Tribological and thermo-mechanical properties of optical coatings: From banknotes to satellites

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JT CMO, Palaiseau, le 27 janvier 2011

Colors

Pleasure and imagination

L. Martinu, Colors from Europe, America and Asia

Colors

Admiration

Colors

Food

Antireflective (AR) coatings

The AR council (www.arcouncil.org)

Security devices

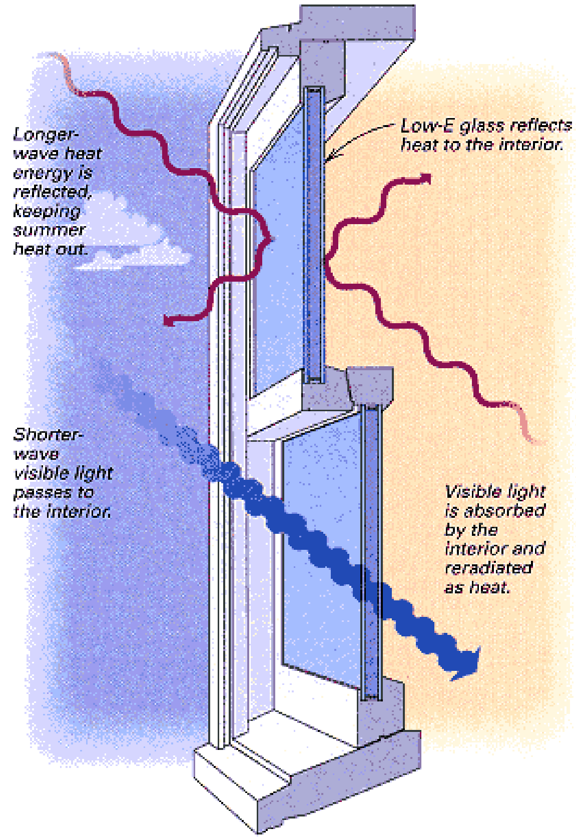
Bank of Canada
(www.banqueducanada.ca)

US Bureau of Engraving and Printing
(www.moneyfactory.com)

Architectural glass, automotive glazing

Schott (www.us.schott.com)

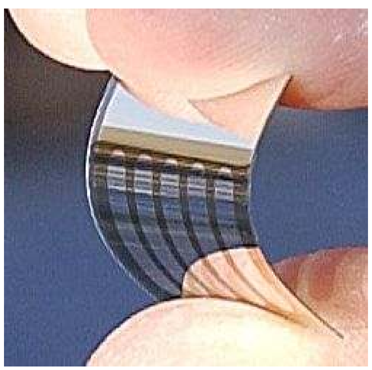
FIGURE 2. Glazing on a building may be the most important component of the building's exterior aesthetic quality, which leads to thin-film glass-coating effects on incident light.



Paul Fisette, «Understanding Energy-Efficient Windows», *Fine Homebuilding,* no. 114, pp. 68–73.

Light generation and conversion

Solar cells



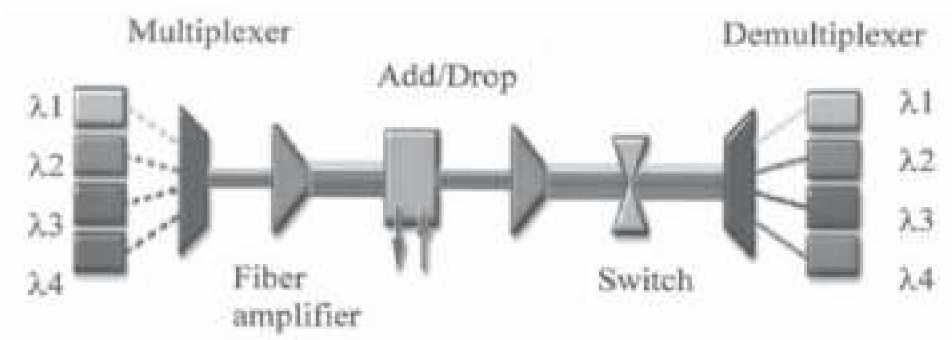
Large area lighting

Displays and visors

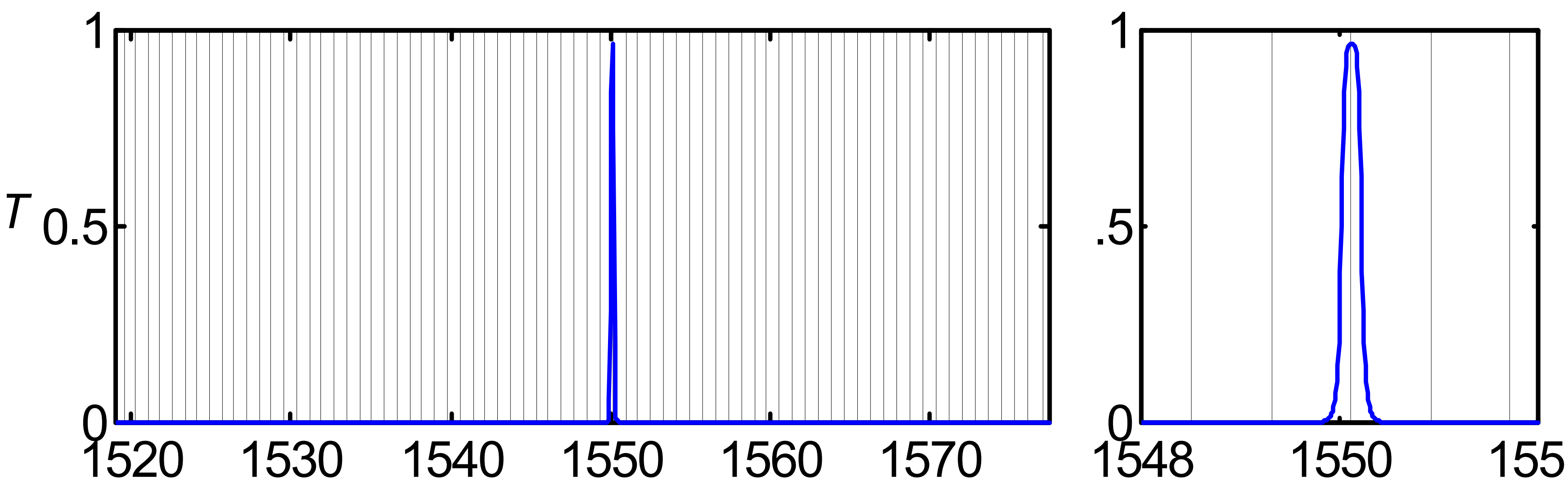
Optically variable devices – OVD
Color effects, decorative coatings

Colorshift (www.colorshift.com)

Telecommunications



N.A. O'Brien *et al.*, «Recent Advances in Thin Film Interference Filters for Telecommunications», *SVC 44th Annual Tech. Conf. Proc.*, 2001, p. 255–261.



Present and future trends – driving forces

<u>Applications</u>

- Optical coatings on plastics (AR, UV protection, mechanical protection)
- Tunable optical filtres
- High power (laser) applications
- Displays, lighting
- Photovoltaics
- Control of environment – smart windows, automobile glazings
- IR and DUV optics
- Space optics and astronomy – satellites, telescopes
- Biomedical engineering, sensors
- Micro-opto-electro-mechachanical systems (MOEMS)
- Organic electronics

Each application represents specific environmental stability and functional properties criteria:

a) Need for better understanding
b) New metrology
c) New solutions

Optical coatings – from design to manufacture

Applications

•...

Properties

- Optical: n, k, loss, colors
- Mechanical (CTE, ν_f)
- Functional: tribological, electrical, surface energy,...

Microstructure

- Packing density (porosity)
- Crystallinity
- Composition
- Roughness
- Homogeneity
- Surfaces and interfaces

Process control and monitoring

- *In situ*, real time
- Timing, QCM
- Optical monitoring

Optical design strategies

- Discrete multilayer desing
- Graded (inhomogeneous) or hybrid design

Fabrication processes

- Plasma-based processes
- Effect of ion bombardment
- New techniques
- Coating plastics

Optical coatings – from design to manufacture

Applications (examples):
- Interference security image str.
- Inhomogeneous optical filters
- Decorative/protective coatings
- Smart IR radiators

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- **Mechanical (CTE, ν_f)**
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Refractive index of PECVD and PVD coatings

Interference filters:

High, low, medium refractive index:

