PHS6317
NANO-ENGINEERING OF THIN FILMS

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Winter 2024

Bienvenue - Welcome

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Ludvik Martinu

Professor in the Department of Engineering Physics, Polytechnique Montréal, QC, Canada,
Chairholder - Multisectorial Industrial Research Chair in Coatings and Surface Engineering,
Founder and Director - Functional Coating and Surface Engineering Laboratory,
Director - Thin Film Science and Technology Research Center, Campus of the UdeM,
Guest Professor – U. Leoben, U. Coimbra, U. Sydney, U. Uppsala, U. Marseille, City U. Hong-Kong,
Former President – Society of Vacuum Coaters

He specializes in the **physics and technology of thin films, coatings, surfaces and interfaces** and is known for his contributions to **plasma processing of nanostructured materials**, **plasma-surface interactions**, and **surface engineering for optical, optoelectronic, tribological, biomedical, aerospace and space applications**, as well as nanostructured **passive and active (smart) materials**.

His research resulted in more than 400 publications and a close collaboration in partnership with industry.

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Concepts of Advanced Materials

Thin Films and Surface Engineering

Historical perspective:

Economic and societal development

Scientific and technological challenges

Incremental and disruptive developments

Main trends:

Introduction of surfaces and interfaces

Multiscale approaches

Functional and multifunctional materials

Nanoscience and Nanotechnology

Development of advanced materials:

Introduction of surfaces and interfaces

Great inventions of the 20th century:

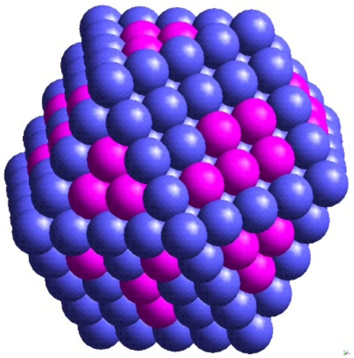
- transistor
- laser
- giant magnetoresistance for memory storage
- optical fibers …

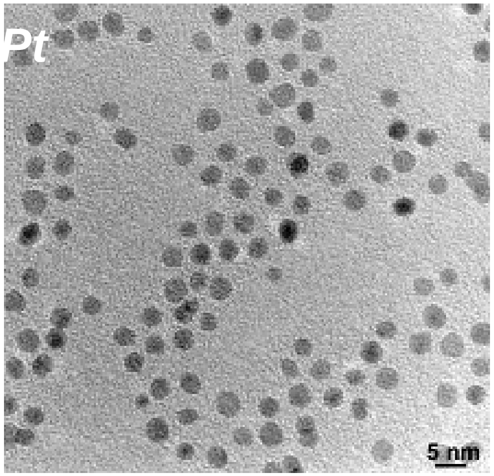
Areas of research and technology of the 21st century:

- micro/nanotechnologies
- optics, photonics, telecom,
- biomedical
- energy
- internet of things, machine learning
- sustainable development, environment – ‘low carbon footprint’

Why surfaces?

Only surface-interface atoms are active





Source: Jean-Paul Salvetat, CNRS-Orléans

Surface of the Earth : 1,44x10^{14} m^2

Volume required to obtain the same surface with particles having a diameter of:

1 mm : 46 billion m^3

(8 m thick layer at the surface of the Montreal Island)

1 µm : 46 million m^3

(20 times the volume of the Olympic Stadium in Montreal)

5 nm : 250 000 m^3

(60% of the Main Building of Polytechnique Montreal)

1 nm : 46 000 m^3

(50 % of the J.A. Bombardier Building)

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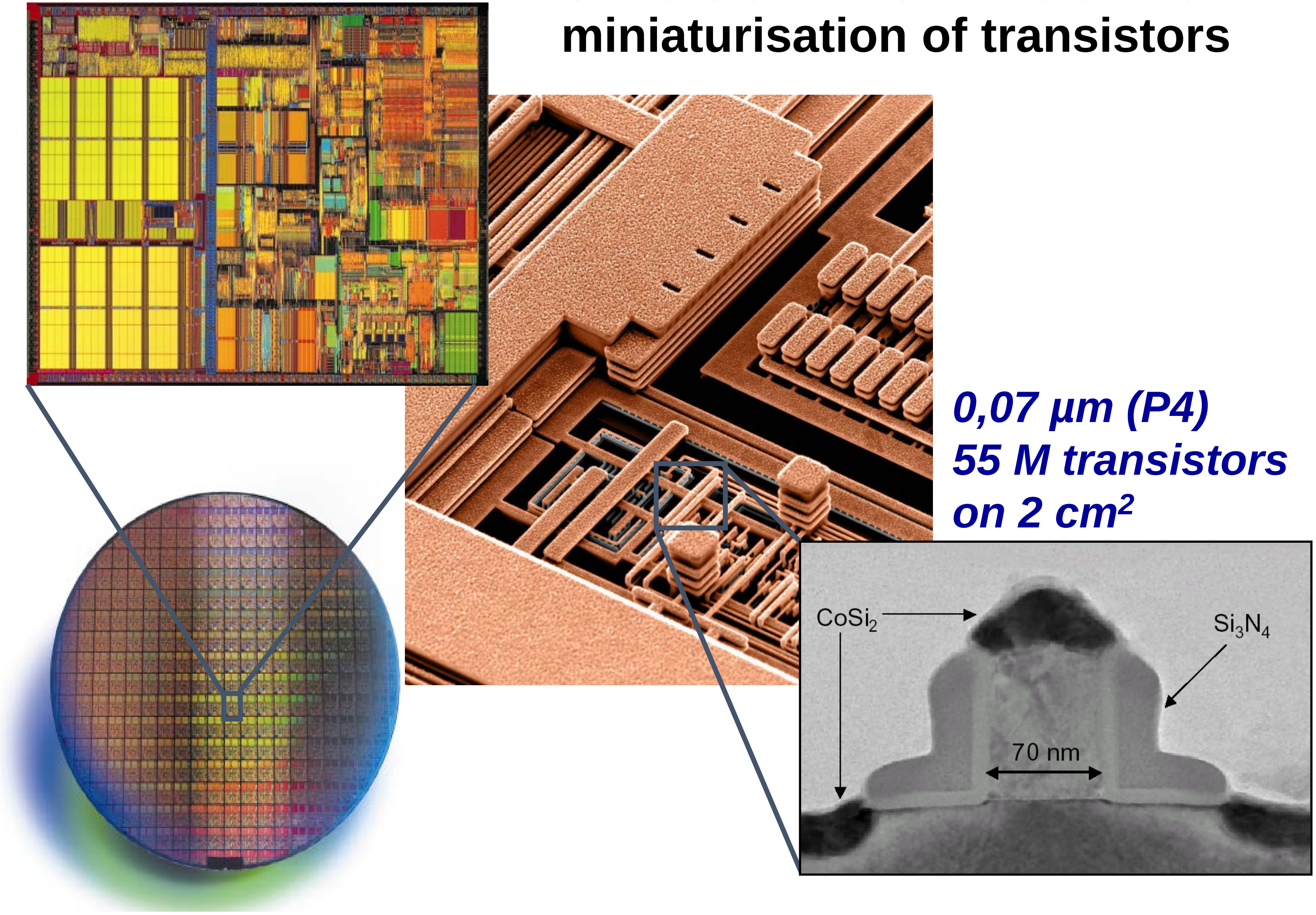
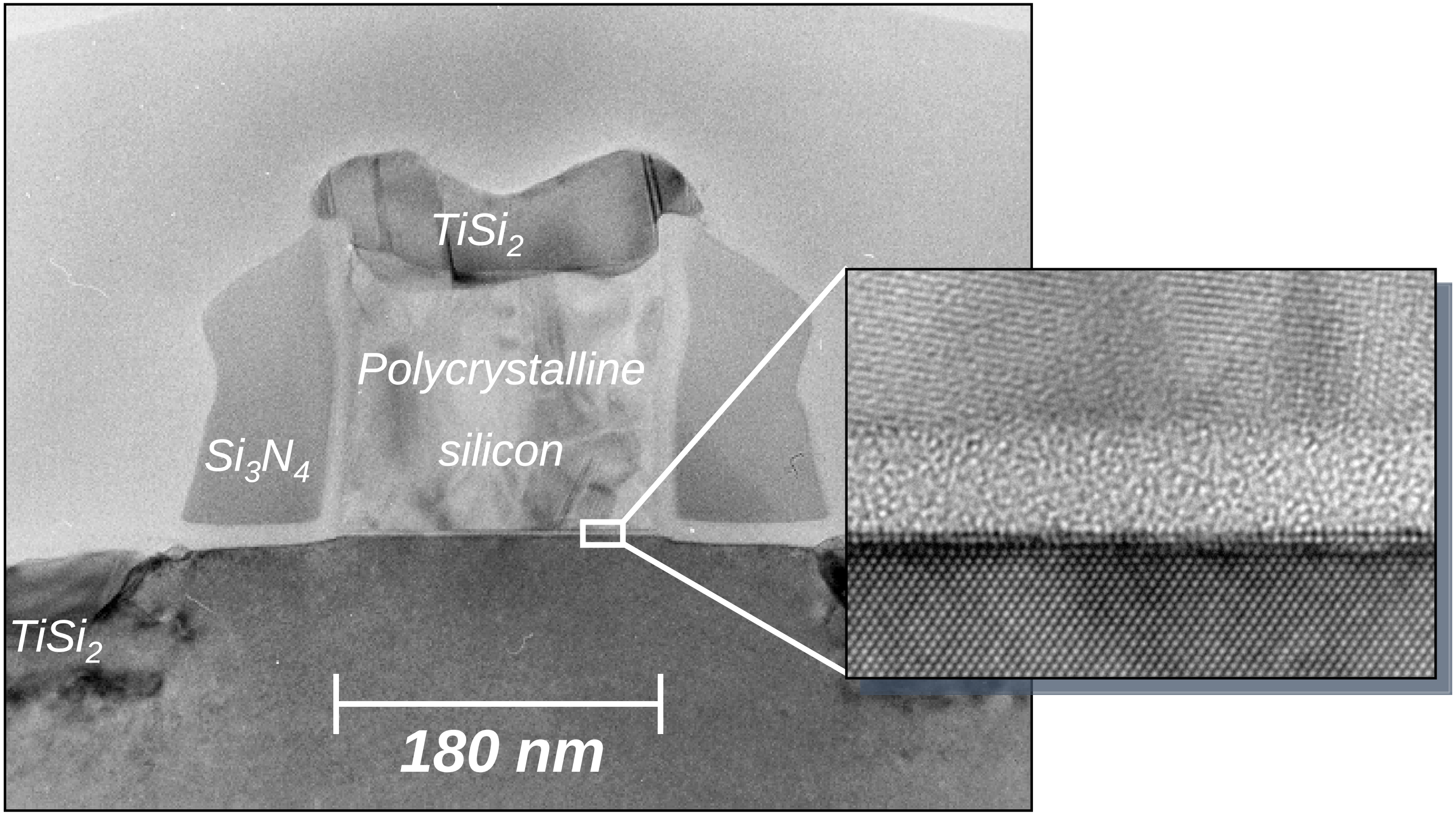
Understand the limits of the miniaturisation of transistors



0,07 µm (P4)
55 M transistors
on 2 cm^2

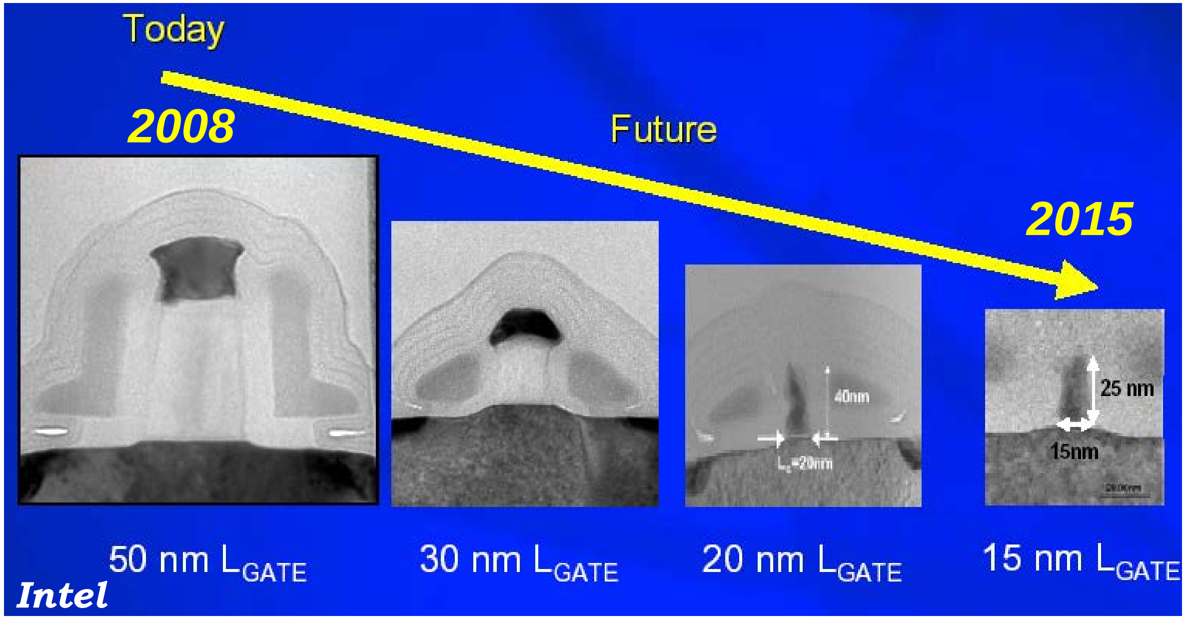
Source: IBM et Intel

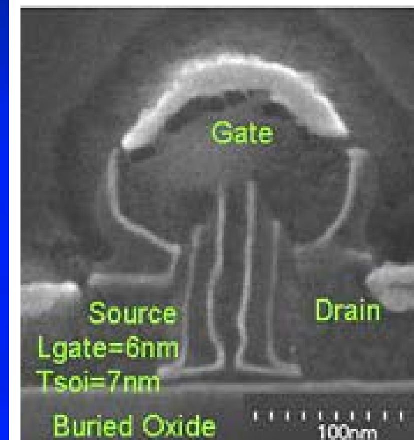
Understand the limits of the miniaturisation of transistors



Source: Intel

Understand the limits of the miniaturisation of transistors





IBM, Dec. 2002

↘

July 2015

Objectives for 2016 (ITRS 2008):

3x10^9 transistors on 2 cm^2, speed : 30 GHz, Memory: 64 GB

→ **today: 2.85x10^9 t / 2 cm^2**

Miniaturisation is not sufficient:

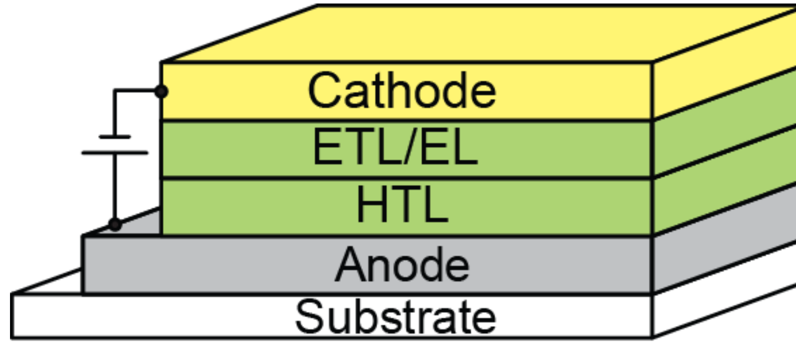
- The behavior of materials changes with size
- Need to develop new materials to respond to precise requirements

