Advanced Nanotechnology Thin Film Approaches for the Food and Medical Industry:

an overview of current status

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OUTLINE

Length scale and Nanostructured Materials

Applications in Nanotechnology

PVD and PACVD Nanocomposites Coatings

Advanced Packaging, Barrier layers, Smart labels

Conclusions

Global market for nanotech products

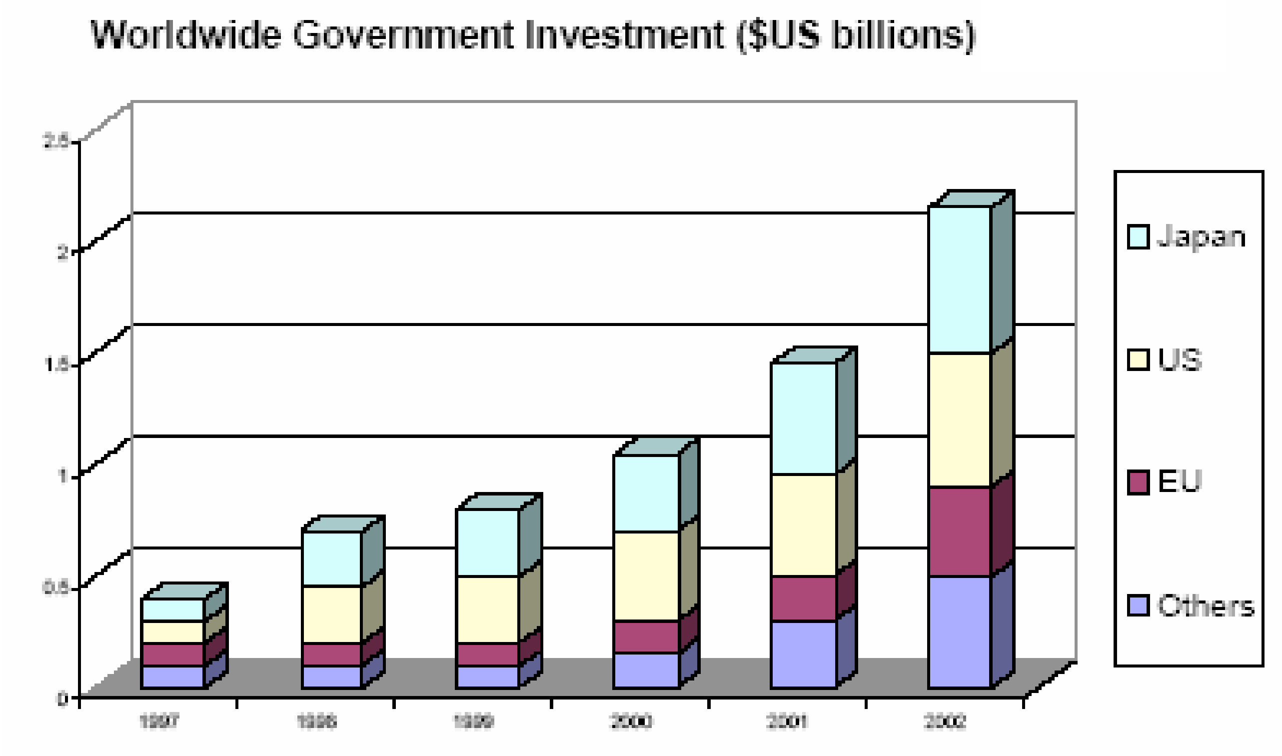
The US National Science Foundation predicts that the total global market for ***nanotech products and services will reach $1 trillion by 2015***, which represents nearly 10% of the present US gross domestic product and will require a workforce of 2 million.

Nanotechnology related industries are expecting a **revenue of $25.6 billion by 2006**.

The US nanotechnology market is an emerging market, with a significant R&D effort

The most prominent fields of nanotechnology are *nanobio, nanomaterials, surfaces, electronics*, *IT* and *instrumentation*.

~400 nanotechnology companies in the US.