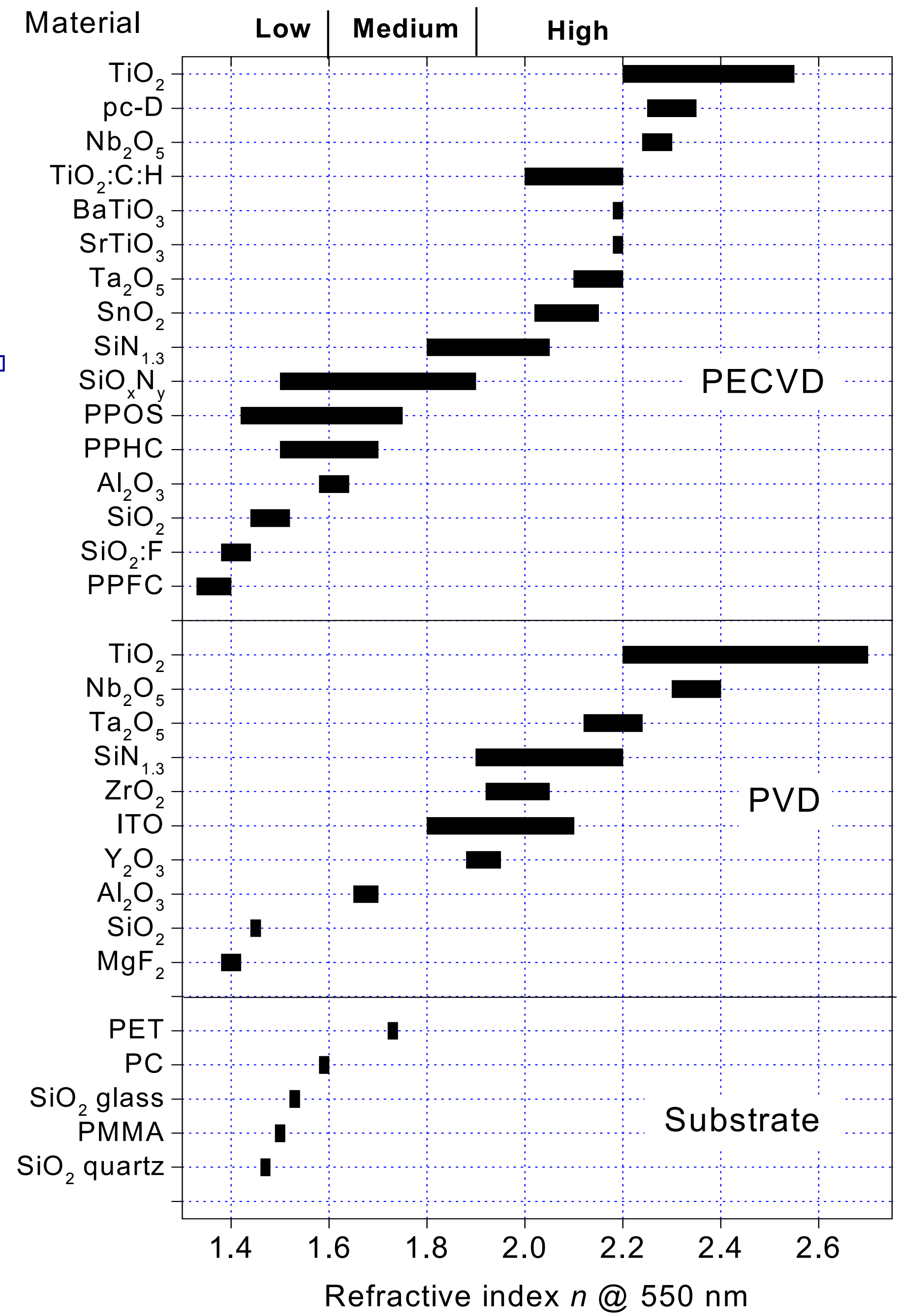
n_H, n_L, n_M

$k < 10^{-5}$

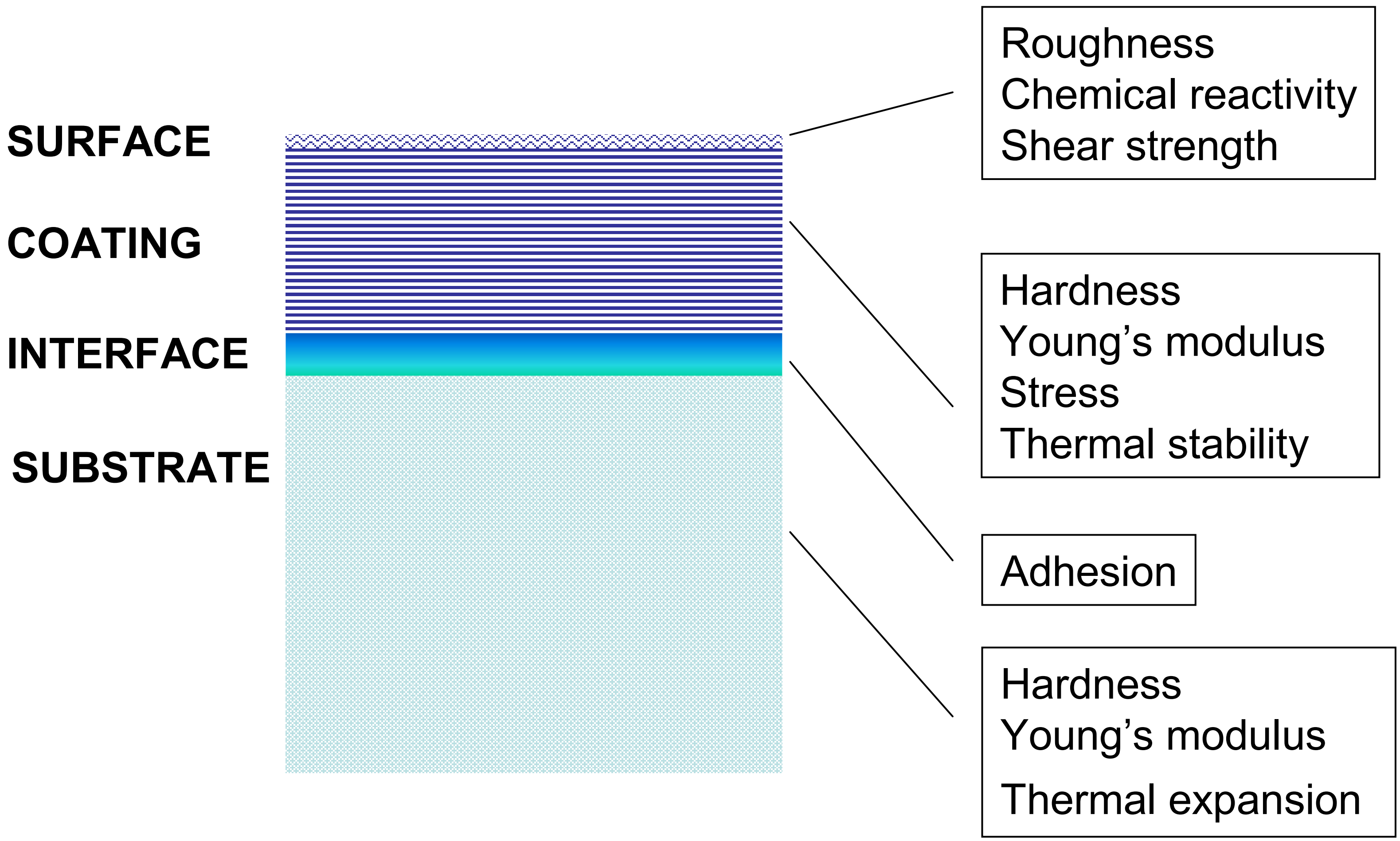
$\alpha = 4\pi k / \lambda$

Dispersion curves: $n(\lambda)$, $k(\lambda)$

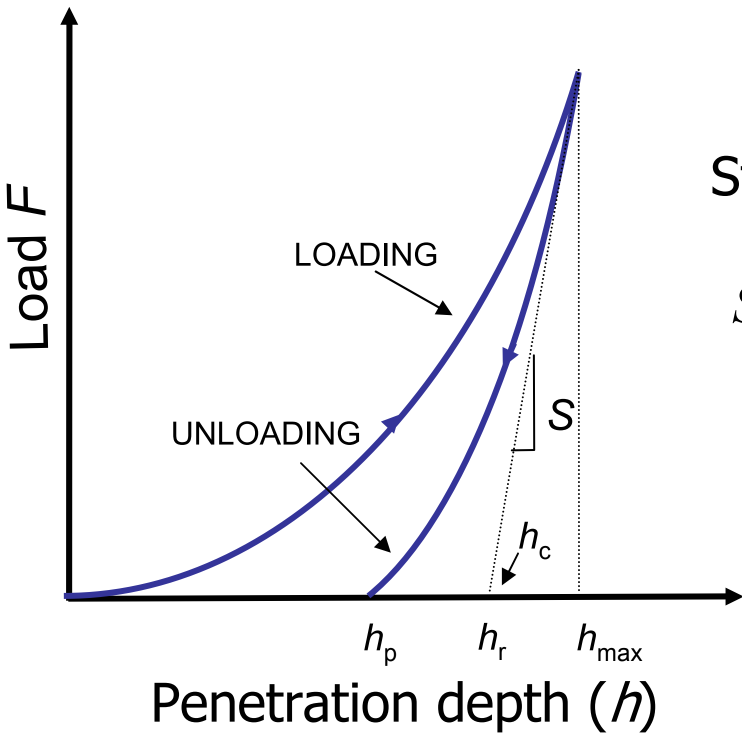
L. Martinu et al., in Handbook of Thin Film Deposition Technologies, P.M. Martin, ed., Elsevier 2010



Important properties of optical film-substrate systems



Load-displacement curve



$F \propto (h_{max} - h_p)^m$

$1<m<2$

Stiffness:

$$S = \frac{dF}{dh}$$

Hardness (H):

$$H = \frac{F_{max}}{A}$$

Elastic modulus (E):

$$E_r = S\frac{\sqrt{\pi}}{2\sqrt{A}}$$

$$\frac{1}{E_r} = \frac{1-\upsilon^2}{E} + \frac{1-\upsilon_i^2}{E_i}$$

Tip area function:

$A = f(h_c)$

for a "perfect" Berkovich indenter

$A = 24.5\ h_c^2$

h_p : Residual depth
h_c : Contact depth
h_r : Intercept of the initial slope
h_{max} : Maximum depth

1. ISO 14577-1 (2002)
2. Oliver W.C., Pharr G.M., J. Mater. Res., 7 (1992) 1564-1583
3. Doerner M.F., Nix W.D., J. Mater. Res., 1 (1986) 601-609

Coefficient of thermal expansion & Poisson's ratio

Thermal stress:

$$\sigma(T) = \sigma_i + (\alpha_s - \alpha_f)\left(\frac{E_f}{1-\nu_f}\right)(T - T_d)$$

Two-substrate technique to determine:

- **CTE - Coefficient of thermal expansion**
- **Poisson's ratio, ν_f**
- **Measured E**

$$\alpha_{film} = \frac{\alpha_{s2}\left(\frac{d\sigma}{dT}\right)_{s1} - \alpha_{s1}\left(\frac{d\sigma}{dT}\right)_{s2}}{\left(\frac{d\sigma}{dT}\right)_{s1} - \left(\frac{d\sigma}{dT}\right)_{s2}}$$

$$\nu_f = \left(\frac{1}{E_r} - \frac{1-\nu_i^2}{E_i}\right)\frac{d\sigma}{dT}\frac{1}{\alpha_s - \alpha_f} - 1$$

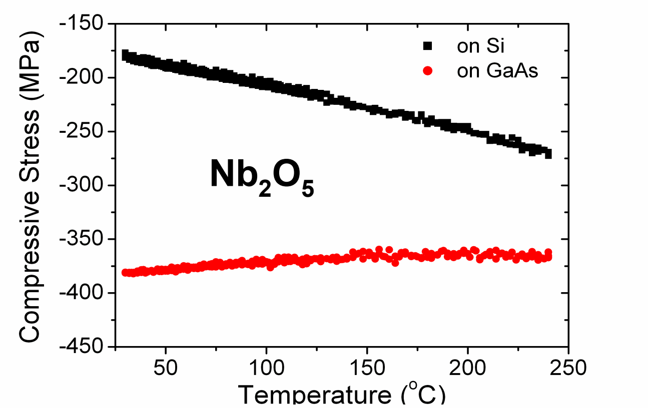
Substrates: $\alpha_{Si} = 2.6\times10^{-6}\ {}^{o}C^{-1}$, $\alpha_{GaAs} = 5.1\times10^{-6}\ {}^{o}C^{-1}$

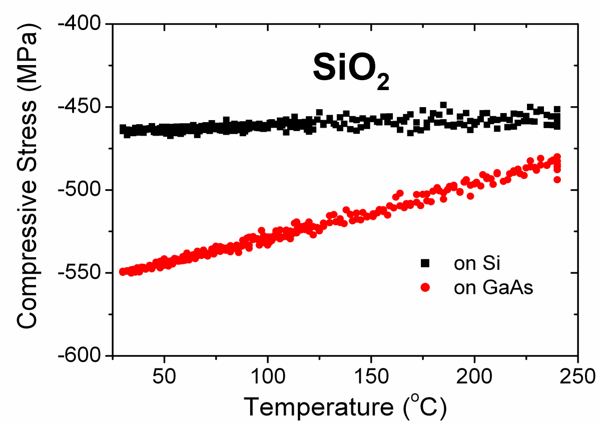
Example for Nb_2O_5, Ta_2O_5 and SiO_2 films:

$\alpha_{Nb2O5} = 4.9\times10^{-6}\ {}^{o}C^{-1}$, $\alpha_{SiO2} = 2.1\times10^{-6}\ {}^{o}C^{-1}$