Source: IBM et Intel

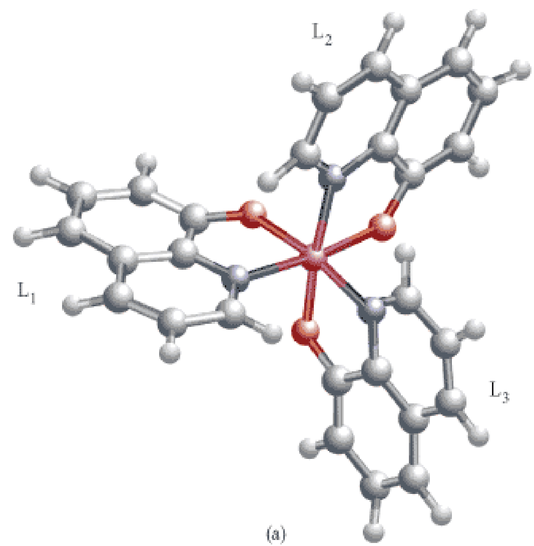
Organic electronics

Challenges:

- *Conductive transparent anode*
- *Stability*

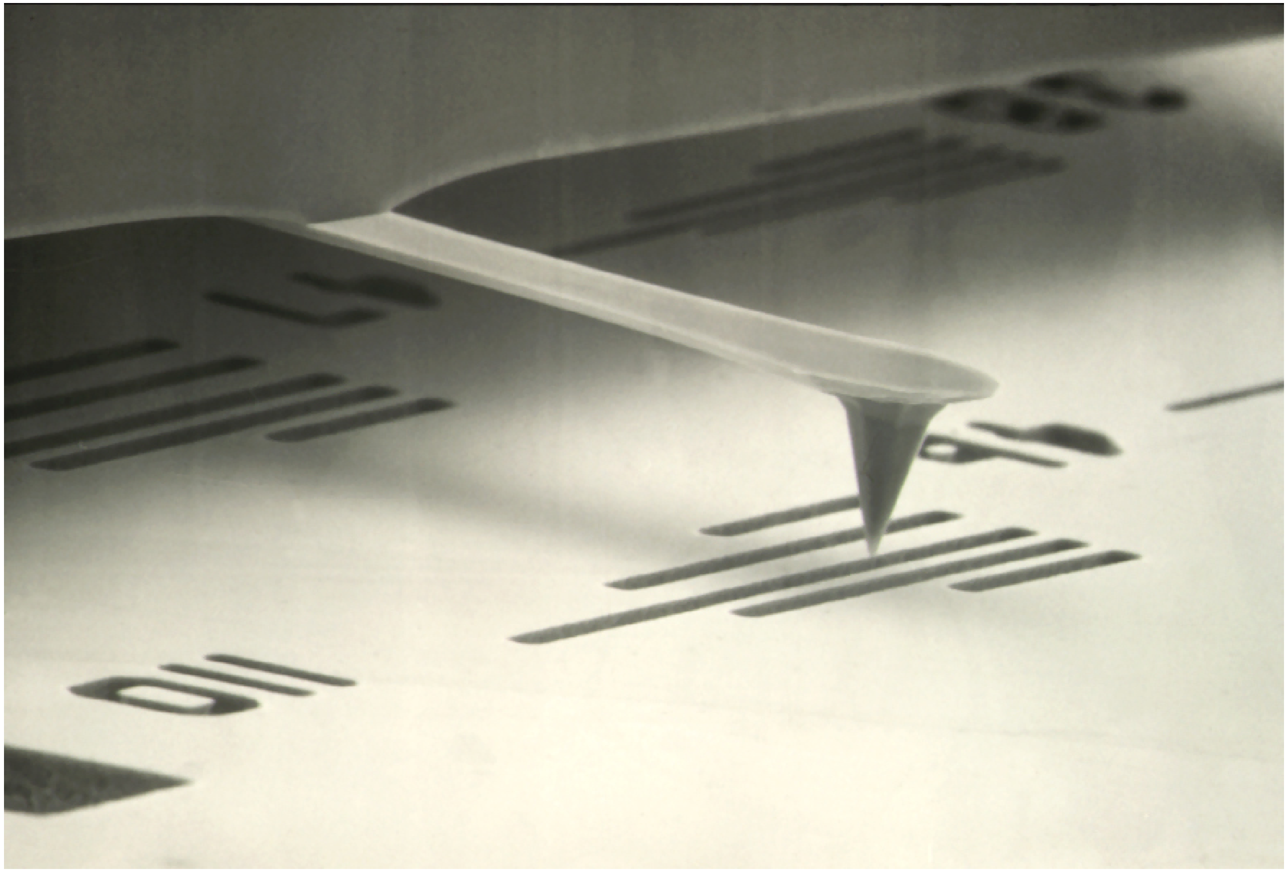


Sony



Atomic scale observations

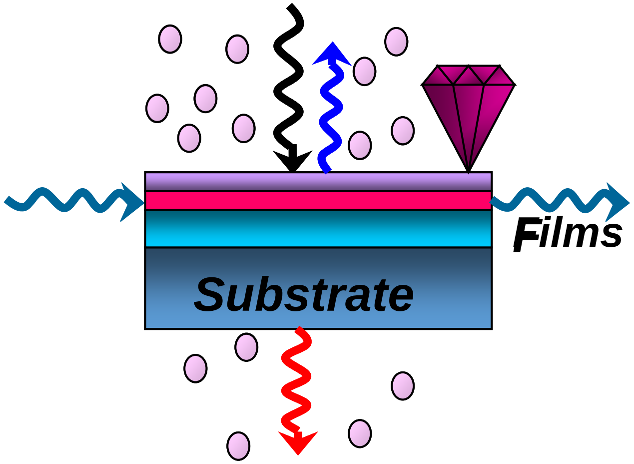
Atomic Force Microscopy and Scanning Tunneling Microscopy



Evolution of the inventions: Funtional materials, nanomaterials

(Multi)functional material:

- Nanomaterials
- Smart materials
- Hybrid materials
- Organic electronics
- Biomaterials



"Green" fabrication technologies

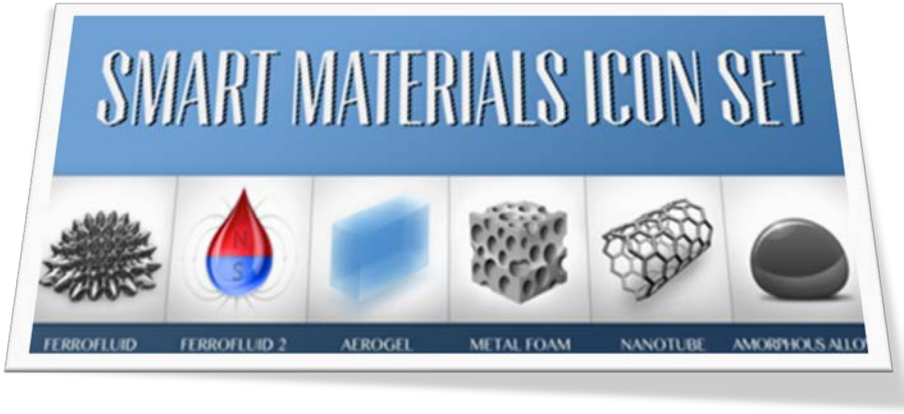
Environmental stability and durability

Industrial scale

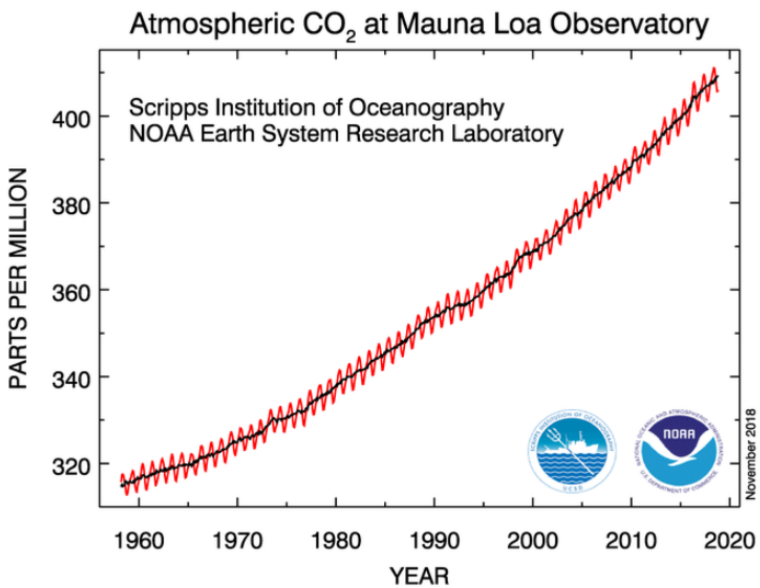
Cost

Globalisation of the world economy

Life cycle analysis

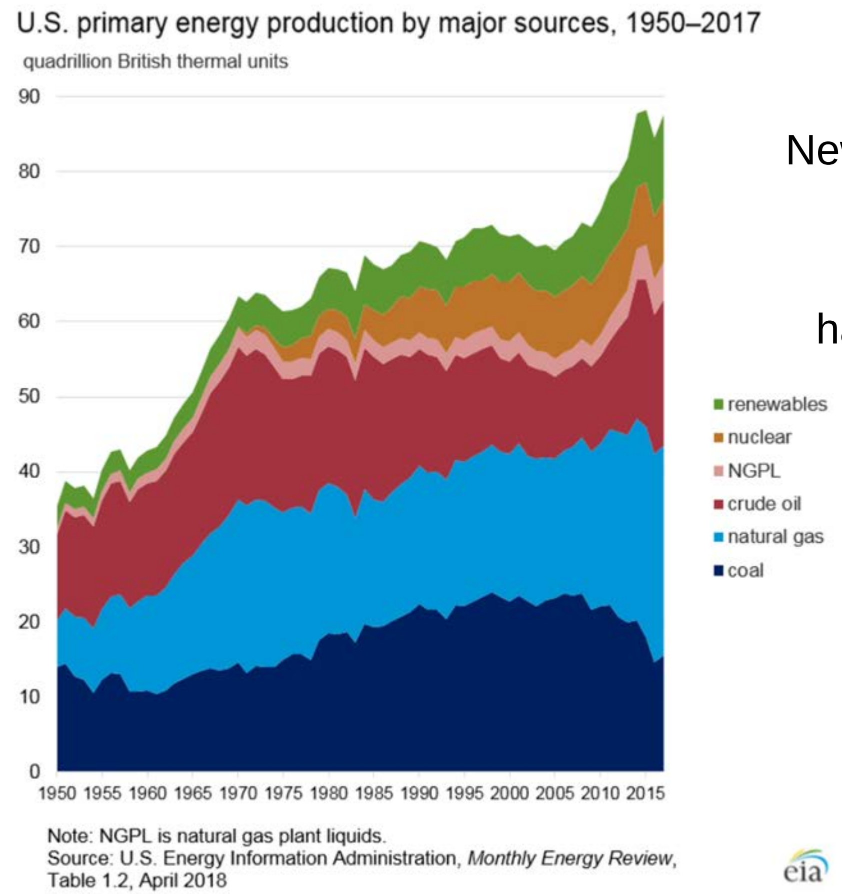


Context – energy and environment



U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Earthscan System Research Laboratory, Global Monitoring Division.

https://www.esrl.noaa.gov/gmd/ccgg/trends/full.html



New energy sources

Energy harvesting

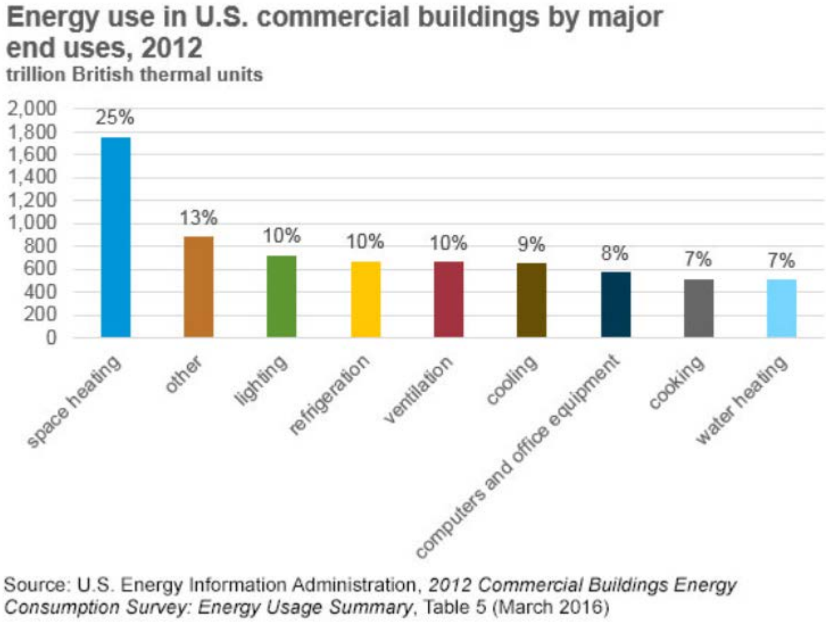
Energy storage

Energy saving

"… the CO_2 concentration has risen from ~315 ppm at the end of the 1950s so that it now exceeds ~400 ppm, with no change of this trend yet in sight. It is widely understood that growing amounts of atmospheric CO_2 lead to global climate change and rising sea levels and that there are numerous secondary and often harmful side effects. Another important trend of significance for solar energy materials is the rapid growth of the global population and its ongoing accumulation in mega-cities whose local climate is altered and often considerably warmer than in surrounding rural regions."

C.G. Granqvist, G.A. Niklasson, Solar Energy Materials and Solar Cells 180 (2018) 213–226

Energy in built environment



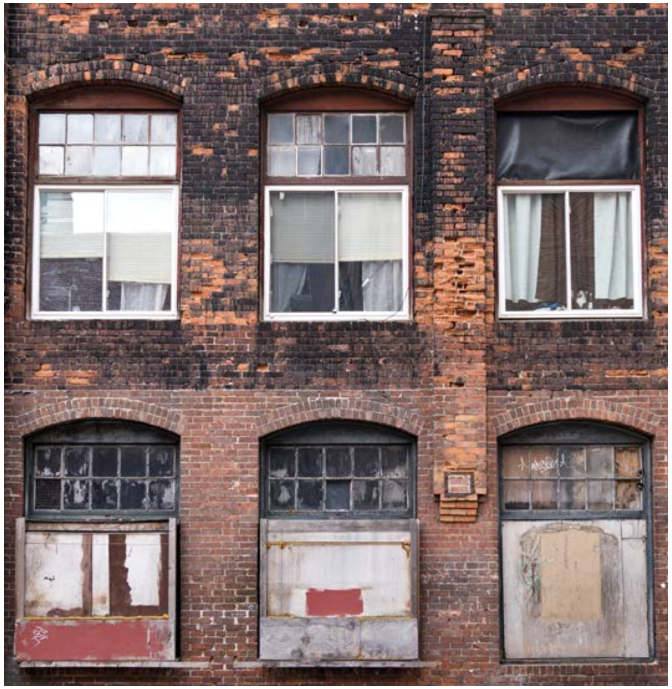
“The building sector contributes up to 30% of global annual green house gas emissions and consumes up to 40% of all energy. Given the massive growth in new construction in economies in transition, and the inefficiencies of existing building stock worldwide, if nothing is done, **greenhouse gas emissions from buildings will more than double in the next 20 years.”**

“The full extent of the life-time emissions of a building can best be understood by using the **life-cycle (LCA) approach**. The LCA approach reveals that over 80 percent of greenhouse gas emissions take place during the operational phase of buildings, when energy is used for heating, cooling, ventilation, lighting, appliances, and other applications.”

United Nations Environmental Programme, Buildings and Climate Change: Summary for Decision-makers, UNDP Sustainable Buildings & Climate Initiative, Paris, France, 2009.

Examples:

Buildings and built environment



Related subjects:
Growing population and demographics of our planet,
Energy consumption, comfort

Introduction

Energy
-
Buildings

vs.

"The Battle for the Wall"

ww.gsa.gov/gpg

According to DOE, 30% of energy in buildings in the US is lost - this corresponds to about 42b$ annually.

