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**
18***	*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**

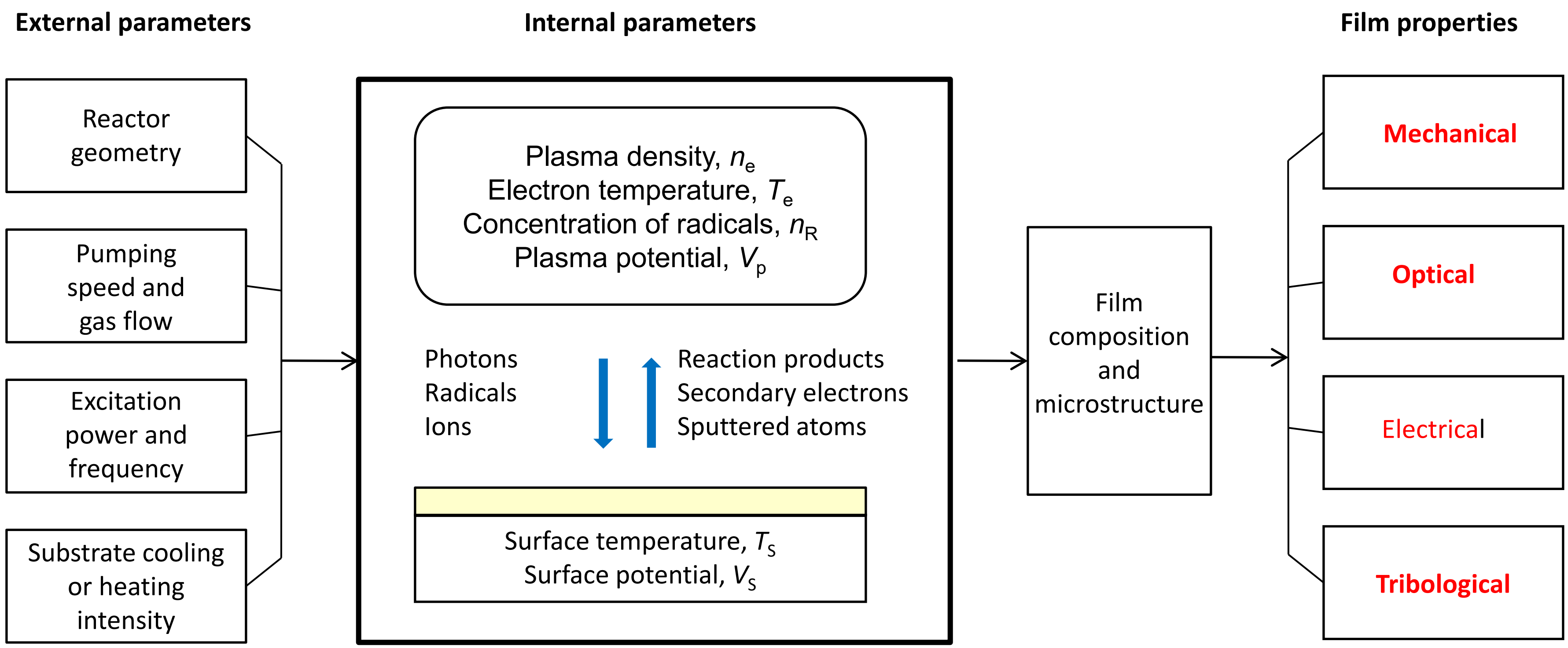
Presentation: **18 April p.m.**

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

Project #3: Applications of nanostructured films and coatings

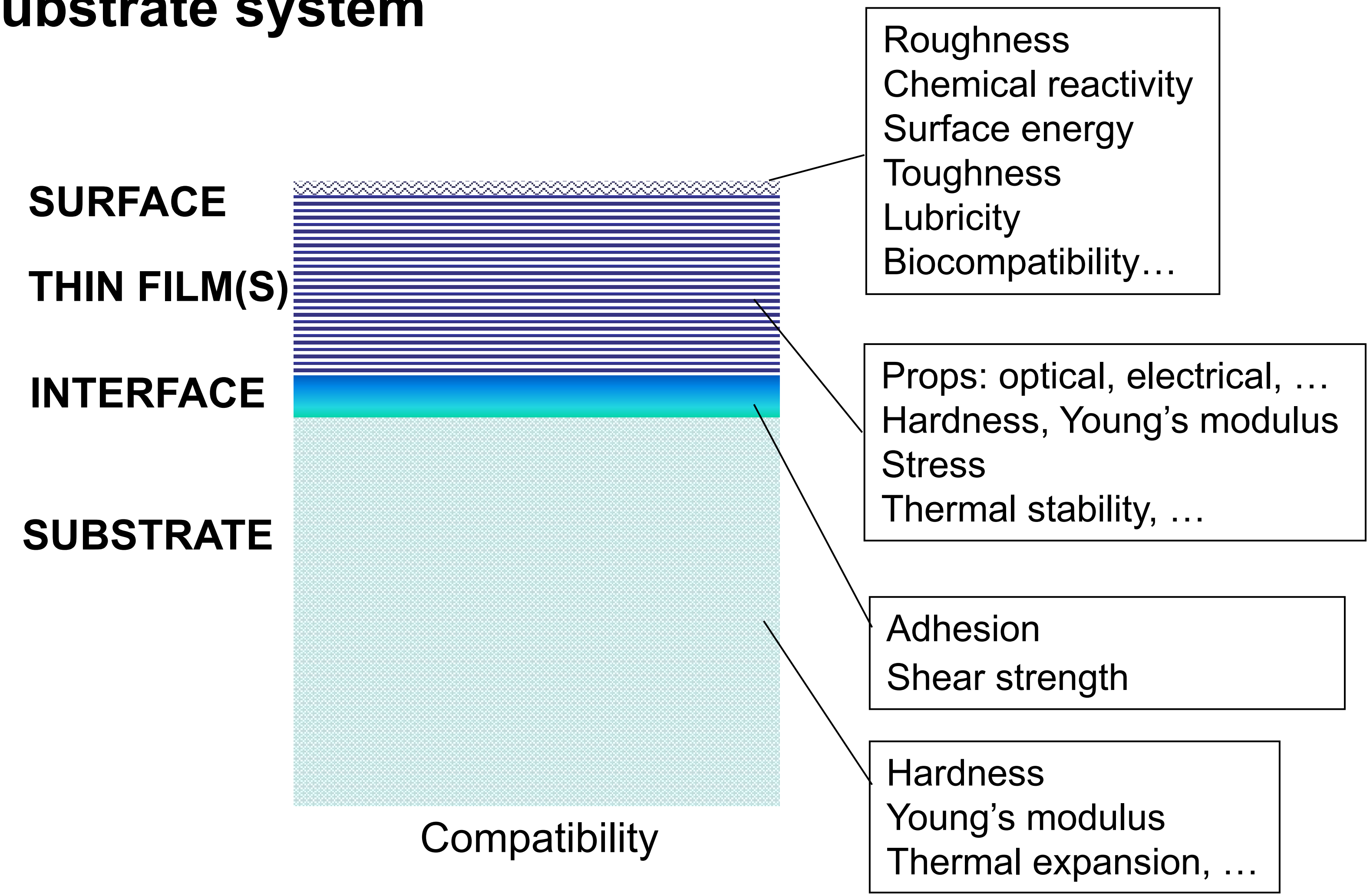
- Thomas Sicotte and Alexandre Gamache - Cellules photovoltaïques à pérovskite
- Alexandre Lussier - Fenêtres intelligentes thermochromiques
- Mohamed Ammari - Thermal barrier coatings for aerospace gas turbine engine
- Luc Montpetit - Passivation of CdZnTe for x-ray detectors
- Veronika Cervenkova - Solar-thermal energy conversion - Transition metal nitrides
- Émilien Martel - Electrochromic, photochromic and gasochromic coatings for consumer optics
- Étienne Tremblay et Nathan Sasseville - Couches minces pour l'électronique organique – OLEDs
- Thomas Lapointe - Photodétecteurs et leur conception/optimisation à l'aide des couches minces
- Alexandre Carrière et Youssef Ben Mami - Électrodes transparentes pour la fabrication des cellules solaires
- Arghavan Yazdanpanah Ardakani - Nanoengineering thin-films to produce hydrophobic coatings for aircraft surfaces
- Mathieu Bruzzese – Oxidation-resistance barrier coatings for aerospace applications
- Bastien Izacard – Atomic oxygen barrier coatings for satellites
- Alexandre Fall - Carbon nanotubes for sodium-ion batteries
- Alexandre Pinel - Couches minces d'hydroxyapatites pour les implants en biomedical
- Christelle Abou Zeidan – Carbon nanotubes for flexible electronics

Plasma system and process and materials control

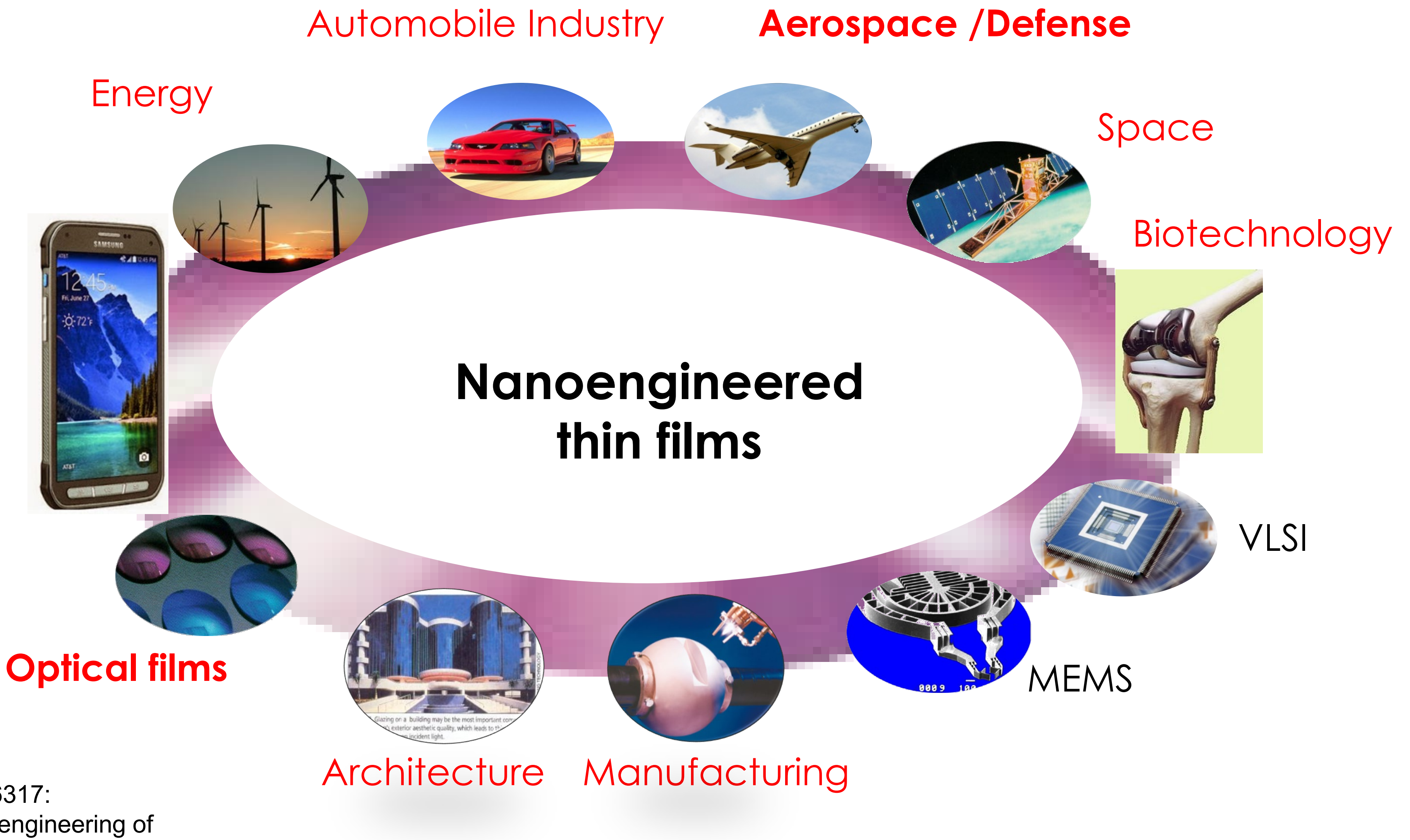


L. Martinu et al., Chapter 9 in "*Handbook of Thin Film Process Technology*", P.M. Martin, ed., Elsevier, 2010.

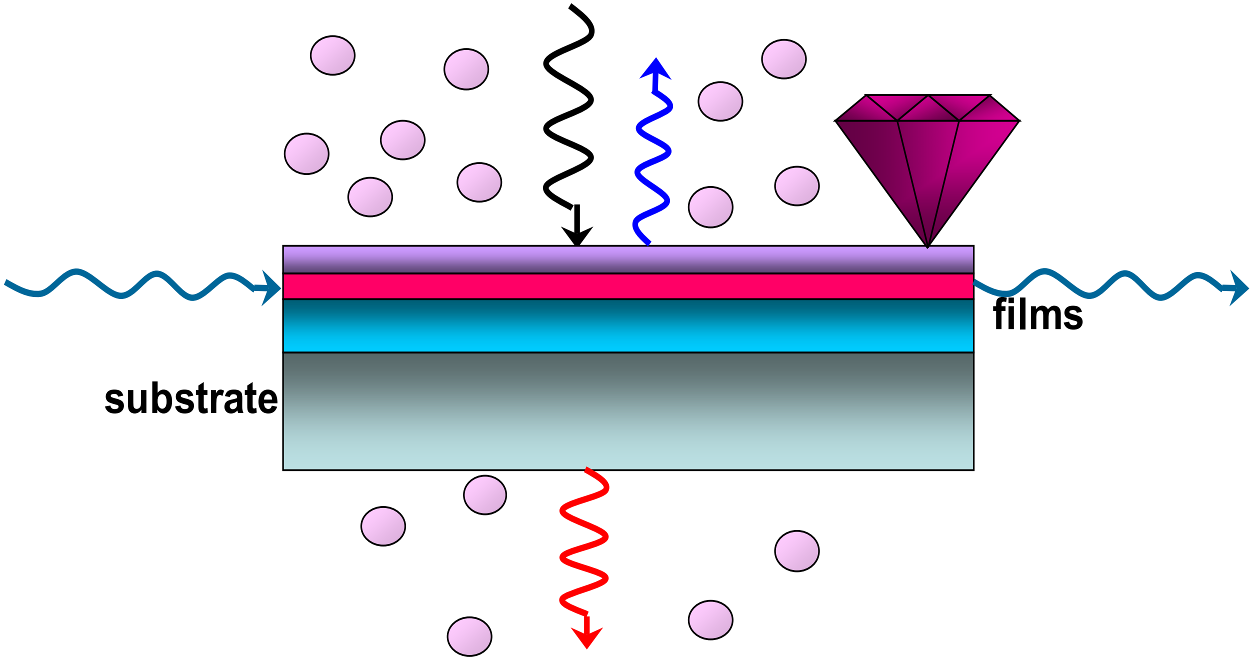
Control of the properties through the microstructure: Film-substrate system



Multisectorial character of advanced materials



Nanostructured functional and multifunctional thin films



The concept of nanostructured functional and multifunctional coatings

-

“We are limited only by our imagination”

Challenges

Main/complementary properties
Compatibility (substrate, process,…)
Process control
Stability
Industrial scale, cost

Deposition technologies

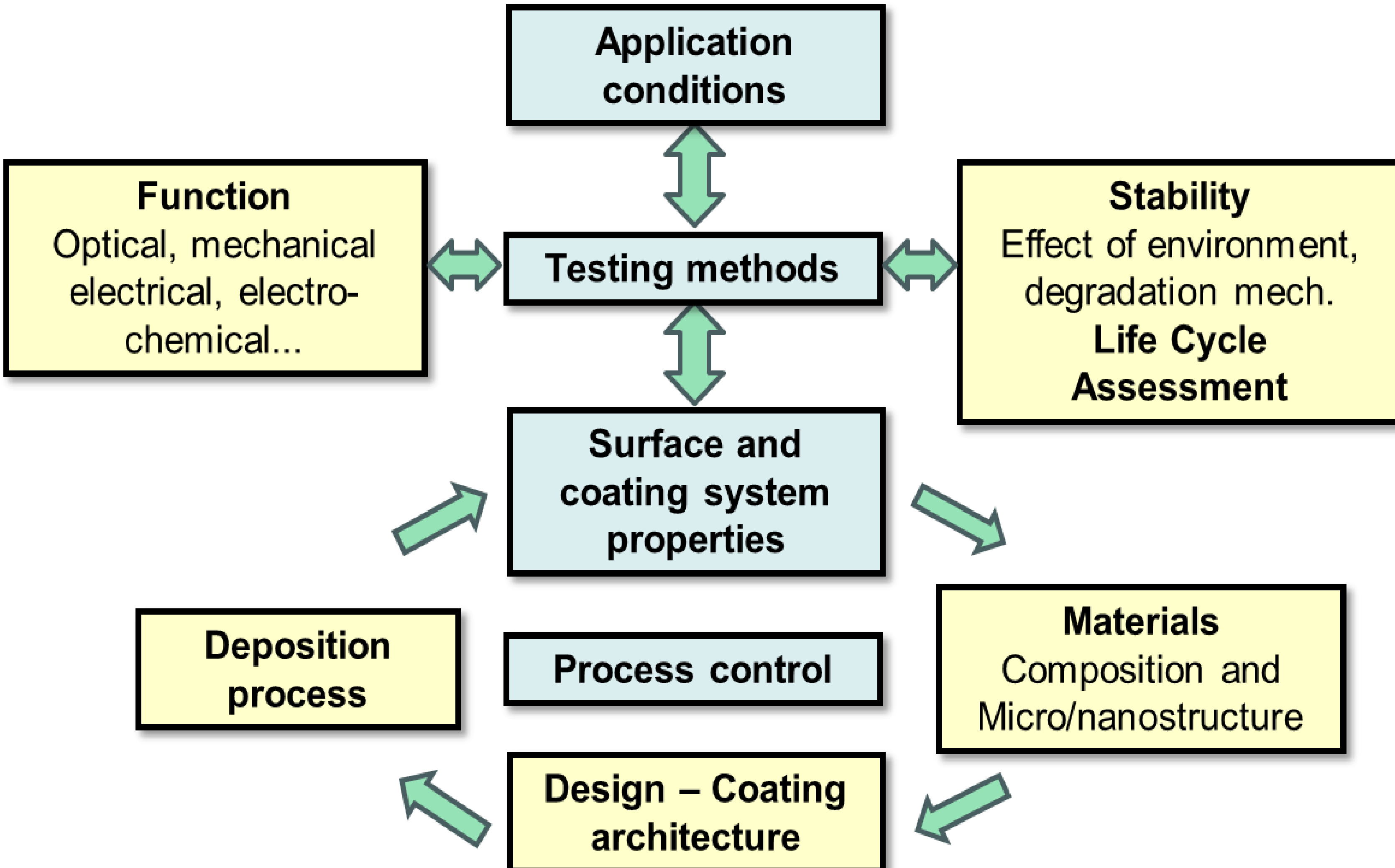
New materials:

- passive functional
- active - smart,
- compounds, nano-materials, nanocomposites

Coating architectures:

- single layers
- (discrete) multilayers
- graded layers
- nanostructures
- control of interfaces

The **holistic approach** to surface engineering



Development of passive thin films

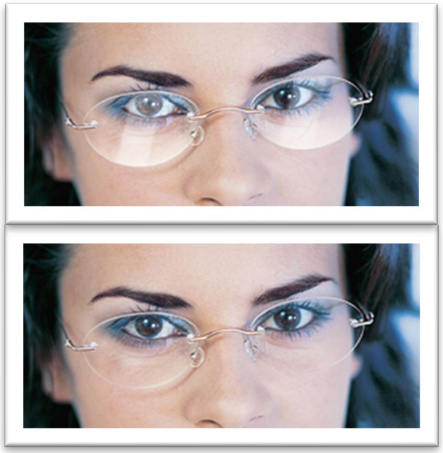
Optical coatings:

- Choice of the fabrication technique
- New technologies

Gas and vapor diffusion barriers:

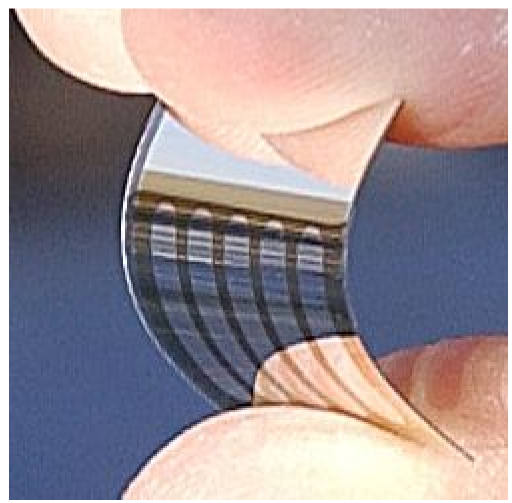
- Thin films on plastics

Optical coatings



The AR council
(www.arcouncil.org)

Bank of Canada



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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

Fabrication processes

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

Optical design strategies

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

Requirements for optical films

1. **Optical properties** – complex refractive index

$$N = n - ik$$

x.xx — filters
x.xxx — waveguides
$\leq 10^{-5}$ — transparent

2. Mechanical and tribological properties
3. Environmental stability (T, RH, …)
4. Functional properties (hydrophobicity/hydrophilicity, electrical conductivity, gas/vapor permeation barriers …)
5. Active properties (electrochromic, thermochromic, photochromic and other properites)