$\nu_{f\ Nb2O5} = 0.22$, $\nu_{f\ SiO2} = 0.11$

σ-*T* plots





E. Cetinorgu et al., Applied Optics 2009

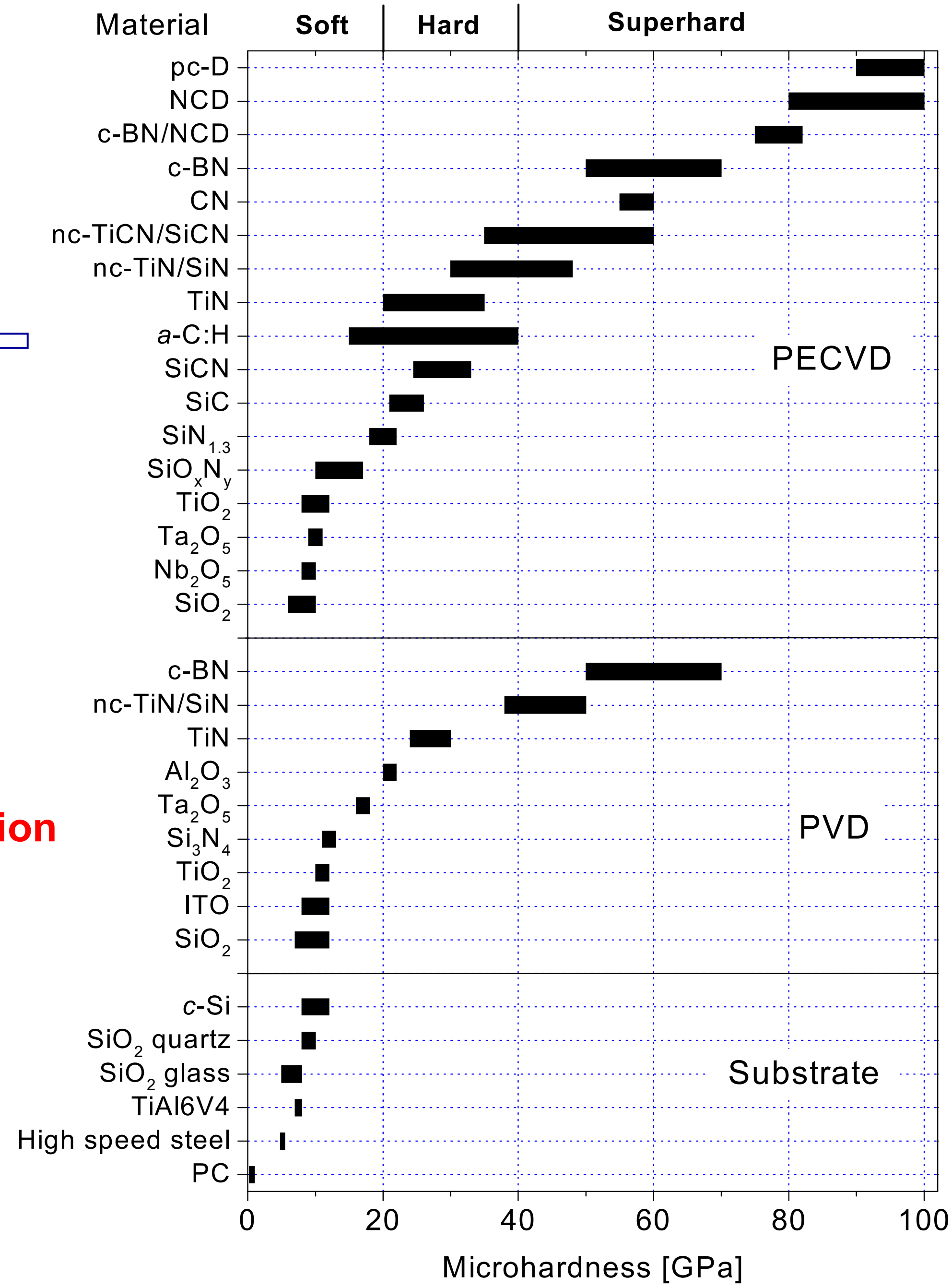
Microhardness of PECVD and PVD coatings

Mechanical requirements:

Adhesion
Stress
Compatibility (plastics)
Scratch and wear resistance:

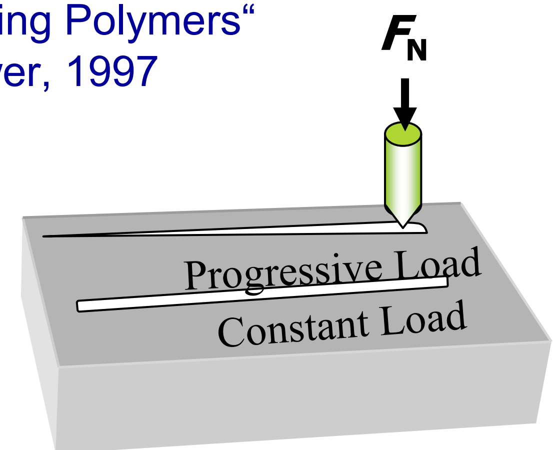
~ H/E - elastic strain to failure
~ H^3/E^2 - resistance to plastic deformation

L. Martinu et al., in Handbook of Thin Film Deposition Technologies, P.M. Martin, ed., Elsevier 2010



Scratch test

L. Martinu, in "Plasma Processing Polymers“
R. d'Agostino et al., eds., Kluwer, 1997



Micro-scratch test (MST)

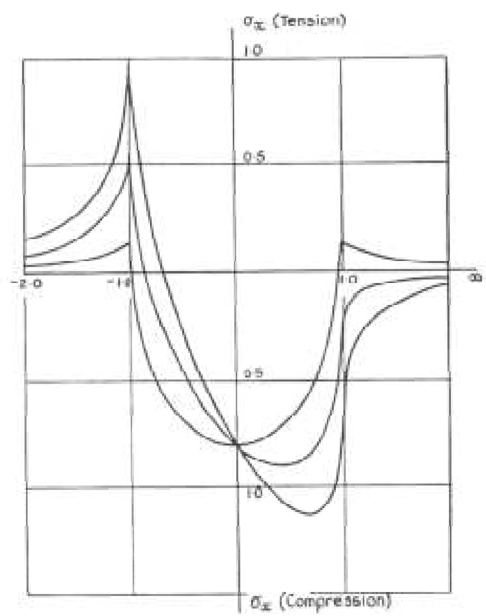
Adhesion measurements: Critical load $\Rightarrow F_C [\mathrm{N}]$

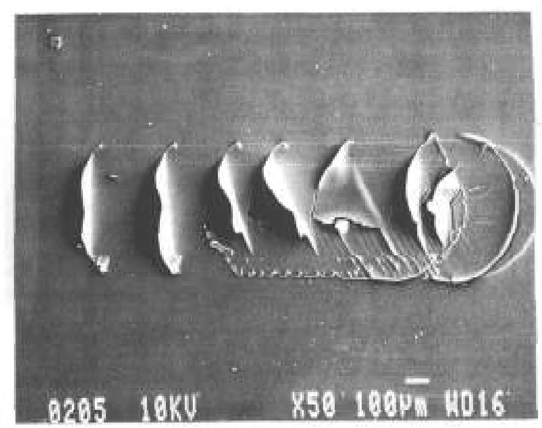
Tip: *hemispherical Rockwell C diamond*
Tip radius: r = 50, 100, 200 μm
Load rate: v = 3 N/min
Load range: F_N = 0 - 30 N

Friction coefficient

$$\mu = \frac{F_T}{F_N}$$

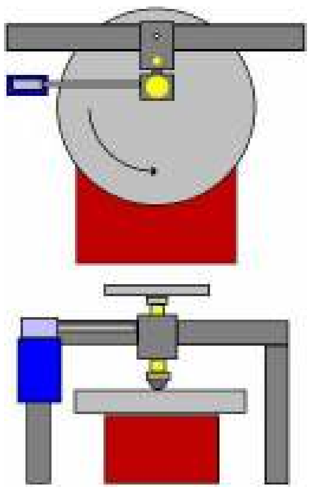
Force: F_N = 1 N
Tip radius: r = 200 μm
Speed: v = 1 cm/min
Scratch length: l = 1 cm





Tribological testing

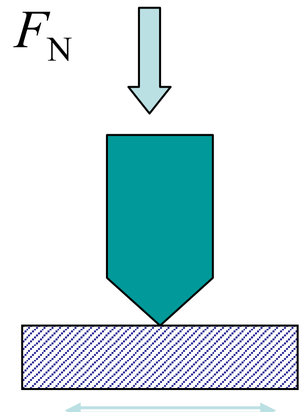
Pin-on-disc

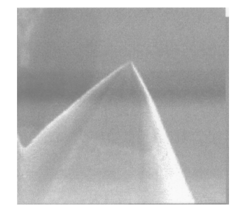


sapphire - 18 GPa
$SiN_{1.3}$ - 17 GPa
Al_2O_3 - 15 GPa
HS steel - 0.9 GPa
$r \sim 3$ mm

Wear test parameters :
frictional force F_T
sliding speed 0.3 cm/s
load F_N = 0.3 - 10 N
RH = 50 %

Triboindenter





diamond tip
$r \sim 3$ μm

Wear test parameters :
load, F_N = 100 μN
scan rate: 24 μm/s
scan size: 4 μm x 4 μm (x30)
distance moved, s = 59,300 μm

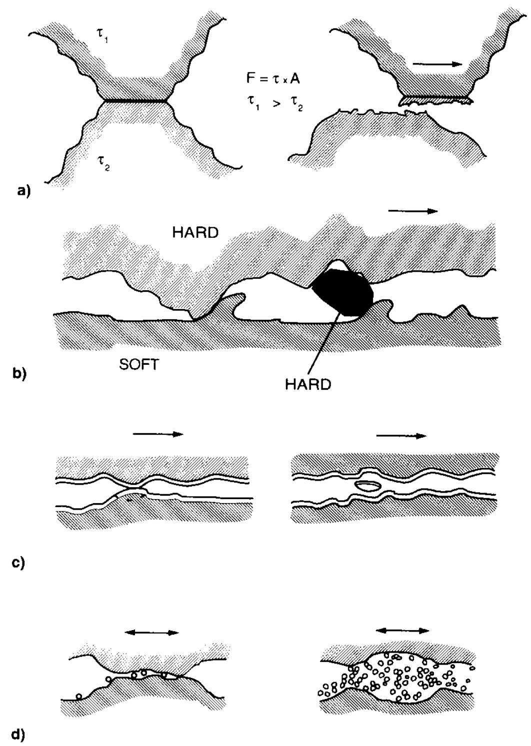
Wear rate: $$K = \frac{V}{F_N s}$$

V – worn volume

Reference: K_{FS} = 10.6 ± 0.9 x 10^{-6} mm^3/Nm

Wear mechanisms

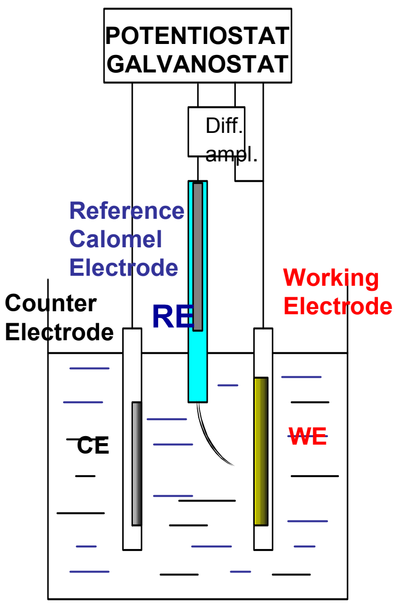
- adhesive
- abrasive
- fatigue
- chemical
- delamination
- brittle fracture
- erosion
- cavitation



