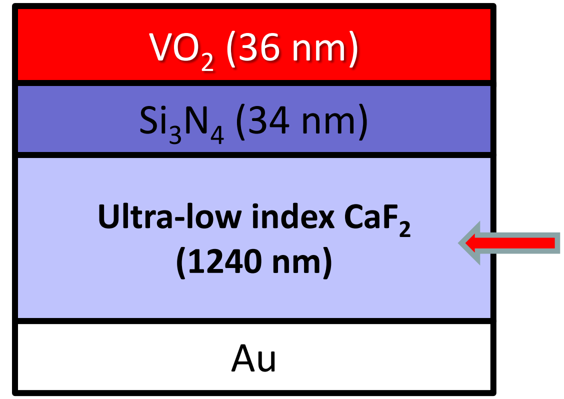
Temperature requirements	
Batteries	-5 to 20°C
Propulsion components	5 to 40°C
Cameras	-30 to 40°C
Solar arrays	-150 to 100°C
IR spectrometers	-40 to 60°C

Can active materials with variable emittance be a solution ?

Design-based smart radiator device with $\Delta\varepsilon = \varepsilon_H - \varepsilon_L \geq 60\%$ for 2.5 µm < λ < 25 µm

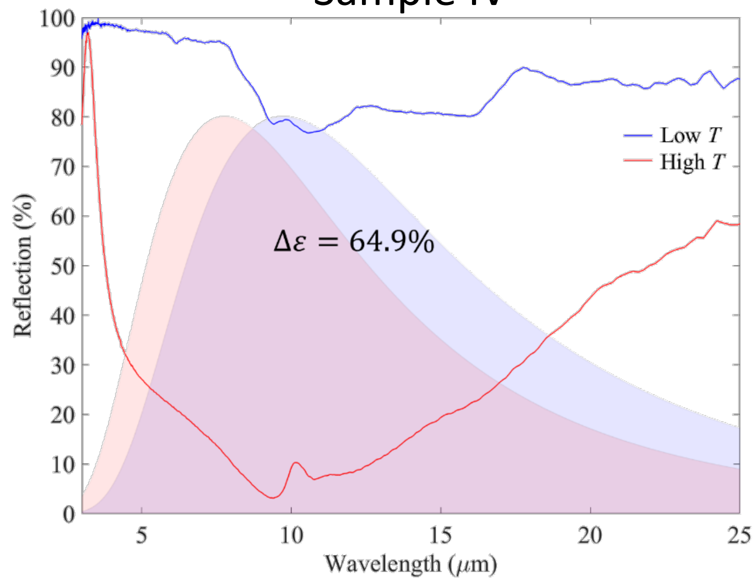
Sample	ε_L (%)	ε_H (%)	$\Delta\varepsilon$ (%)
I	14.1	80.1	**66.0**
II	16.8	79.4	62.5
III	17.5	78.9	61.4
IV	14.8	79.6	64.9
V	13.9	78.2	64.4