Refractive index of optical coatings

L. Martinu and D. Poitras
J. Vac. Sci. Technol. A 18,
2619-2645 (2000)

L. Martinu et al., Chapter 9 in the "Handbook of Film Deposition Technologies",
P.M. Martin, ed., Elsevier 2010

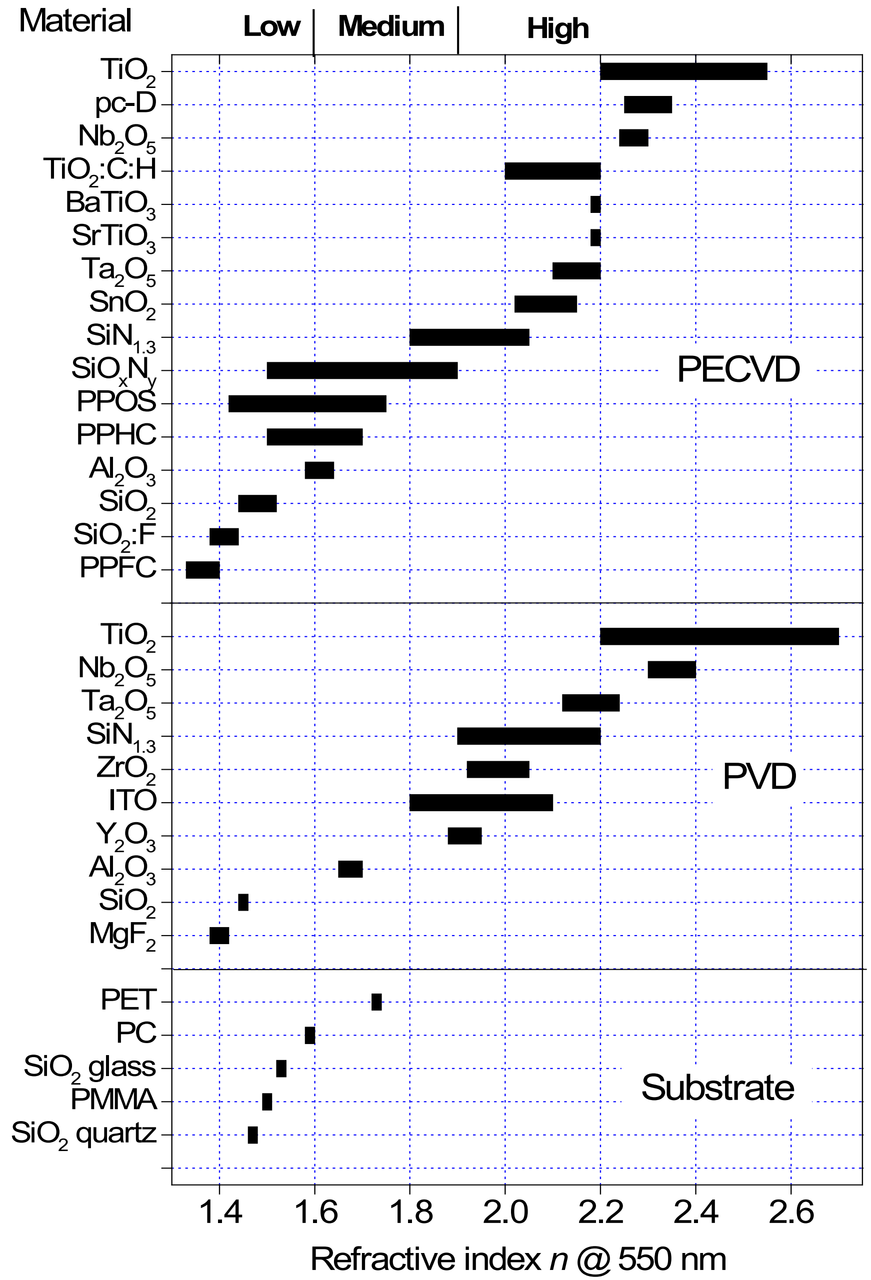
Requirements:

Choice of n_H and n_L

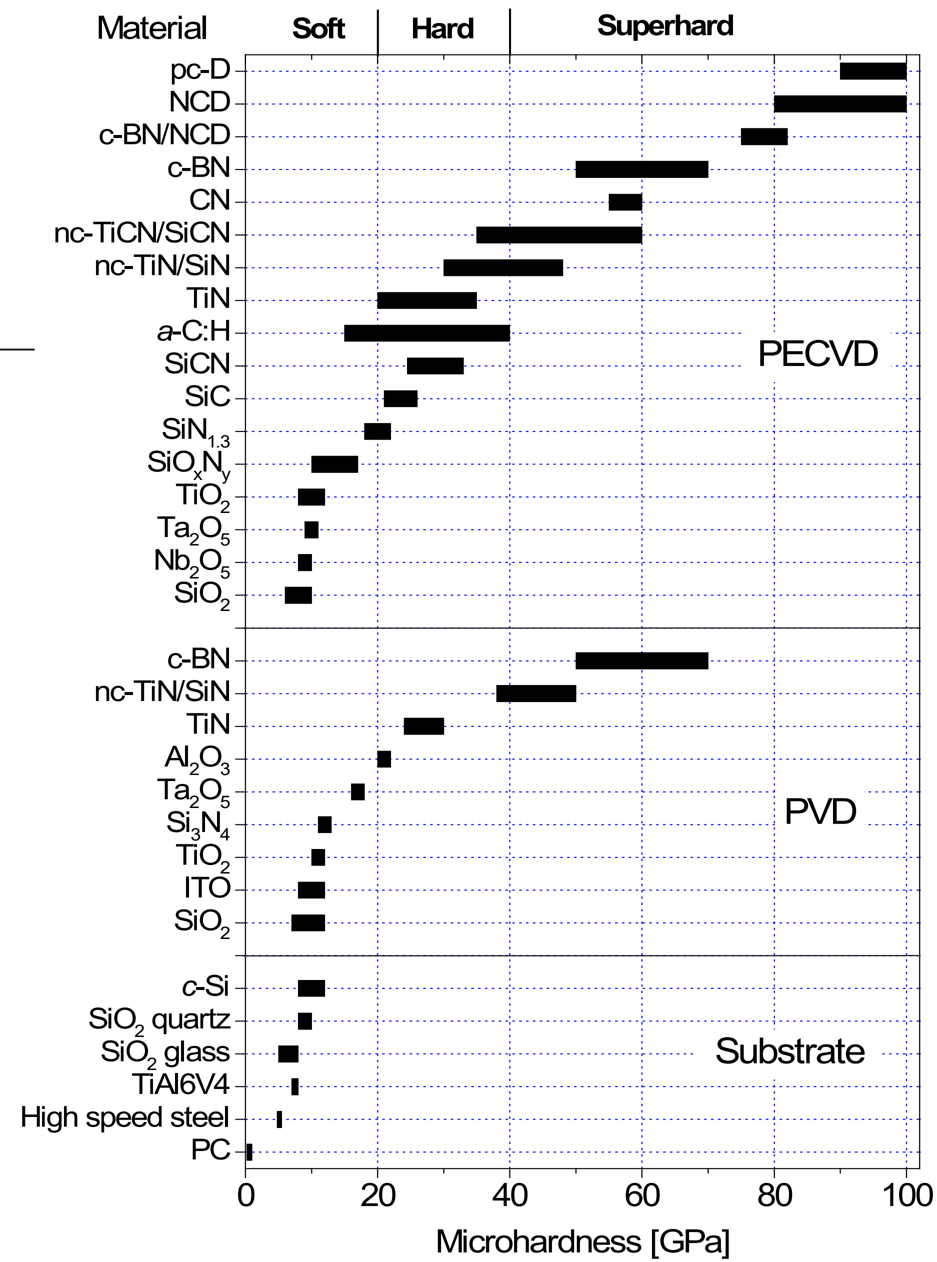
Compatibility with substrates

Durability and environmental stability

Compatibility with other process technologies



Microhardness of different coatings



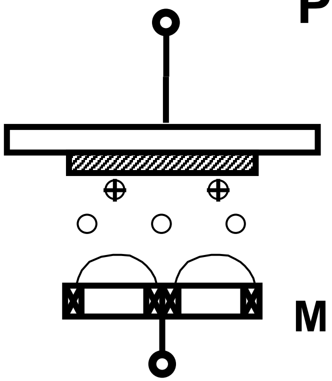
L. Martinu and D. Poitras
J. Vac. Sci. Technol. A, 18 (2000) 2619

L. Martinu et al., Chapter 8 in “Handbook of Film Deposition Technologies, P. Martin, ed., Elsevier 2010

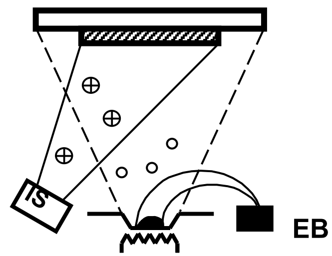
J.E. Klemberg-Sapieha et al., Appl. Optics 43 (2004) 2670

Comparison of different deposition techniques

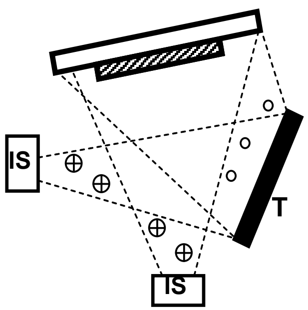
PVD



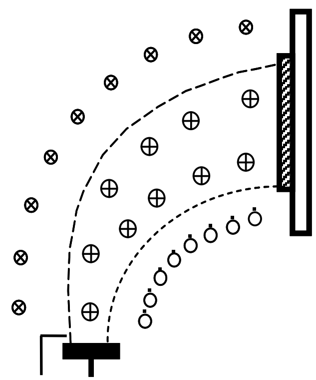
MS: DCMC, PDMS,
RFMS, HiPIMS



IBAD

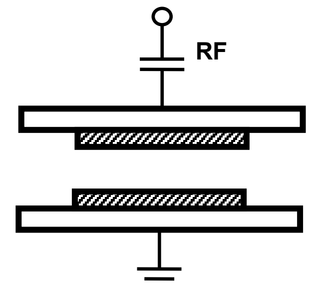


DIBS

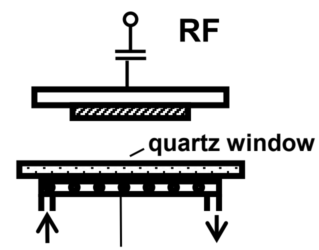


FCAD

PECVD



RF/AC PECVD



Dual mode MW/RF
PECVD

J.E. Klemberg-Sapieha et al., Appl. Opt., 43 (2004) 2670
L. Martinu et al., in 50 Years of Vacuum Coatings, SVC, 2007
L. Martinu et al., in Handbook of Thin Film Deposition Technology, Elsevier, 2010

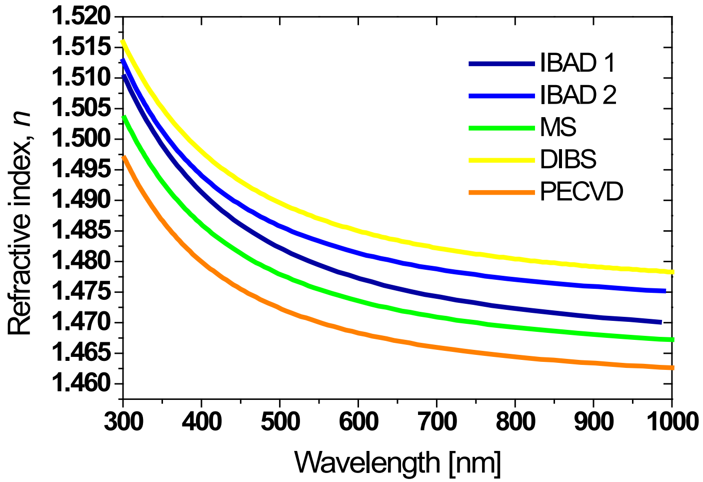
Deposition techniques and parameters

Deposition technique	Coating	Conditions					
		p [Torr]	T_S [°C]	V_B [V]	E_i [eV]	*I* [μA/cm²]	r_D [nm/s]
IBAD 1	SiO_2	$6.0x10^{-5}$	60	0	200	100	0.15
	TiO_2	$1.1x10^{-4}$	100	0	150	185	0.07
IBAD 2	SiO_2	$1.2x10^{-4}$	60	0	115	65	0.20
	Ta_2O_5	$1.5x10^{-4}$	100	0	115	65	0.20
	TiO_2	$1.3x10^{-4}$	80	0	105	100	0.35
MS	SiO_2	$3.1x10^{-4}$	80	0			0.23
	Ta_2O_5	$3.5x10^{-4}$	80	0			0.25
	TiO_2	$3.8x10^{-4}$	80	0			0.13
DIBS	SiO_2	$2.4x10^{-4}$	100	0	300	200	0.37
	Ta_2O_5	$2.4x10^{-4}$	100	0	300	200	0.53
PECVD	SiO_2	$6.0x10^{-2}$	30	600	240	80	2.30
	Ta_2O_5	$2.5X10^{-2}$	30	600	300	90	0.80
	TiO_2	$2.5x10^{-2}$	30	450	225	70	0.60
FCAD	TiO_2	$2.6x10^{-3}$	30	120	50	2500	1.70

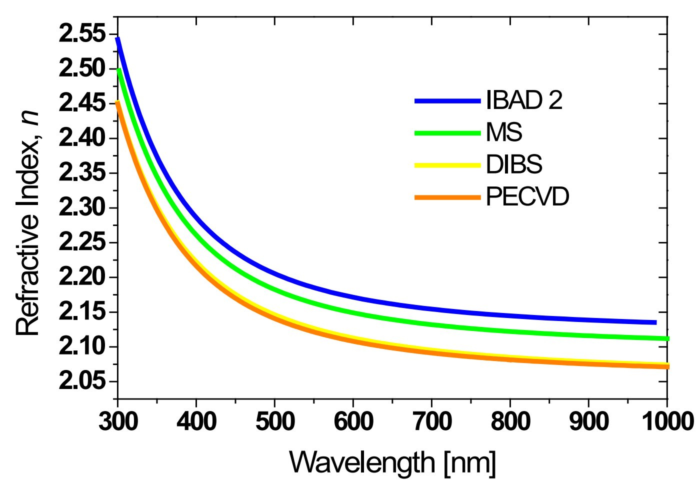
Thickness *d* ~ 1000 nm
Two types of pre-characterized substrates: c-Si (50 mm diameter) and FS (25 mm diameter)

Refractive index dispersion curves

SiO_2



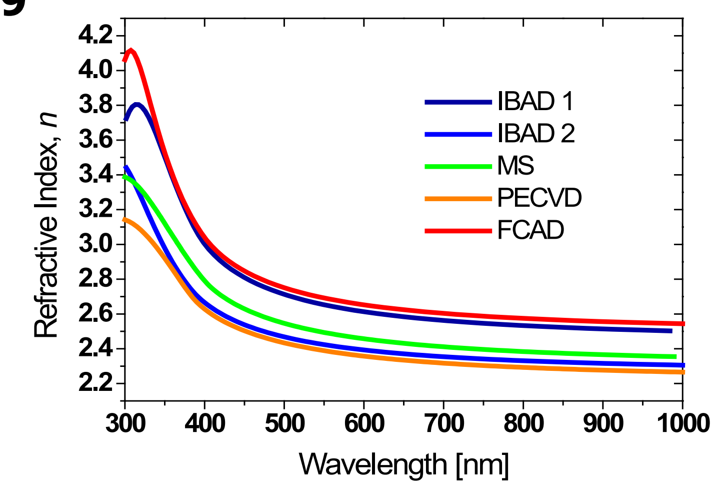
Ta_2O_5



n_{550} = 1.47 – 1.49

n_{550} = 2.13 – 2.19

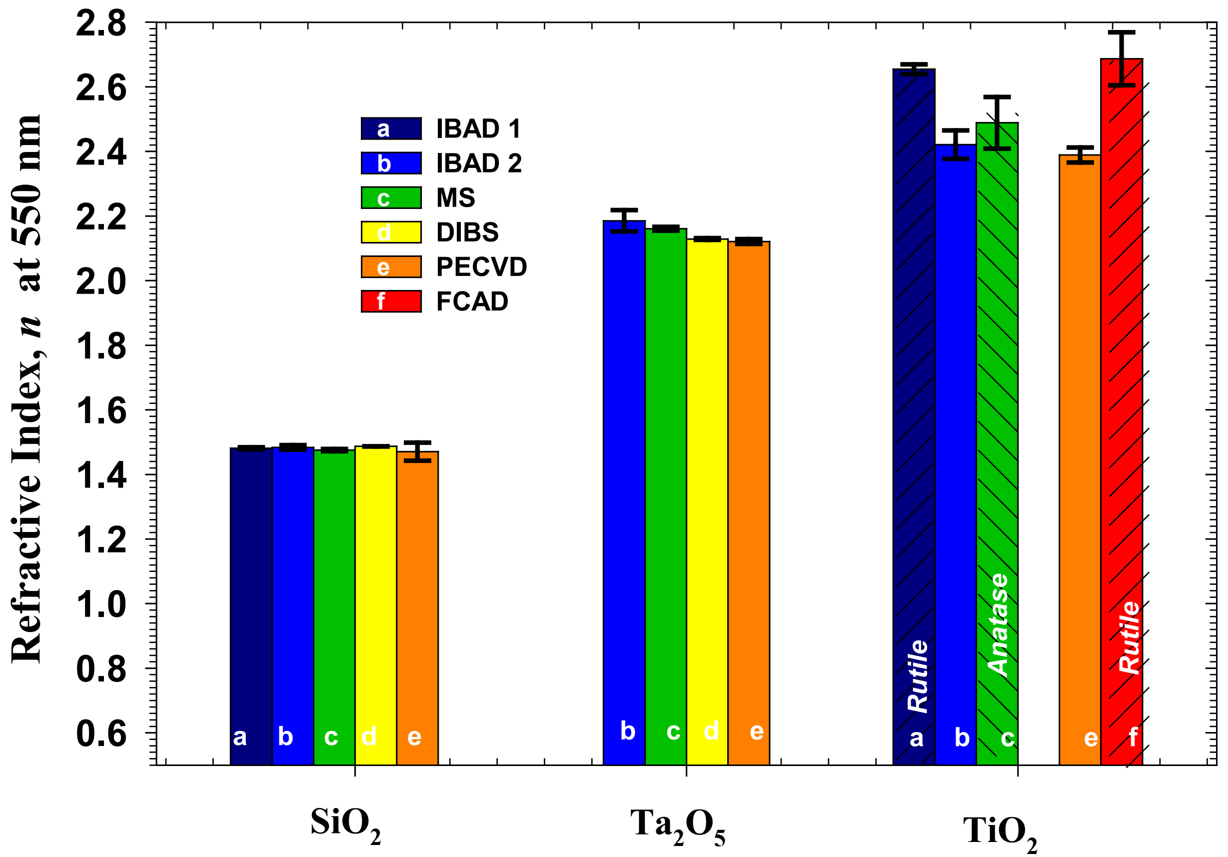
TiO_2



n_{550} = 2.35 – 2.70

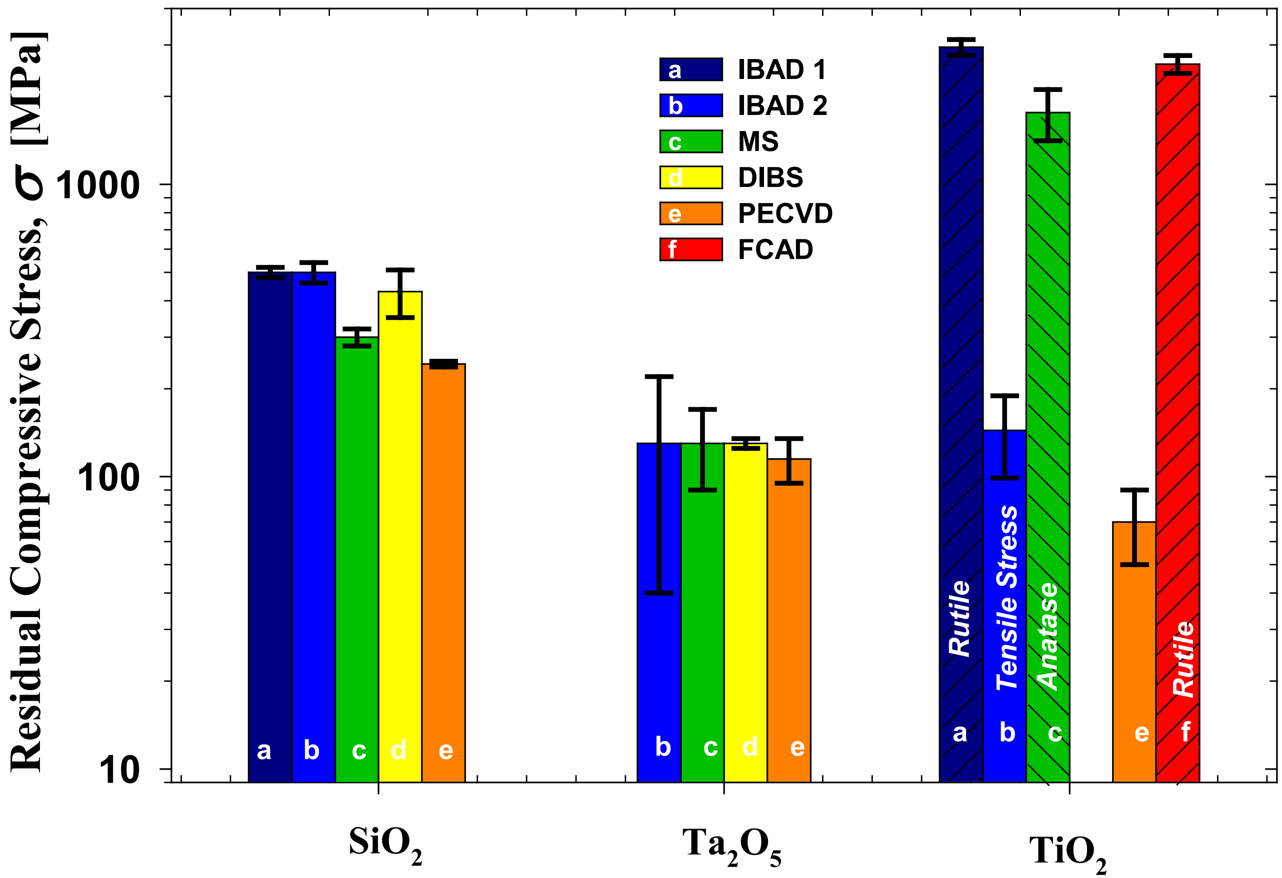
$k < 10^{-5}$

Comparison of n_{550} values



SiO_2	Ta_2O_5	TiO_2
Δn: ~0.5 %	Δn: ~1.6 %	Δn: ~6.8 %
n~1.478	n~2.155	n~2.511

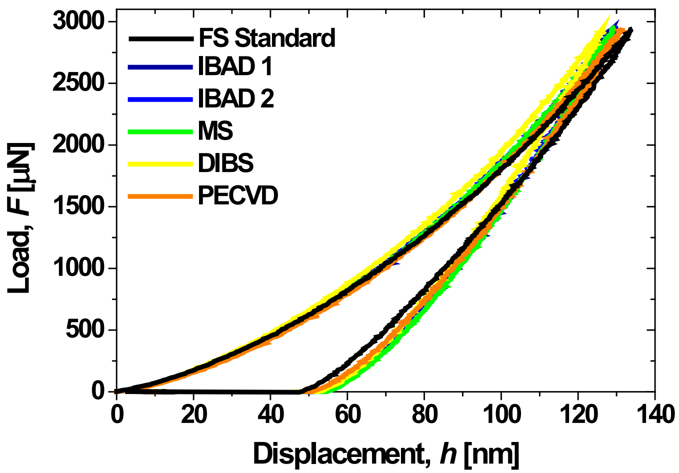
Residual stress



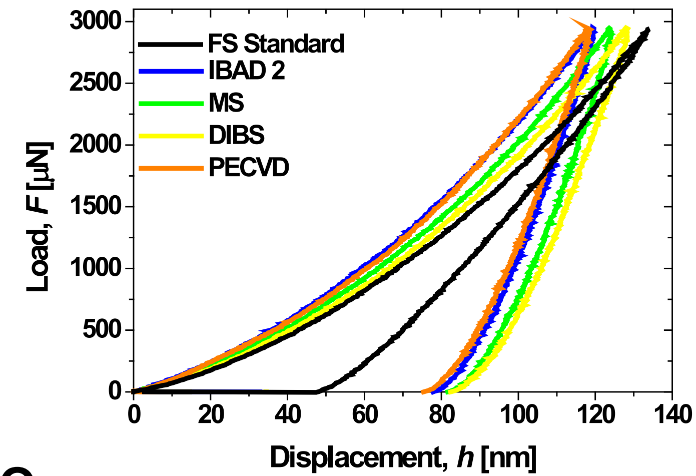
σ ~ (-230, -450) MPa σ ~ -120 MPa σ~ (+120 MPa; -2 GPa)