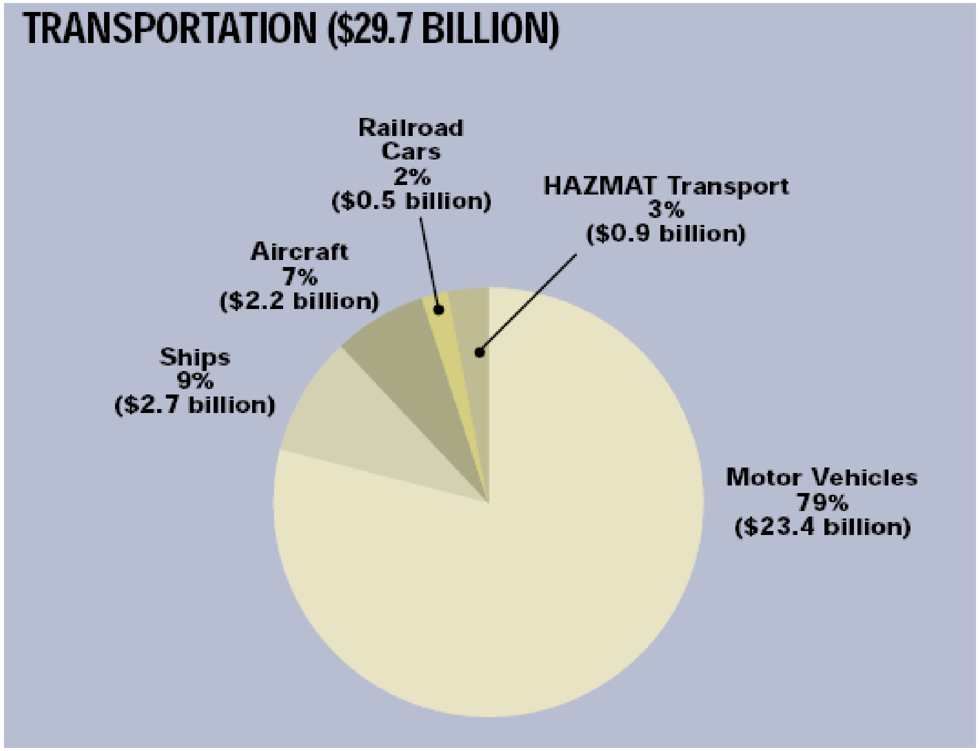
vs.

Courtesy of Brent Boyce, Guardian Industries, 2014

Introduction

- **Wear and corrosion** are the most important failure mechanisms in industry. Repair and replacement of components lead to a significant decrease in performance, efficiency and safety, and substantially increase production cost.
- According to NACE (National Association of Corrosion Engineers), the cost of **corrosion, wear and other materials deterioration** in USA in 2013 exceeded **$1 trillion US$** (6.1% of the GDP).

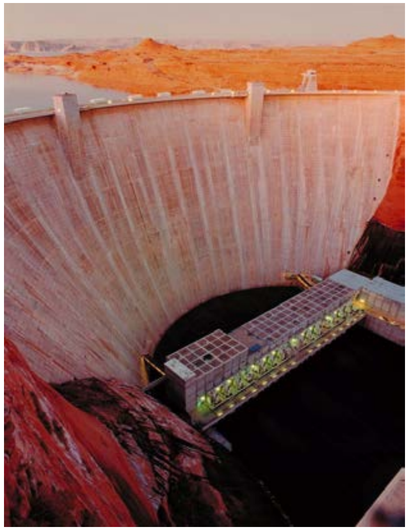
- Similar studies show that **Wear** imposes a cost level of **100 billion US$** (0.7 % of the GDP).
- This cost can be enormously reduced through better **understanding of failure mechanisms** and **Surface Engineering.**



Corrosion-related costs in the US transportation sector

Industrial infrastructures

Dams and reservoirs



Pipelines

Bridges

Railways

Related subjects:
New and aging infrastructure
Maintenance
Environment

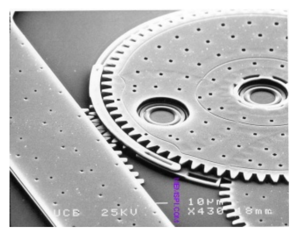
Turning machines, hard functional materials

Machining

<u>Characteristics:</u>
- wear resistance
- chemical and thermal stability
- hardness
- toughness

<u>Materials:</u>
TiN, TiC, TiCN, TiAlN,…

Microelectronics MEMS



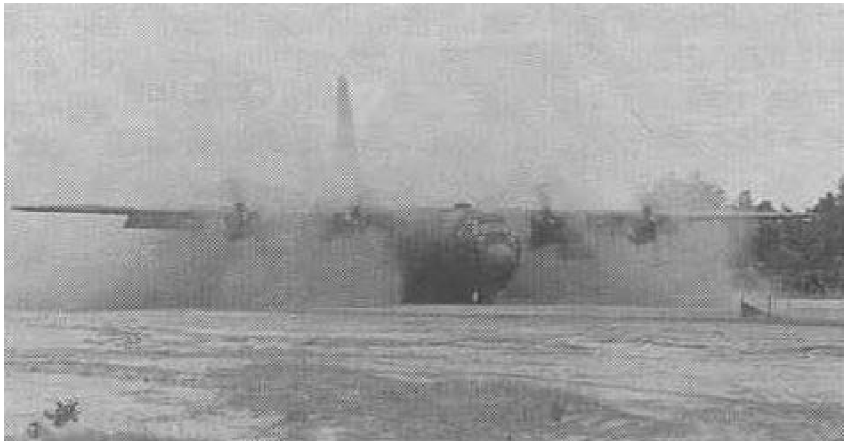
<u>Characteristics:</u>
- low friction
- wear resistance
- controlled mech. Properties
- heat conductivity

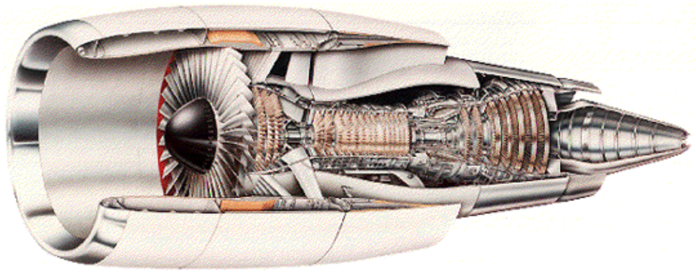
<u>Materials:</u>
TiN, $SiN_{1.3}$, DLC, CN_x

Automobile components; functional materials

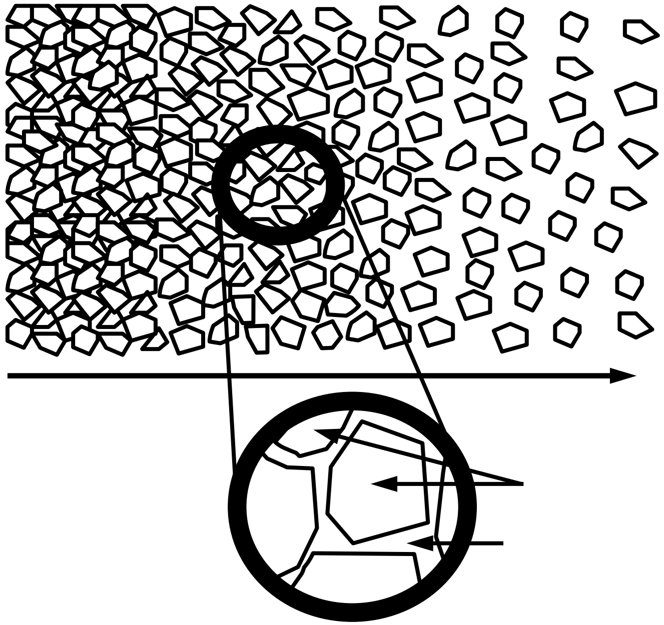
1. Car body, engine components
2. Decorative elements (electrochemical plating vs vapor-vacuum deposition)
3. Electronic components
4. Optical components – mirrors, windows, windshields

Erosion aircraft engine components

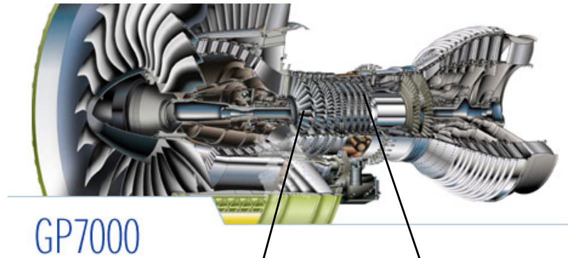




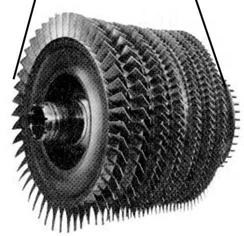
Microstructure: nanocomposites



Engines – aerospace, automobiles, hard materials



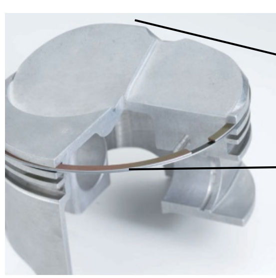
Aerospace industry
Pratt and Whitney
Engine GP7000
for Airbus A380

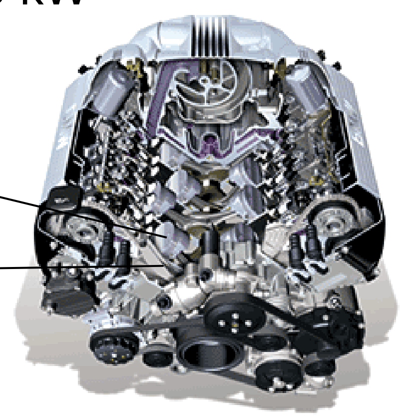


Characteristics:
- abrasion resistance
- thermal barrier

Materials:
ZrO_2, CaO, MgO, Y_2O_3
(turbine blades)

Automobile industry
BMW 8 cylinder, 200 kW
engine

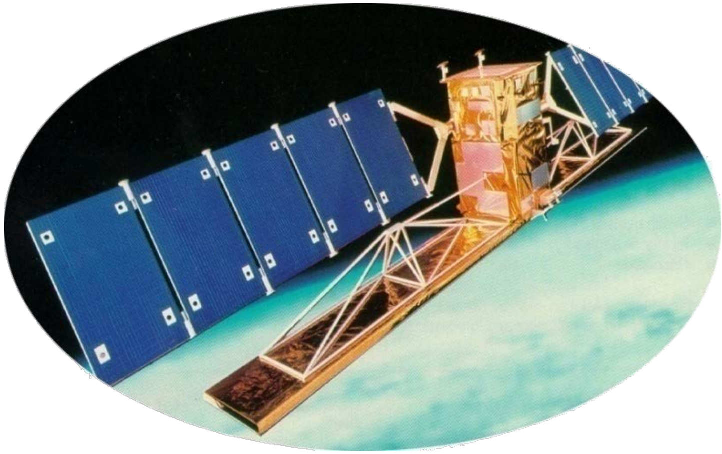


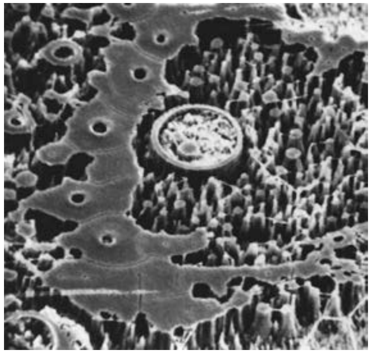


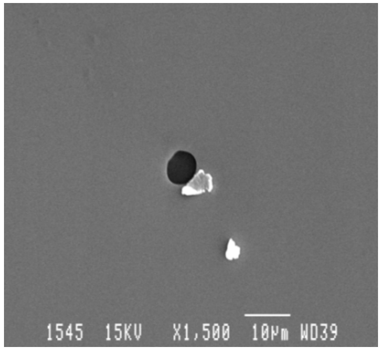
Characteristics:
- low friction
- wear resistance

Materials:
DLC (piston)

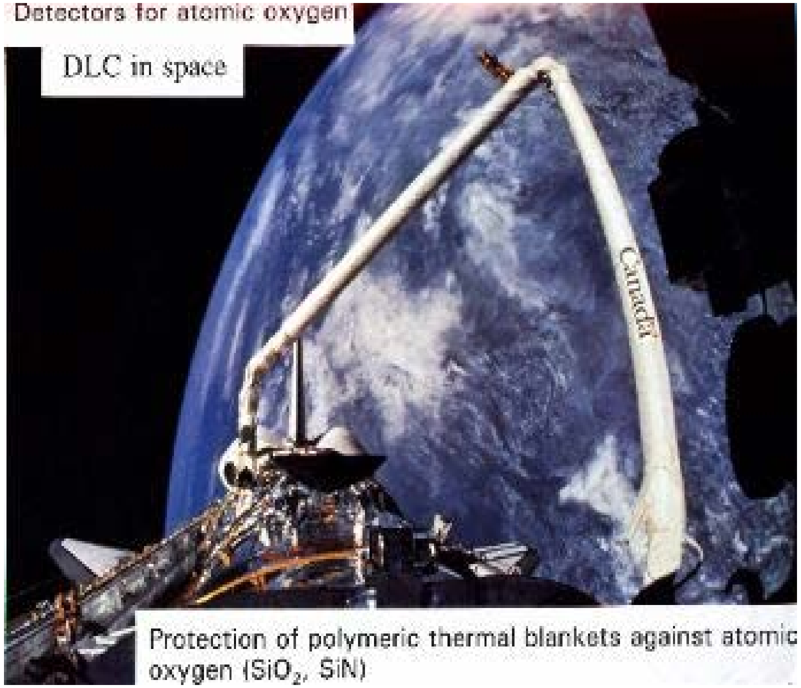
Space exploration







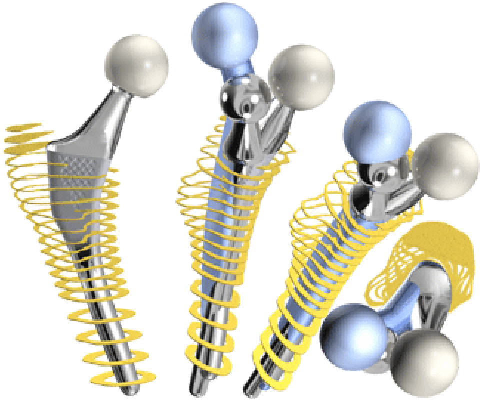
Polymers: Polyimide (DuPont Kapton)
Without protection and with a SiO_2 film



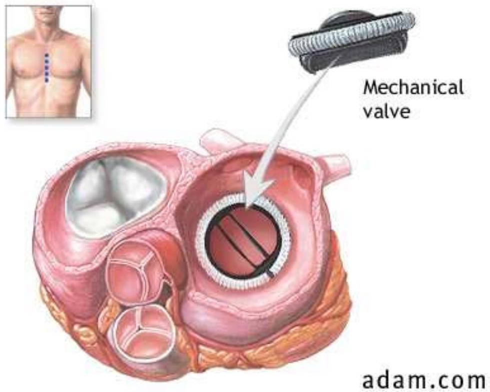
Erosion by atomic oxygen
Smart IR radiators