Nanotechnology and Packaging

- Longer shelf life

  - Improved barrier, absorbing compounds, UV absorters

- Hot fill

  - Improved high temperature performance

- Flexible packaging – thin films
- Functionality

  -Anti-counterfeit, anti-tamper, anti-microbial, sensors (temperature, moisture, light, decay), integrated power (intelligent tags, self-healing containers)

- Increasing use for:

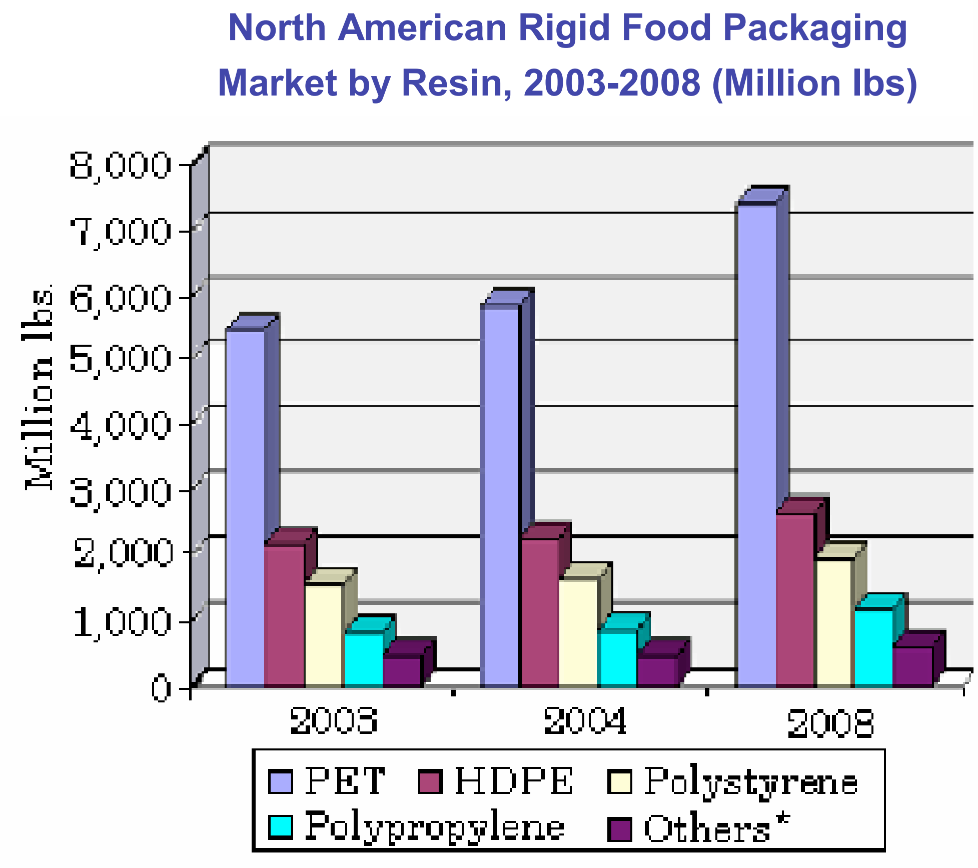
  -Gas barrier

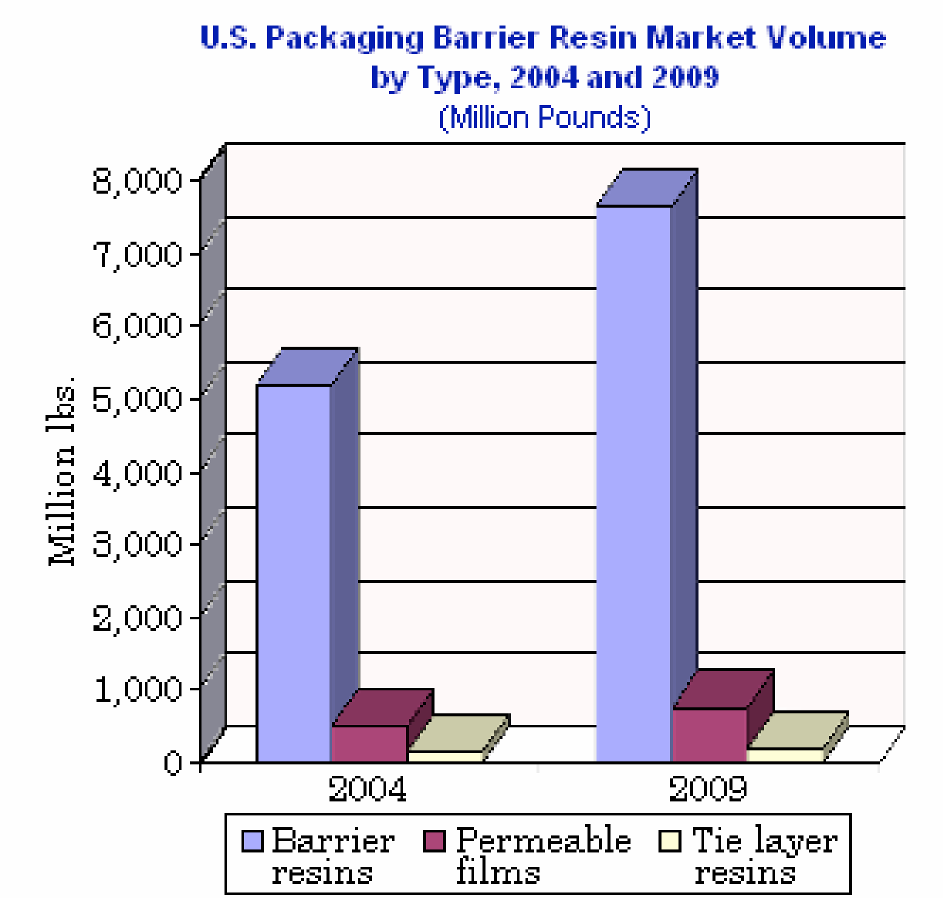
  -Oxygen barrier

  -Food packaging

  -Films

Packaging Market





***Includes LDPE, polycarbonate, SBCs, PVC and others.**

Source: BCC, Inc.