Load-displacement curves

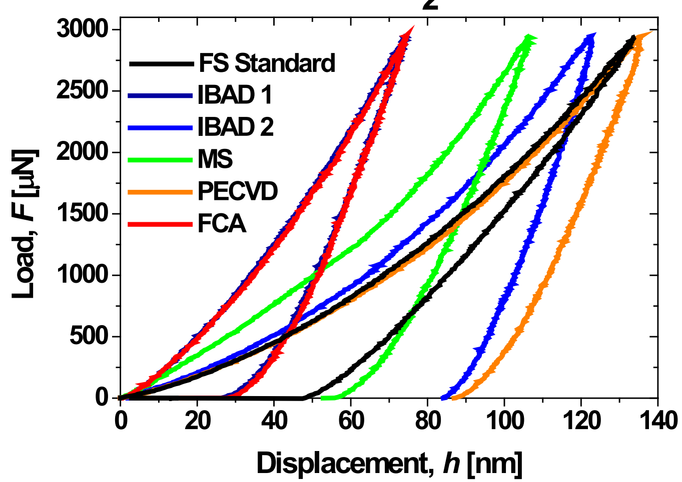
SiO_2



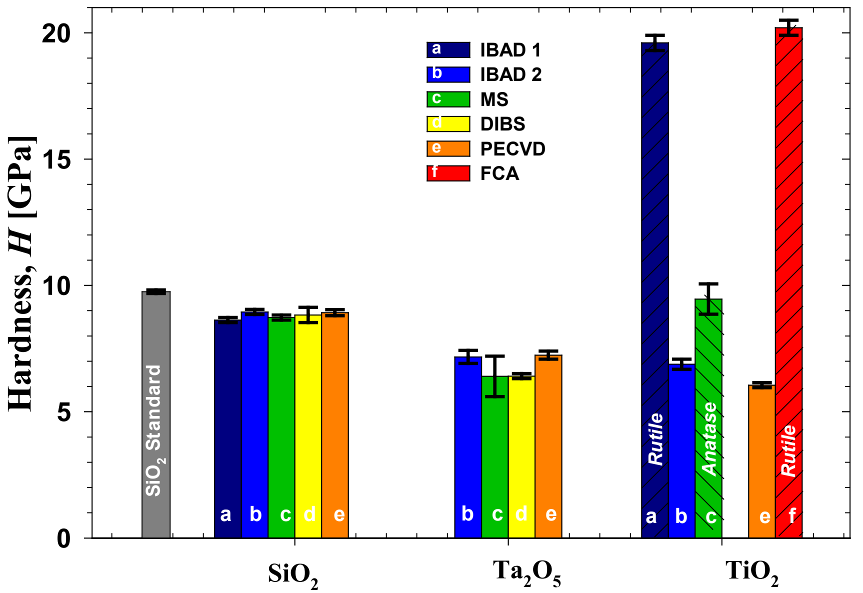
Ta_2O_5

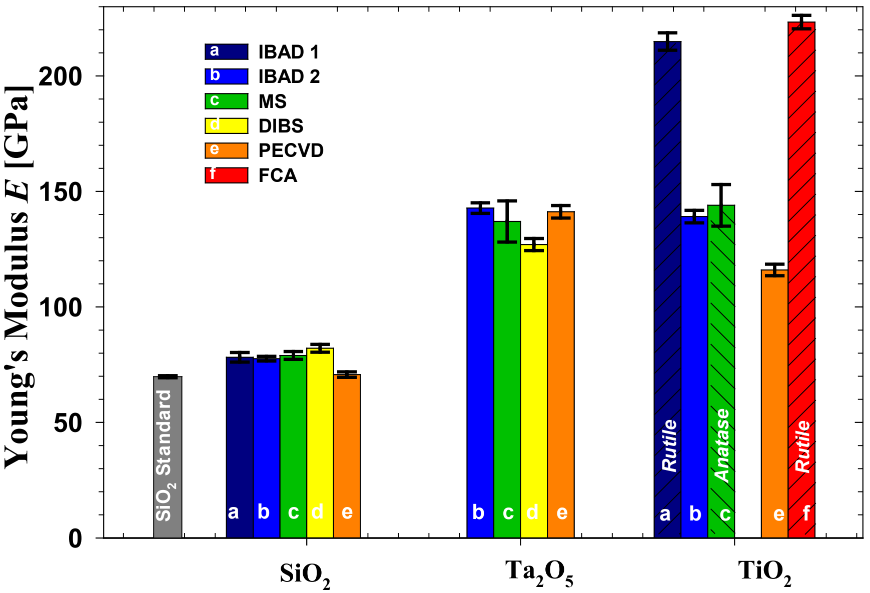


TiO_2

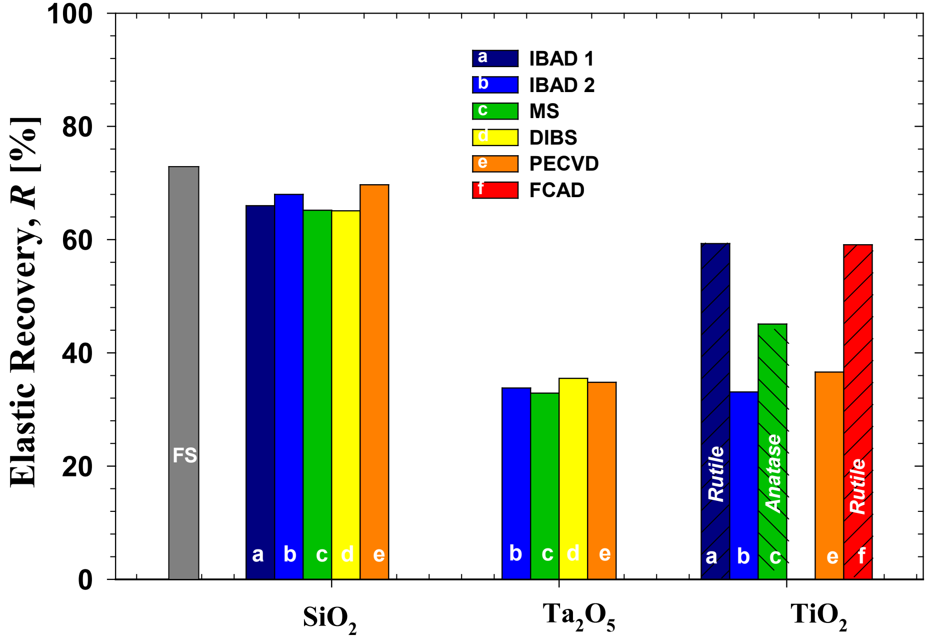


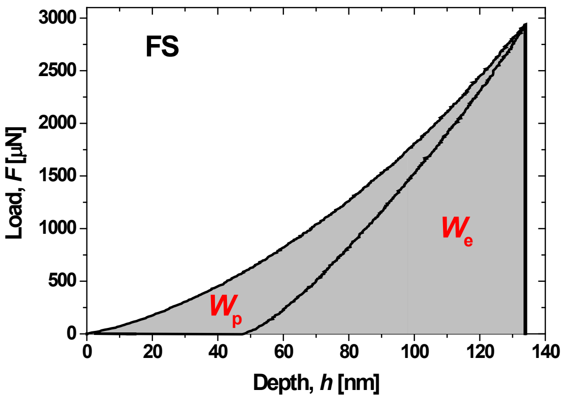
Hardness and Young's modulus





Elastic recovery

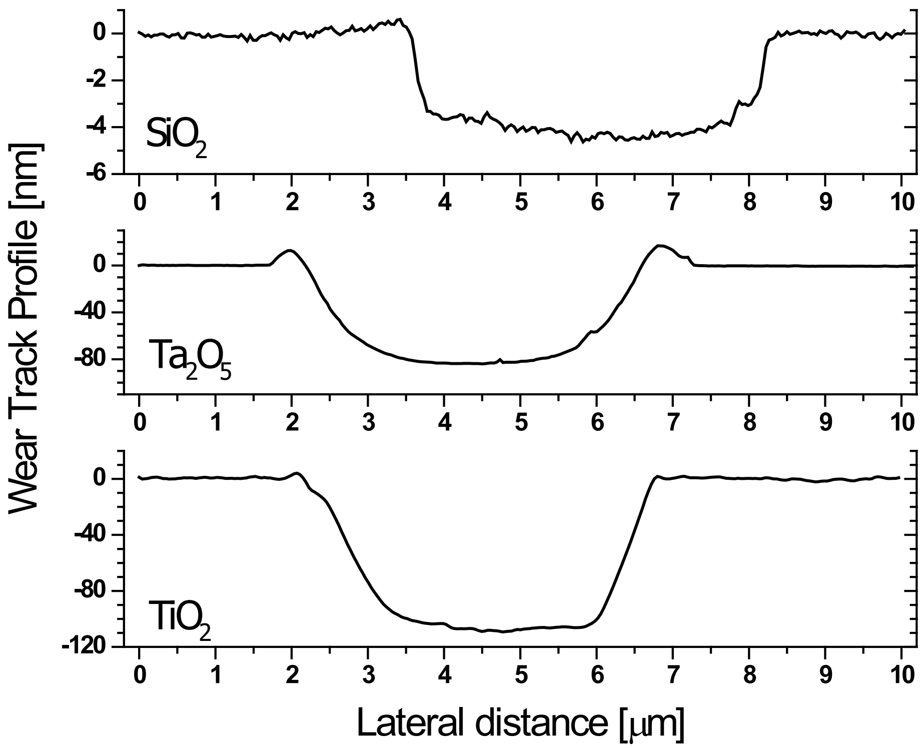


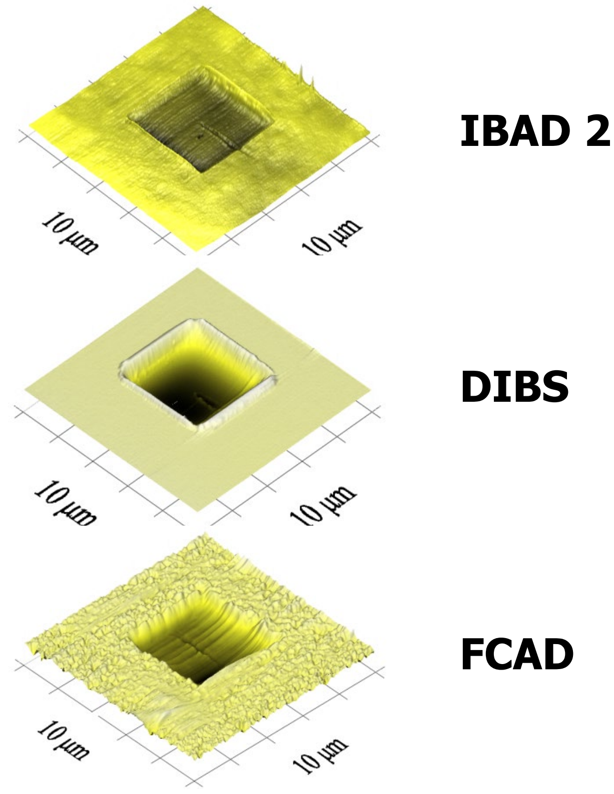


$$R = \frac{W_e}{W_{Tot}}$$

R ~ 70 % R ~ 35 % R ~ 35 - 60 %

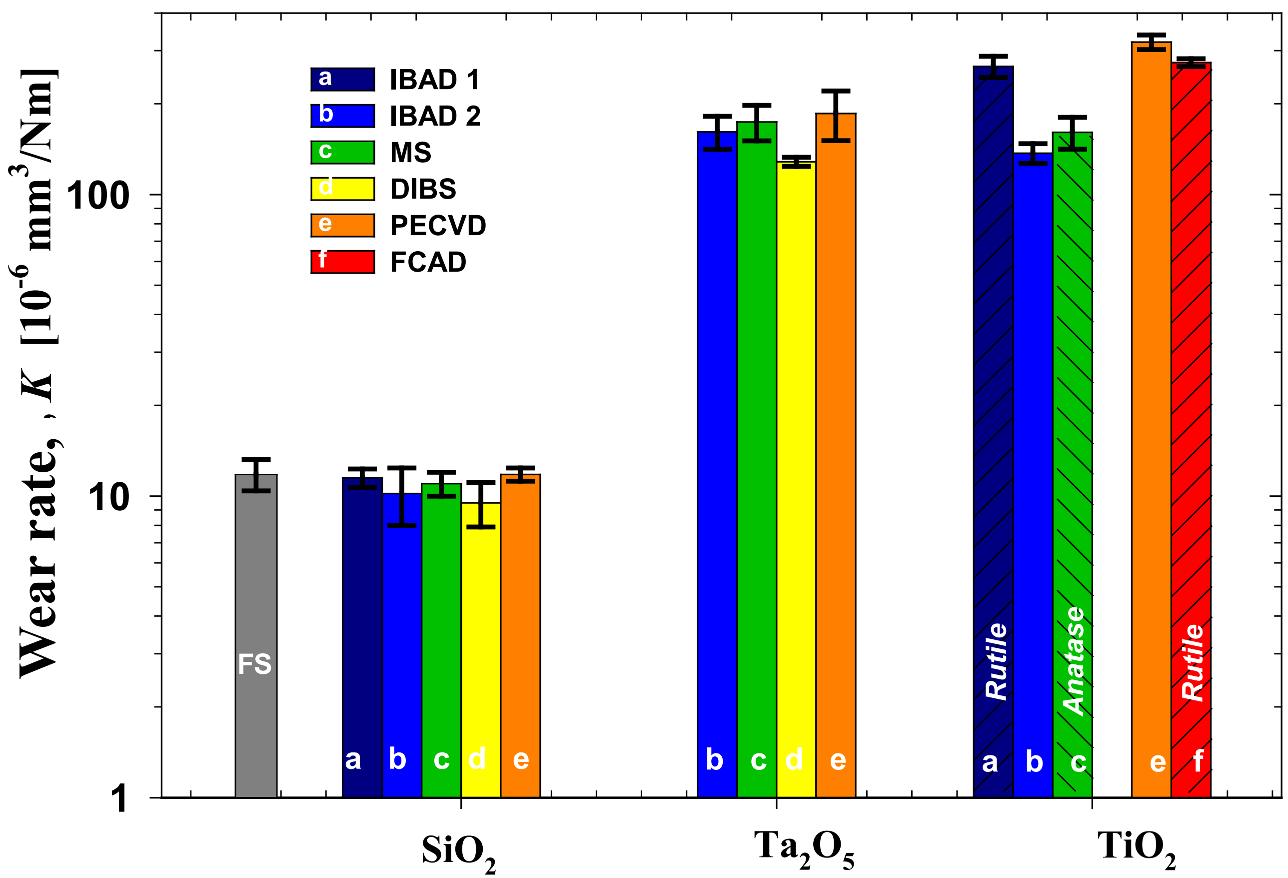
Wear test





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

Wear rate


Wear rate, , K [10^-6 mm^3/Nm]
100
10
1
IBAD 1
IBAD 2
MS
DIBS
PECVD
FCAD
FS
a
b
c
d
e
f
Rutile
Anatase
SiO2
Ta2O5
TiO2

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Energetic conditions during the film growth

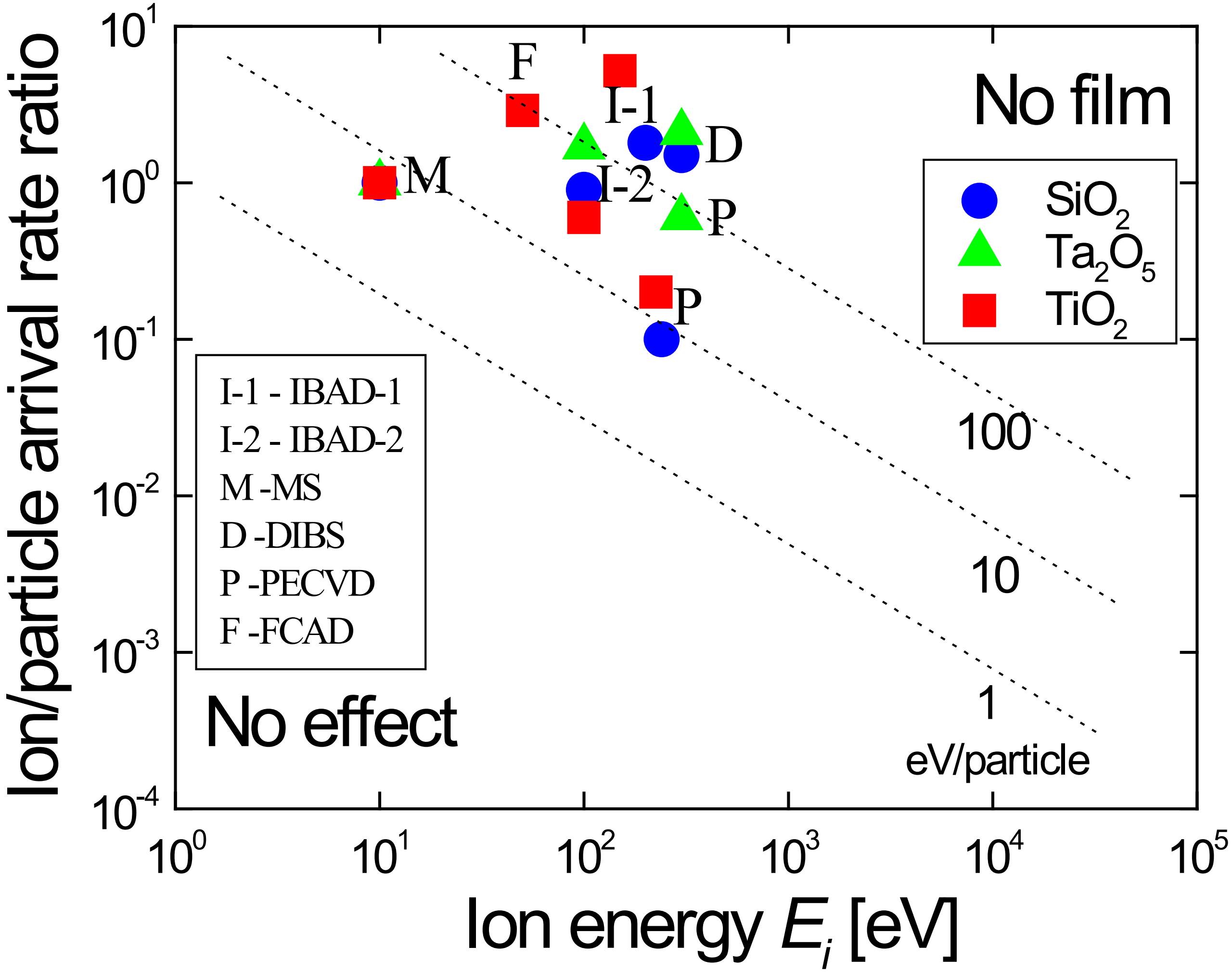
Technique	SiO_2		Ta_2O_5		TiO_2	
	E_i [eV]	Φ_i/Φ_N	E_i [eV]	Φ_i/Φ_N	E_i [eV]	Φ_i/Φ_N
IBAD-1	200	1.8	-	-	150	5.2
IBAD-2	100	0.9	100	1.7	100	0.6
MS	10 ?	1 ?	10 ?	1 ?	10 ?	1 ?
DIBS	300	1.5	300	2.1	-	-
PECVD	240	0.1	300	0.6	225	0.2
FCAD	-	-	-	-	50	2.9

Energy per deposited particle:

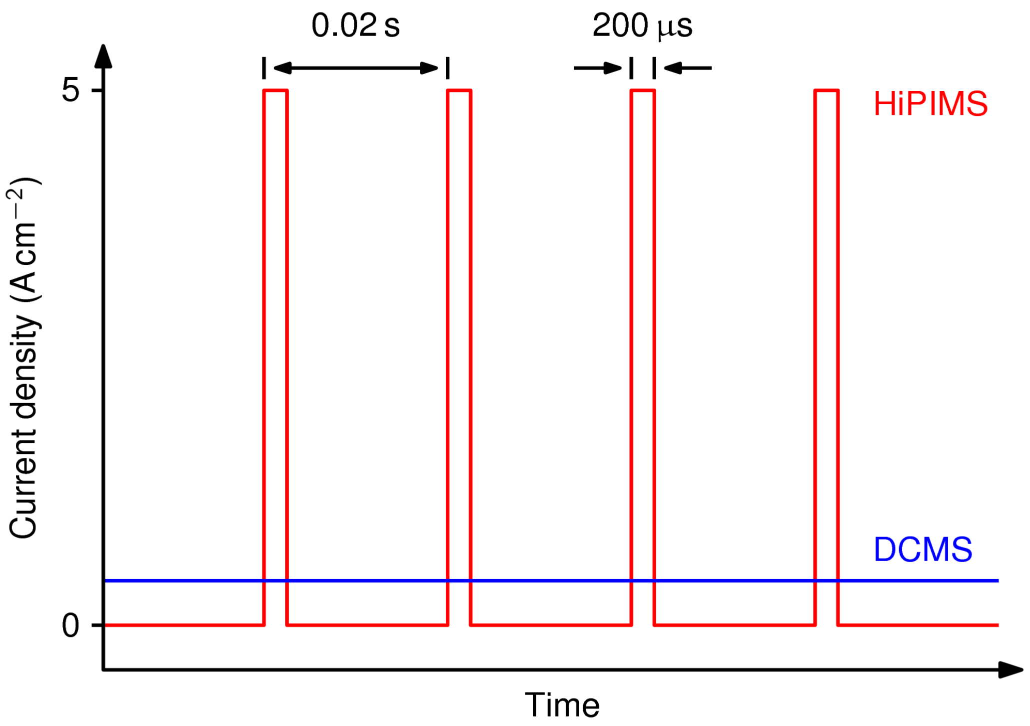
$$E_p \sim E_i \frac{\Phi_i}{\Phi_N} \qquad \Phi_N = r_D \frac{\rho N_A}{m_A}$$