Biomedical applications

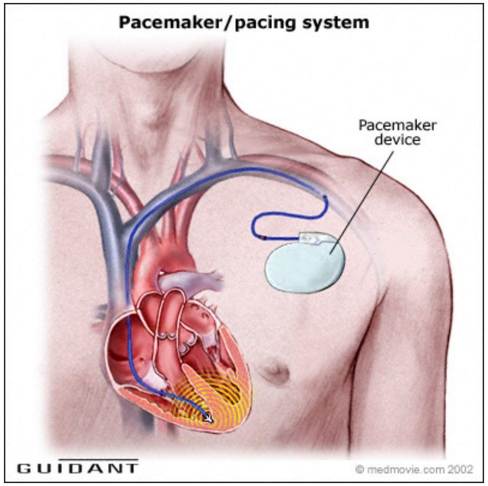
Joint replacements



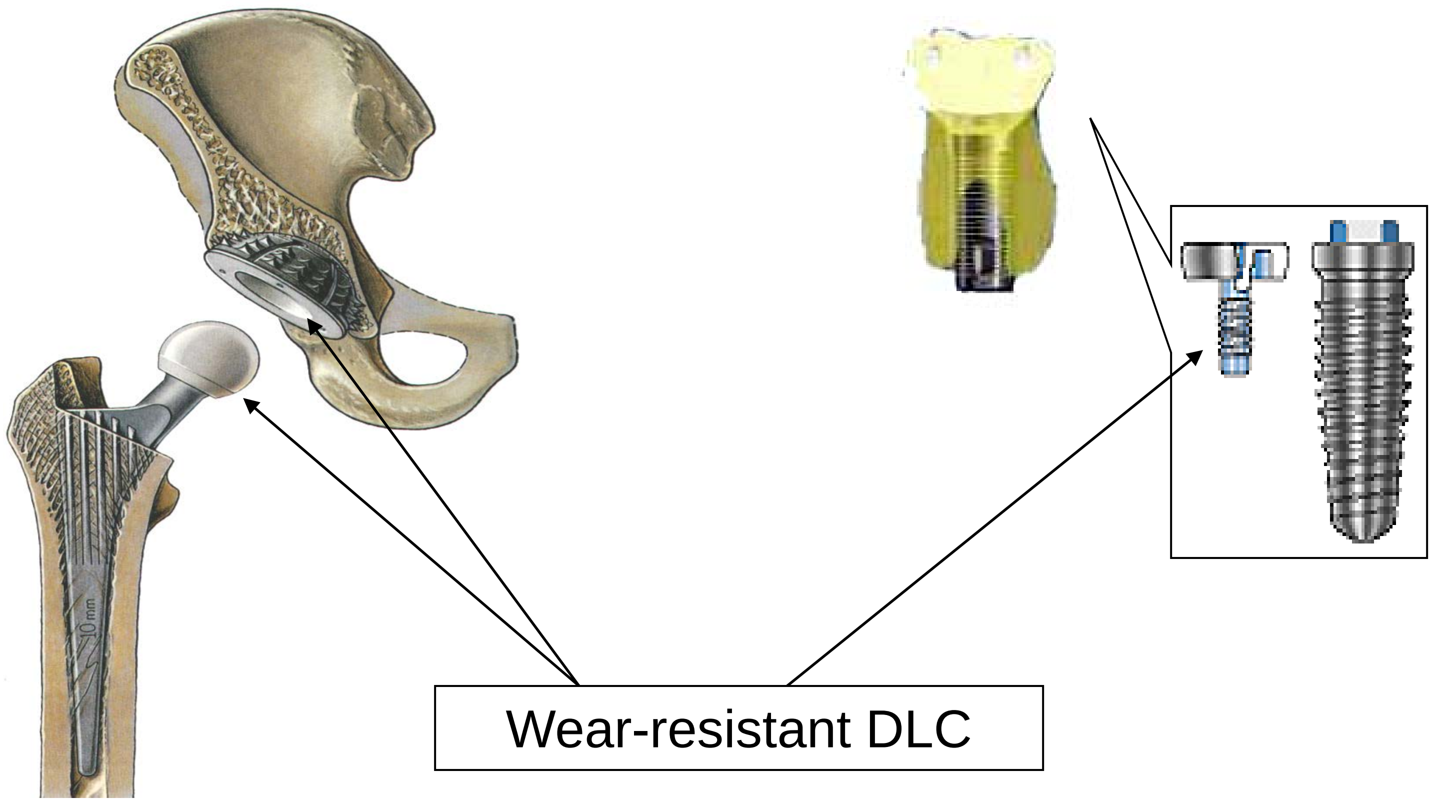
Heart valves



Pacemakers

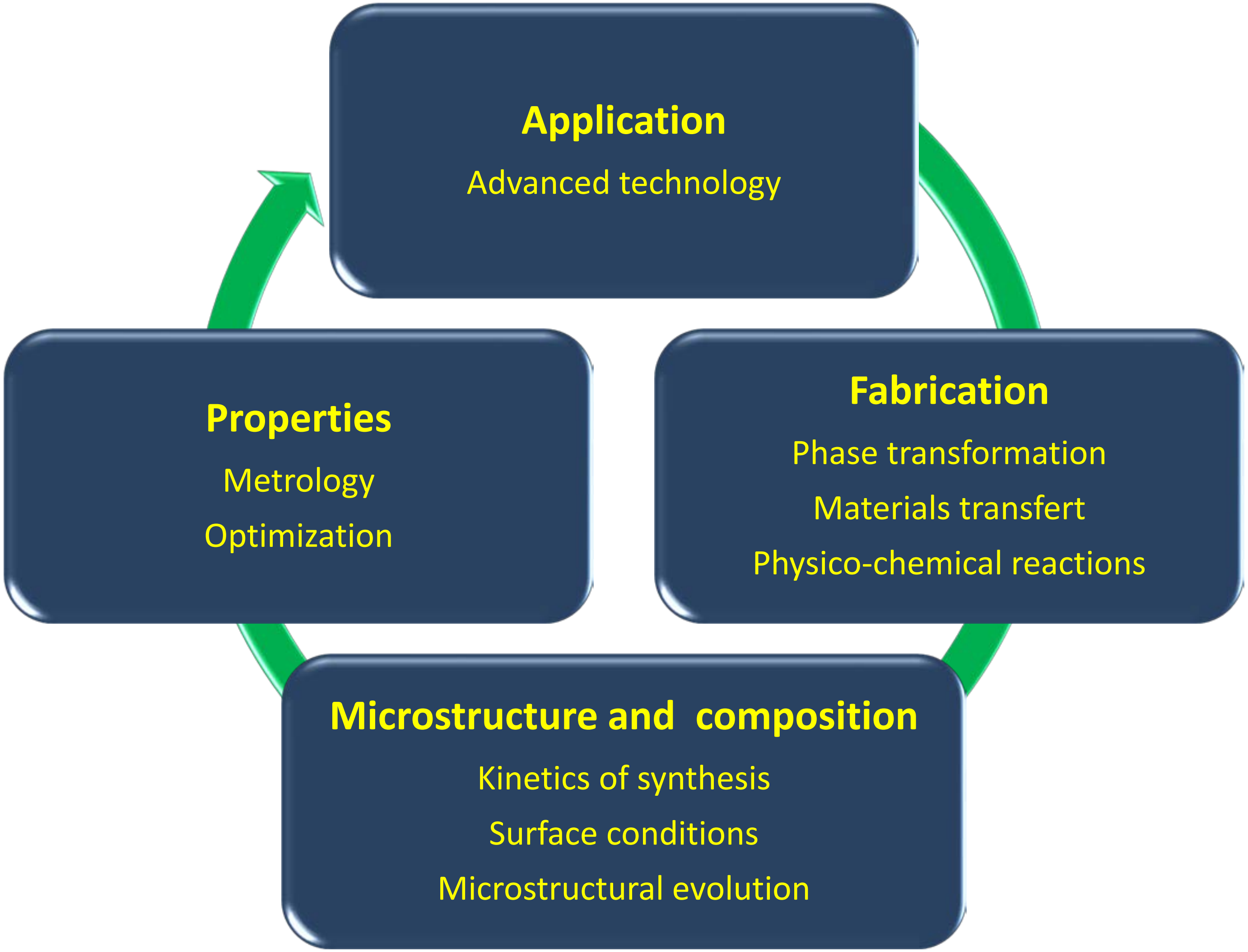


Biomedical applications



Pharmaceutical products and tests

Development of films and coatings



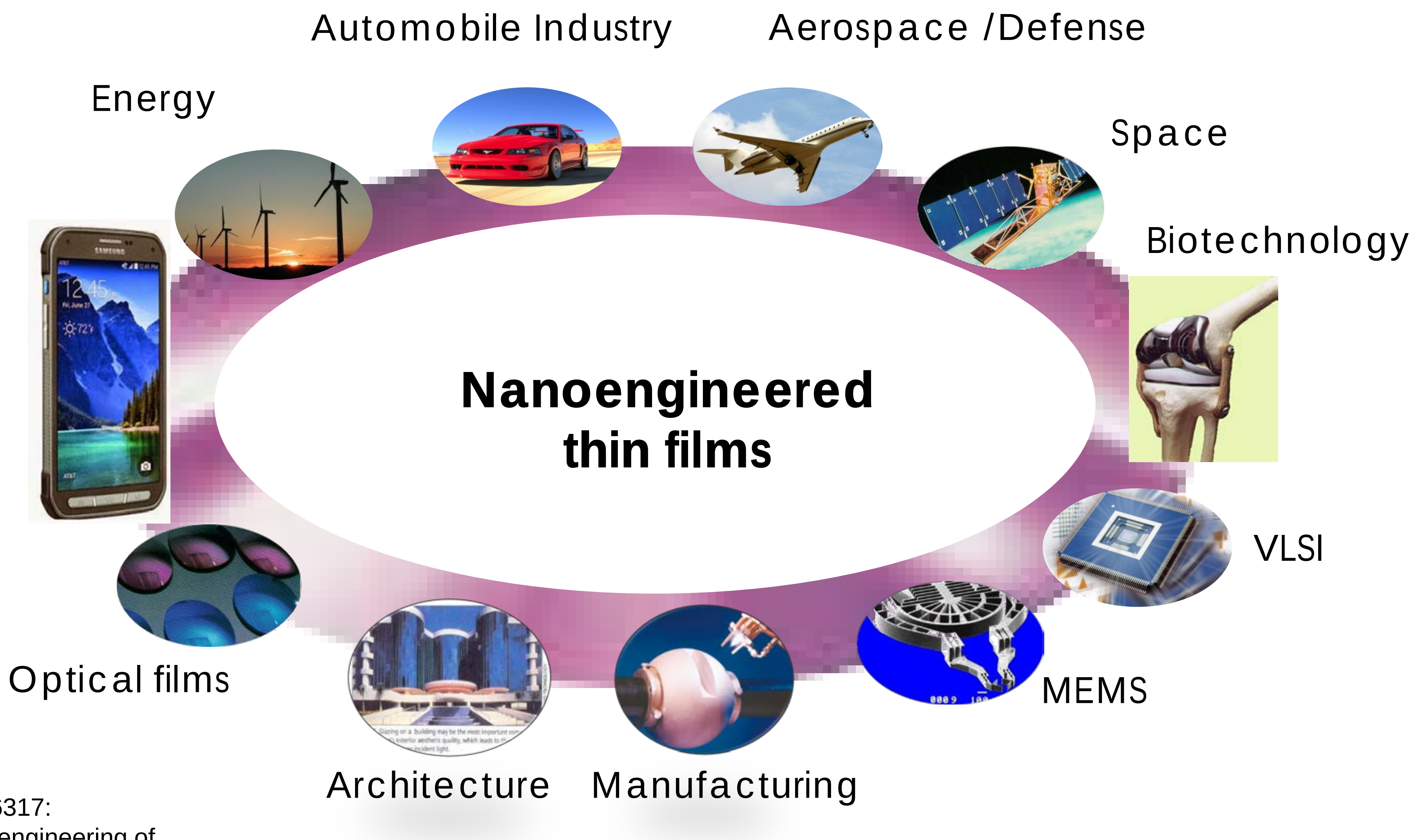
Film functions

Mechanical	Tribological properties (lubrication; wear resistance, erosion, abrasion; diffusion barriers, microsystems …)
Optical	Optical filters, optical waveguides (examples: optical communication, reflective surfaces, antireflective coatings, energy control, architecture, automobile, energy conversion …)
Electrical	Conductivity, contacts, active and passive solid components, insulators, supraconductors
Magnetic	Information storage, security devices, sensors
Chemical	Corrosion resistence, catalytic effects, protective coatings
Esthetic	Decorative effects - spectacles, jewelry, consumer products, fashion, branding, …

Technological and economic motivation for the progress in advanced materials

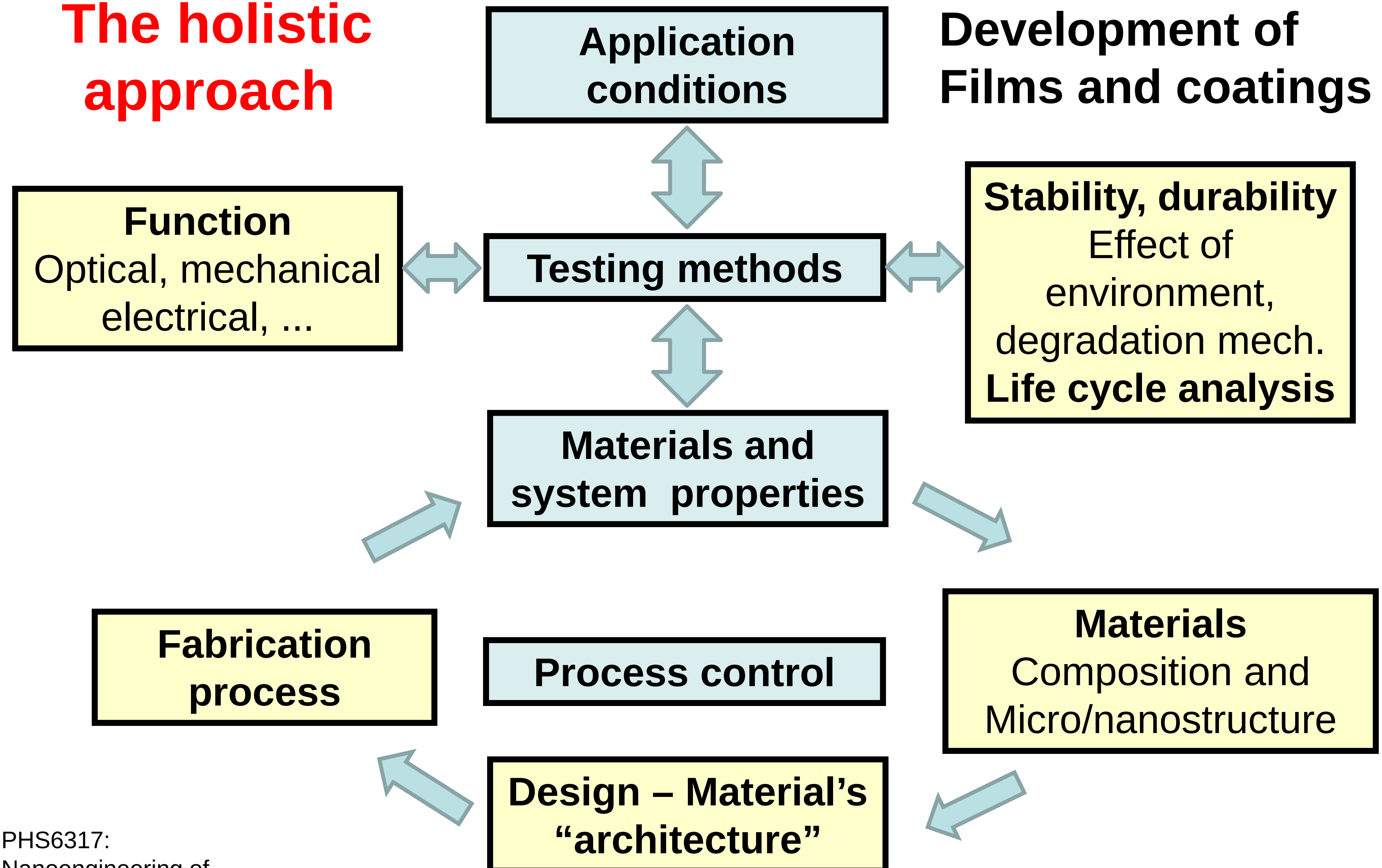
- New products (new materials, new properties, new functions)
- New engineering problem solutions
- Improved "functionality" of existing products
- Preservation of rare and expensive materials
- Environmental considerations (waste reduction; decrease in energy consumption, low pollution)