K. Holmberg, A Matthews, *Coatings Tribology: Properties, Techniques and Applications in Surface Engineering,* Elsevier 1994

Tribo-corrosion characterization

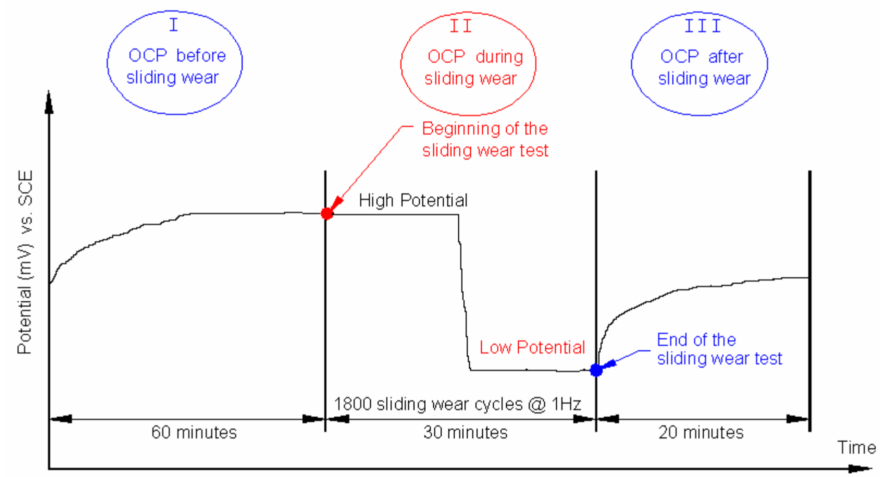
- Structural and compositional analyses (XRD, SEM, EDX, ...)
- Mechanical properties: (hardness, *H,* Young;s modulus, E_r), wear coefficient: *K*
- Corrosion: E_b, i_{corr}, R_p (Potential of WE is measured with respect to RE)
- **Tribo-corrosion:** **Wear test in a liquid environment:**



Three-electrode configuration

M. Azzi et al., Wear 2009

- Reciprocating frequency: 1 Hz
- Normal load: 9 N
- Counterface: Alumina ball 4.5 mm dia.
- Number of cycles: 1800
- Stroke length: 10 mm
- Medium : 1% NaCl in water



The normal force, frictional force, number and rate of cycles and the electrochemical parameters, current and potential, are continuously monitored during the test.

Optical coatings – from design to manufacture

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- Inhomogeneous optical filters
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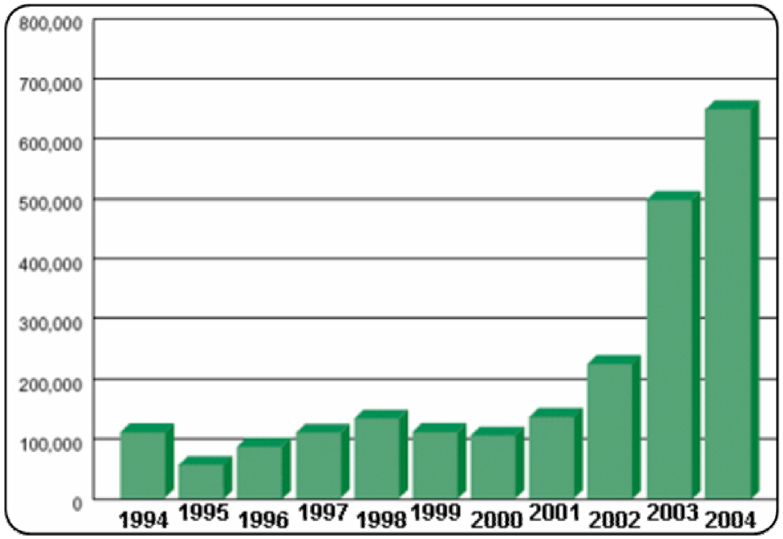
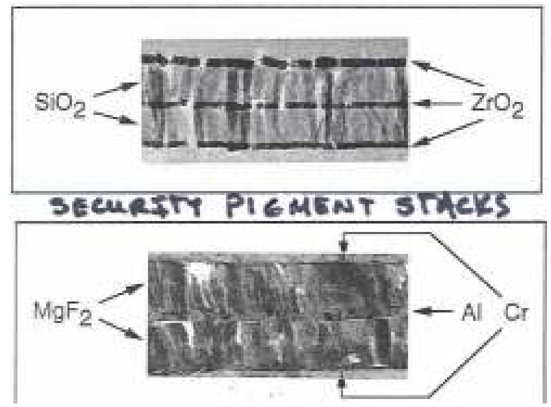
Interference security image structures - ISIS



Total number of Canadian banknotes passed and seized
http://www.rcmp.ca/scams/counter_e.htm



Optically variable devices - OVDs

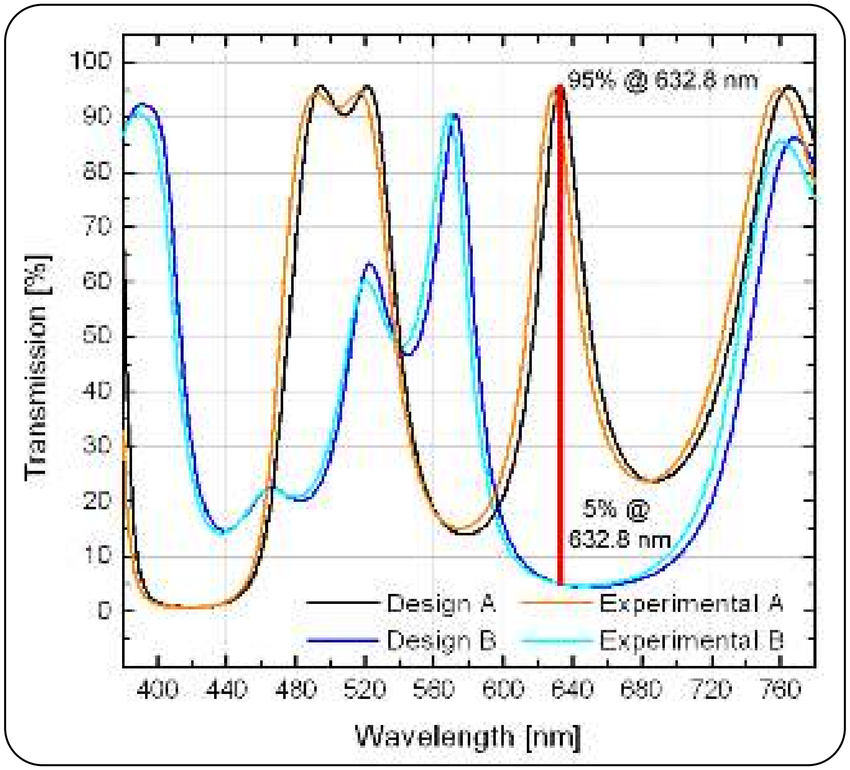
Canadian banknote

US banknote - Optically variable ink

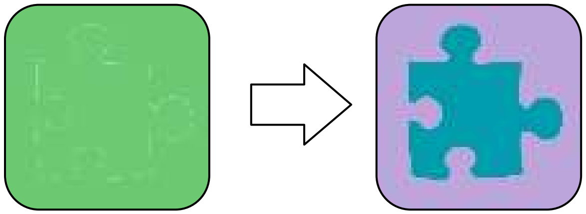
Metameric interference filters

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



Hidden image concept
(0 and 50 degrees)

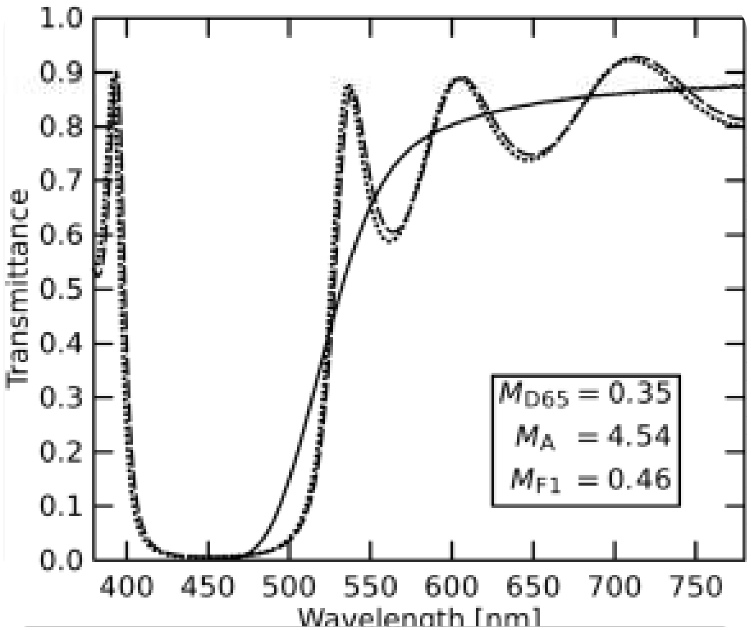


• Pairs of complex metameric filters are **highly sensitive to deposition errors**.

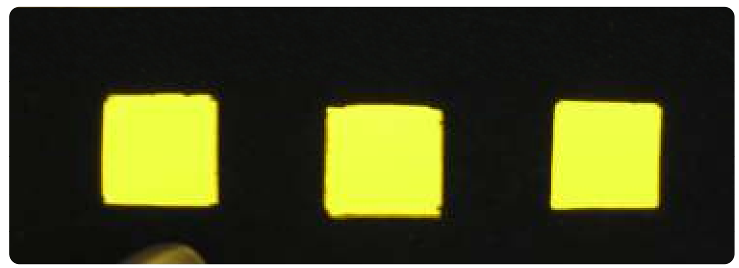
Metamerism in transmission:
Polymer film and interference filter

One of the filters is replaced by a **simple non-iridescent material** (NIM) - <u>Benefits:</u>

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

Structure and color coordinates of four color filters: A-D

Sample	Layers	Total thickness (nm)	Color coordinates (xyY)	Color
Filter *A*	Ta_2O_5/SiO_2 (13 layers)	790	(0.494, 0.453, 48.85)	
Filter *B*	Nb_2O_5/SiO_2 (19 layers)	1600	(0.416, 0.278, 33.80)	
Filter *C*	$Cr/SiO_2/Nb$ (3 layers)	372	(0.196, 0.151, 11.32)	
Filter *D*	$Al/SiO_2/Nb_2O_5/Nb$ (4 layers)	305	(0.380, 0.318, 65.62)	

Substrates: Glass, polycarbonate

Fabrication process: Dual ion beam sputtering,
Magnetron sputtering

Stability tests of the OVDs

(i) immersion into 100% acetone for 24 hours at room temperature

(ii) immersion into a bleach (*4% Sodium Hypochloride*) solution for 24 hours at room temperature