Φ_i – flux of ions
Φ_N – flux of condensed particles
ρ – density
m_A – molecular weight

Energetic conditions during the film growth



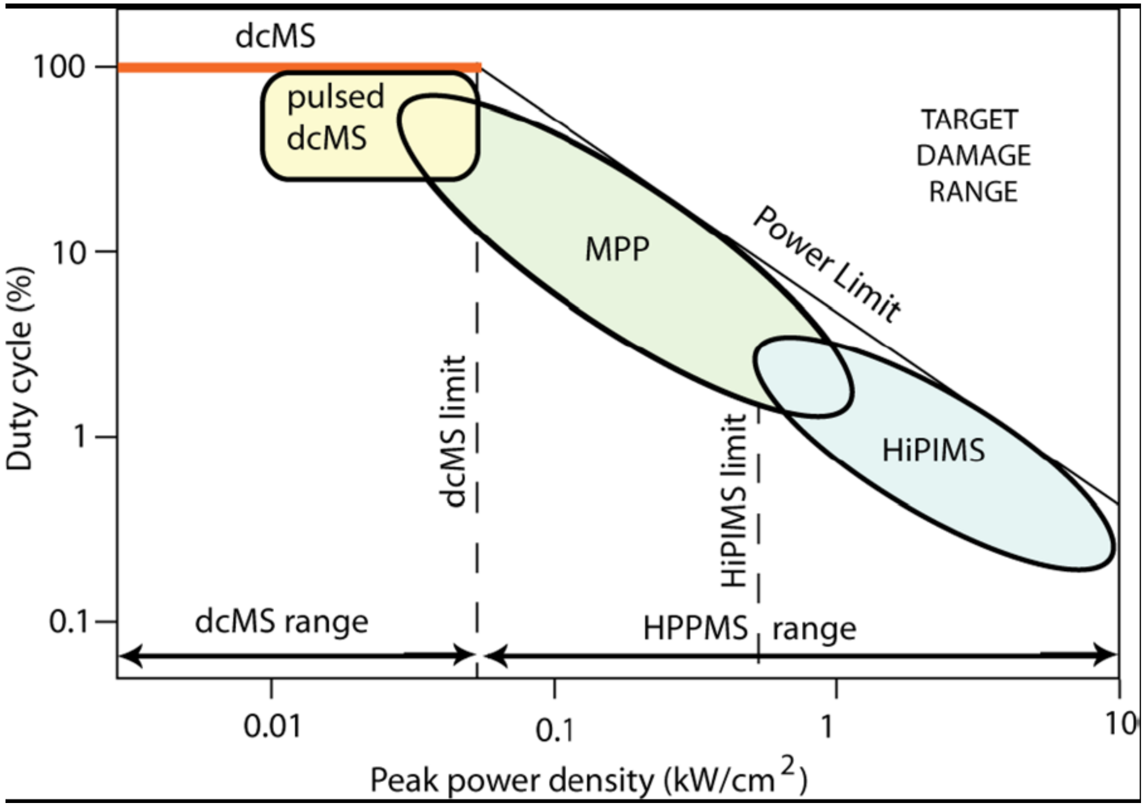
High Power Impulse Magnetron Sputtering - HiPIMS



<u>New coating properties due to:</u>

- high density plasmas – films obtained from ionized species
- high ion fluxes toward the substrate
- effect of ion bombardment on the microstructural evolution

Pulsed discharges



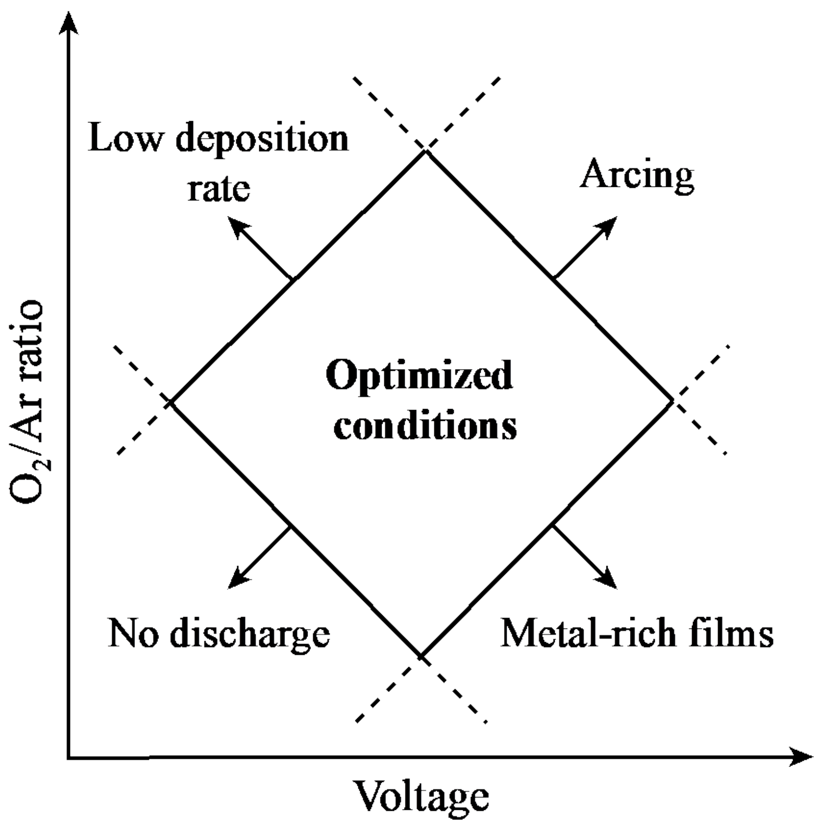
Nomenclature for pulsed discharges

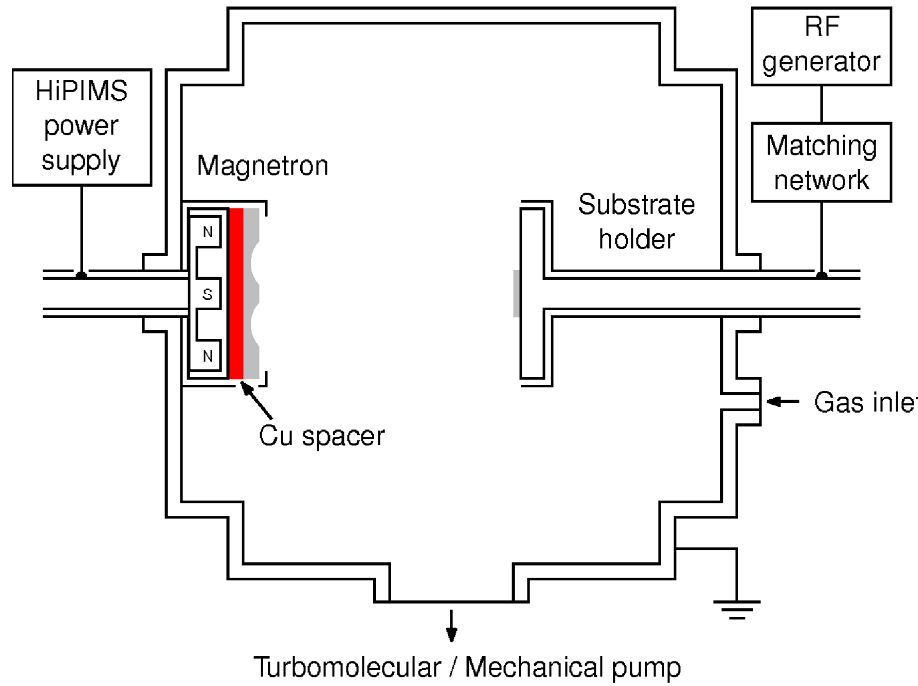
Recent review articles and comparisons:

- J.T. Gudmundsson, N. Brenning, D. Lundin and U. Helmersson, J. Vac. Sci. Technol. A 30 (2012) 030801-1-35 (above)
- A. Anders, Surf. Coat. Technol. (2011), J. Vac. Sci. Technol. A 28 (2010) 783
- K. Sarakinos et al., Surface & Coatings Technology, 204 (2010) 1661
- MPP vs. HiPIMS: M. Hala et al, SCT 2012, JPD-AP, 45 (2012) 055204

HiPIMS process optimization

Parameter space



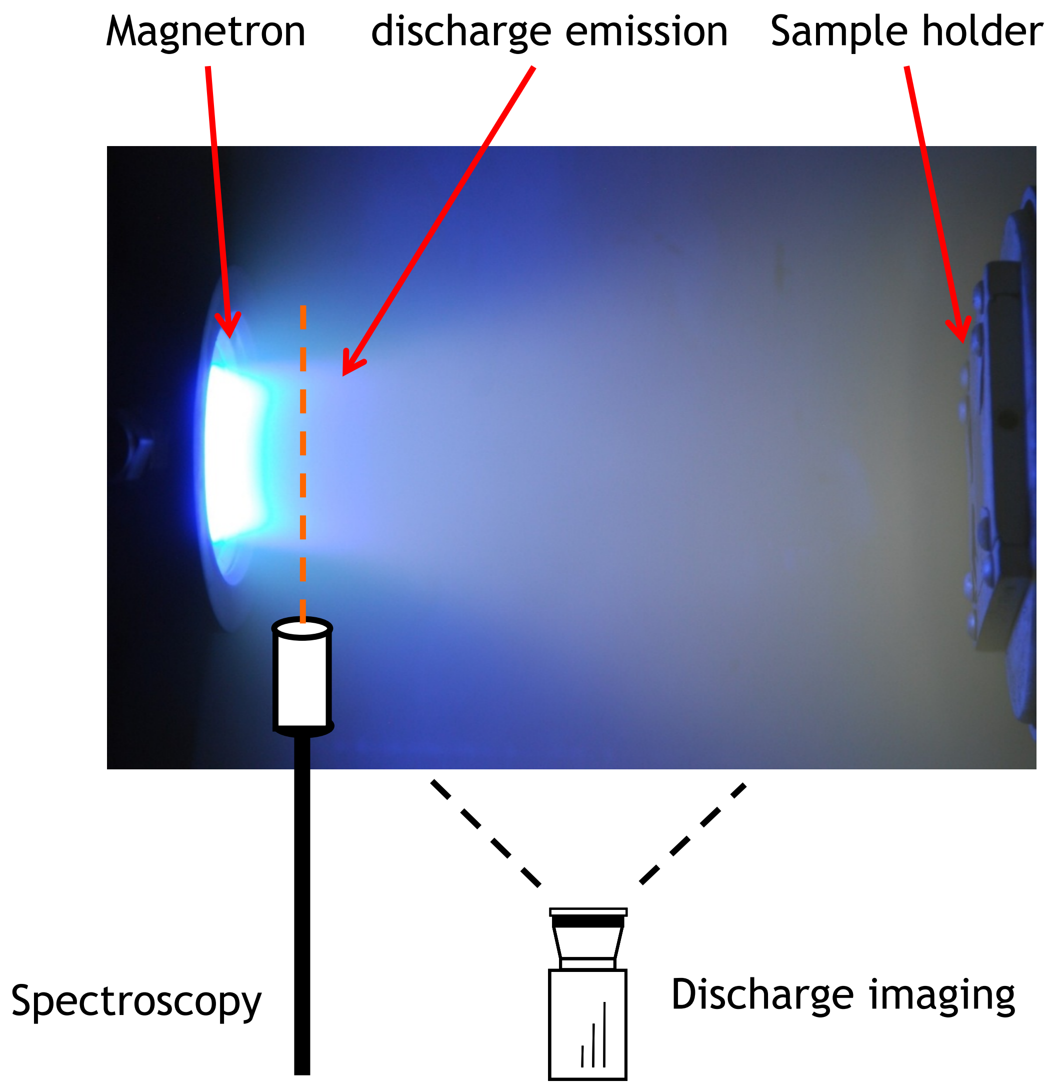


Effect of magnetic field:
J. Capek et al., J. Appl. Phys., 111 (2012)

Hysteresis suppression:
M. Hala et al., J. Phys. D: Appl. Phys., 45 (2012)
M. Hala et al., Surf. Coat. Technol. 2012

Time and space resolved OES:
M. Hala et al., IEEE Trans. Pl. Sci., 38 (2010)

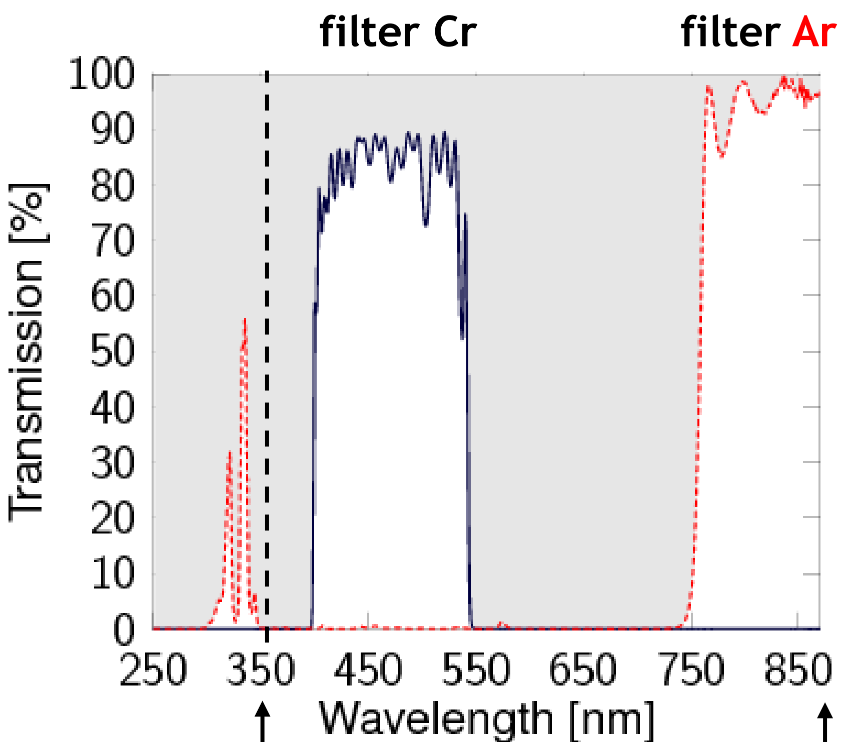
OES diagnostics – from the target to the substrate



Reactive HiPIMS:

Pure O_2 typical in optical coatings

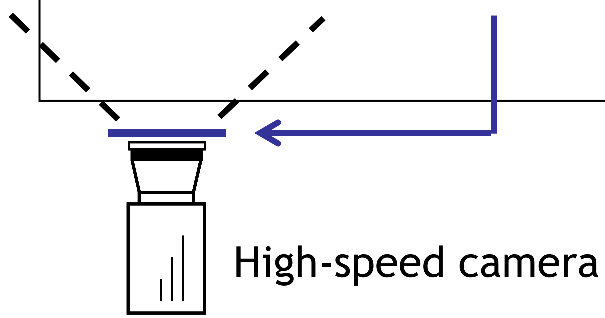
HIPIMS: Optical filters for species-resolved imaging
Filter performance and application



cut-off of the camera objective | CCD

Introduction of custom-made band-pass interference filters

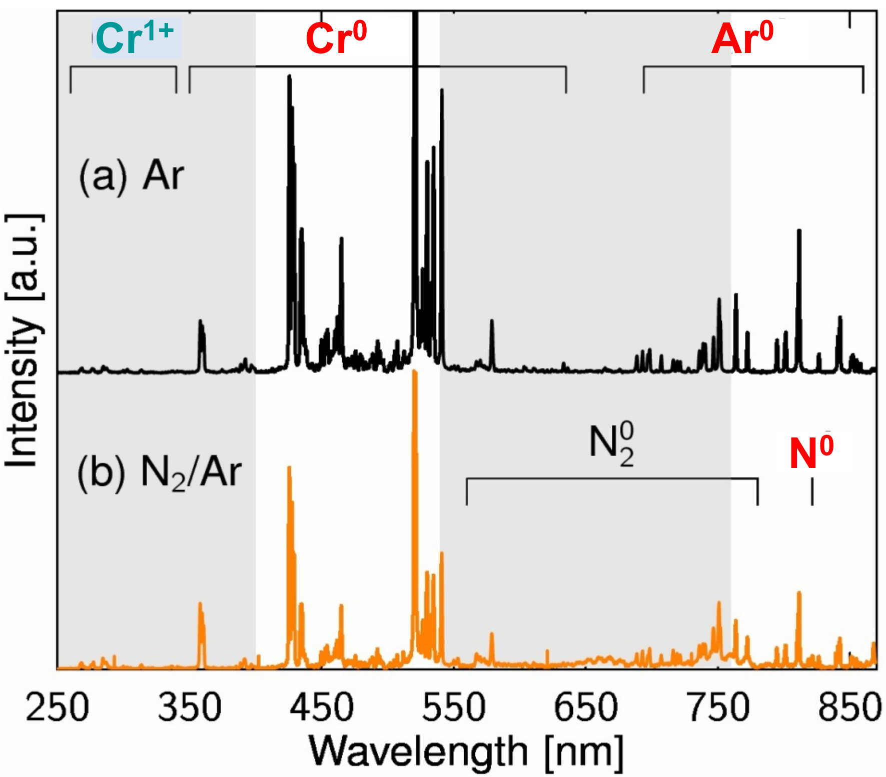
- **high-transmission regions:**
- **400 to 540 nm - filter Cr**
- **above 750 nm - filter Ar**



M. Hala et al., IEEE Trans. plasm. sci. (2010)

HIPIMS with a Cr target: Discharges in Ar, N_2, and in Ar/N_2 mixtures

5-cm magnetron p = 4 Pa (30 mTorr)
U_c = -2000 V   OES at d = 3 cm



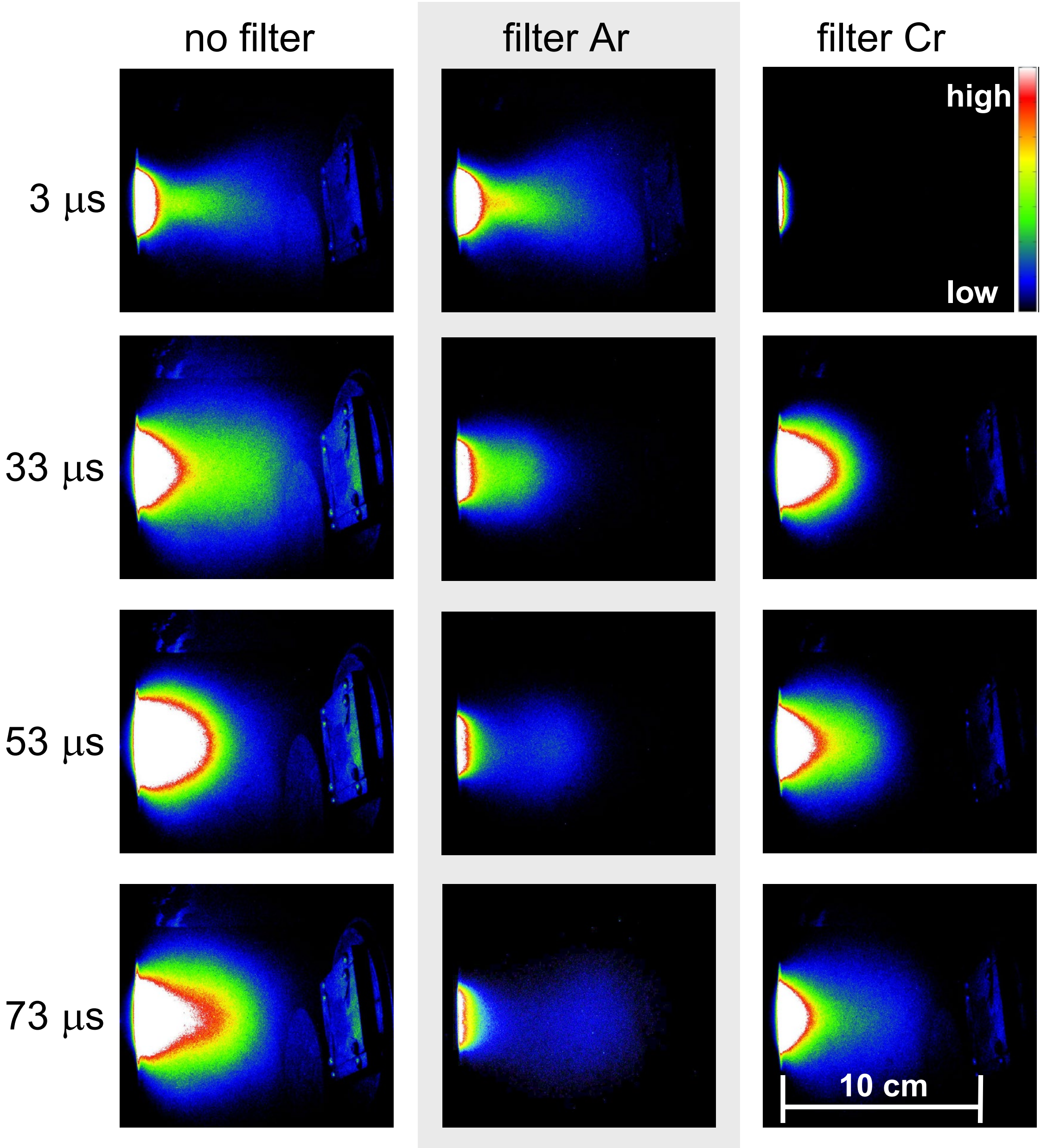
Sputtering of Cr

Two spectral regions of interest selected

- neutral chromium emission lines
- neutral gas emission lines and bands

M. Hala et al., IEEE Trans. Pl. Sci., 38 (2010) 3035

Dynamics of the HiPIMS discharge in Ar



Ignition phase

Electron avalanches and

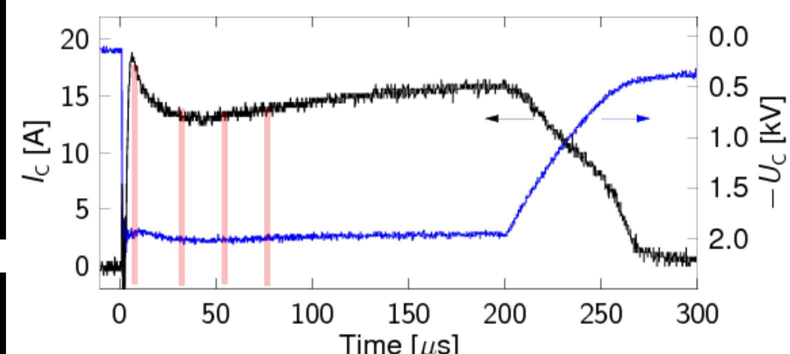
working-gas ion generation

Metal-dominated phase

Self-sputtering process

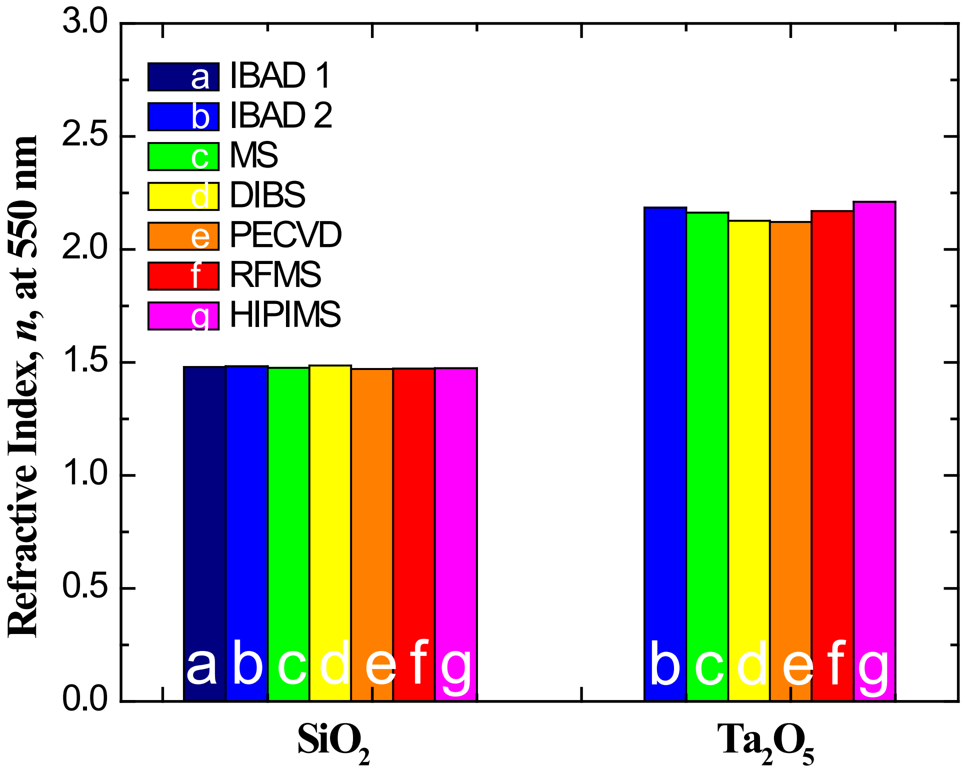
Plasma rich in sputtered Cr expands outwards the target