Multisectorial character of advanced materials



The holistic approach

Development of Films and coatings



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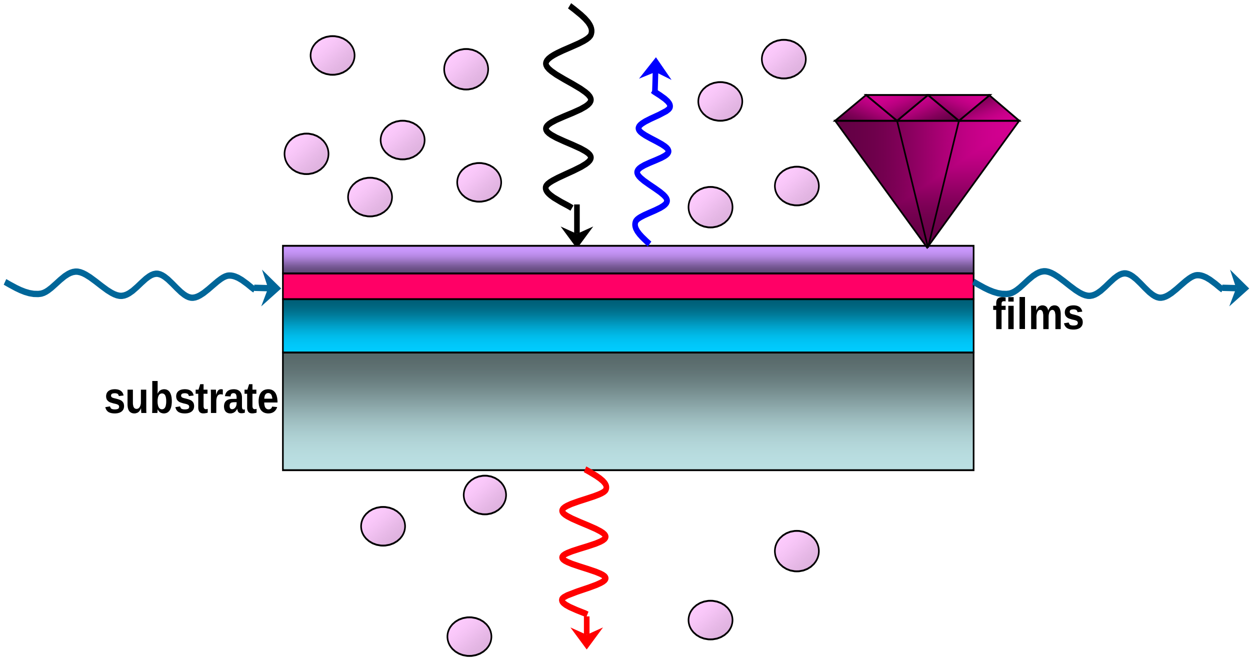
Nanostructured functional and multifunctional thin films



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

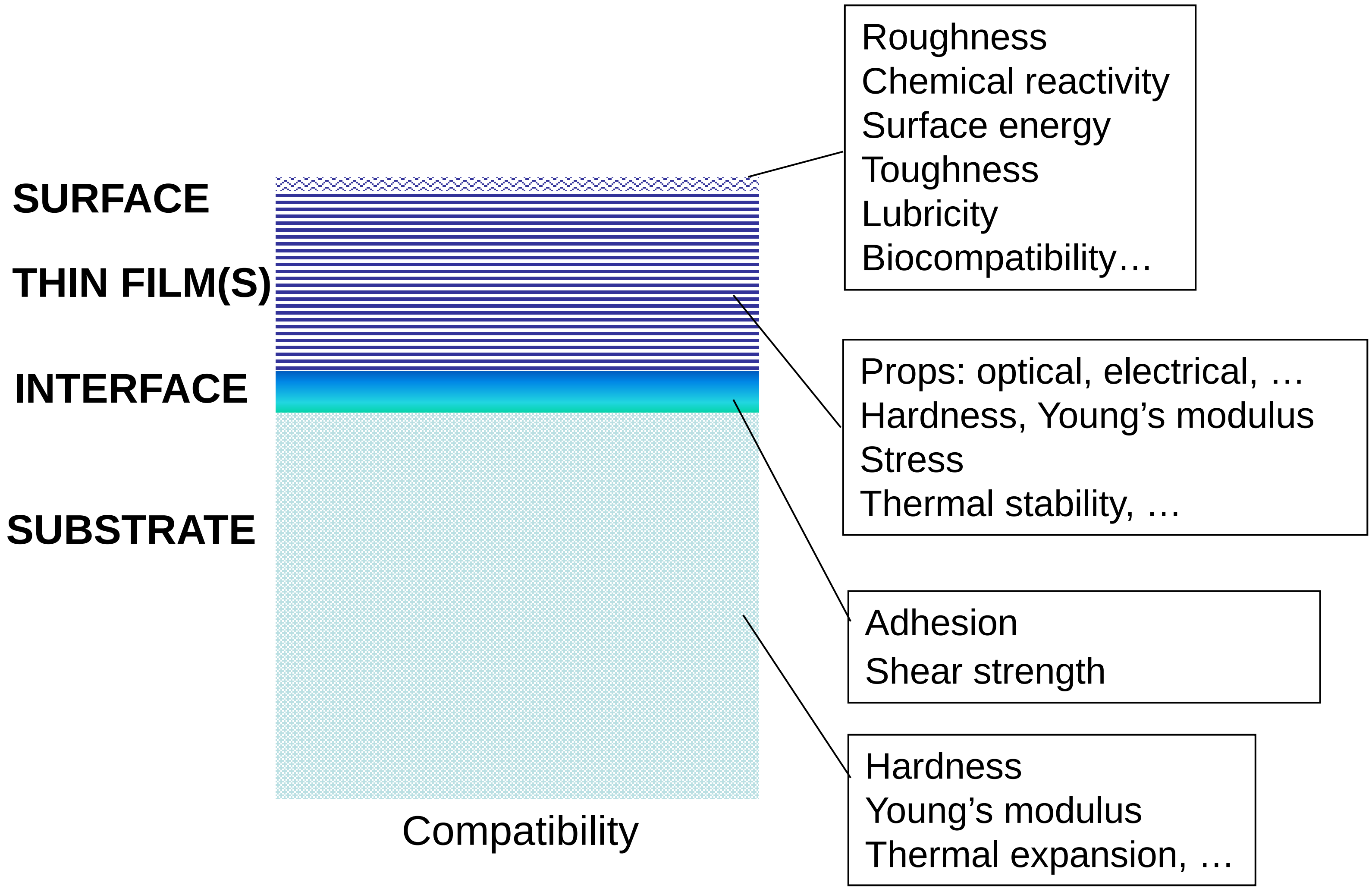
Deposition technologies
New materials:

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

Coating architectures:

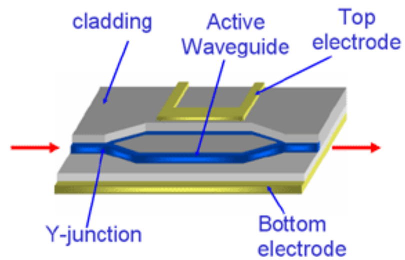
- single layers
- (discrete) multilayers
- graded layers
- nanostructures
- control of interfaces

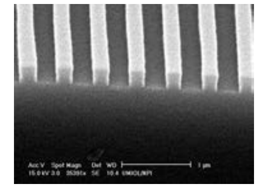
Control of the properties through the microstructure: Film-substrate system



Applications of optical coatings

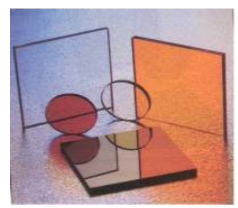
- Optical waveguides





- Decorative coatings

- Optical filters



- Energy control

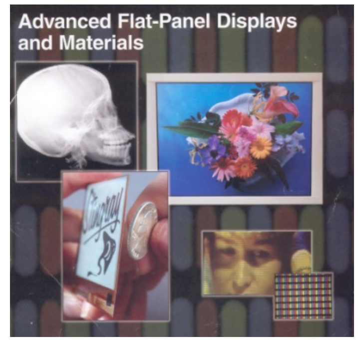
FIGURE 2. Glazing on a building may be the most important component of the building's exterior aesthetic quality, which leads to thin-film glass-coating effects on incident light.

- Optical MEMS

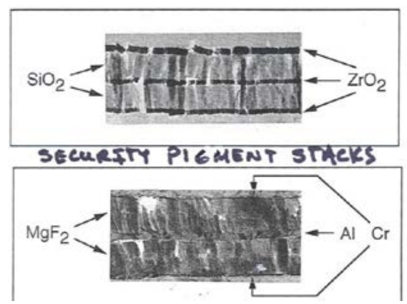
Optical coatings on plastics

Interference effects cause residual reflected-light color, which can be a striking feature of thin-film coated eyeglass lenses.

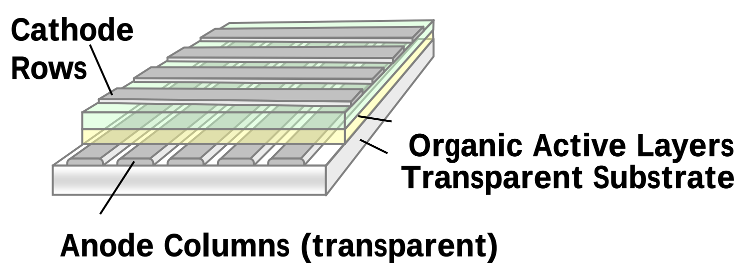
- Lenses, optical components
- Displays



- Security devices



- OLEDs



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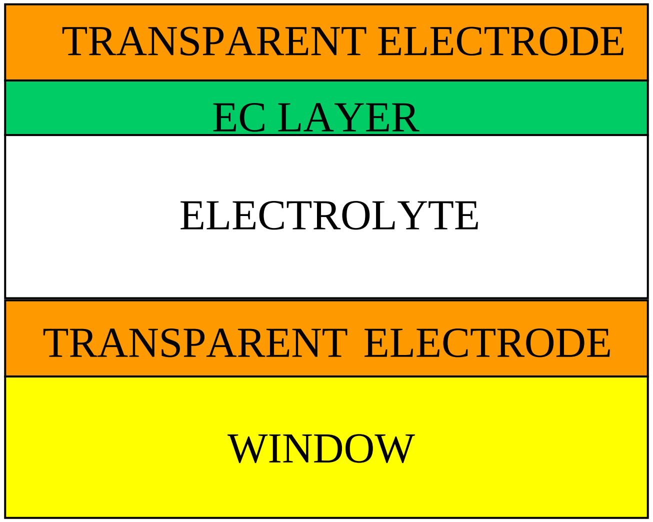
Colorshifting paints

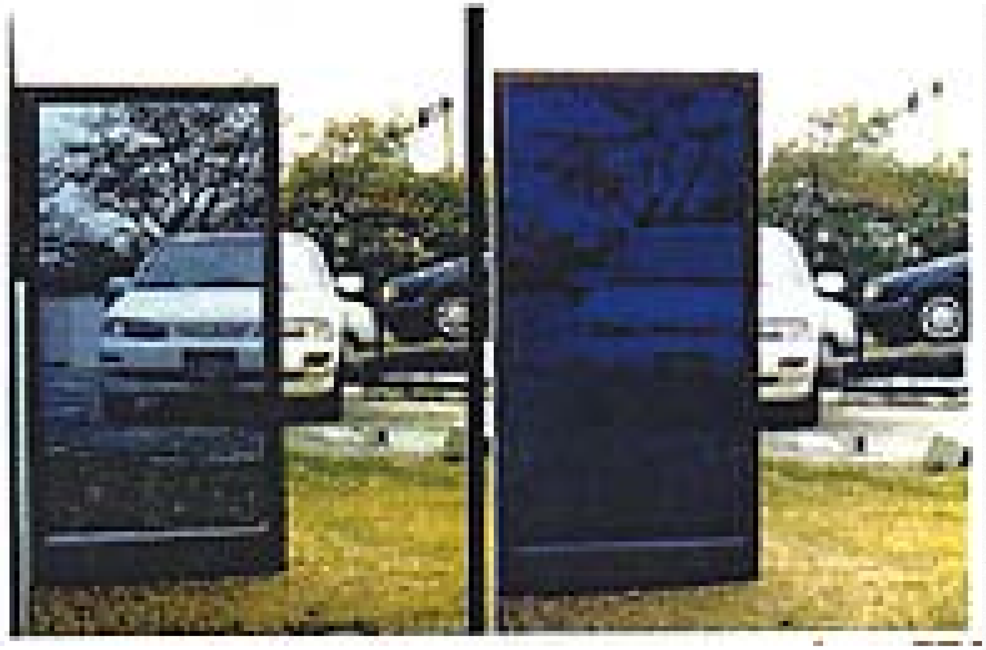
Electrochromic thin films

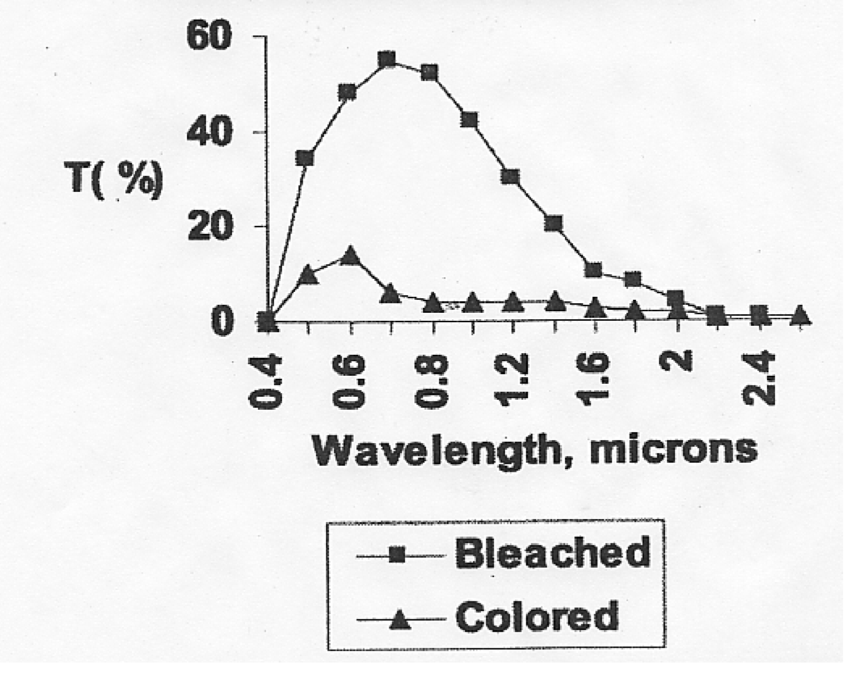
- Darken with applied voltage
- Bleach with reverse bias
- Reversible process
- Multilayer coatings
- Applications: architectural glass, automobile mirrors, sunglasses

EC Window Structure



Electrochromic windows





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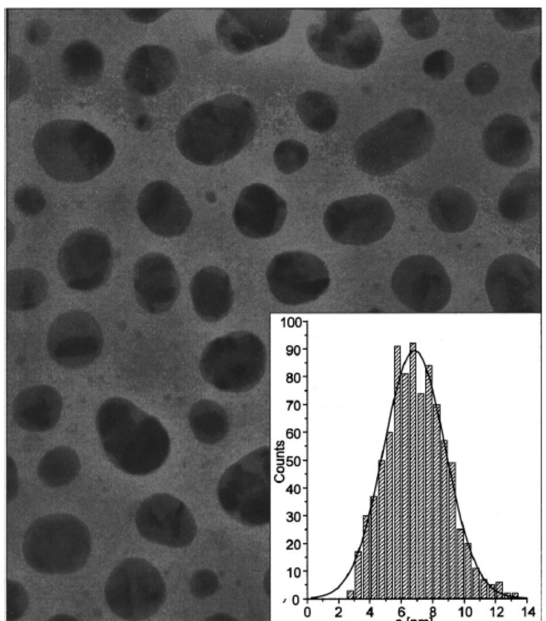
Nanocomposite materials - Au/SiO_2