Tie layer resins: adhesive resins used to bond dissimilar resins together

Length scale and Nanostructured Materials

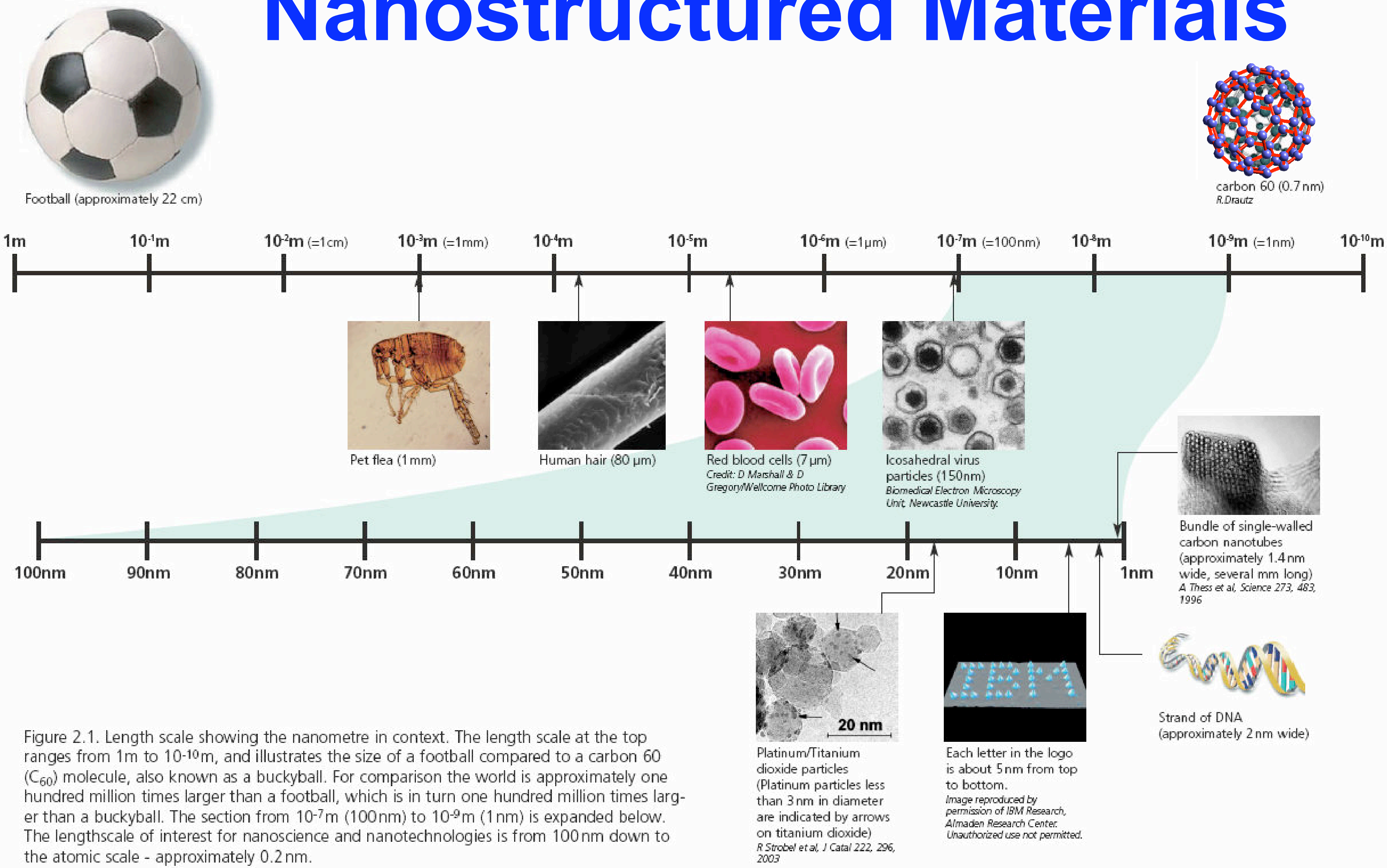


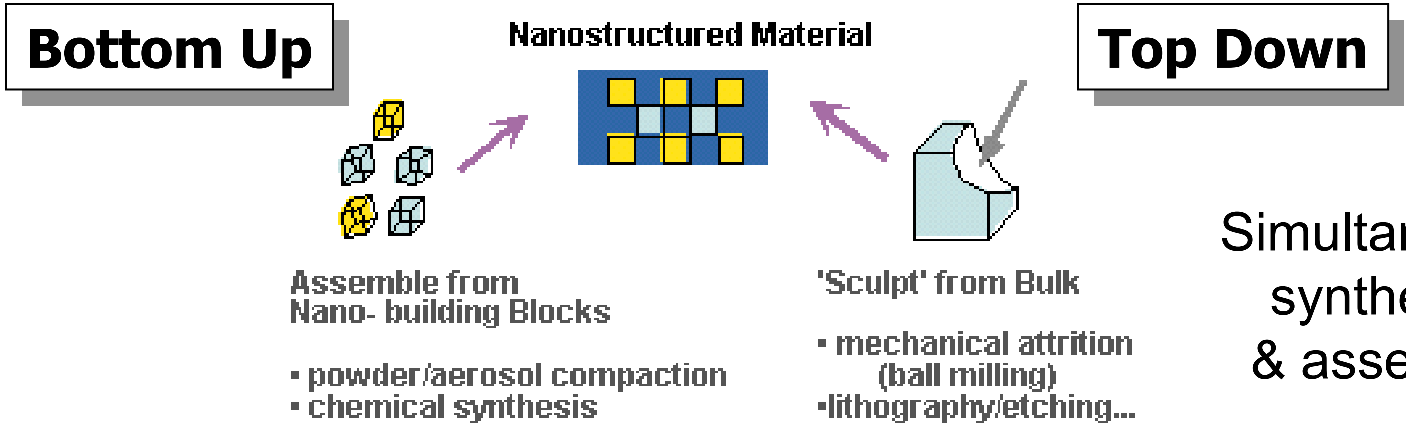
Figure 2.1. Length scale showing the nanometre in context. The length scale at the top ranges from 1m to 10^{-10}m, and illustrates the size of a football compared to a carbon 60 (C_{60}) molecule, also known as a buckyball. For comparison the world is approximately one hundred million times larger than a football, which is in turn one hundred million times larger than a buckyball. The section from 10^{-7}m (100nm) to 10^{-9}m (1nm) is expanded below. The lengthscale of interest for nanoscience and nanotechnologies is from 100 nm down to the atomic scale - approximately 0.2 nm.

The Royal Society & The Royal Academy of Engineering (2004), Nanoscience and nanotechnologies.