Current and voltage waveforms



M. Hala et al., IEEE Trans. Pl. Sci. 38 (2010)

Comparison of n_{550} values



Comparative study:

Pre-characterized substrates – c-Si, FS

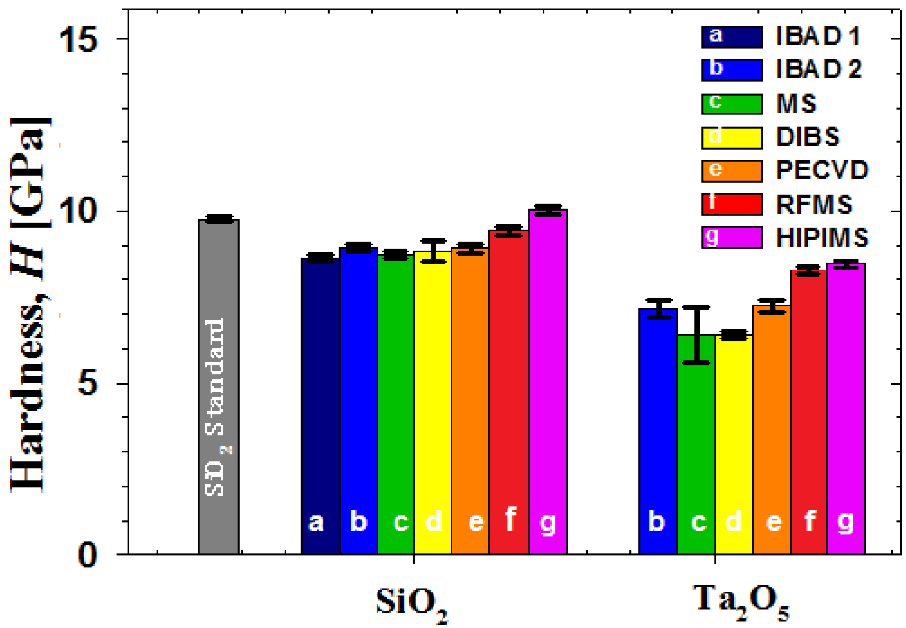
Coating thickness: 1 μm

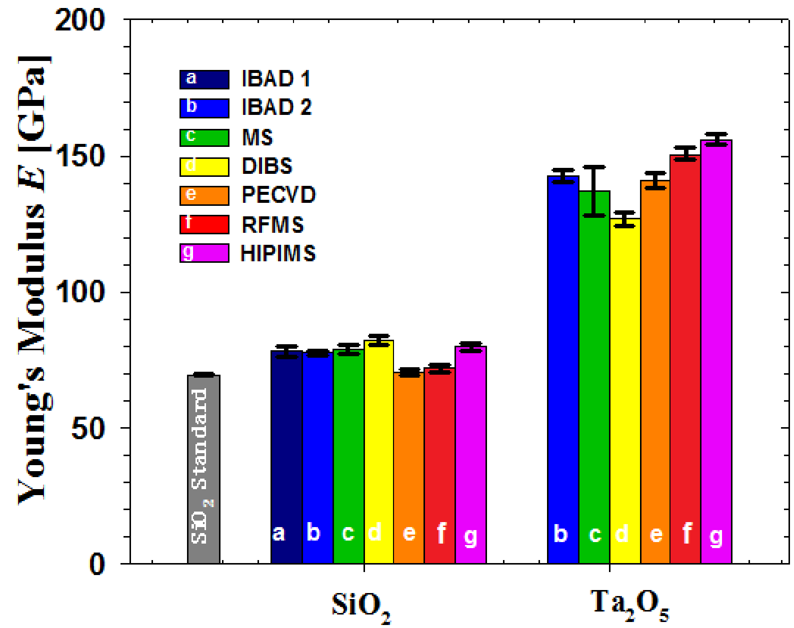
Characteristics suitable for high-end optical filters

HiPIMS vs other techniques:

Comparison with J.E. Klemberg-Sapieha et al., Appl. Opt., 43 (2004) 2670

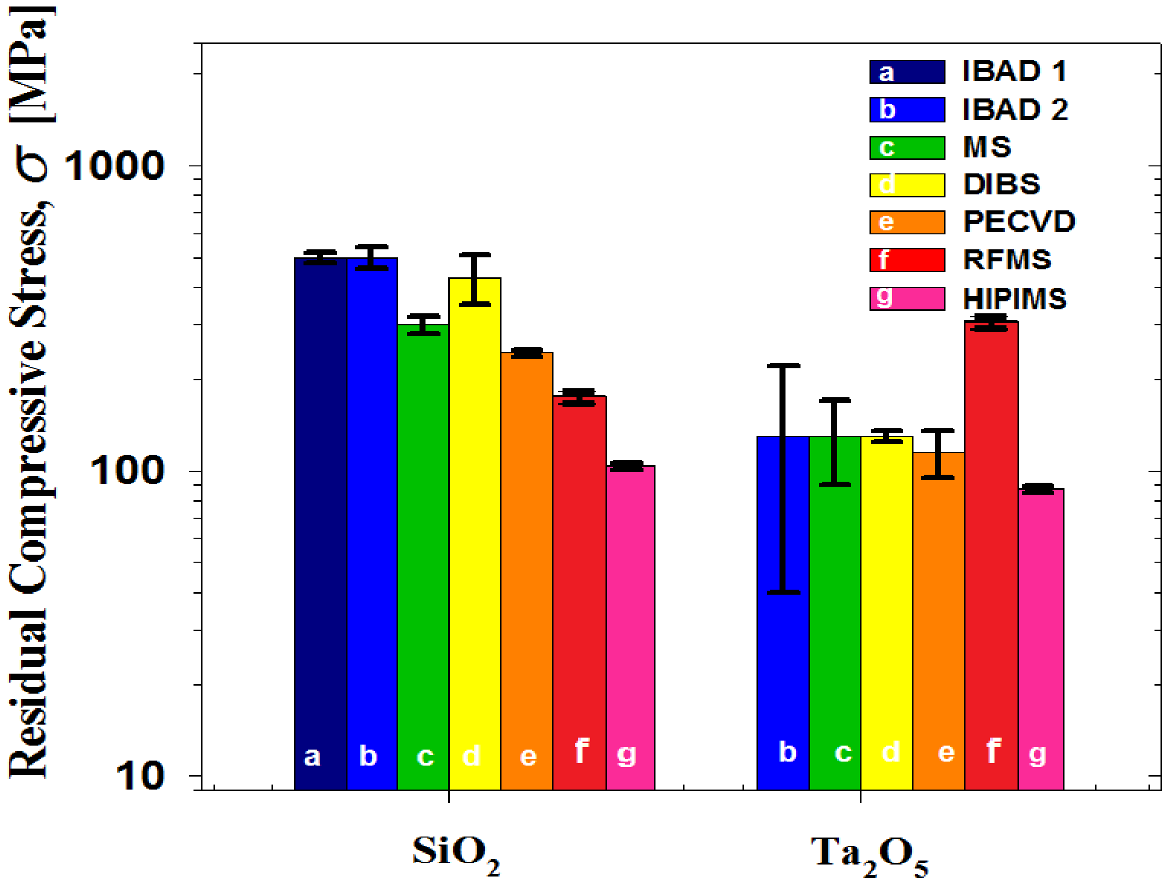
Hardness and Young's modulus





HiPIMS vs other techniques:
Comparison with J.E. Klemberg-Sapieha et al., Appl. Opt., 43 (2004) 2670

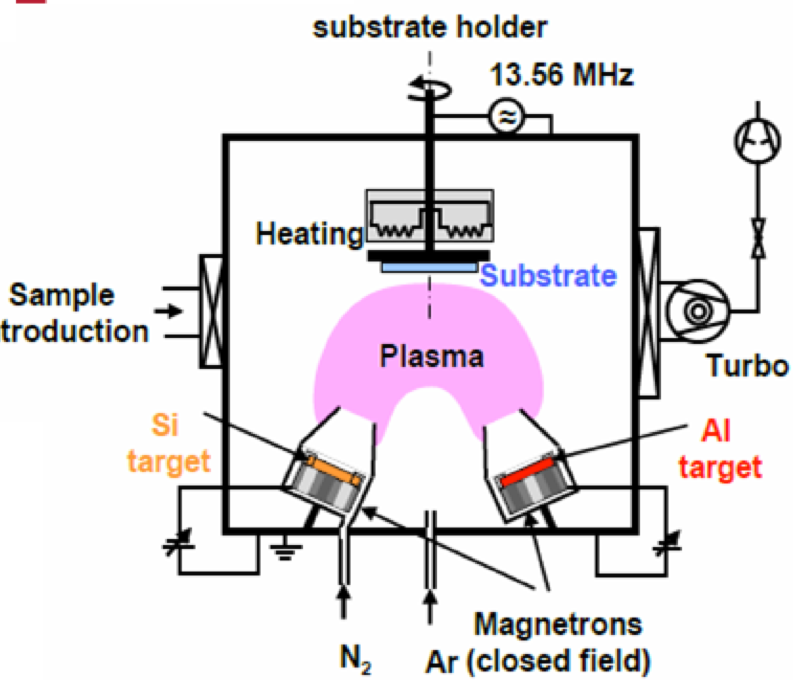
Residual stress



HiPIMS vs other techniques:

Comparison with: J.E. Klemberg-Sapieha et al., Appl. Opt., 43 (2004) 2670

Nanocomposite Al-Si-N films

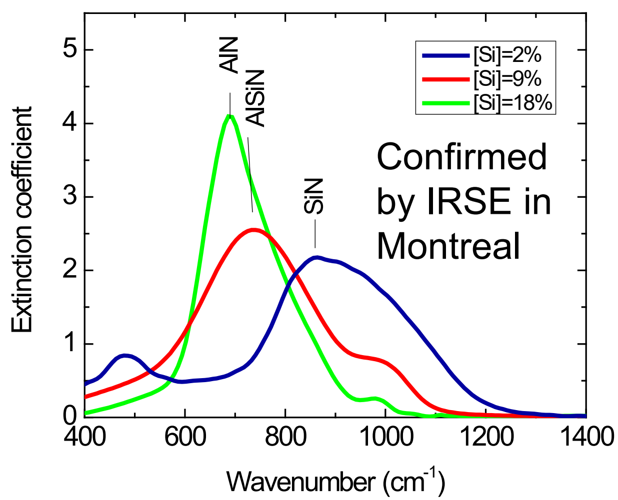


Reactive UBM sputtering from Al and Si targets

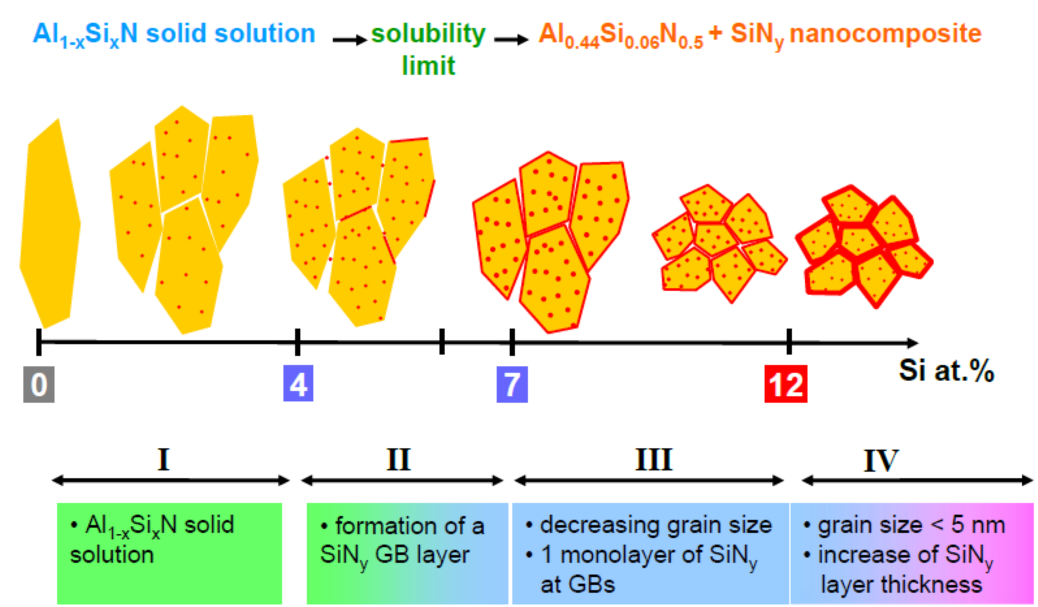
Pressure: ~0.3 Pa
Substrate Temp: 200 ^{O}C
Deposition rate: ~250 to 650 nm/h
Thickness: ~1-2 μm

AlN to Al-Si-N with up to 23 at.% Si

Formation of nanocomposite at [Si]> 6 at.%
$Al_{0.88}Si_{0.12}N$ with Si_3N_4

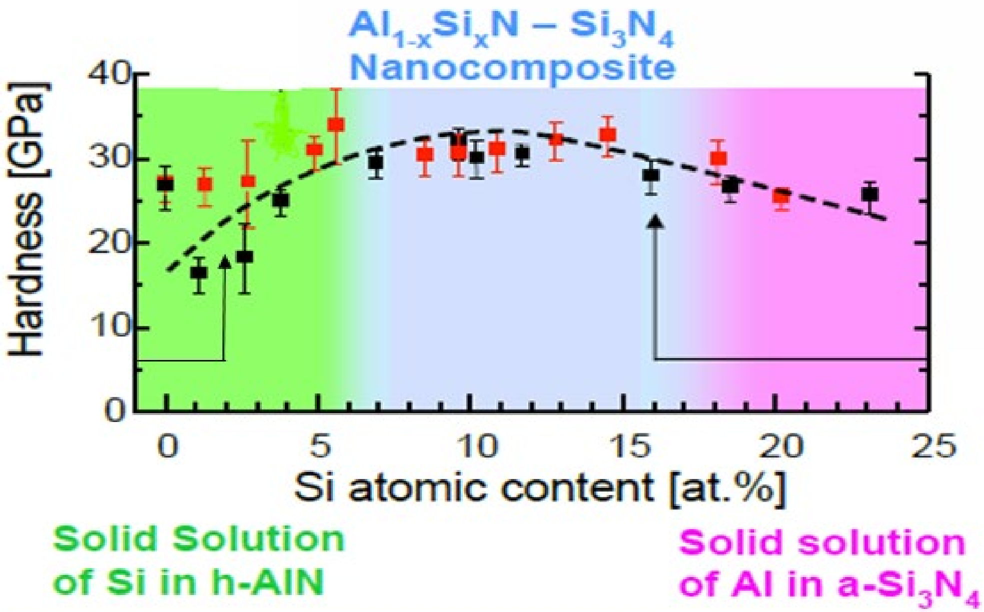


Structural evolution of Al-Si-N films



A. Pélisson, Doctoral thesis, University of Basel, Basel, 2009

Mechanical properties of Al-Si-N

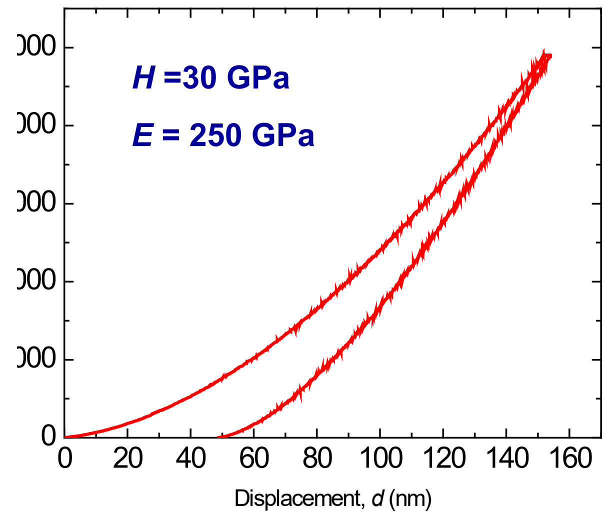


Hardness of Al-Si-N depends on composition:

- Solid soluton hardening
- Nanocomposite, small grain size. but structural similarities of AlN and Si_3N_4:
  → no sharp interfaces?
- Approaching the hardness of Si_3N_4

A.Pélisson, M. Parlinska-Wojtan, H.- J. Hug, J. Patscheider, *Surf. Coat. Technol.* 202 (2007) 884–889

Al-Si-N with 9 at.% of Si deposited at 200 ^{O}C



***H*/*E* - elastic strain to failure**

***H*/*E* = 0.12**

H^3/E^2 - resistance to plastic deformation

H^3/E^2 = 0.43 GPa

***R* ~ 80%**

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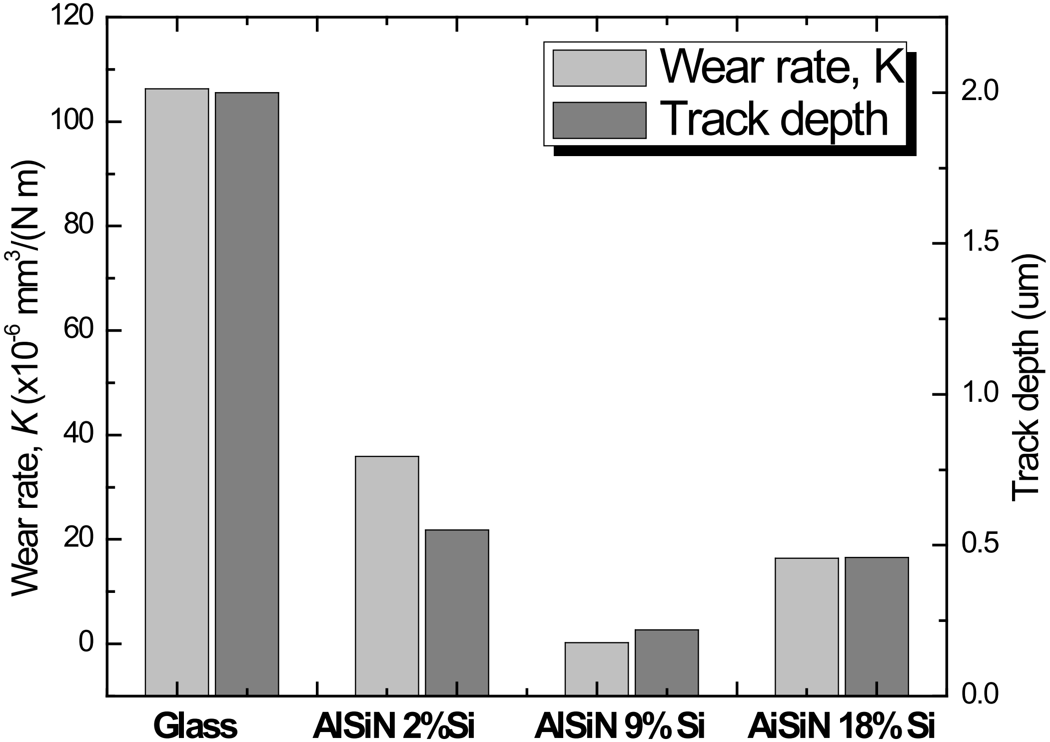
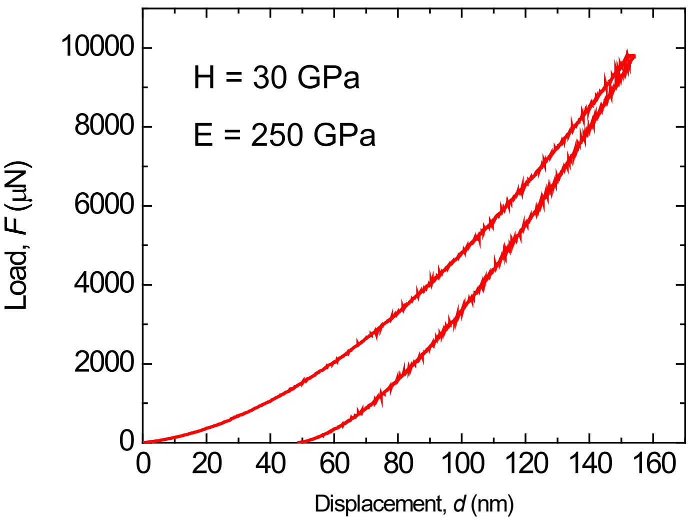
Wear resistance of Al-Si-N films





Al-Si-N: 9 at.% of Si

H/E = 0.12

H^3/E^2 = 0.43 GPa

R ~ 80%

J.E. Klemberg-Sapieha, ... J. Patscheider, …,
SVC Ann. Tech. Conf., Santa Clara, May, 2012.