Lycurgus cup, 300 AD,
Photo: British Museum, London

Maxwell-Garnett 1904:
effective medium

Mie 1908: Maxwell's equations
in spherical coordinates



nc-Au/SiO_2 at Polytechnique in Montreal: Dalacu *et al.*, JAP, 87 (2000) 228

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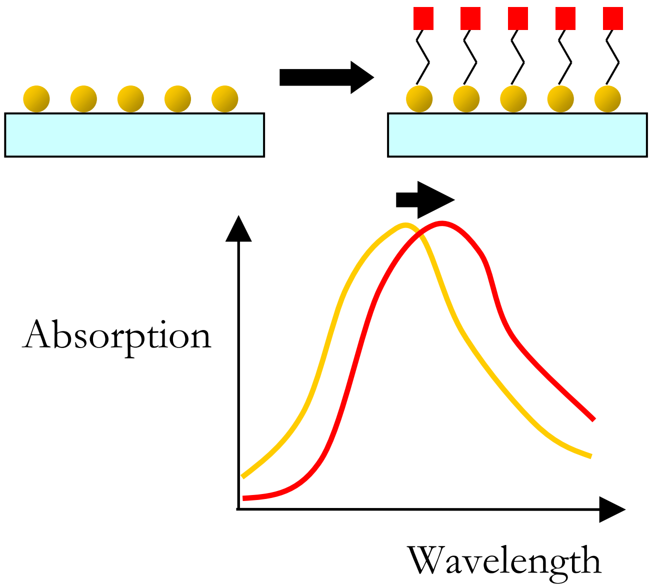
Attractive applications

Selective absorbers
Heterogeneous catalysis
Non-linear optics

Chemical sensors:

Surface plasmon resonance: SPR



Work in Montreal:

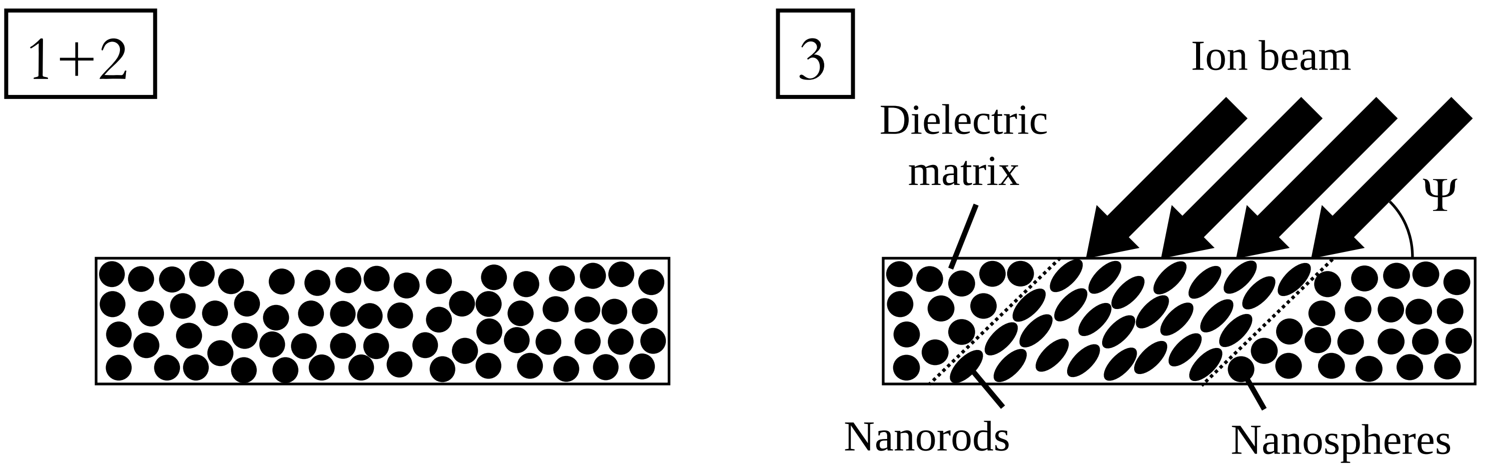
Aligned Au nanorods in a SiO_2 matrix

Polarization-dependent NLO characteristics

Example: Anisotropic nanocomposite Au/SiO_2 materials

Fabrication:

1. Hybrid PECVD/sputtering deposition
2. Thermal annealing
3. Heavy ion irradiation

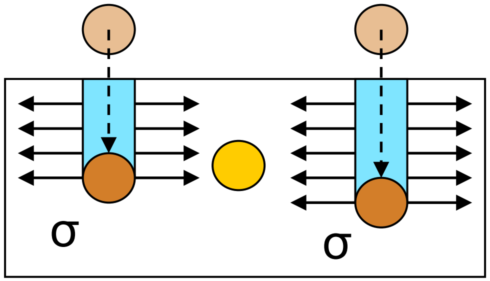


J.-M. Lamarre *et al.*, Thin Solid Films, 479, 2005, p. 232

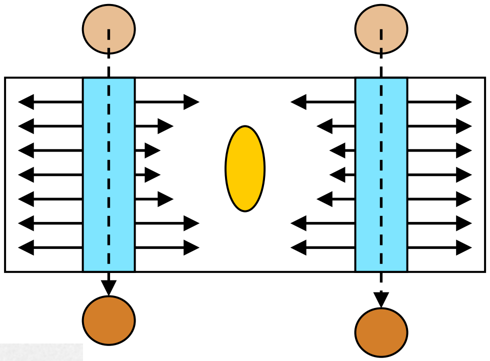
Shape-controlled nanoparticles

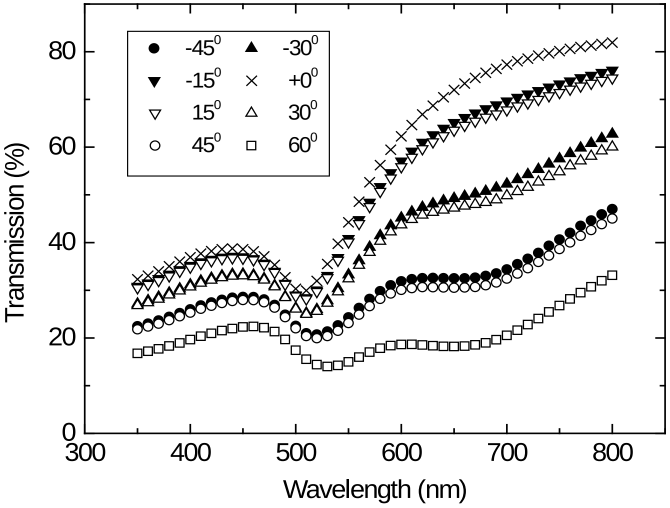
Heavy ion irradiation of Au/SiO_x

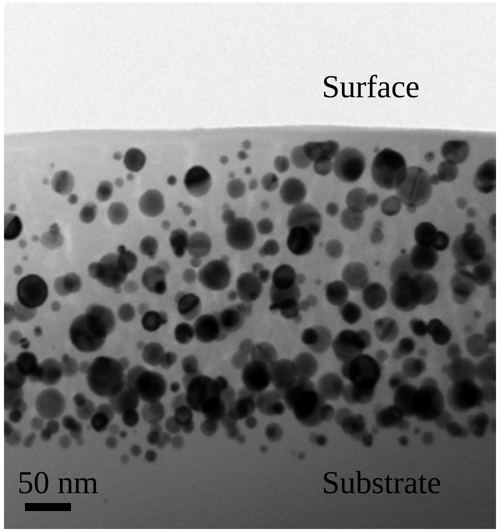
30 MeV copper ions

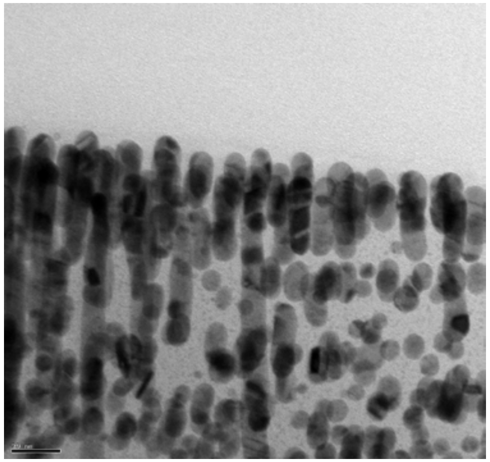


After deformation









Parameters: 30 MeV Cu^{5+}, variable irradiation angle, dose: 10^{15} ions/cm^2

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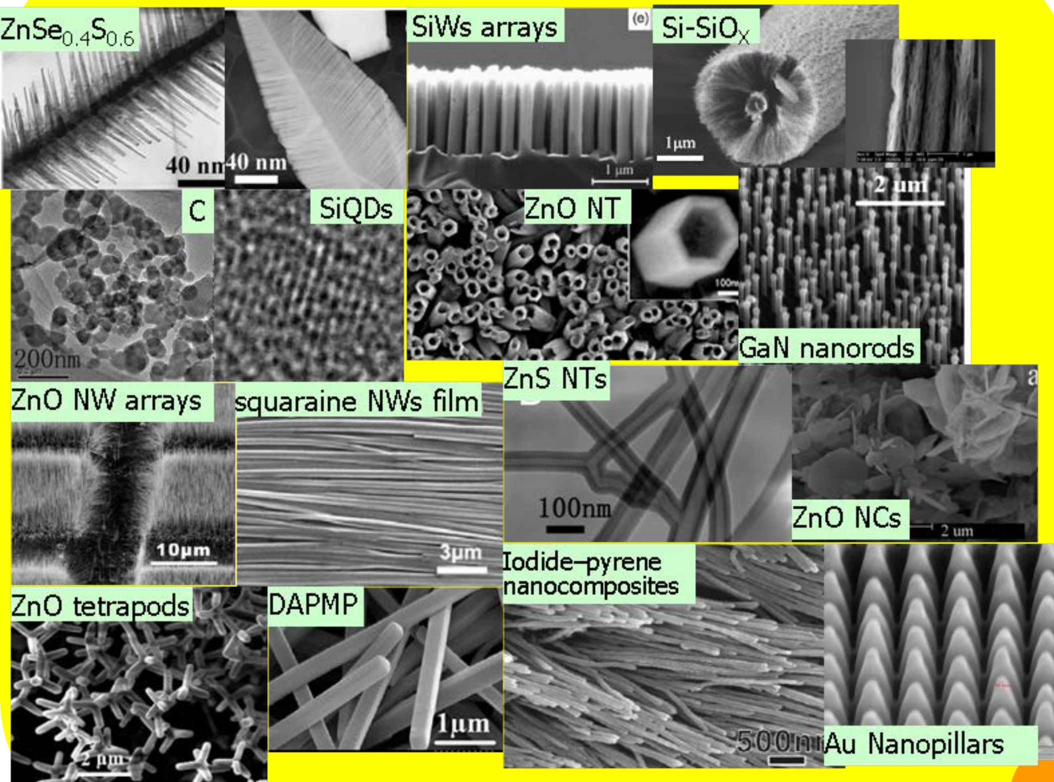
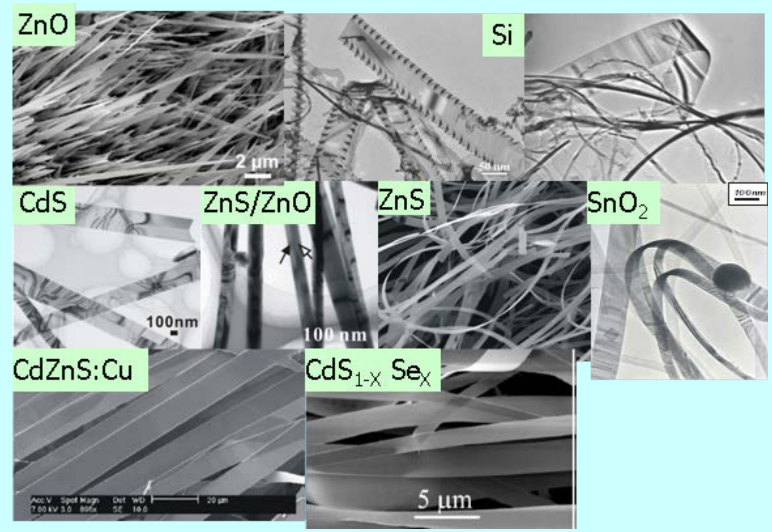
Research on Nanomaterials at the City University of Hong Kong