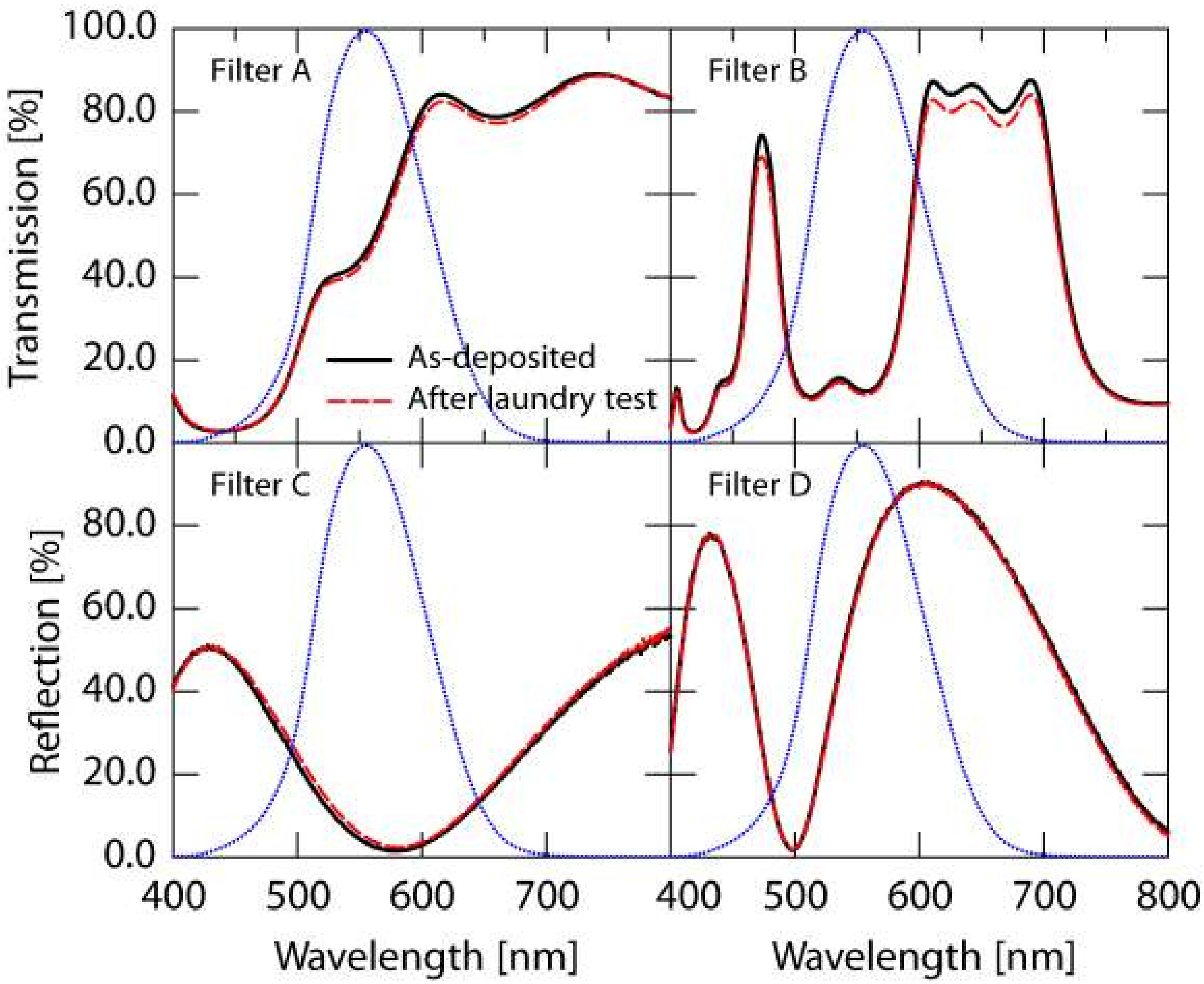
(iii) laundry machine test done at 60^{o}C for two cycles (20 minutes each) using the standard detergent load

(iv) humidity test performed at 80 ^{o}C in a 100% relative humidity environment for 24 h and 480 h

(v) durability test consisting of keeping the samples at 55^{o}C in ambient air for an extended period of time.

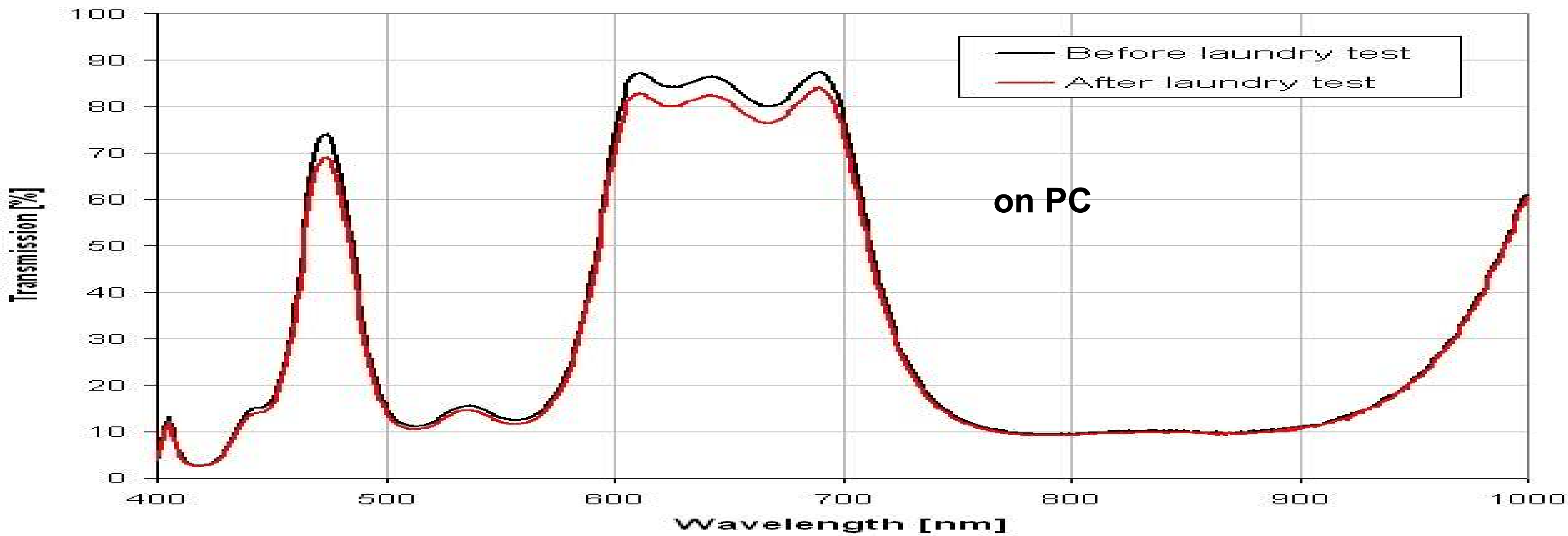
Stability of the OVDs

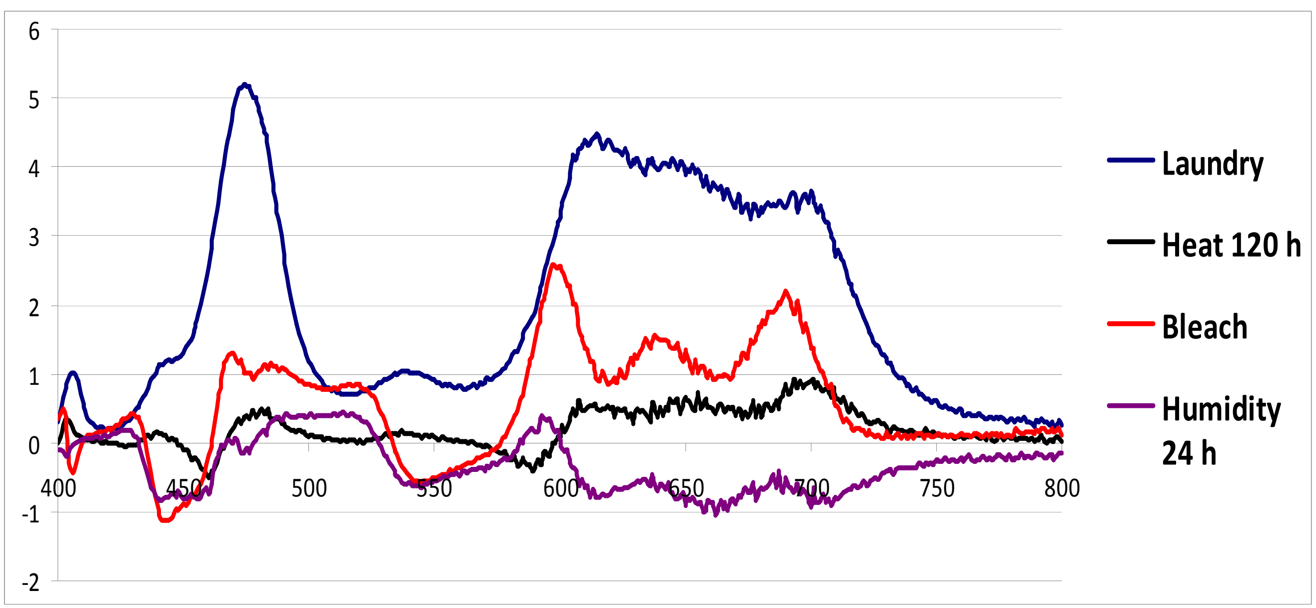
Color effects related to the sensitivity of human eye



E. Cetinorgu,
B. Baloukas et al.,
In preparation, 2011

Evaluation of the stability of filter B





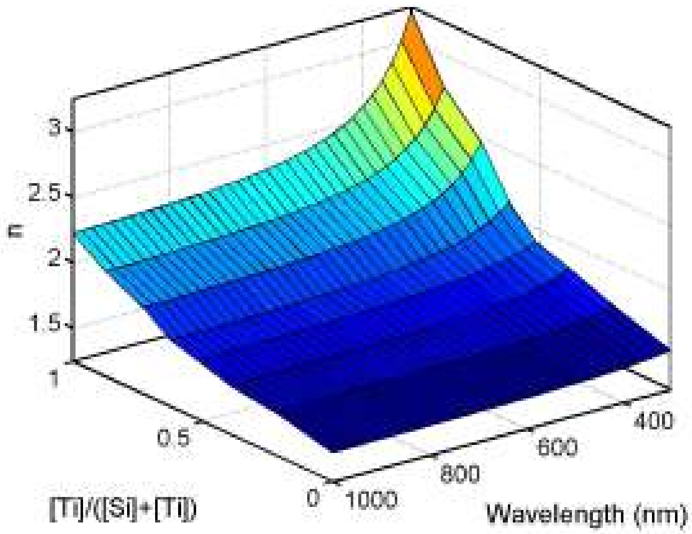
E. Cetinorgu,
B. Baloukas et al.,
In preparation 2011

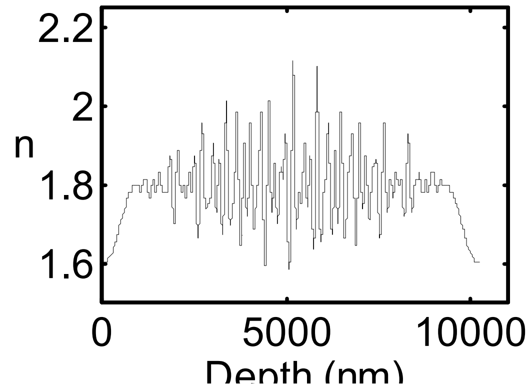
Color difference between the original filters' color and that obtained after each individual test for three different illuminants