Highest reported emissivity modulation



Si_3N_4 : seed layer for growth

Sample IV

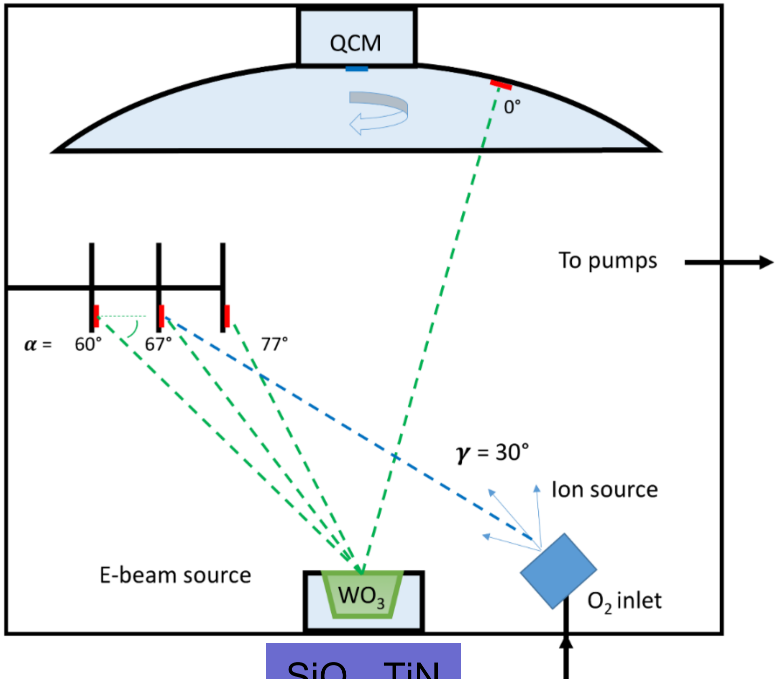


PHS6317: Nanoengineering of Thin Films - W2024

*R. Beaini et al, Solar En. Mat. Solar Cells, **205** (2020) 110260*

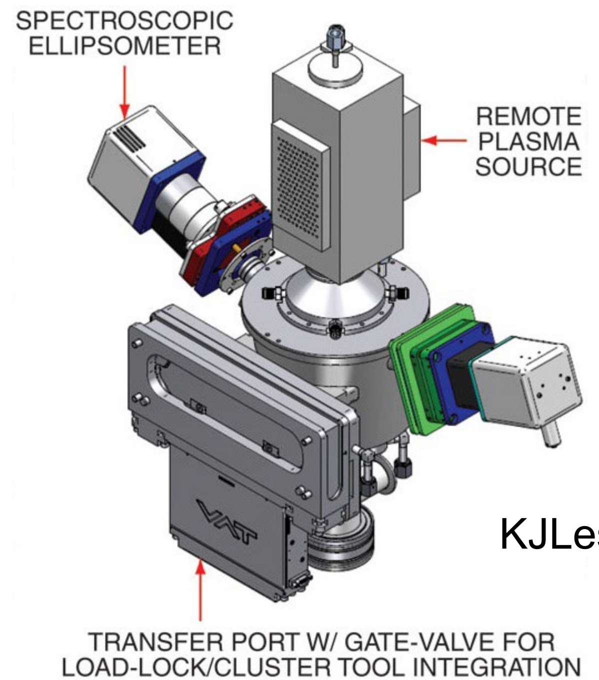
Angle-selective optical films

Ion-assisted glancing angle deposition - GLAD



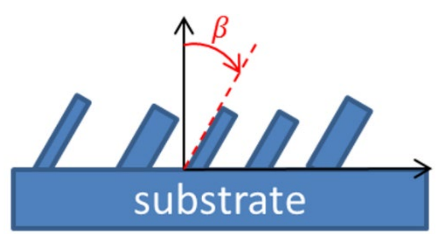
SiO_2, TiN

Plasma Enhanced ALD



Observations:

- s-pol is symmetric;
- p-pol is highest at the angle of the columns;
- p-pol is asymmetric.