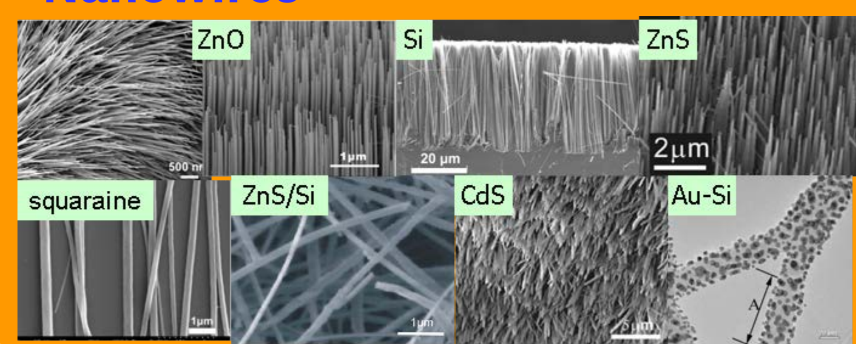
Nanostructures



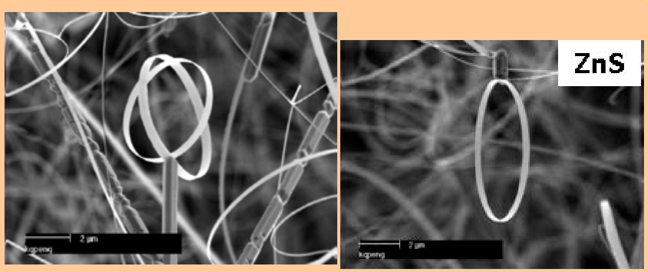
Nanoribbons



Nanowires

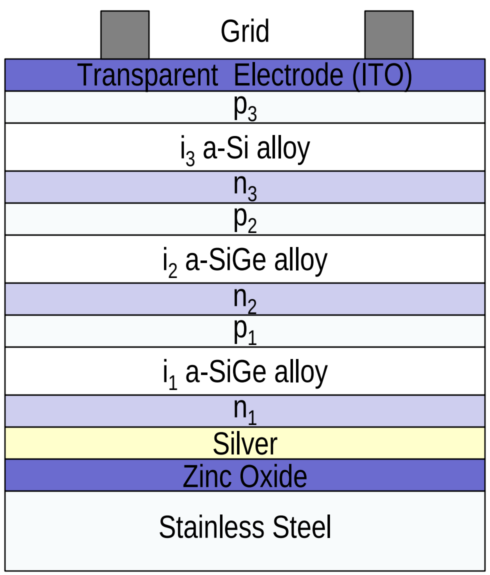


Nanorings

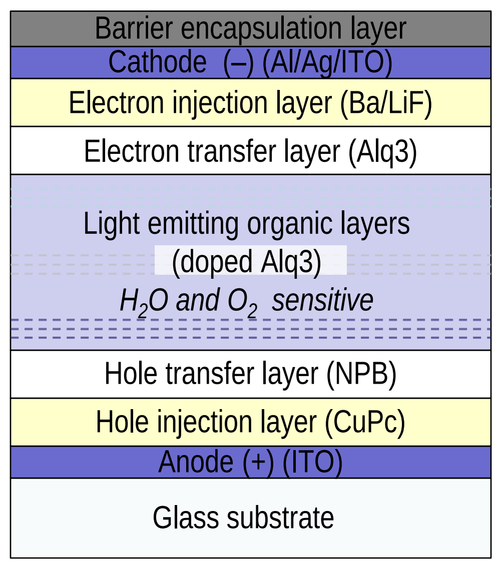


Integration of thin films

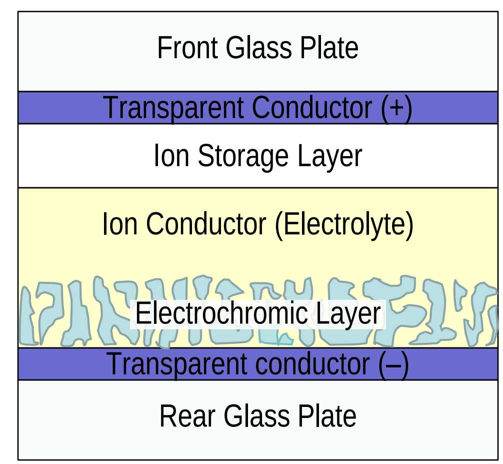
Thin film solar cell



Display



Smart windows



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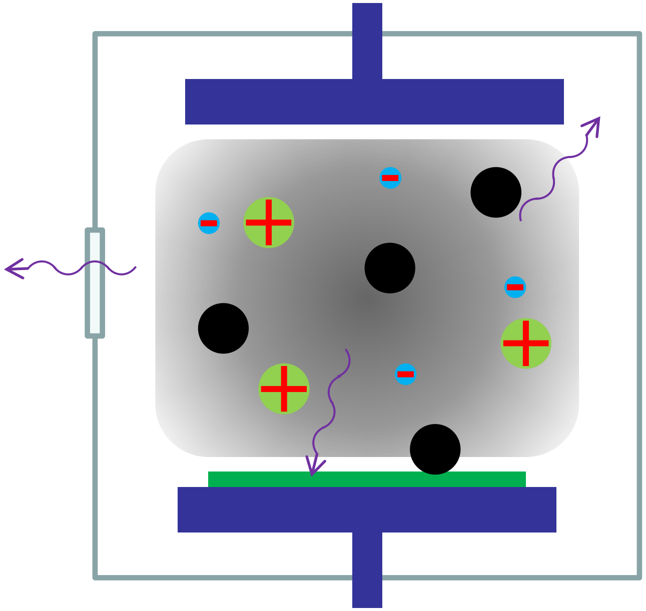
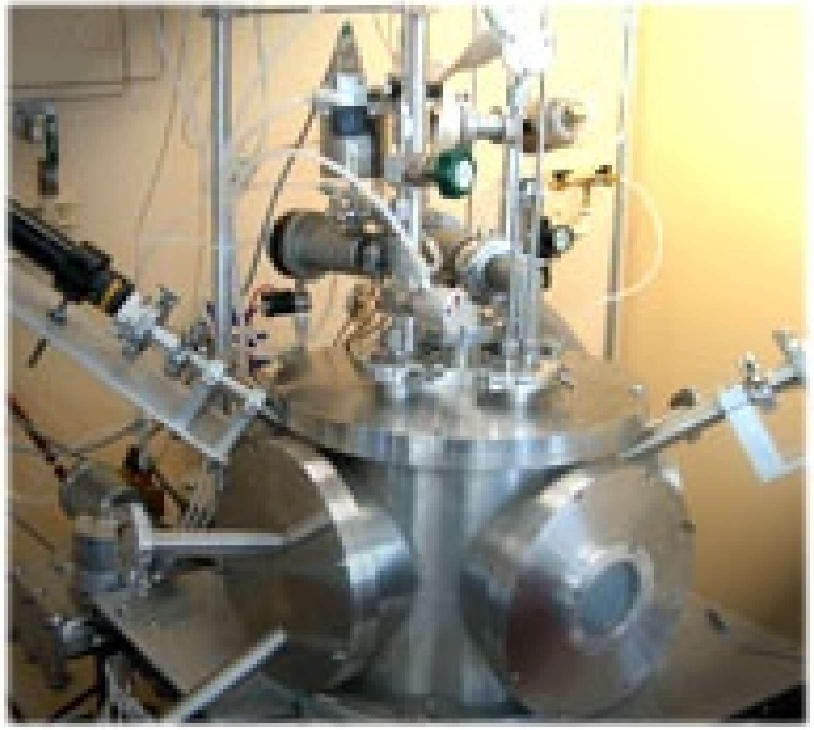
Plasma processes



Low pressure plasma

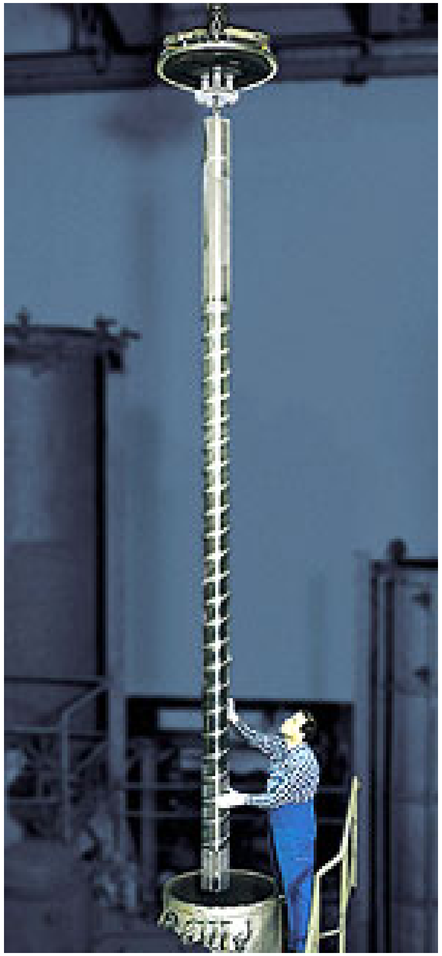
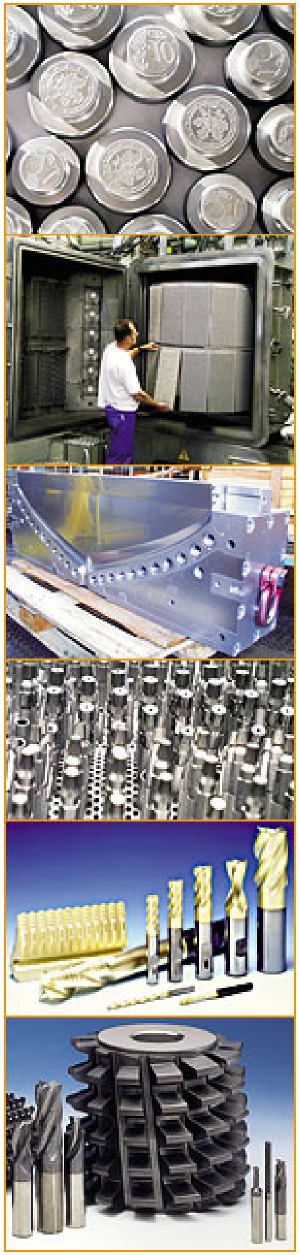
Quasineutrality, collective behavior, non-equilibrium
Plasma-surface interactions (ions, photons…)

Deposition systems:
from laboratory to industrial scale



Examples of the fabrication systems

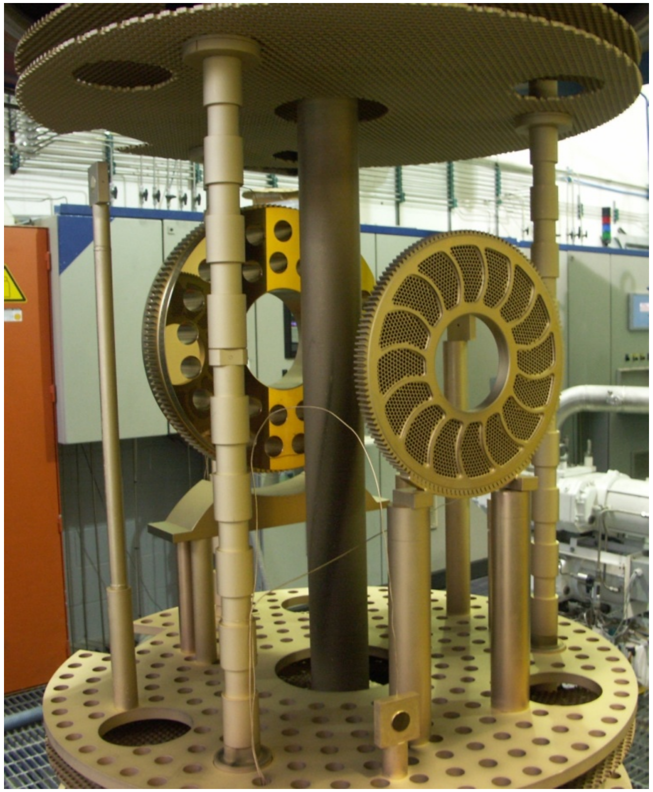


Multi-zone PECVD-PVD system

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)**

Roll-to-roll PECVD deposition system

Large area roll-to-roll deposition system for the fabrication of triple-junction photovoltaic cells: 2,500m, 36 cm wide and 125 μm SS foils; 4 compartments: a) washing, b) back reflector sputtering (Al, ZnO), c) PECVD of 9-layer triple junction – nc-Si and SiGe, d) AR coating – ITO. System: 90m long, 3m tall, web speed 30 cm/min, 14,5 km of solar cells in 72 hrs. (Courtesy of United Solar Ovonic, USA)

Thin Film Physics and Technolgy Research Center
University of Montreal Campus

GCM

- Founded in 1984
- Affiliated Institutions: Polytechnique (eng. phys., el. and chem. eng.) UdeM (phys., chem.)
- Members: 35 Professors, ~180 collaborators (students, post-docs, professionals)
- *Since 2003: member of the government-supported « Quebec research cluster on advanced materials » (70 professors, 500 other personnel)*

Research themes:

1. Micro- and nanoelectronics
2. Photonics and optoelectronics
3. Sensors actuators
4. Coatings and functional surfaces
5. Nano-engineering of surfaces
6. Magnetism and spintronics
7. Organic electronics

TOF SIMS

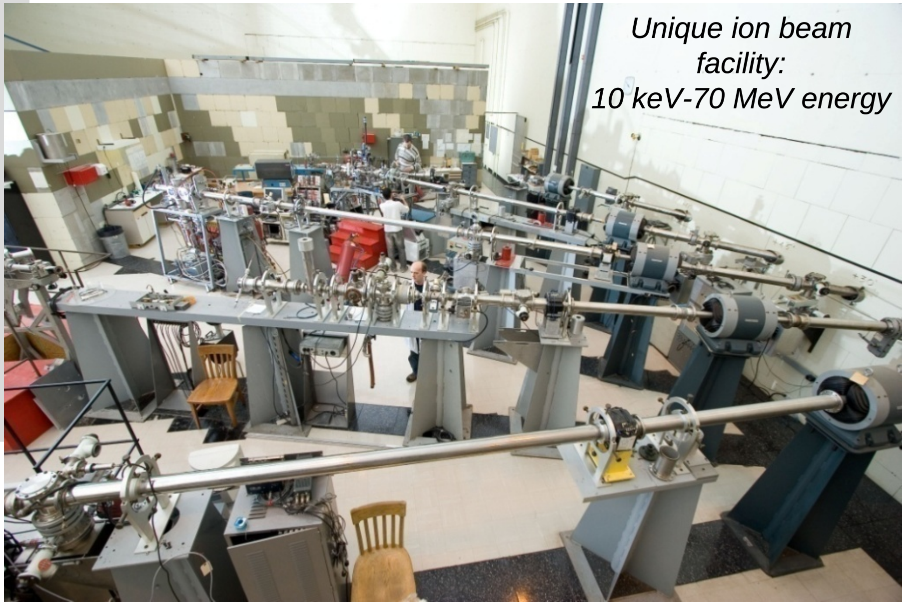
Central facilities (open access, user fee-based)

(50 M$ equipment, 1.6 M$ budget, 450+ users/y.)

Laboratoires:

- Microfabrication (LMF)
- Surface analysis (LASM)
- Ion beams (LFI)
- AFM, Raman and infrared facility (LCM)
- Optical and Tribo-mechanical Metrology (LOTM)

Website: gcm.phys.polymtl.ca



Unique ion beam facility: 10 keV-70 MeV energy

Contacts:
ludvik.martinu@polymtl.ca
francois.schiettekatte@polymtl.ca

GCM Lab

Central Facilities: One stop – One shop

Université de Montréal

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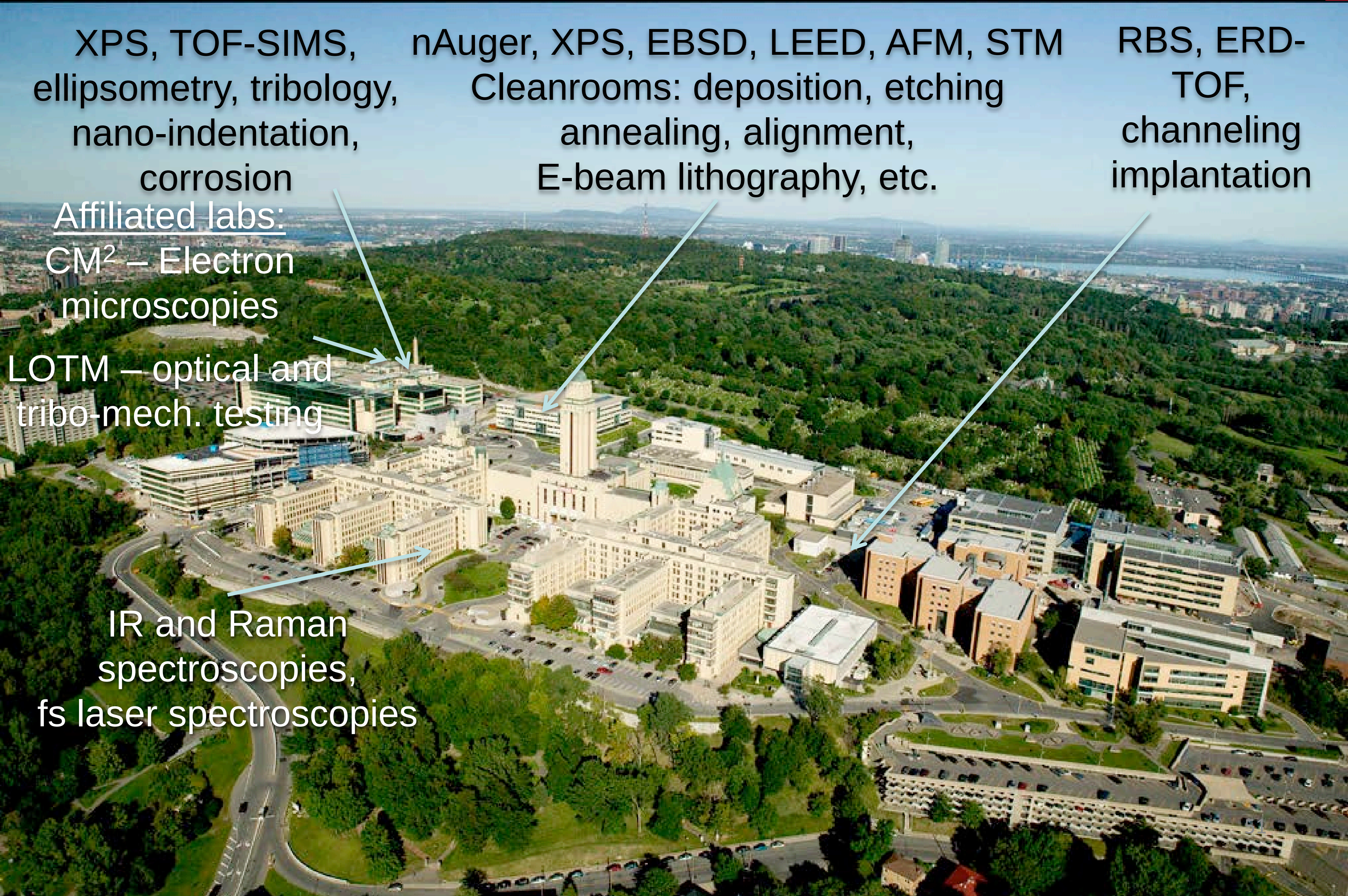
LE GÉNIE EN PREMIÈRE CLASSE



Functional Coating and Surface Engineering Laboratory

larfis.polymtl.ca

Directors

Ludvik Martinu
514-340-4099
lmartinu@polymtl.ca

Jolanta Sapieha
514-340-5747
jsapieha@polymtl.ca

Mission

To develop new fabrication techniques and new materials for thin film systems and coatings possessing tailored optical, optoelectronic, micro- and nano-mechanical, tribological, and protective properties, and other functional characteristics

Team

20 students
5 post-docs
5 research associates
3 technicians

Plasma- and ion-based processes

Plasma enhanced chemical vapor deposition PECVD

High power pulsed magnetron sputtering - HiPIMS

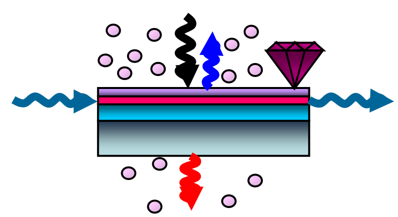
Roll coating

Dual ion beam

Plasma-enhanced chemical vapor deposition, pulsed magnetron sputtering, dual ion beam sputtering, hybrid processes, reactor design, new materials, plasma surface processing, plasma diagnostics and monitoring.