What is Nanotechnology

-Manipulation of objects at the atomic scale
-Dimensions not exceeding 100 nanometers

Key approaches to fabrication:



Simultaneous
synthesis
& assembly

Bottom up approach:

- **Synthesis** of building blocks
  (nanoparticles, macromolecules, layers…)
- **Assembly** of building blocks to nanostructures

Nanostructured Materials

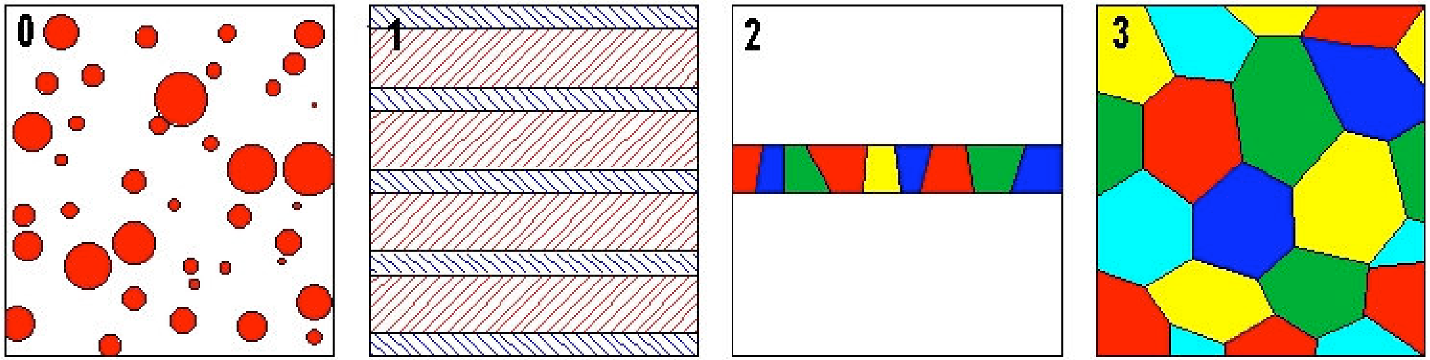
A broad class of materials, with microstructures modulated in zero to three dimensions on length scales less than 100 nm

Unifying features

-synthetic materials with modulated structures in 0 to 3 dimensions.

-size constraint ("confinement") <100nm in at least one dimension.

-significant volume fraction (>1%) of interfaces.



R.W. Siegel, Nanophase Materials, Encyclopedia of Applied Physics, VCH Publishers 1994

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Nanocomposite and Nanolayered Coatings

Conventional materials have grain sizes ranging from microns to several millimeters and contain several billion atoms each.

Nanometer sized grains contain only about 900 atoms each.

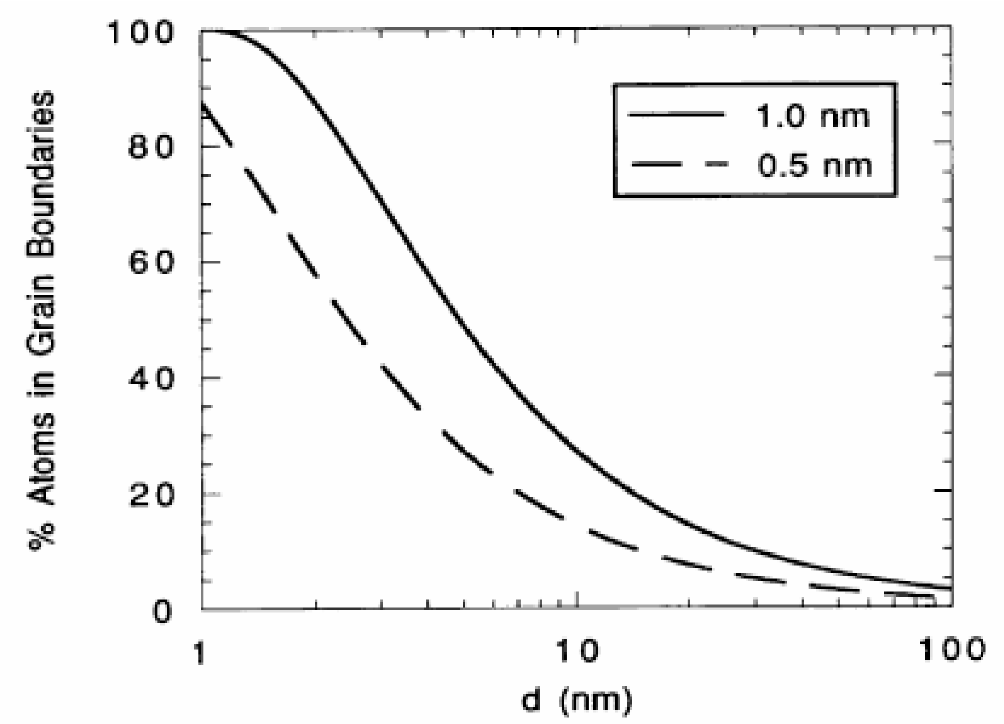
As the grain size decreases to the nanometer range, there is a significant increase in the volume fraction of grain boundaries or interfaces.