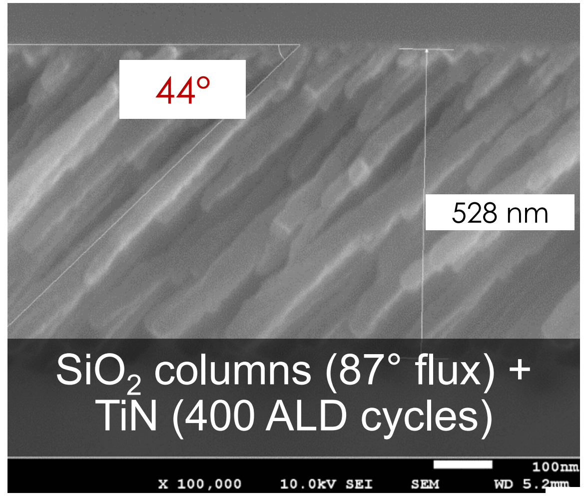
GLAD – shadowing effects

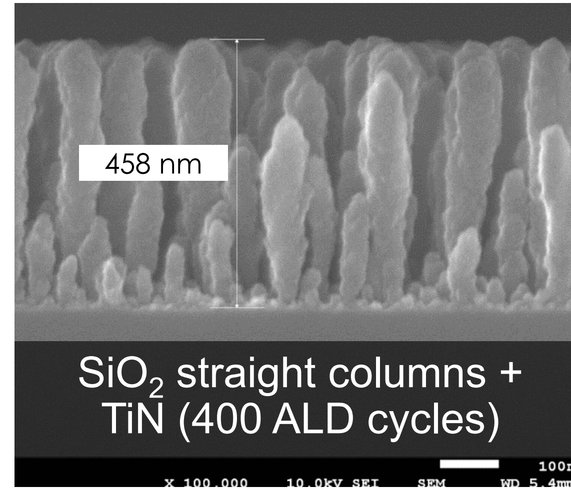
S. Woodward-Gagné et al., SVC 2018

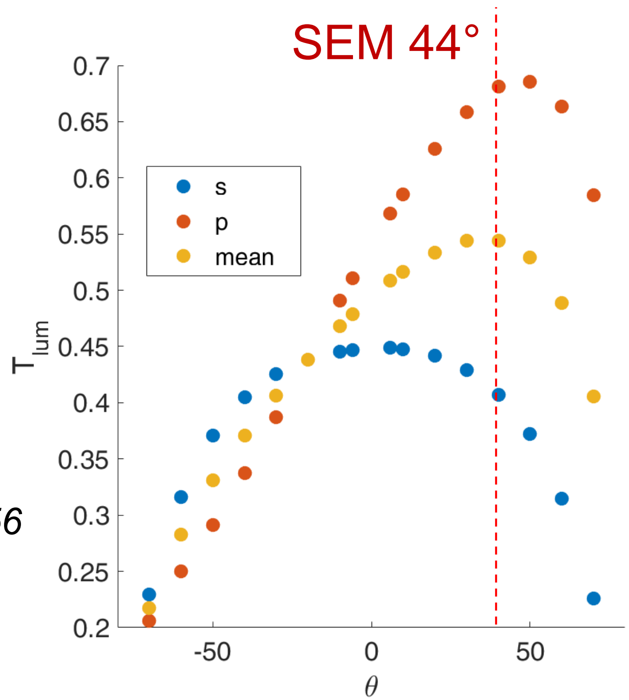
Angular selectivity – Controlling absorption by ALD

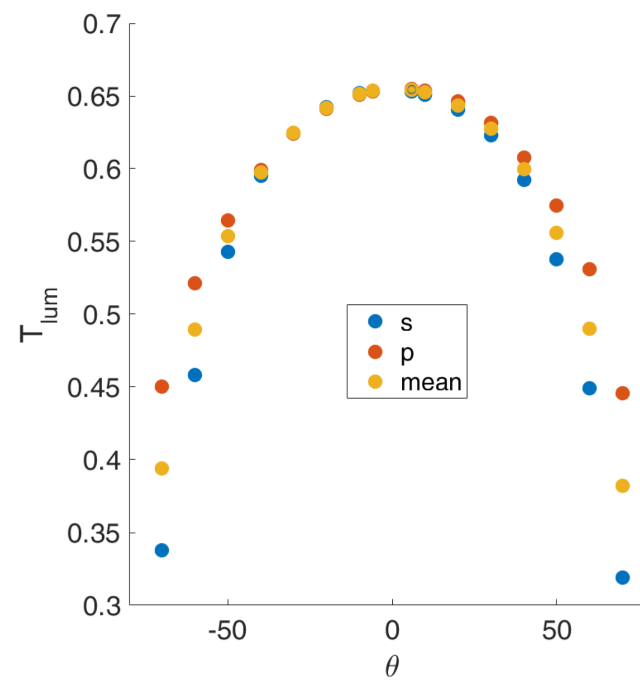
Dielectric **GLAD** coatings overcoated by an absorbing film by **ALD** promise **additional control**.

- ALD-TiN on SiO_2 GLAD columns obtained from e-beam evaporation*
- Number of cycles allows one to precisely tune the level of absorption for a GLAD film of constant thickness.