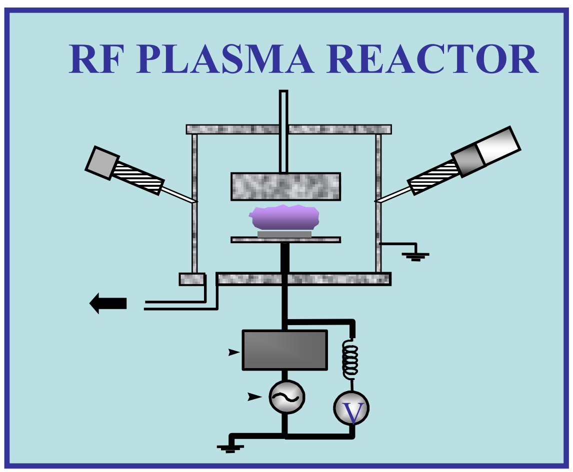
Sample	Illuminant	ΔE$_{(L^*a^*b)}$												
		Bleach		Acetone	Laundry		Heat				Humidity			
		Glass	PC	Glass	Glass	PC	Glass 120 h	Glass 720 h	PC 120 h	PC 720 h	Glass 24 h	Glass 480 h	PC 24 h	PC 480 h
Filter A	D65	1.11	7.26	0.47	0.60	2.40	0.13	0.22	0.45	0.49	2.68	2.18	1.24	3.21
	A	0.99	6.61	0.42	0.50	2.15	0.13	0.23	0.43	0.45	2.43	1.86	1.27	2.88
	F1	1.18	7.57	0.50	0.63	2.56	0.13	0.21	0.41	0.47	2.90	2.36	1.20	3.40
Filter B	D65	0.38	0.73	0.09	1.06	1.72	0.38	0.41	0.11	0.26	0.44	0.76	0.28	3.42
	A	0.42	0.79	0.18	0.67	1.79	0.38	0.47	0.17	0.27	0.78	0.70	0.20	3.72
	F1	0.68	0.73	0.09	1.12	1.64	0.46	0.54	0.04	0.20	0.96	1.06	0.25	3.09
Filter C	D65	Fully delaminated		4.67	12.78	6.88	1.65	10.28	2.41	11.05	21.49	69.24	-	-
	A			3.96	10.47	5.57	1.34	8.07	1.94	9.41	17.26	56.14	Strong	-
	F1			4.89	14.12	7.57	1.93	10.86	2.67	11.93	22.09	72.01	Change?	-
Filter D	D65	Fully delaminated		1.25	1.11	0.73	0.74	1.40	2.22	1.47	Partially delaminated		Partially delaminated	
	A			1.08	0.75	0.54	0.52	1.05	1.65	1.52				
	F1			1.01	1.12	0.74	0.78	1.04	2.03	1.54				

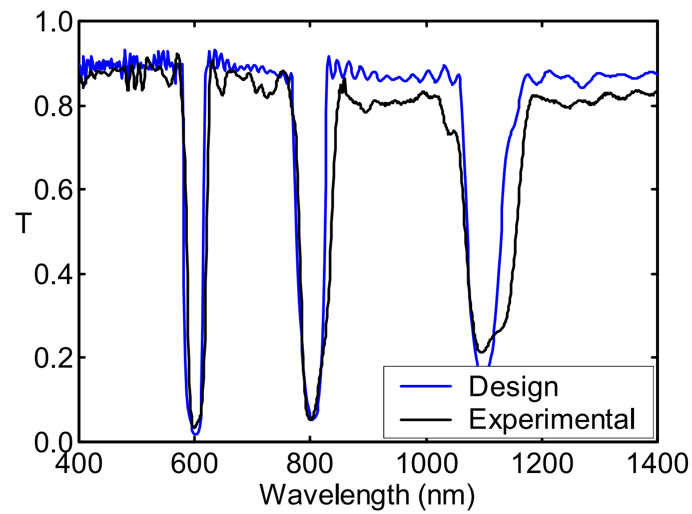
Filter *A* : Ta_2O_5/SiO_2 (13 layers)
Filter *B* : Nb_2O_5/SiO_2 (19 layers)
Filter *C* : $Cr/SiO_2/Nb$ (3 layers)
Filter *D* : $Al/SiO_2/Nb_2O_5/Nb$ (4 layers)

Design and fabrication of inhomogeneous filters







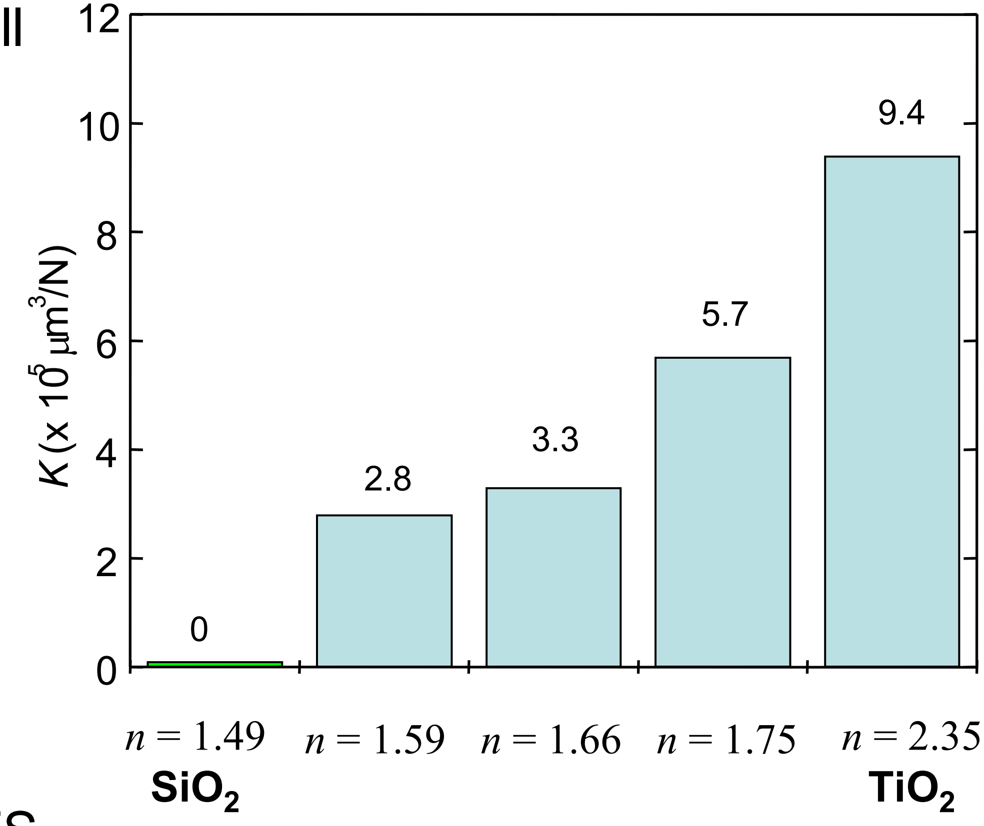


OpenFilters: S. Larouche et al, Appl. Opt., 2008; S. Larouche et al., Appl. Opt. 2004

Wear rate for TiO_2/SiO_2 films with different *n*

Sapphire ball

F = 0.3 N



Substrate: FS

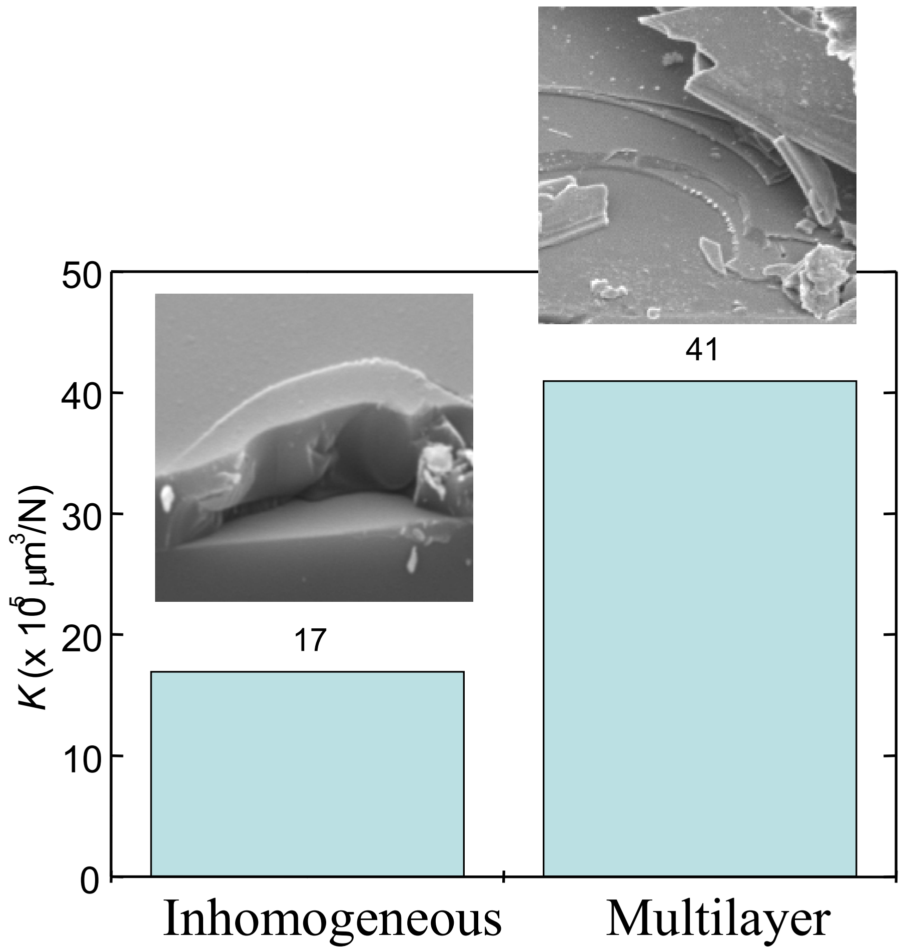
d = 1.0 μm

M.-A. Raymond et al., Proc 44th Tech. Conf., SVC, 2011

Wear rate for multilayer vs inhomogeneous systems

Sapphire ball

F = 0.3 N



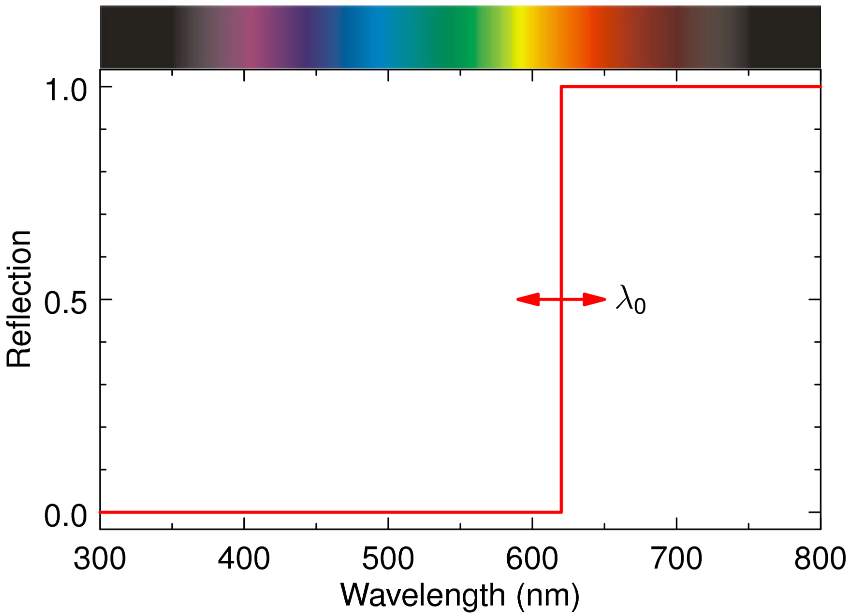
Substrate: FS

d = 1.0 µm

Wear rate ratio $K_{(multi)}/K_{(inhom)}$ = 2.4

M.-A. Raymond et al., Proc 44th Tech. Conf., SVC, 2011

Quest for the red color



Requirements:

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

Ideal reflection spectrum

Target color coordinates

3 layer design

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, Collab. with Hauzer Techno Coating

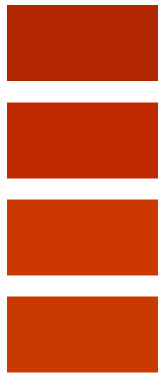
Reflection spectra of deposited coatings

Sample 1

Sample 2

Sample 3

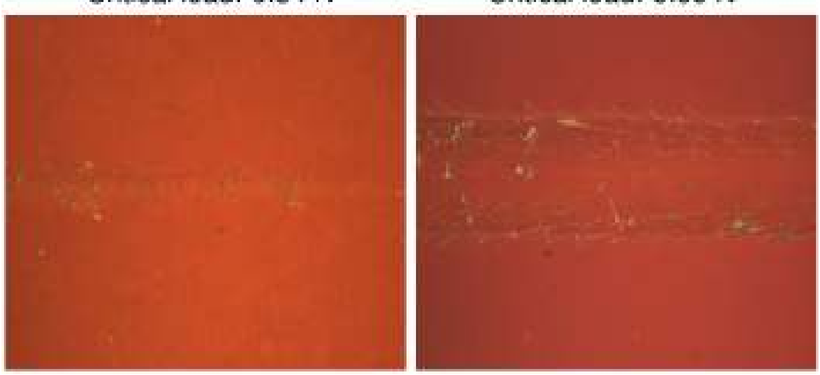
Sample 4



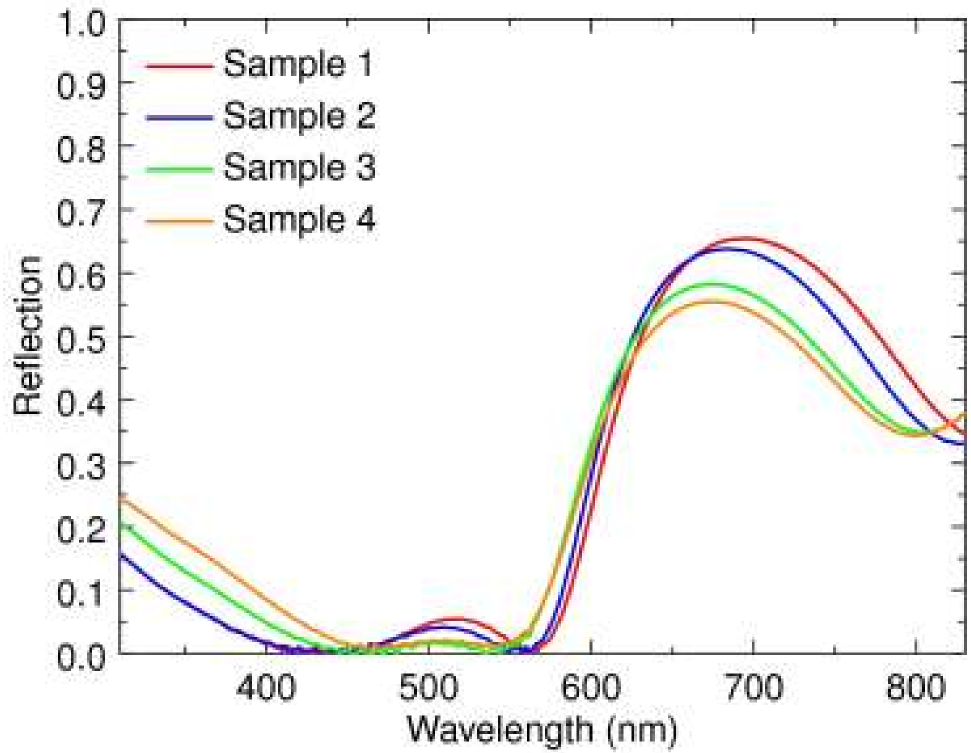
Enhancement of the scratch resistance

Fe_2O_3/SiON coating
Critical load: 0.34 N

TiN/Fe_2O_3/SiON coating
Critical load: 5.65 N

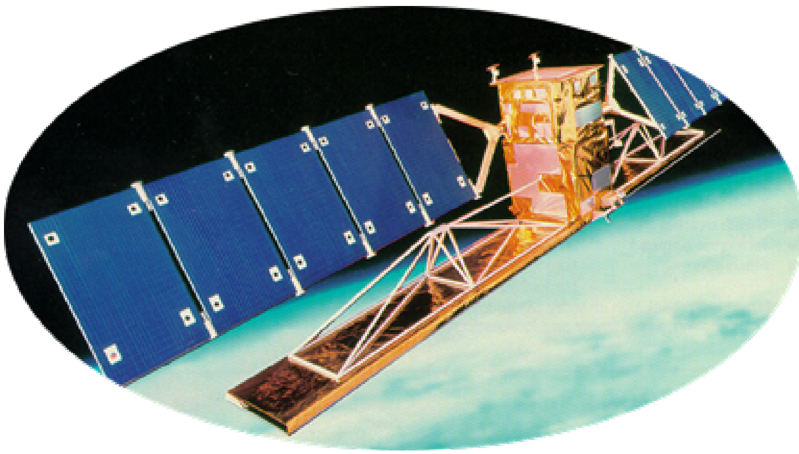


Reflection spectra of red coatings measured by spectrophotometry



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

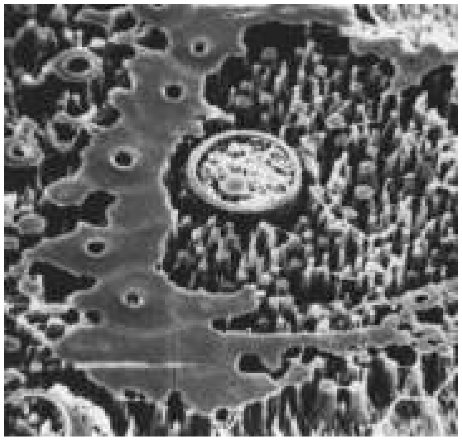
Outer space applications: Characteristics of the space environment



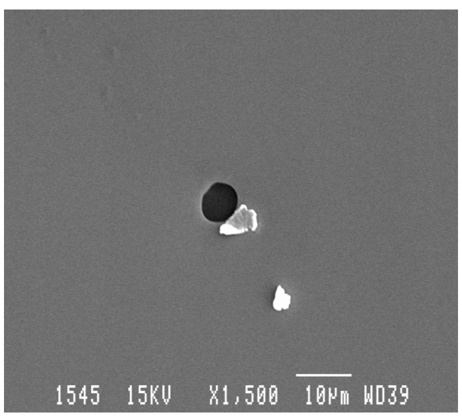
- Atomic oxygen (90% at an altitude of 300 km)
- Pressure (10^{-6} Torr)
- Intense ultraviolet radiation
- Cyclic changes of temperature (-150° C to 150°C)
- Build-up of surface electric charge
- Micrometeorites

Protection against atomic oxygen

Uncoated Kapton



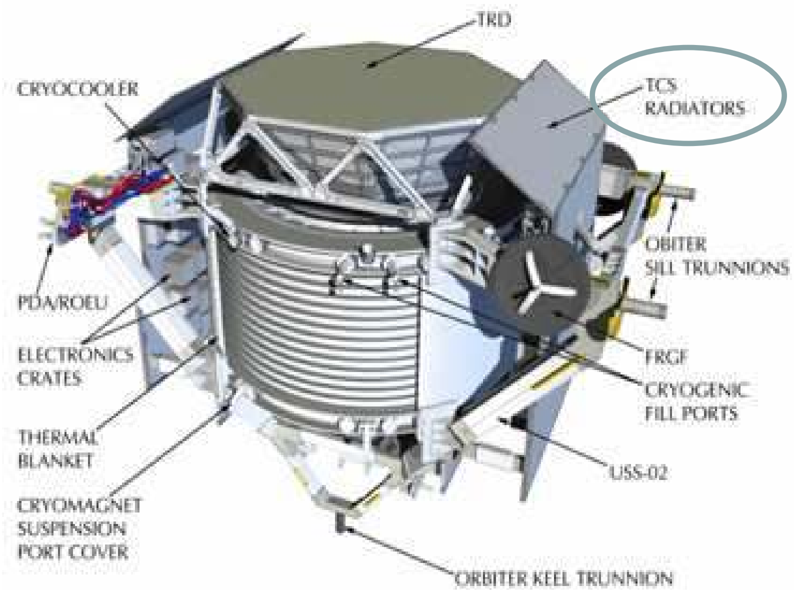
SiO_2-coated Kapton after 6 months in space



Diamond-like carbon atomic oxygen sensors with controlled concentrations of bonded and unbonded hydrogen

Participation in 6 Space Shuttle flights since 1990's
Collaboration with the CSA and NASA

Energy management in satellites



<u>Space environment heat load:</u>

Sun side 1300 W/m^2

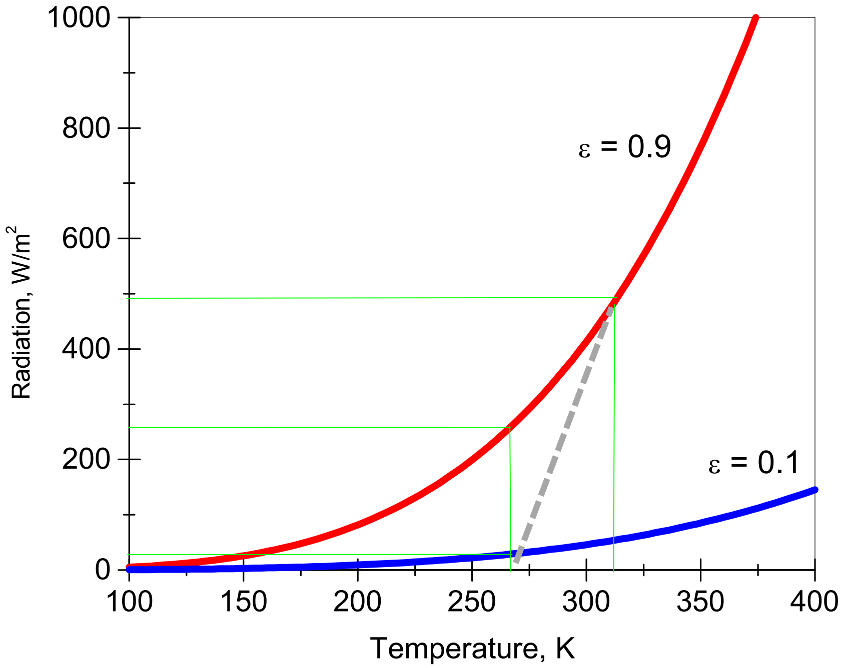
Dark side 5 W/m^2

Radiation is the only way to release the excess energy

Spacecraft Thermal Control Handbook, Vol. 1: Fundamental Technologies The Aerospace Press , 2002