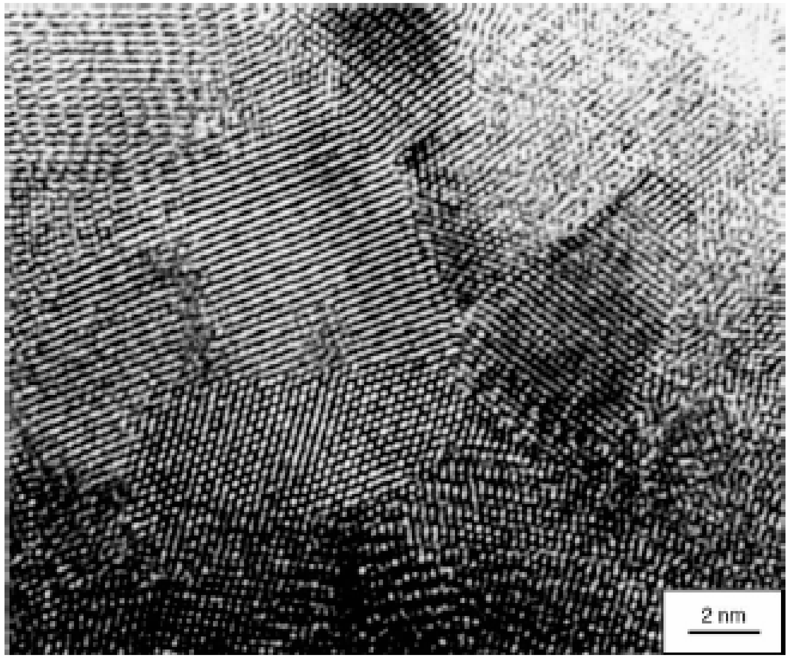
A nanostructured crystalline material is one in which the spacing between lattice defects approaches inter-atomic distances.

These characteristics strongly influence the chemical and physical properties of the material.

For example, is has been found that nanostructured ceramics are sometimes tougher and stronger than the coarser grained ceramics and nanophase metals exhibit significant increases in yield strength and elastic modulus.

% of atoms in grain boundaries of a nanocrystalline materials





HRTEM image of a region of nanocrystalline palladium

Range of percentage of atoms in grain boundaries of a nanocrystalline solid as function of grain diameter, assuming that the average grain boundary thickness ranges from 0.5 to 1.0 nm

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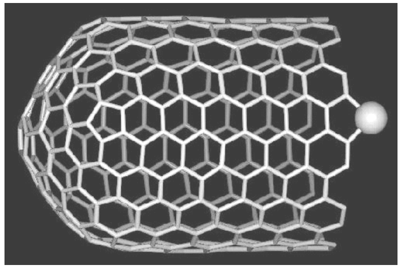
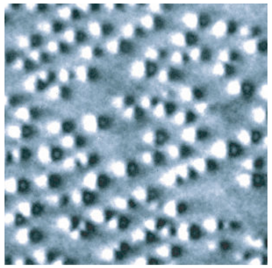
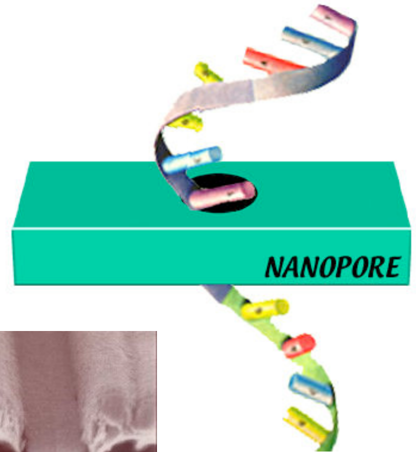
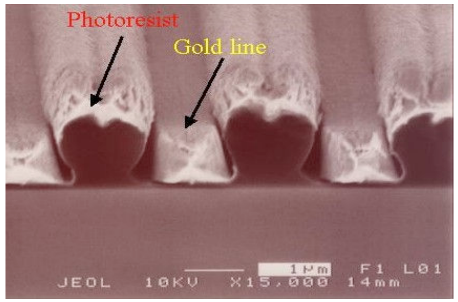
Applications in Nanotechnology