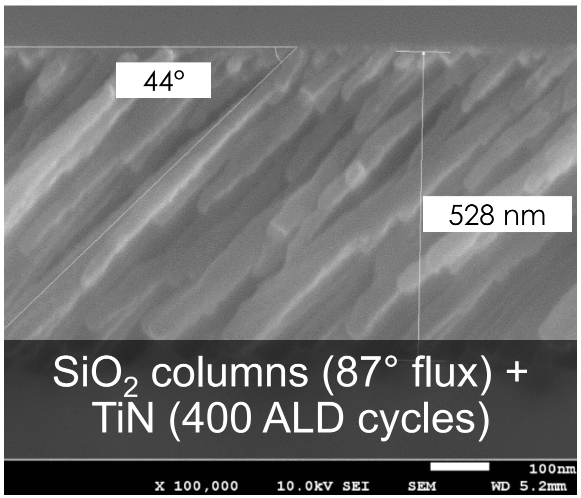


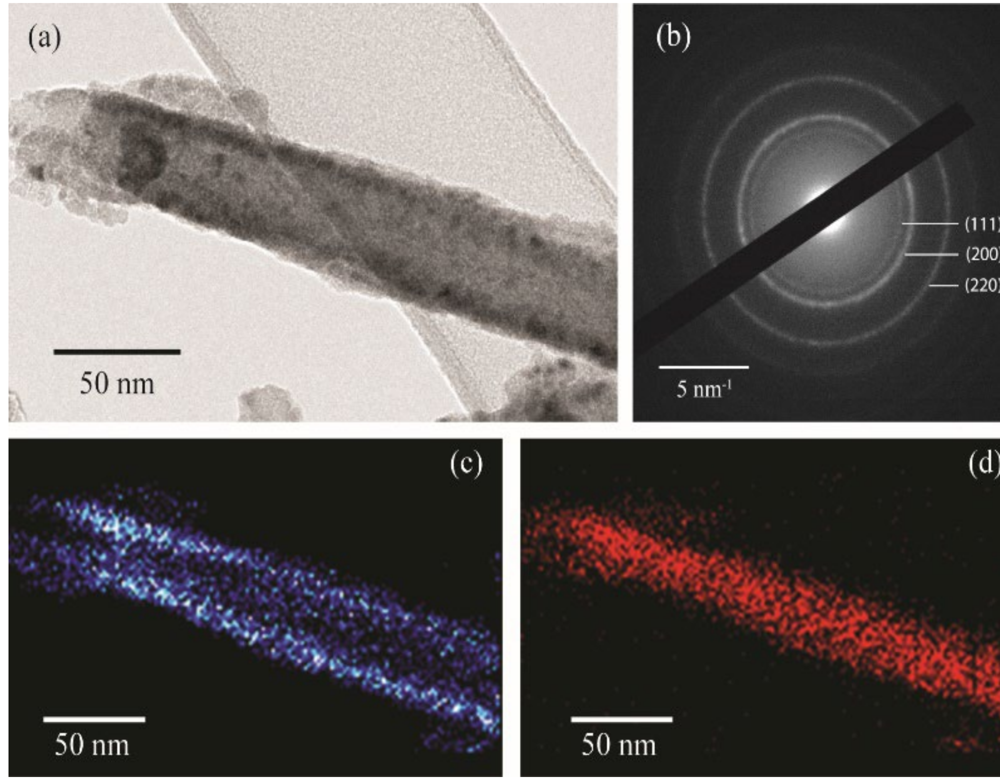


*S. Woodward-Gagné et al., *Opt. Mat. Express*, ***9*** *(2019) 4556*

Slanted columnar core shells

Tuning the thickness of ALD-TiN films around the GLAD-SiO_2 slanted columns





TEM micrographs of a TiN-coated SiO_2 nanocolumn:

(a) TEM bright field nanocolumn image
(b) Selected-area electron diffractogram over the TiN-coated SiO_2 nanocolumn, and mapping of titanium (c) and silicon (d)

*S. Woodward-Gagné et al., Opt. Mat. Express, **9** (2019) 4556*

Further challenges and opportunities

Low-E architectural glass coating line

Courtesy of Guardian Industries

<u>Total world annual production:</u>

About 500,000,000 m^2 of coated glass
typically 10 to 20 layers, 5-20 nm thick; glass 6 m x 3.2 m.

Towards future green cities

"**Vincent Callebaut's Smart City** was commissioned as part of the Climate Energy Plan of Paris, and it shows how the **Paris of 2050** could embrace sustainability to create a healthier future while retaining its historical aesthetic and meeting its long-term energy goals."

Climate energy plan of Paris

http://inhabitat.com/futuristic-paris-smart-city-is-filled-with-flourishing-green-skyscrapers/
http://vincent.callebaut.org/

POLYTECHNIQUE MONTRÉAL
UNIVERSITÉ D'INGÉNIERIE

PHS 6317 Nanoengineering of thin films

Course schedule – Winter 2024

12 January	Introduction – Scientific and technological challenges
19	Fabrication methods – Vacuum physics and vapor-phase techniques
26*	Fabrication methods – Plasma processes and process optimization
2 February	Fabrication methods - Plasma-surface interactions and diagnostics
9**	Fabrication methods – Thermal/Plasma spray technologies
16*	Optics of thin films 1, optical characterization, *Miniquiz1 (5%)*
23*	Optics of thin films 2, design of optical filters
1*** March	*Presentations – Emerging fabrication techniques (30%)*
	March 4-8 - Winter/Spring break
15**	Tribo-mechanical properties of films and coatings
22**	Electrochemical properties – corrosion and tribo-corrosion *(filter-20%)*
5 April	Functional films and coatings – Part 1, *Miniquiz 2 (5%)*
12	Functional films and coatings – Part 2
16	Life cycle analysis and environmental impact, **visits**
19***	*Presentations – Emerging applications of nanostructured films (40%)*