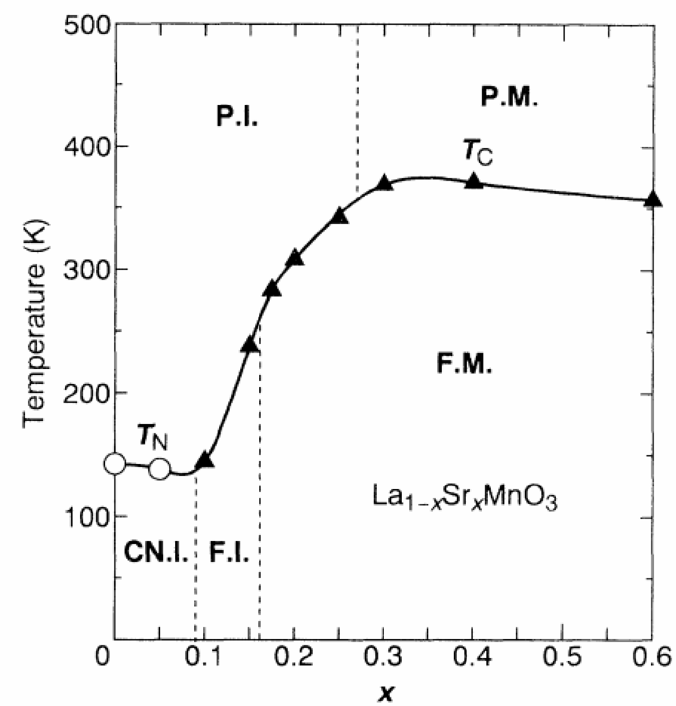
Passive	Active
Constant conductance or diode heat pipes	Variable conductance heat pipes, looped heat pipes, or capillary pumped loops
Hardwired heaters (fixed and variable-resistance, such as auto-trace or positive temperature-coefficient thermistors)	Resistance heaters with commandable mechanical or electronic controllers
Thermal storage devices (phase change or sensible heat)	Heat pumps and refrigerators
	Stored coolant systems
Thermal insulation (multilayer insulation, foams, or discrete shields)	Pumped fluid loops
Radiators (fixed, articulated, or deployable) (with louvers or pinwheels)	Thermoelectric coolers
Surface finishes (coatings, paints, treatments, second-surface mirrors)	

Variable emissivity for temperature stabilization



<u>Ways to change ε:</u>

- Louvers
- MEMS
- Electrochromics
- **Thermochromics**

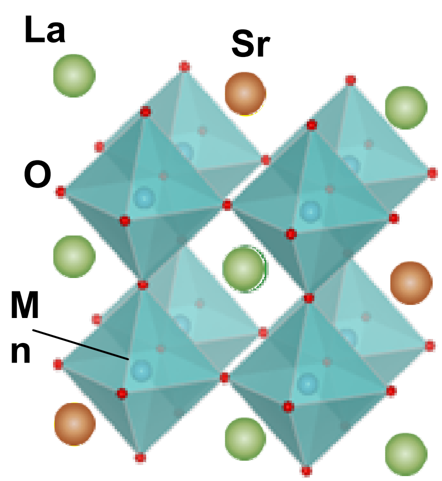


A. Urushibara, Phys. Rev. B, **51 (1995)** 14103

$La_{1-x}Sr_xMnO_3$ – LSMO

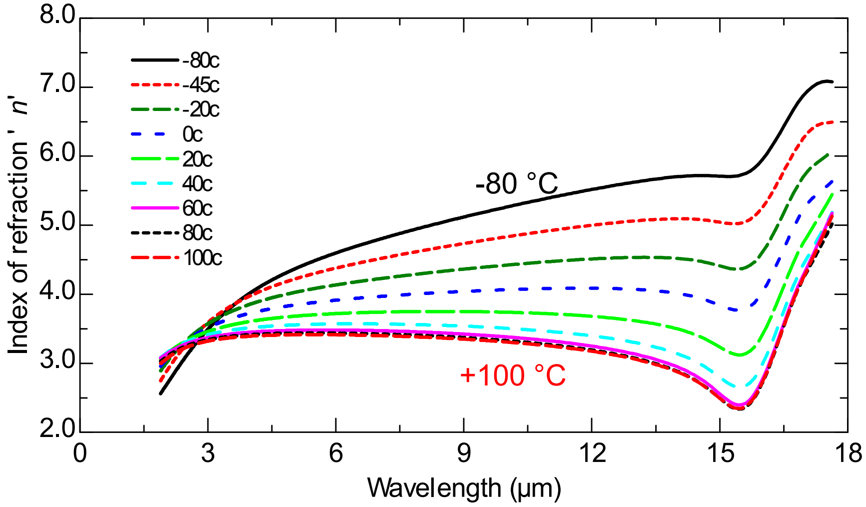
Metal (low ε) to insulator (high ε) phase transition (MIT): - 10 °C to + 100 °C

T_{MIT} depends on the Sr concentration (x)

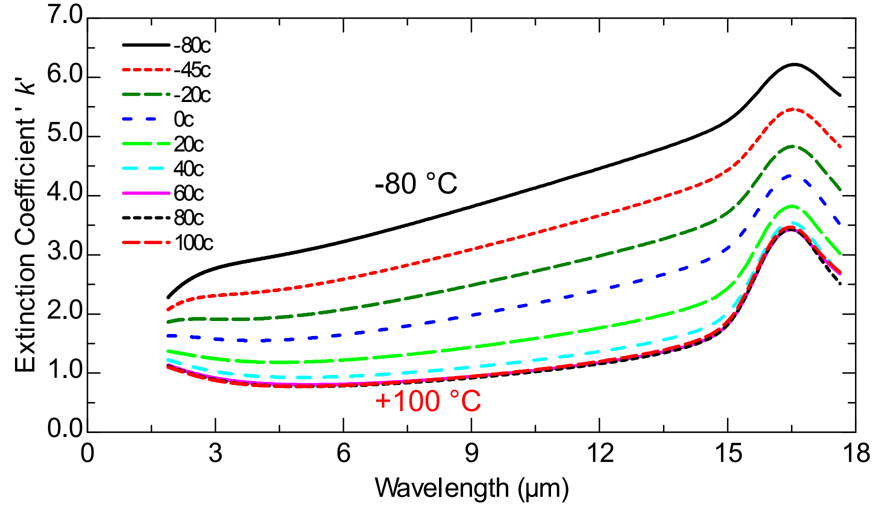


Temperature dependent optical constants

n (λ, T)



k (λ, T)



2.2 < n < 5.8 @ 15 µm

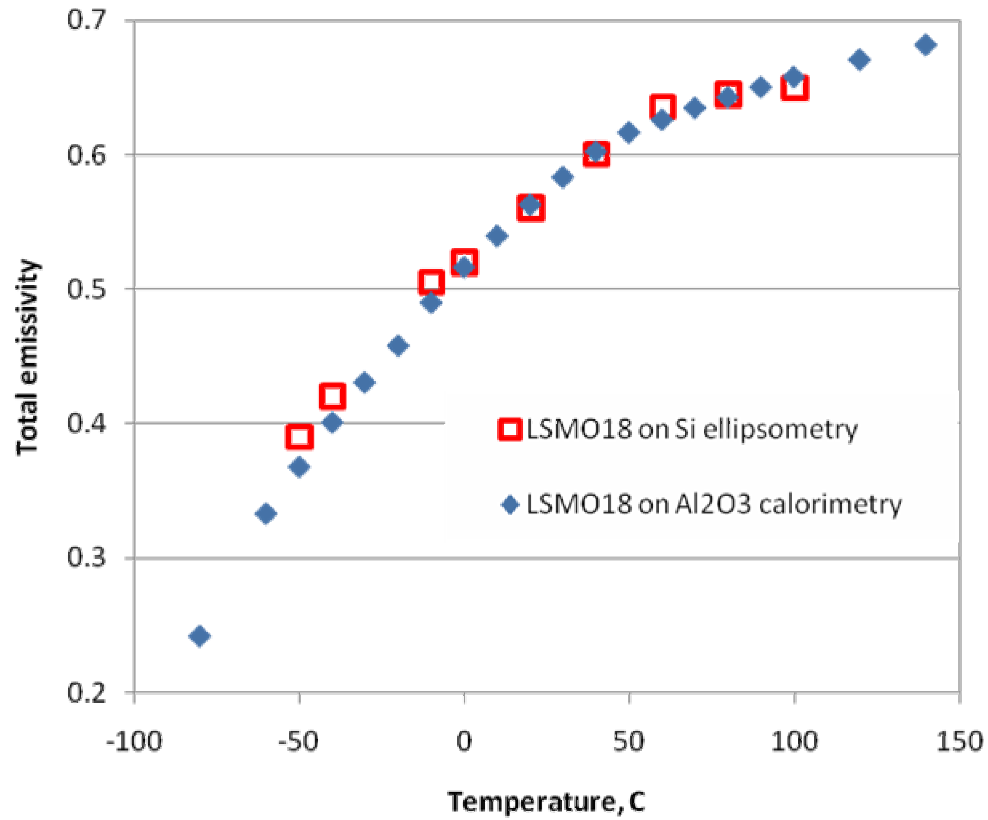
This allows one to calculate specular:

Reflection: (λ, T,θ,s-p, d, ….)
Transmission: (λ, T,θ,s-p, d, ….)
Adsorption (λ, T,θ,s-p, d, ….)

on different substrates or in multilayers

O. Zabeida et al., Proc. SVC, 2010

Emissivity from ellipsometry and calorimetry measurements



RADARSAT is being lowered into the Thermal Vacuum Chamber during thermal qualification at the Canadian Space Agency's David Florida Laboratory in Ottawa. Courtesy of: Communications Research Center Canada

- **Excellent agreement between two methods: Ellipsometry and calorimetry**
- **$\Delta\varepsilon \approx 0.4$**

O. Zabeida et al., Proc. SVC, 2010

Conclusions

Each optical application represents specific environmental stability and functional properties criteria:

a) Need for better understanding – multitechnique approaches

b) New metrology – applicable to optical coatings

c) New solutions – materials, processes, design strategies

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Oleg Zabeida

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6th Symposium on Functional Coatings and Surface Engineering,
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- Thin films with tailored optical, mechanical, tribological, electrical, thermal and other functional properties
- Smart coating materials and film systems
- Vacuum and non-vacuum deposition processes, process control and diagnostics
- Plasma processes and plasma-surface interactions
- Thin film systems for passive and active optical filters and waveguides
- Protective tribological coatings with enhanced wear, scratch, abrasion, erosion and corrosion resistance
- Characterization methods of the microstructure and of the functional properties
- Thin film materials and systems for optical, optoelectronic, aerospace, energy-control, biomedical, micro-system, sensor and other applications
- Surface and interface engineering approaches for the control of adhesion, stress and environmental stability

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