Thermo-elastic characteristics of films and coatings
Thermal expansion coefficient & Poisson's ratio

Two substrate method: Thermo-elastic constants of the films were obtained from the σ - T plots

Total $\sigma(T)$ in the film:

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

Assumption: E_f and α_f - independent of T

σ_i - independent of substrate

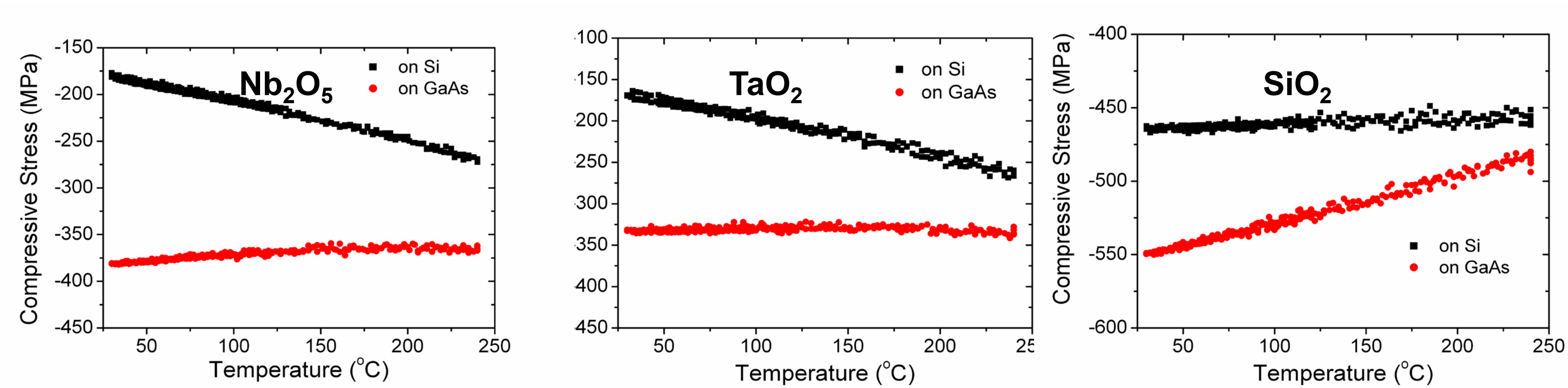
$$\left(\frac{d\sigma}{dT}\right)_{s1} = \frac{E_f}{1-\nu_f}(\alpha_{s1} - \alpha_f) \quad \Rightarrow \quad \alpha_{film} = \frac{\alpha_{s2}\left(\frac{d\sigma}{dT}\right)_{s1} - \alpha_{s1}\left(\frac{d\sigma}{dT}\right)_{s2}}{\left(\frac{d\sigma}{dT}\right)_{s1} - \left(\frac{d\sigma}{dT}\right)_{s2}}$$

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

E. Çetinörgü et al., Applied Optics, 48 (2009) 4536

Coefficient of thermal expansion & Poisson's ratio

σ-*T* plots : Nb_2O_5, Ta_2O_5 and SiO_2 prepared by DIBS



Temperature range : 30-240 °C

Heating and cooling cycles (3 x) 1.5 °C/min in N_2 ambient

Substrate: c-Si, GaAs

CTE : α_{Si} = 2.6×10^{-6} °C^{-1} and α_{GaAs} = 5.12×10^{-6} °C^{-1}

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

Results were used to calculate:

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

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

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Results – Comparison with published data

Film Material	$E_f/(1-n_f)$ (GPa)	E_f (GPa)	CTE $\times 10^{-6}$ (°C^{-1})	ν_ϕ	References
Nb_2O_5	139	130	4.9	0.22	This work
	–	–	1.52	–	[33]
	–	60	5.8	0.20	[34]
	–	–	-2.0	–	[35]
	–	125	–	0.23	[39]
Ta_2O_5	143	136	4.4	0.27	This work
	1549	–	2.45	–	[17]
	–	–	2.3 to 5.6	–	[36] [37] [38]
	1549	–	2.42	–	[1] [36]
	–	–	6.72	–	[38]
SiO_2	93	87	2.1	0.11	This work
	3257		0.38	–	[17]
	–	86	3.10	–	[21]
	–	75	0.55	0.16	[34]
	–	72	–	0.17	[39]

1. Thien et al OC **198** 2001.
17. Lee et al RSI **72**(4) 2001.
21. Thielsch et al AO **41**(16)2002.
33. Thien et al JMO **47**(10) 2000.
34. Chen et al JAP 101, 2004.
35. Choosuwan et al, JAP **91**, 2002.
36. Weyant et al, J. Am. Ceram. Soc. **88**, 2005.
38 al J. Mater Sci. **41**, 2006.
39. Chudoba et al Surface Coat. Technol. **127**, 2000.

Development of passive thin films

Optical coatings:

- Choice of the fabrication technique
- New technologies

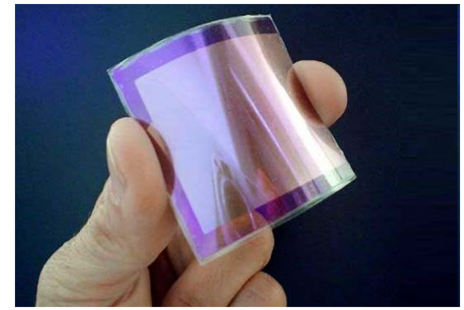
Gas and vapor diffusion barriers:

- Thin films on plastics

Applications of optical coatings on plastics

lenses
optical components

displays



flexible solar cells

flexible electronics

optical security devices

aerospace

automotive

Why plastics?

- **Cost**
- **Flexibility**
- **High strength-to-weight ratio**
- **Lightweight**
- **Safety**
- **Roll based processing**

Problem: Coating-substrate compatibility

Properties of selected optical plastics

Polymer	*n* [@550nm]	*ρ* [g/cm³]	WA [%]	CTE [µm/m°C]	ST [°C]	*H* (DSI) [GPa]	E [GPa]
PC	1.58	1.20	0.15	68-70	122-132	0.2;118*-122*	2.1-2.3
PMMA	1.49	1.17-1.19	0.30-0.45	52-60	71-91	0.2;63*-93*	1.7-3.0
PET	1.66	1.40	0.05	59	80-100	130*	3.8
PTFE	1.35	2.17	0.03	86	260-290	58*	0.5
FEP	1.34	2.10	0.01	140	60-204	25*	0.4
PVDF	1.42	1.78	0.03	140	68-170	75*	1.8
PS	1.59	1.04	0.1	90	80	110*	2.4
PEN			<0.05		155	0.2	5.0
COP	1.53	1.01	<0.01	60-70	125		
COC	1.53	1.02	<0.01	60-70	75-170	184*	3.1
Fused silica	1.46	2.20		0.40		9.5	110
Glass	1.52	2.18		0.75		7.2	68
Diamond	2.42	3.52		1.80		98	980

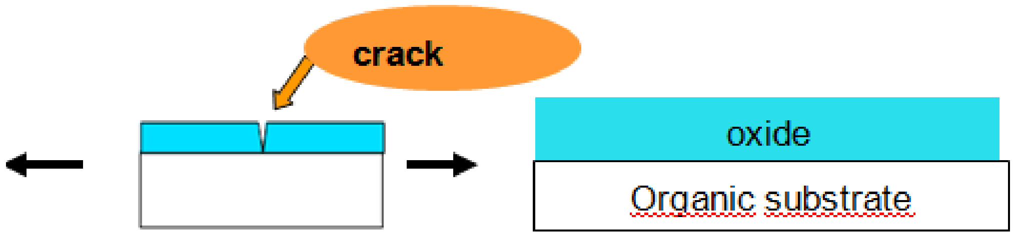
n_{550} refractive, ρ density, *WA* water absorption, *CTE* coefficient of thermal expansion @20°C, *ST* service temperature, *H* (DSI) depth sensing indentation hardness; *Rockwell hardness, *E* elastic modulus.

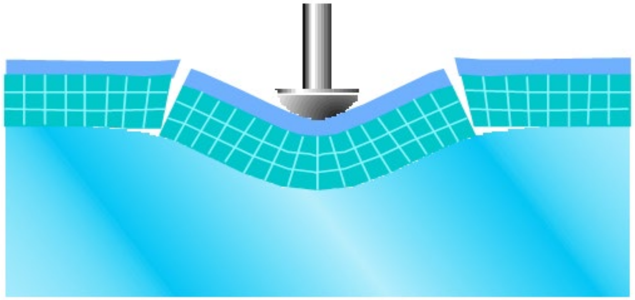
Inorganic optical films on plastic substrates

Problem: Significant mismatch between the mechanical properties of inorganic layers (e.g., anti-reflective (AR) coatings) and plastics substrates (e.g., for ophthalmic applications) may lead to pre-mature failure including cracking, delamination and other adverse effects.

Mechanical sollicitation → deformation of substrate

Strain to failure of oxides < ~ 2 %





Need:

- Tailor mechanical properties of AR layers: make them "deformable" (less brittle)
- Good adhesion (at all interfaces)
- "Perfect" transparency
- Good durability (vs. "crazing", scratches, stress cracking…)
- Environmental stability (UV, humidity, temperature…)

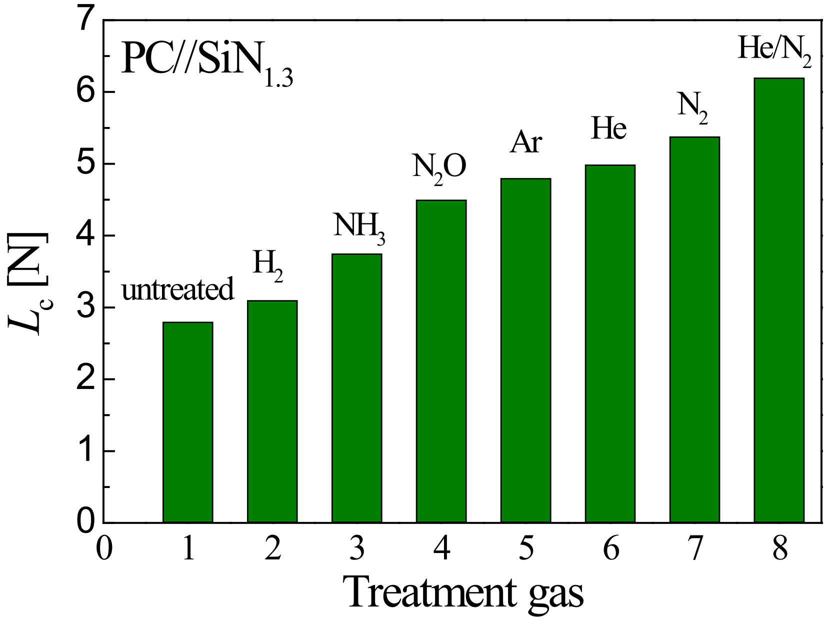
Methods to improve adhesion of coatings to polymeric surface

- Wet chemical treatment
- Mechanical treatment
- Exposure to flames
- UV treatment
- Ion beams
- Corona treatment
- **Low pressure plasma treatment**

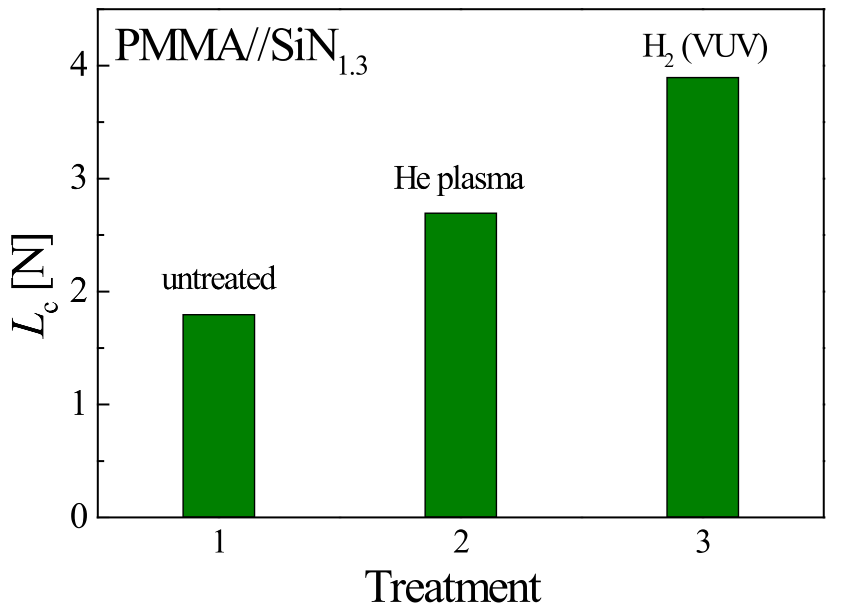
Plasma effects to improve adhesion

1. **Surface cleaning**
   (*removal of organic contamination from the surfaces*)
2. **Ablation**
   (*removal of Weak Boundary Layer, WBL*)
3. **Surface crosslinking:**
   CASING – Crosslinking via Activated Species of Inert
   Gases (*creation of free radicals on polymer surfaces via ion bombardment, VUV photons*)
4. **Surface chemistry modification**
   (*incorporation of chemical functionalities on polymer surfaces*)
5. **Surface electric charge**
6. **Deposition of intermediate layers**
7. **Atomic interface mixing**

Adhesion of Si_3N_4 films on plastics: Case study of PC and PMMA

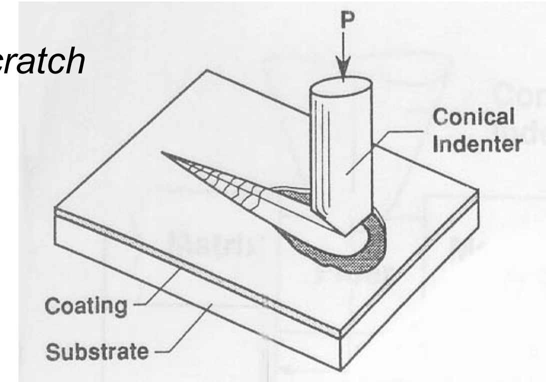


MW plasma pre-treatment in different gases



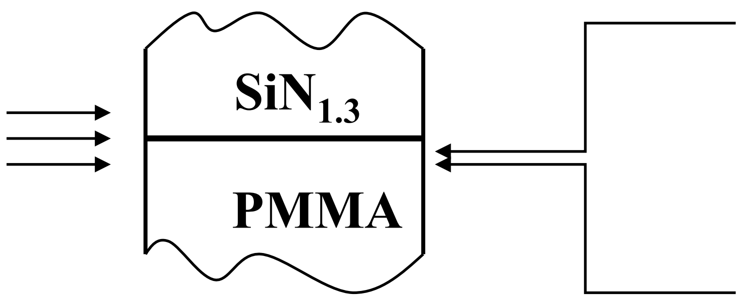
Pretreatment by He plasma or VUV radiation

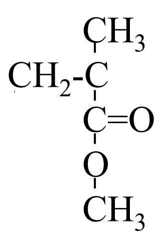
Micro-scratch test

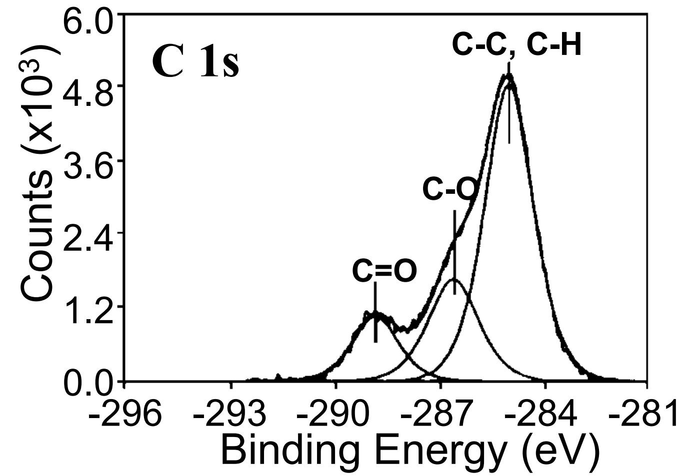


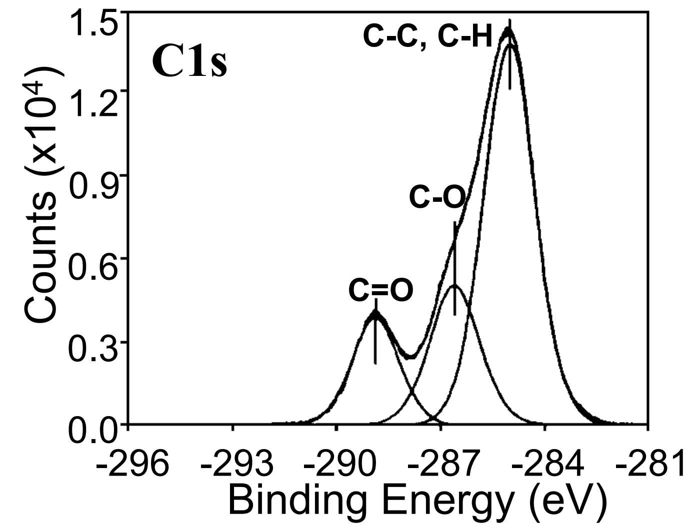
Martinu and Klemberg-Sapieha: "Optical coatings on plastics", in "Optical Interference Coatings", Springer 2003