Optical & tribo-mechanical metrology

Multifunctional coatings



UV-IR ellipsometry
IR reflectometry

Nano-indentation
Nano-tribology

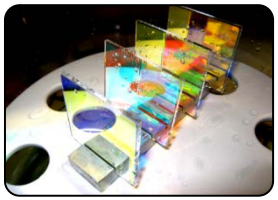
Optical properties: ellipsometry (UV-VIS-NIR-IR), prism coupling, electro-optic measurements, spectrophotometry.

Tribo-mechanical properties: depth-sensing indentation, nanotribology, micro-scratching, adhesion, wear, friction, erosion, tribo-corrosion, functional properties and stability.

Design & fabrication of optical coatings

Smart materials

Metameric filters



Interference filters

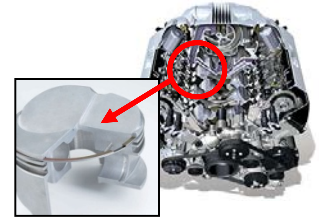
Decorative coatings

Applications: Optical interference filters for optical instrumentation, telecommunication, ophthalmics, security and sensors, smart systems for energy and environmental control, and decorative anticorrosive applications.

Hard and protective coatings

Aerospace and aviation

Automotive

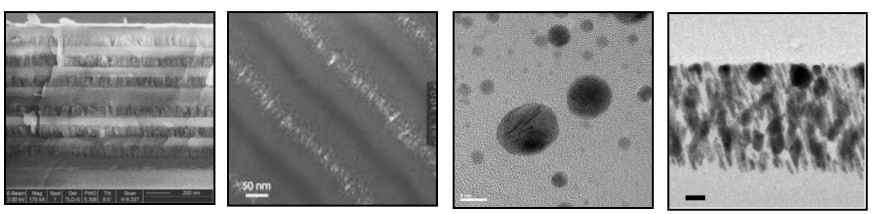


Biomedical

Health and safety

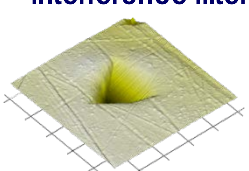
Functional properties: adhesion control, wear, erosion and corrosion resistance, thermal and environmental stability, biocompatibility, etc.

Materials and microstructure



Multilayer and graded index interference filters

Nanoparticles and nanocomposite thin films

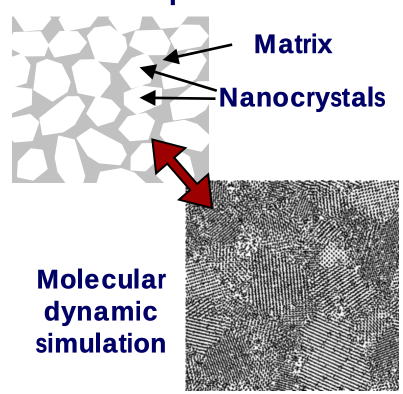


Surface imaging after indentation, wear and corrosion

Microstructure and materials analysis: scanning and transmission electron microscopies, X-ray diffraction, ion beam analysis, X-Ray photoelectron spectroscopy, etc.

Modelling and predictive tools

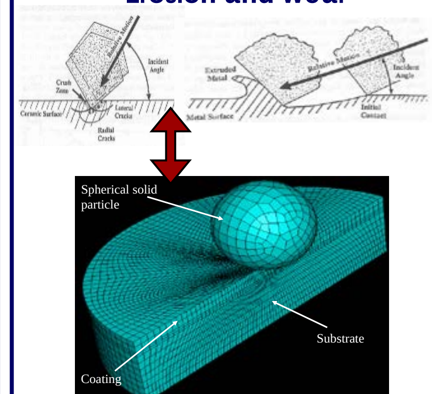
Nanocomposite materials



Molecular dynamic simulation

14 nm (262,000 atoms)

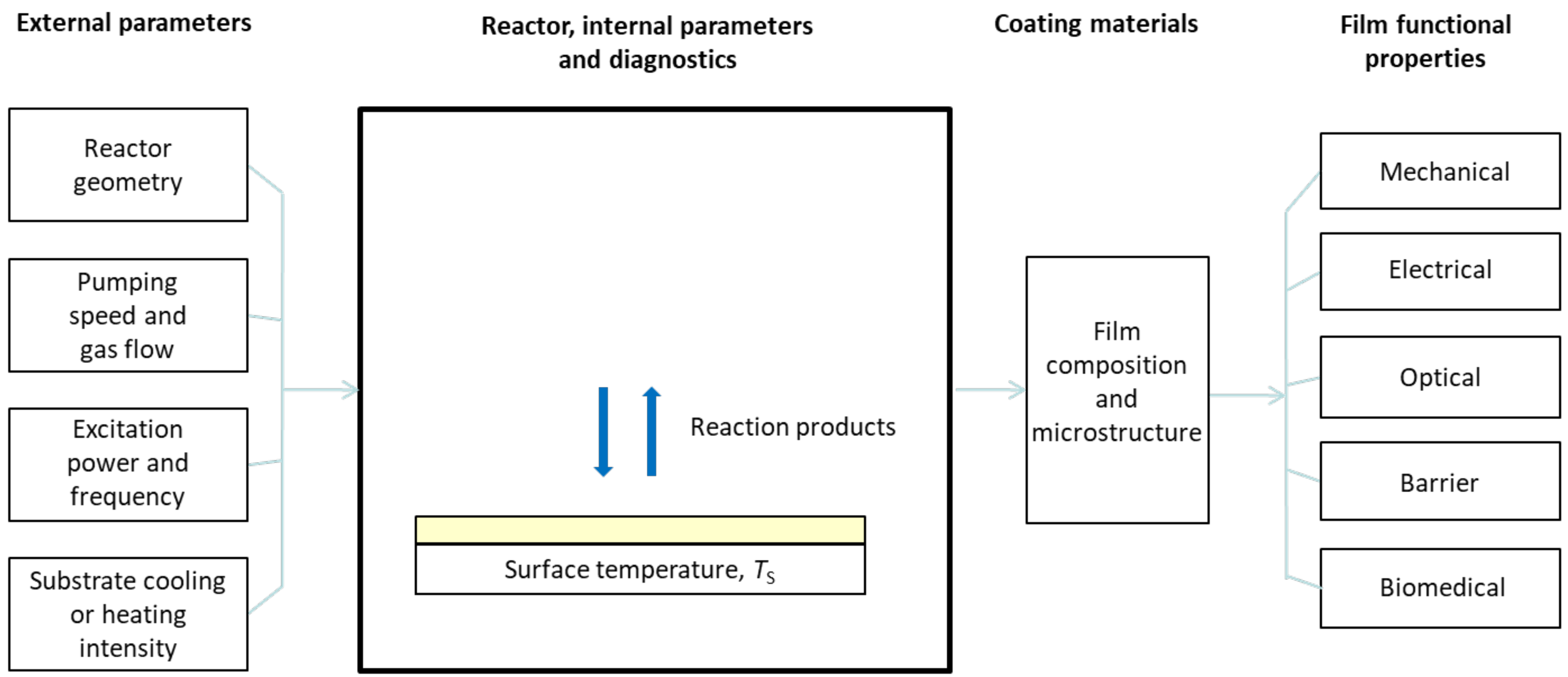
Erosion and wear



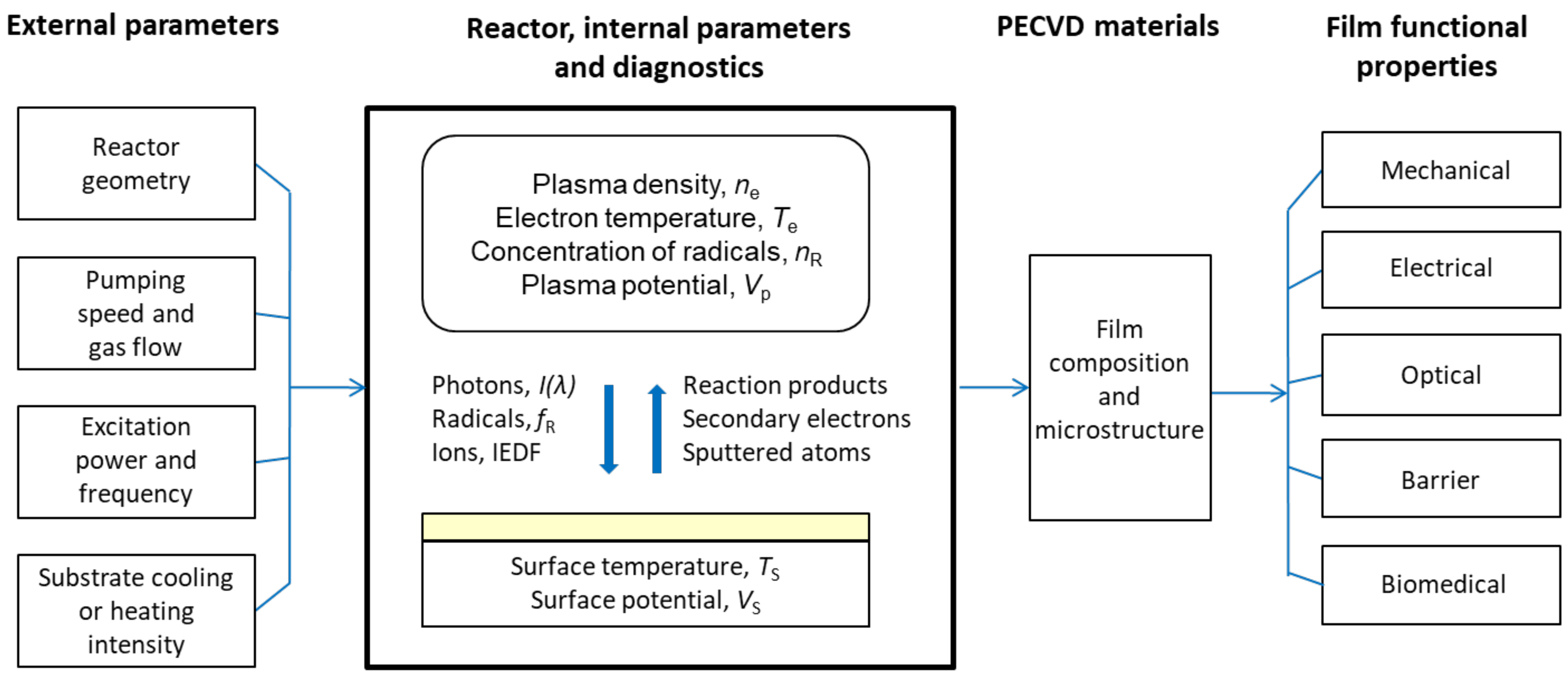
Finite element models

Modelling, simulation, prediction, failure mechanisms, design of coating architectures: multilayers, nanocomposites, graded layers, nanolaminates, nanoporous systems.

Thin film processes



Thin film processes



L. Martinu, O. Zabeida and J.E. Klemberg-Sapieha, "Plasma-Enhanced Chemical Vapor Deposition of Functional Coatings", Chapter 9 in the "Handbook of Thin Film Deposition Technologies", P.M. Martin, ed., Elsevier, Amsterdam, 2010, pp. 394-467

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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
2 February	Fabrication methods - Plasma-surfaces 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***	Tribomechanical properties of films and coatings
22**	Electrochemical properties – corrosion and tribo-corrosion *(filter-20%)*
5 April	Passive functional films and coatings, *Miniquiz 2 (5%)*
12	Active functional films and coatings
16	Life cycle analysis and environmental impact
19***	*Presentations – Emerging applications of nanostructured films (40%)*

Evaluation

1. **Project 1:** Bibliographic research on an emerging fabrication technique of thin films - Report and presentation 30%

2. **Project 2:** Design of an optical filter - Report 20%

3. **Project 3:** Bibliographic research on a specific application of the nano- engineering of thin films - Report and presentation 40%

4. **Miniquiz** 1 and 2 (@ 5%) 10%

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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: **16 February**

Report: **22 March**

Projet #3 – Application of nanostructred thin films:

Choice of the subject: **16 February**

Abstract and references: **15 March**

Report and presentation: **19 April**

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Project 1: Bibliographic reserach on an emerging fabrication technique; Report and presentation (20% + 10% = 30%)

Deliverables: Report – max 10 pages (letter size, 2 cm margins, Times New Roman 12 pts single space)

<u>Structure and contents:</u>

Summary – abstract

Introduction: challenges, possible approaches, choice of the subject and its justification

Scientific description of the fabrication technique: principles of operation, background theory, experimental set up, advantages and disadvantages, open questions

Conclusions

Bibliography – papers from refereed journals

Evaluation:

Scientific depth – 50%
Structure, clarity, consistency, critical sense – 30%
Form – how smooth reading and listening, quality of figures and tables, language – 20%

<u>Deadlines:</u>

Choice of the subject: .... **26 January**
Summary (150 words) and list of references: **9 February**
Report and presentation: .... **1st March**

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Project 2: Design of an optical filter (20%)

<u>Specific requirements:</u>

Deliverables: Report, maximum 8 pages (letter size paper, 2 cm margins, Times new roman 12 pts)

Structure and contents:
- Introduction – describe the choice of the specific filter
- Optical specifications of the filter: spectral characteristics in T and R, tolerances
- Methodology of the design (architecture, materials, optimization,…)
- Discussion of the performance and sensitivity to the fabrication process
- Conclusions

Deadlines:
Choice of the filter: .. **16 February**
Report: …………….. **22 March**

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Project 3: Bibliographic reserach on an emerging application of the nanoengineering of thin films; Report and presentation (30% + 10% = 40%)

Deliverables: Report – max. 16 pages (letter size, 2 cm margins, Times New Roman 12 pts single space)

<u>Structure and contents:</u>

Summary – abstract

Introduction: challenges and problems, possible approaches

Scientific description of the solution: principles of operation, background theory, experimental set up, advantages and disadvantages, impact, open questions

Conclusions

Bibliography – papers from refereed journals

Evaluation:

Scientific depth – 50%
Structure, clarity, consistency, critical sense – 30%
Form – how smooth reading and listening, quality of figures and tables, language – 20%

<u>Deadlines:</u>

Choice of the subject: .... **26 January**
Summary (150 words) and list of references: **9 February**
Report and presentation: .... **1st March**

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References:

- "Materials Science of Thin Films", M. Ohring, Academic Press, New York 1992 (1st edition), 2002 (2nd edition)
- "Handbook of Deposition Technologies for Films and Coatings", R.F. Bunshah, ed., 2nd edition, Noyes Publications, Park Ridge, 1994. P.M. Martin, ed., 3rd edition, Elsevier, 2010;
- "Handbook of Nanotechnology", B. Bhushan, ed., Springer, Berlin, 2003.
- ''Handbook of Thin Film Process Technology'', D.A. Glocker and S.I. Shah, eds, Institute of Physics, Bristol, 2002.
- S. Larouche, J.-M. Lamarre, L. Martinu, "Guide de rédaction de rapports de laboratoire et de projet pour les cours de génie physique à l'École polytechnique de Montréal", École Polytechnique, Montréal, 2002.

International journals

Nature,
Thin Solid Films
Journal of Vacuum Science and Technology
Surface and Coating Technology
Journal of Applied Physics
Applied Physics Letters
Physical Review B
Physical Review Letters
Applied Optics
Optical Engineering
Solar Energy Materials and Solar Cells
Wear….

Societies:

American Vacuum Society (AVS)
Society of Vacuum Coaters (SVC)
Materials Research Society (MRS) ….