PMMA/$SiN_{1.3}$ interface



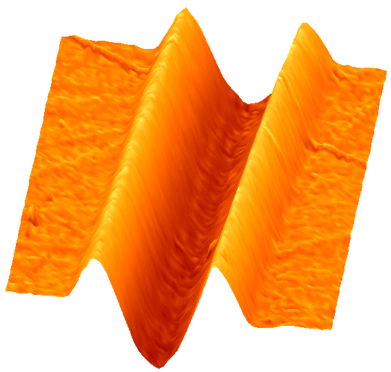




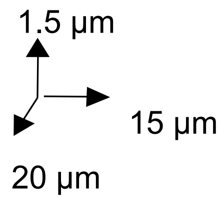


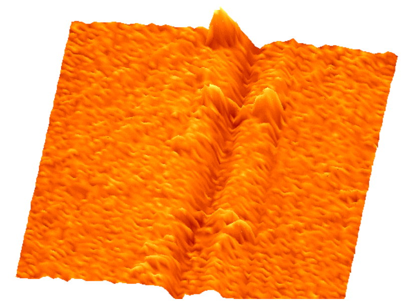
Klemberg–Sapieha et al., MRS Proc. 1998

AFM images of scratch track profiles

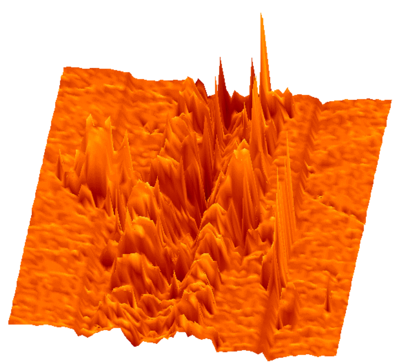


Untreated PC

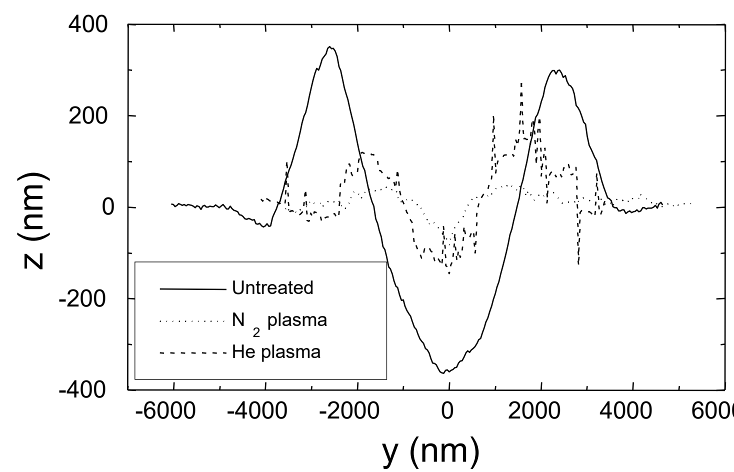




PC/N_2

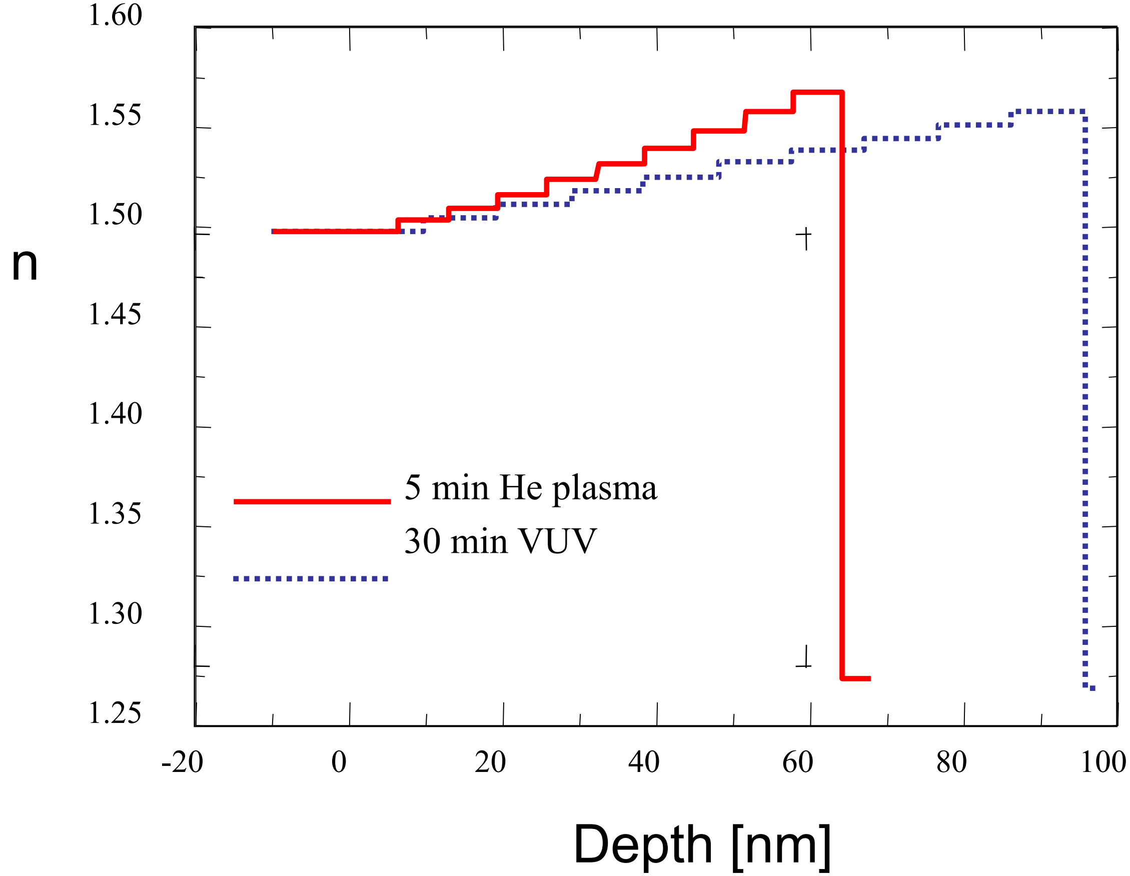


PC/He



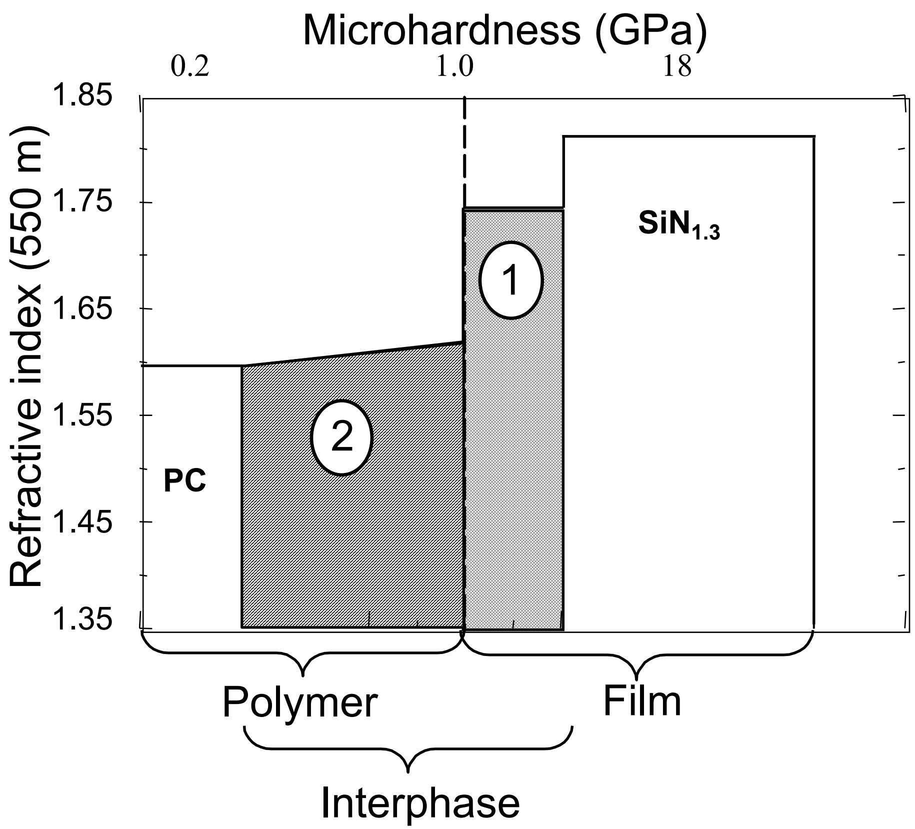
S. Dahl et al., Thin Solid Films, 1999

Refractive index depth profile for PMMA - spectroellipsometry



J. E. Klemberg-Sapieha et al, TSF 1998

Interphase



J.E. Klemberg-Sapieha et al., SVC Proc., 2000

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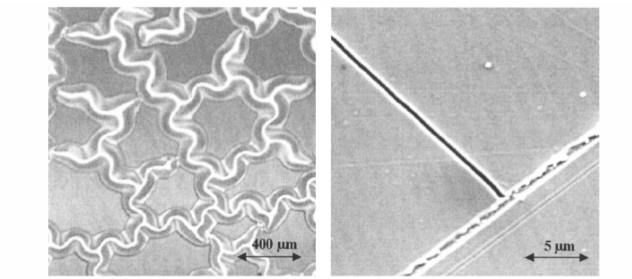
Challenges in coating plastics



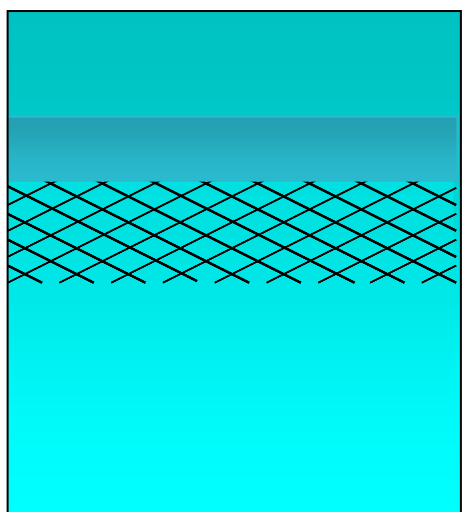
buckling of a coating **tensile-stress cracking**

U. Schulz, Appl. Opt.. 2006

Properties of selected plastics and coatings

Polymer	*ρ* [g/cm³]	CTE [µm/m°C]	*H* [GPa]	*E* [GPa]
PC	1.20	70	0.2	2.0
PMMA	1.18	60	0.2	1.8
PET	1.40	59	0.3	3.8
COP Zeonor	1.01	70		
SiO_2	1.98	2.1	9.5	85
Ta_2O_5	8.20	4.4	7.0	135
Nb_2O_5	4.50	4.9	6.0	125

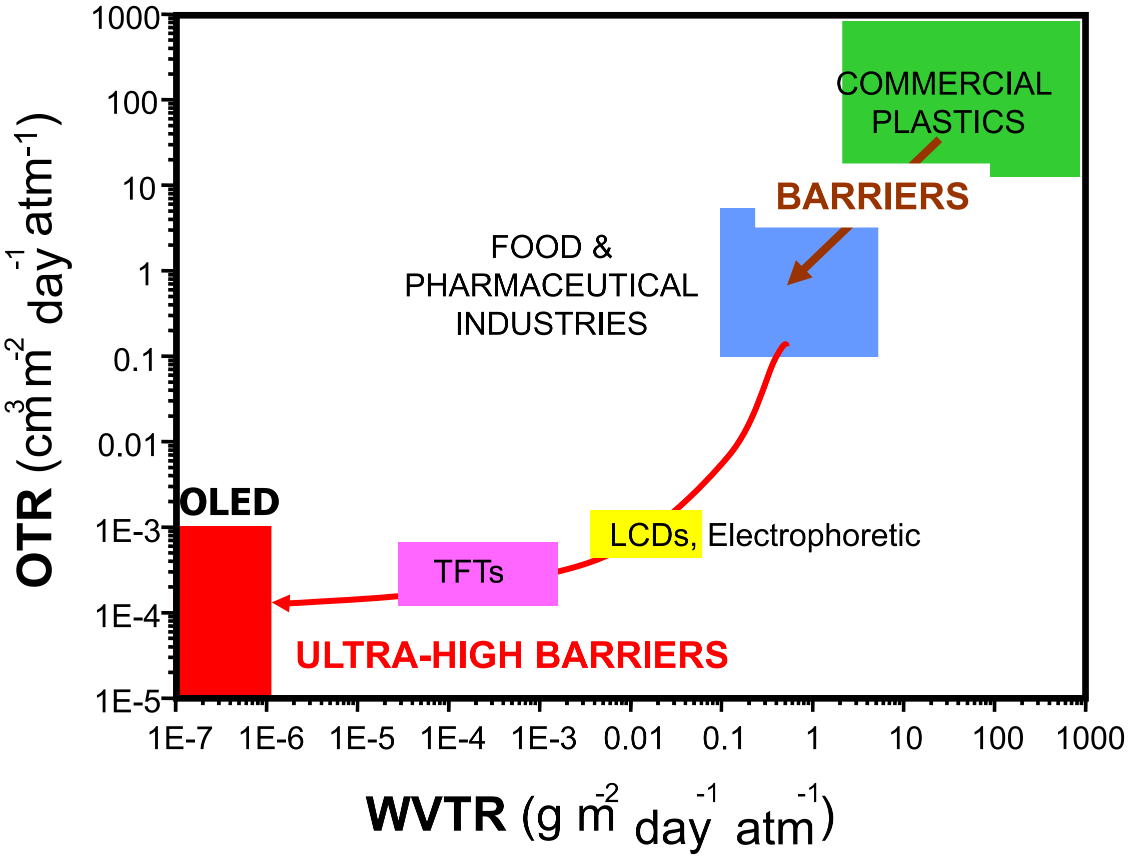
Solution:
Tailoring the interfacial region



Martinu and Klemberg-Sapieha, in Opt. Interference Coatings, Springer, 2003

Permeation barriers on polymer substrates

OTR and WVTR requirements for different applications and the barrier performance provided by available materials.



Barrier requirements

Food & Pharmaceutical Industries:

OTR = 0.1- 1 cm^3/m^2 day atm
WVTR = 0.1- 1 g/m^2 day atm
BIF ~ 100 – 1000

Barrier requirements

Organic Electronics:

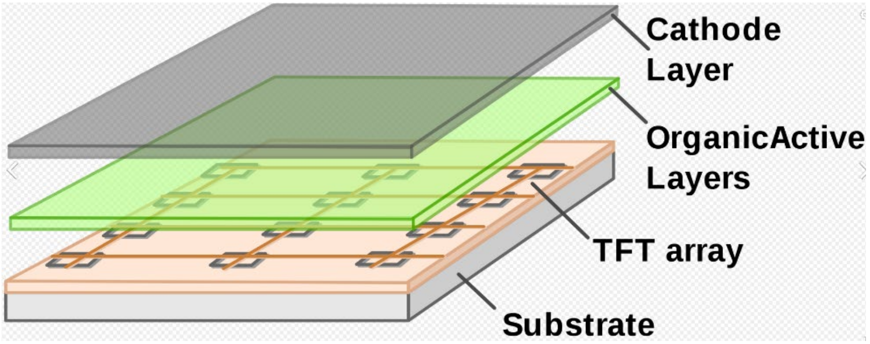
OTR < $\mathbf{10^{-3}}$ cm^3/m^2 day atm
WVTR < $\mathbf{10^{-6}}$ g/m^2 day atm
BIF > $\mathbf{10^5}$ for oxygen
BIF > $\mathbf{10^7}$ for water

$$\text{Barrier Improvement Factor (BIF)} = \frac{\text{Permeation (bare substrate)}}{\text{Permeation (coated film)}}$$

OLED and AMOLED

AMOLED (active-matrix organic light-emitting diode) is a display device technology used in smartwatches, mobile devices, laptops, and televisions. OLED describes a specific type of thin-film-display technology in which organic compounds form the electroluminescent material, and active matrix refers to the technology behind the addressing of pixels.

As of 2008, AMOLED technology has been used in mobile phones, media players and digital cameras, and continued to make progress toward low-power, low-cost and large-size (for example, 40-inch or 100-centimeter) applications



Flexible displays and flexible touch screens continue to grow; it is expected that flexible, curved and foldable displays will have over $75 billion revenue in 2027.

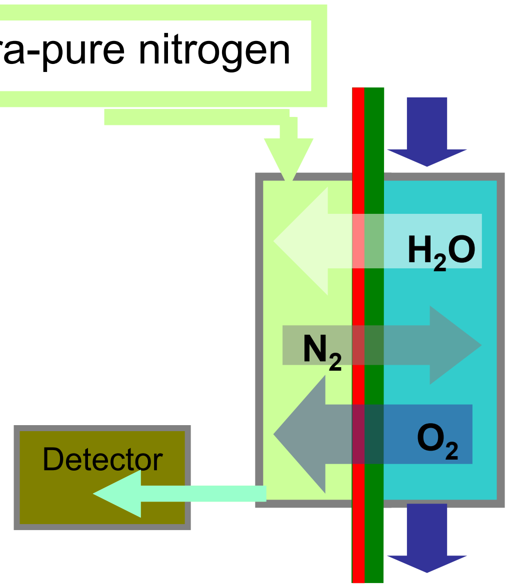
Jennifer Colegrove, Touch Display Research, private communication, May 2019

WVTR and OTR tests

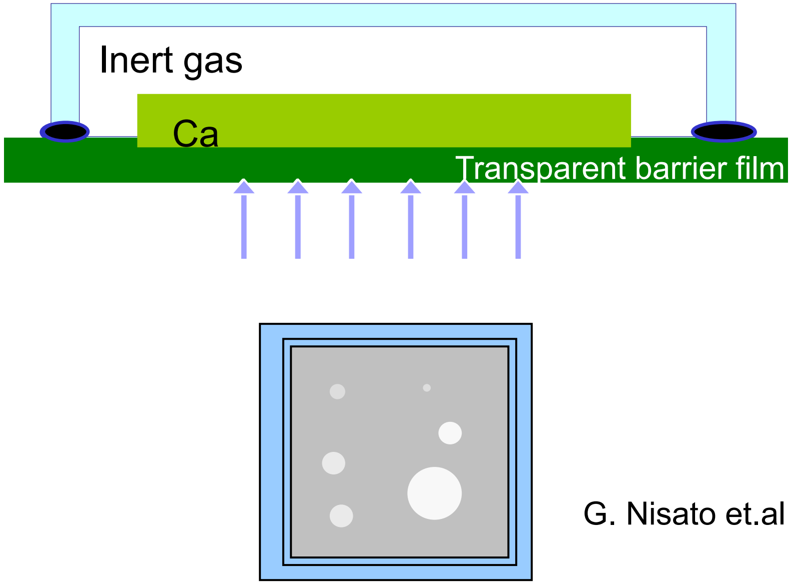
Standard "MOCON" test

WVTR
in
g/m^2day

OTR
in
ccm/m^2day



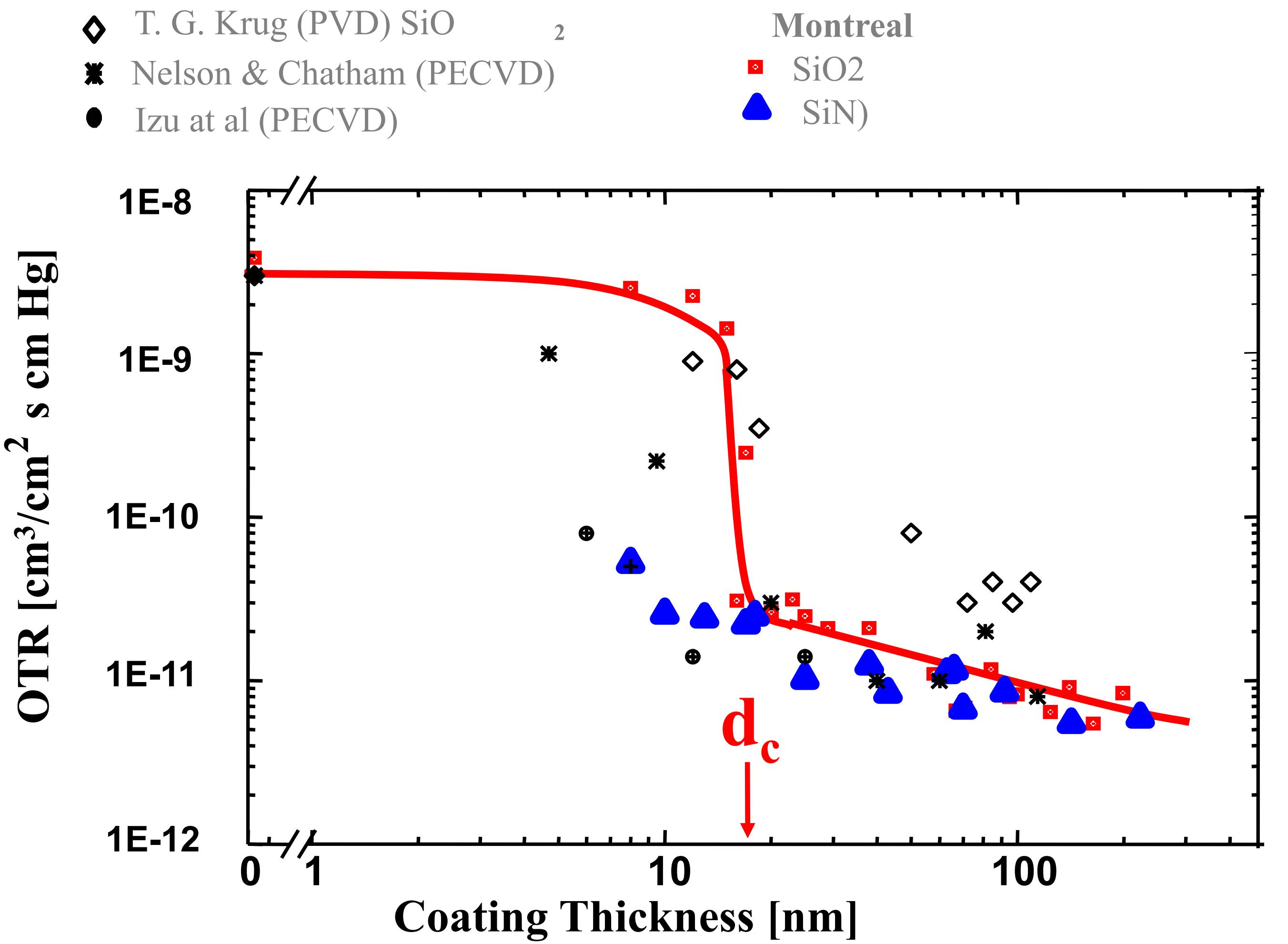
Ca test



G. Nisato et.al

- Standard "Mocon" test
- Calcium test
- QMS measurements (vacuum)
- OLED lifetime test
- Others

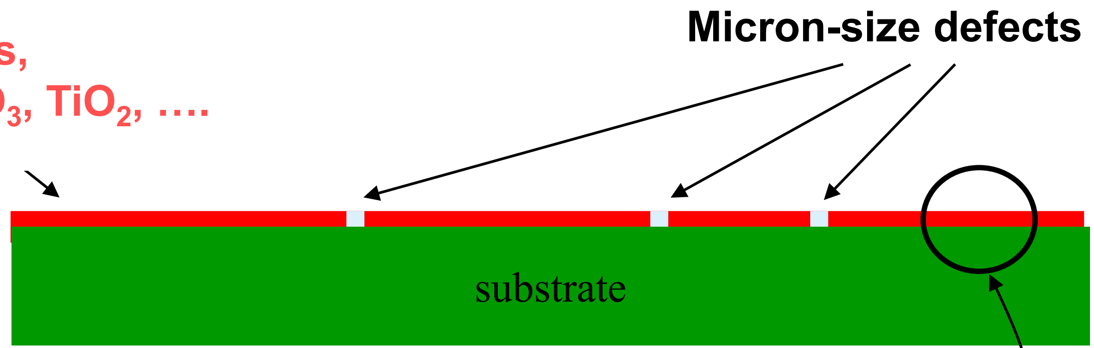
Critical thickness, d_c



* From: H. Chatham, *Surface and Coatings Technology* **78** , 1 (1996).

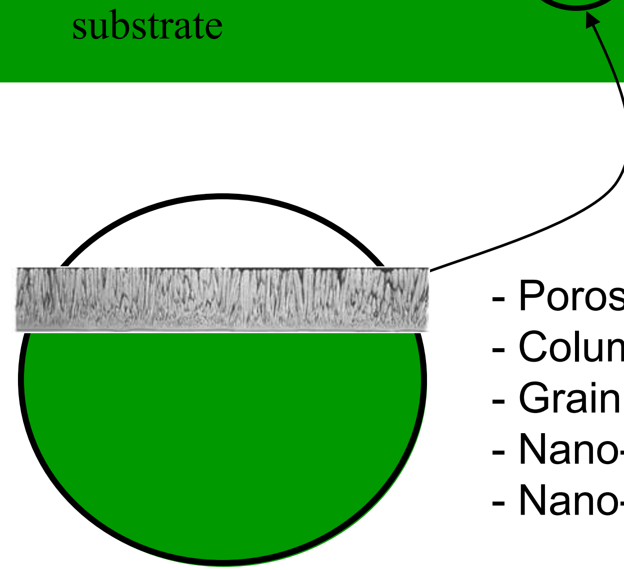
Defect-controlled permeation

Metal oxides, nitrides,
e.g. SiO_2 , Si_3N_4, Al_2O_3, TiO_2, ….

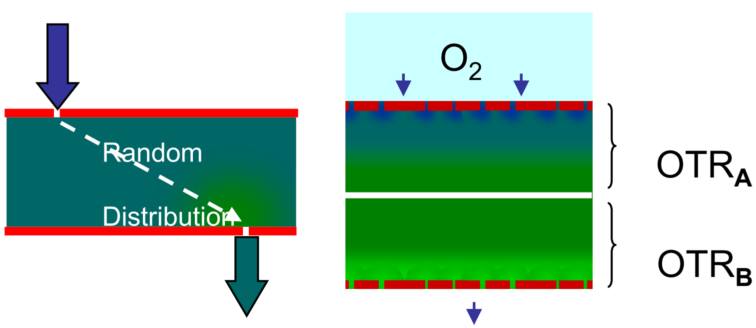


PET E_a ~ 29 kJ/mol

SiO_x Ea > 80-300 kJ/mol



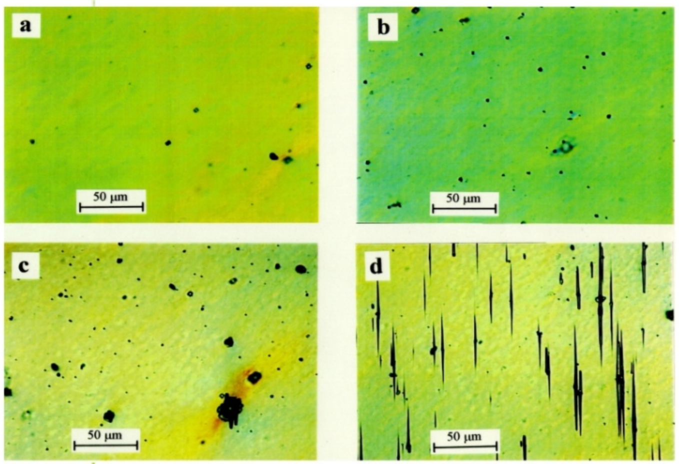
- Porosity;
- Columnar structure;
- Grain boundaries;
- Nano-cracks;
- Nano-breaches.



Permeation of gases through barrier-coated plastic films is controlled by the presence of **micron- and submicron size defects** in the otherwise impermeable coating !!!

Coating – substrates interphase

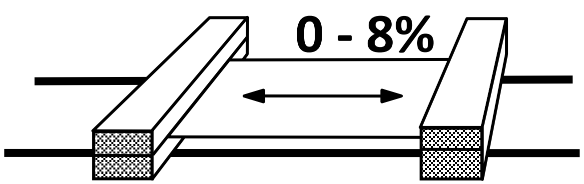
PECVD SiO_2 (200nm)/PET



Sample	Stretching	OTR cm^3/m^2 day
13 µm PET	0 %	159
	4 %	163
SiO_2	0 %	0.3 - 1.1
	2 %	0.7 - 1.0
	3 %	2.2 - 3.3
	4 %	10.3 - 97
	4.8%	117
	5 %	137
	6 %	160
	8 %	160

PVD ← (0.7 - 1.0)
PECVD ← (2.2 - 3.3)

Films Stretching:

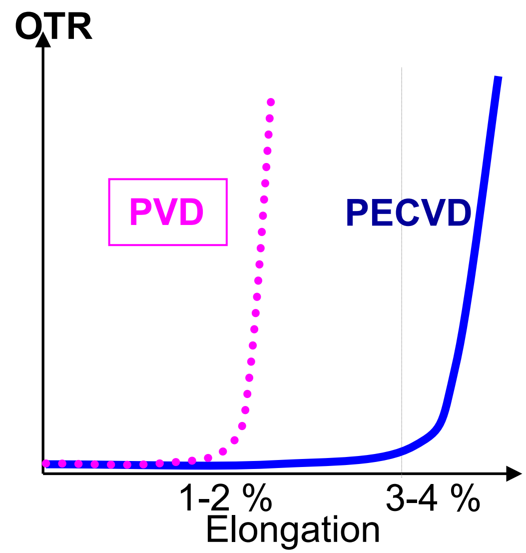


Test carried out using peel-tester 3M90, Instrumentors Inc.)

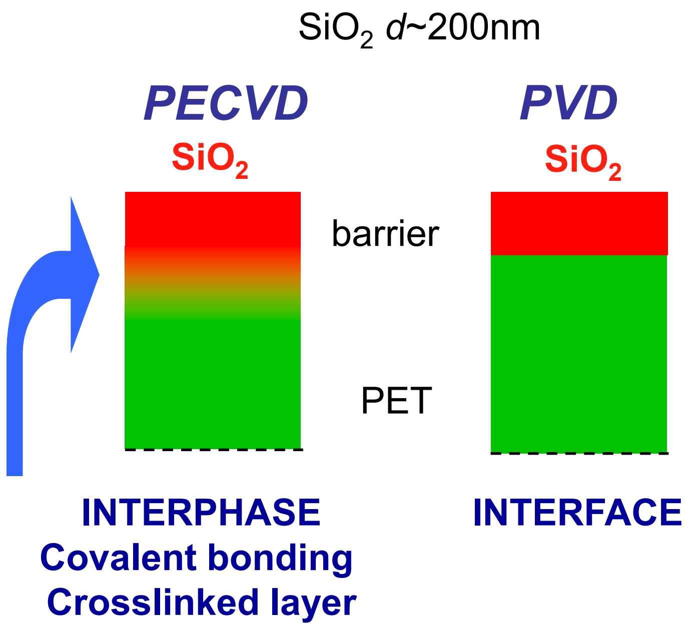
Stretching speed : 0.056 mm/s

Samples width : 9 cm or 2 cm.

G. Czeremuszkin et al., Proc. SVC 46th An. Tech. Conf. (2003)



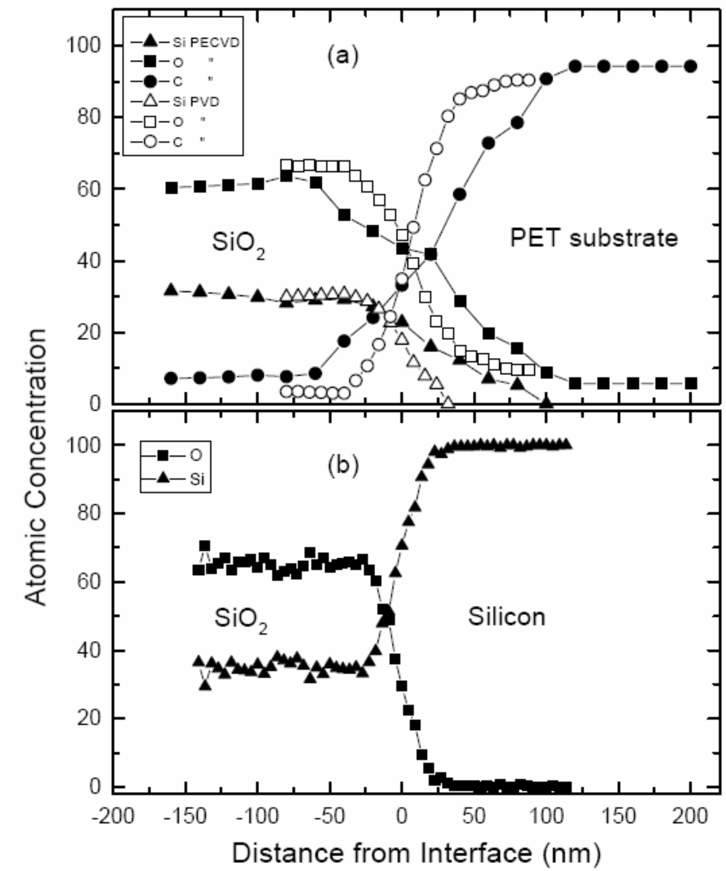
Interfacial region - Interphase



* Thin coatings - thinner interphase 5 ~10 nm;
* Depends on process parameters;

* Interphase: complex structure:
    Likely composed of:
A. Gradient transition layer (silica/substrate) with chemical bonding;
B. Modified substrate layer (UV, VUV, Ions);

PECVD
Improved adhesion;
Increased stretchability;
Increased "bendability" of coated films.



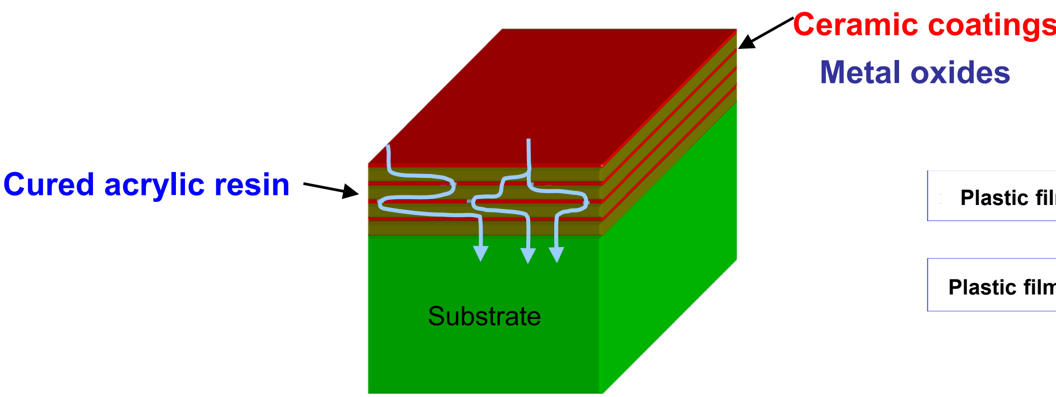
Comparison of compositional depth profiles of the SiO_2/substrate by ERD:
(a) PECVD (320 nm) and PVD (120 nm);
(b) Thermal CVD (200 nm) SiO_2 on c-Si

Da Silva-Sobrinho AS, Schüler N, Klemberg-Sapieha JE, Wertheimer MR, Andrews M, and Gujrathi SC J V S T, A 16 (1998) 3190.

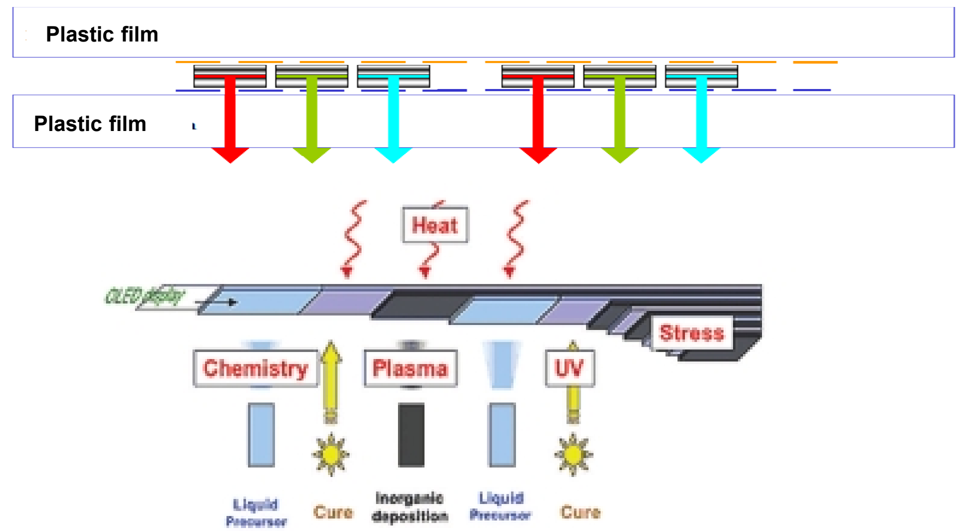
Ultra-high barriers

WVTR = 1 10^{-6} g/m^{2}day atm

corresponds to **<u>0.006 monolayer per day !</u>**



Ultimate goal: encapsulation and flexible substrates for OLEDs



<u>Deposition sequence of ultra barrier:</u>

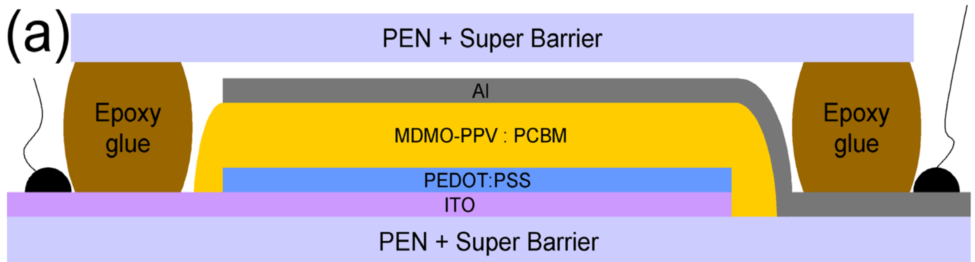
- Plasma surface activation
- Flash evaporate monomer
- UV cure
- Deposit inorganic layer
- Flash evaporate monomer
- UV cure
- Deposit inorganic layer

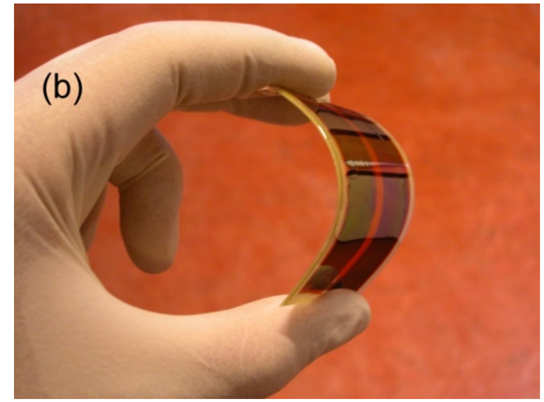
In line vacuum polymer deposition (courtesy of Vitex System)

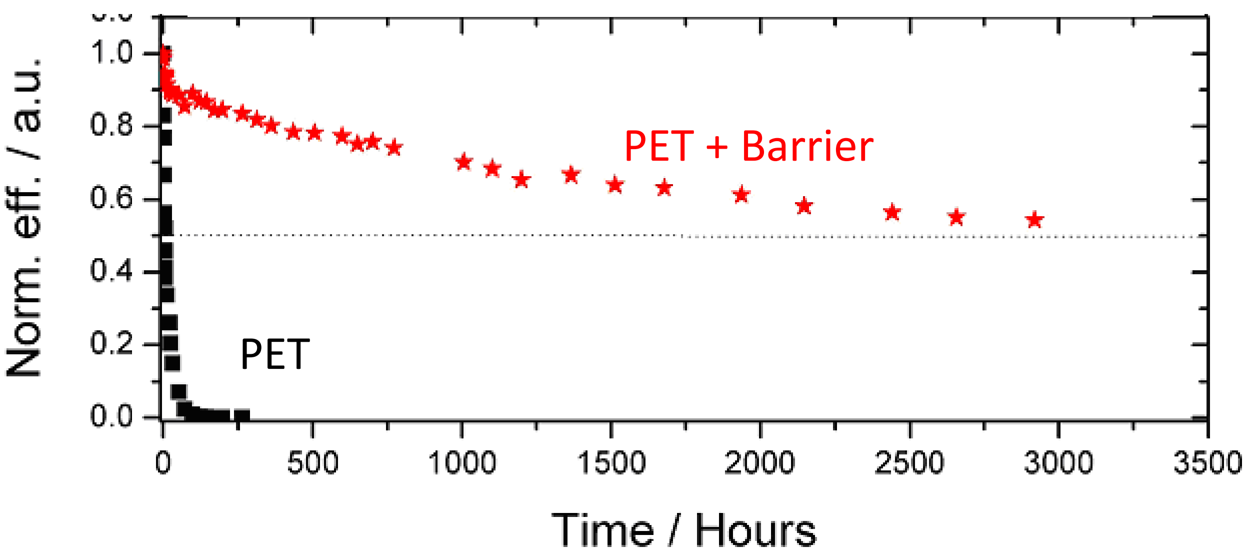
P. Martin, Vacuum Technology & Coating, 2009.

M.E. Gross et al., SVC, 2006.

Ultra-high barriers

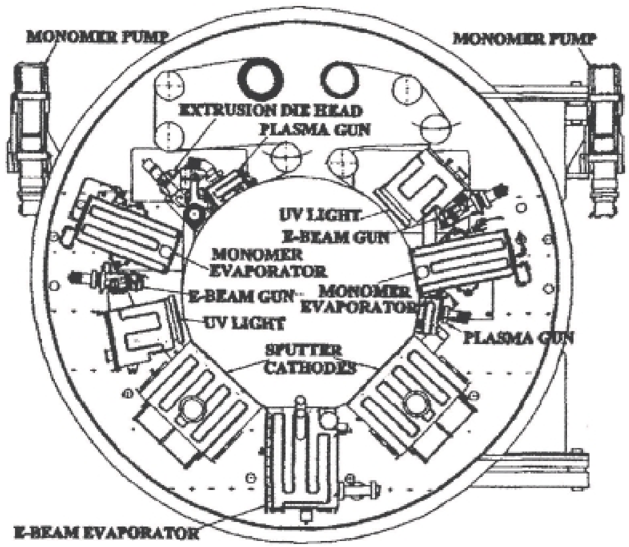




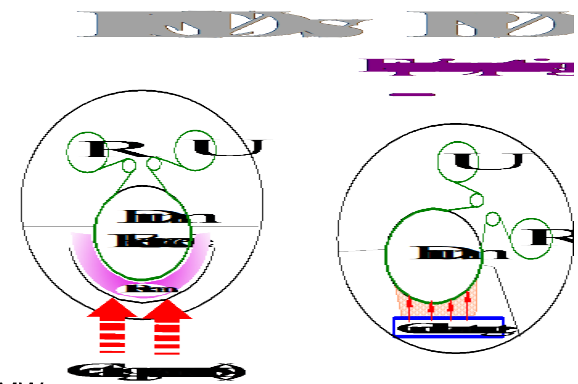


Flexible photovoltaic cell

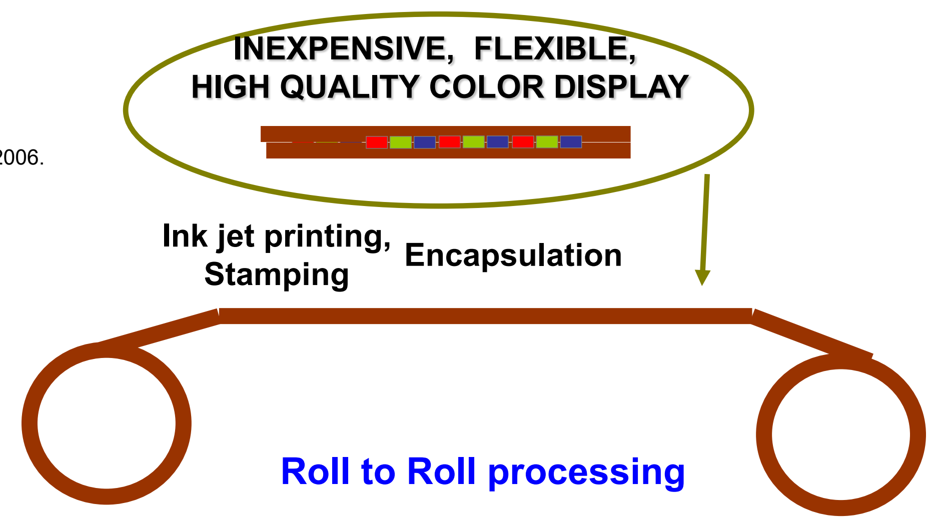
Roll-to-roll technology for transparent barrier

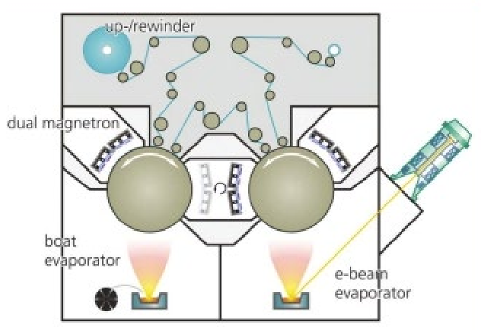


Schematic system which combine: plasma treatment, polymer evaporator, sputtering and e-beam evaporator around the central drum of web coater. M.E. Gross et al., SVC, 2006.



AC, RF, MW,
AC/RF, RF/MW



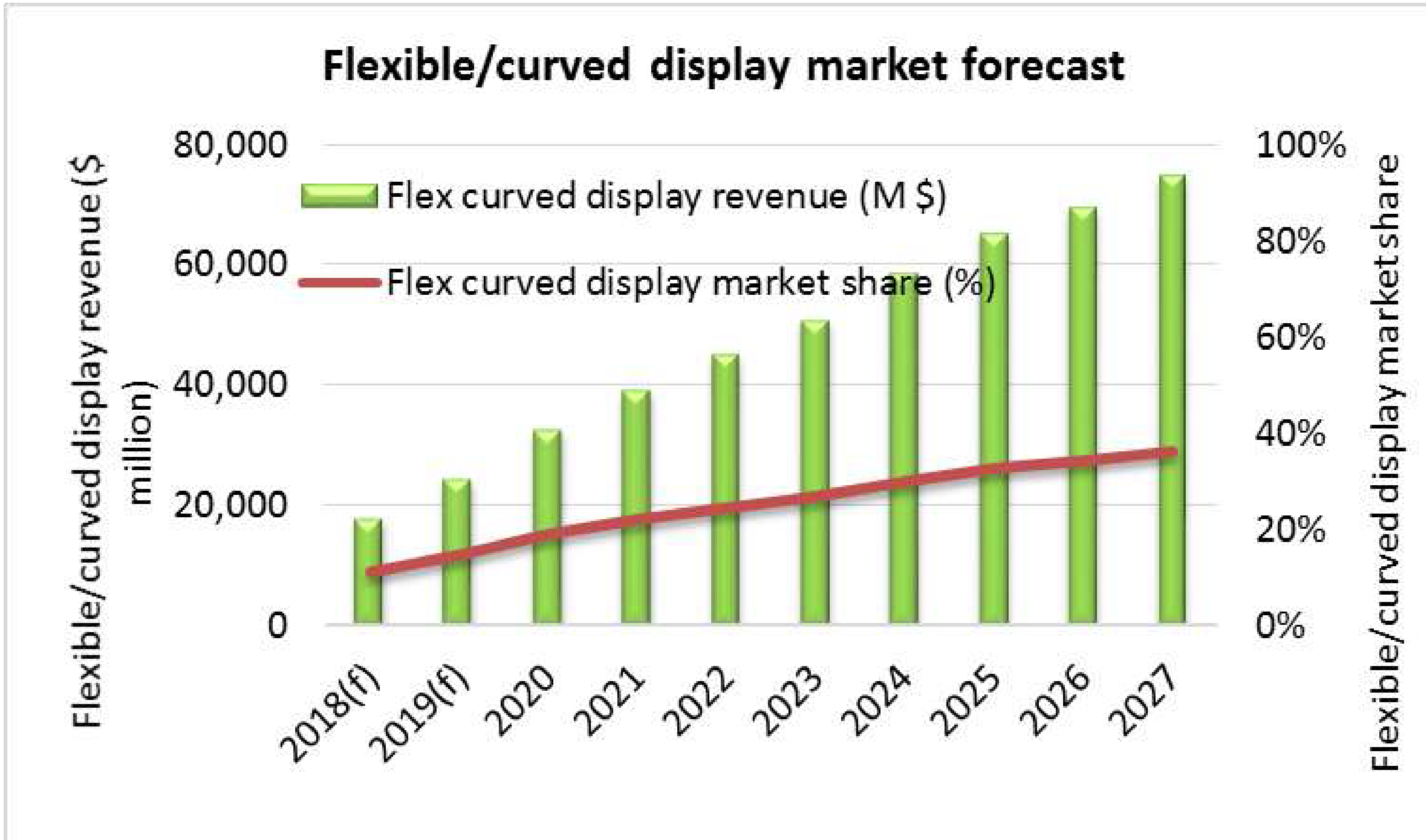


Pilot roll coater novel Flex 600.
N. Schiller et al., Vacuum Technology & Coating, 2009.

G. Czeremuszkin et al., SVC, 2003

Flexible, curved and foldable display market share

It is foreseen that flexible, curved and foldable display will have over $75 billion revenue, which will be about 36% market share in 2027.



Jennifer Colegrove, Touch Display Research, private communication, May 2019

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**
18***	*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: **18 April p.m.**

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

Project #3: Applications of nanostructured films and coatings

Thomas Sicotte and Alexandre Gamache - Cellules photovoltaïques à pérovskite

Alexandre Lussier - Fenêtres intelligentes thermochromiques

Mohamed Ammari - Thermal barrier coatings for aerospace gas turbine engine

Luc Montpetit - Passivation of CdZnTe for x-ray detectors

Veronika Cervenkova - Solar-thermal energy conversion - Transition metal nitrides

Émilien Martel - Electrochromic, photochromic and gasochromic coatings for consumer optics

Étienne Tremblay et Nathan Sasseville - Couches minces pour l'électronique organique – OLEDs

Thomas Lapointe - Photodétecteurs et leur conception/optimisation à l'aide des couches minces

Alexandre Carrière et Youssef Ben Mami - Électrodes transparentes pour la fabrication des cellules solaires

Arghavan Yazdanpanah Ardakani - Nanoengineering thin-films to produce hydrophobic coatings for aircraft surfaces

Mathieu Bruzzese – Oxidation-resistance barrier coatings for aerospace applications

Bastien Izacard – Atomic oxygen barrier coatings for satellites

Alexandre Fall - Carbon nanotubes for sodium-ion batteries

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

Christelle Abou Zeidan – Carbon nanotubes for flexible electronics