- **materials**
  - nanoporous materials
  - nanostructured materials
  - nanocomposites
  - catalysts
  - Multifunction, adaptive, smart materials
- **biotechnology**
  - sensors, nanoprobes of biological function/activity
  - bioelectronics
  - biomolecular machines, drug delivery
  - self-assembling adaptive materials
- **electronics, optics and photonics**
  - quantum confinement
  - Lasers (fiberoptic data communication)
  - molecular scale electronics
  - photonic band gap materials

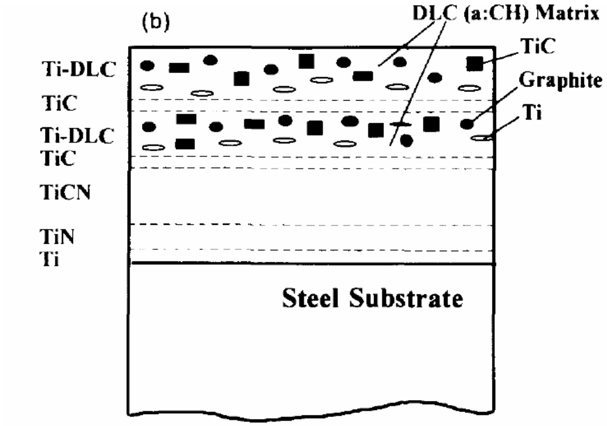




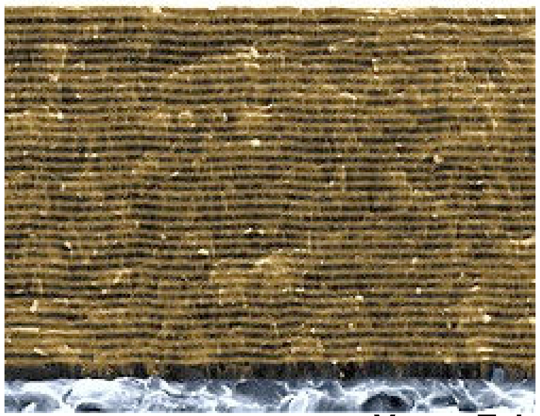


Nanocomposite and Nanolayered Coatings

Interfaces and grain boundaries are key parameters in designing nanolayered coatings. Internal interfaces in materials are extended defects including grain boundaries and interphase boundaries.
On a laboratory scale a great variety of coating concepts for designing innovative, multifunctional nanoscaled PVD thin films with properties tailored to specific applications have been developed, as well as promising advanced coating materials such as:



- **nanocomposite coatings**
- **nanostructured multilayer films**
- **nanomodulated superlattice films**
- **nanocrystalline films**
- **nanostabilised single layers**
- **multilayer films**
- **nanograded films**



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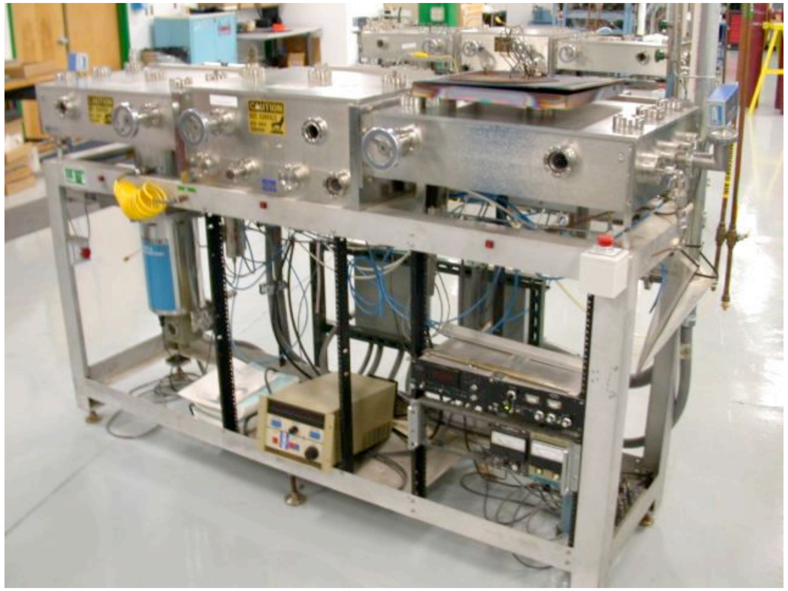
Thin film sputtering lines



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6 chamber thin film sputtering line

in-line PECVD System

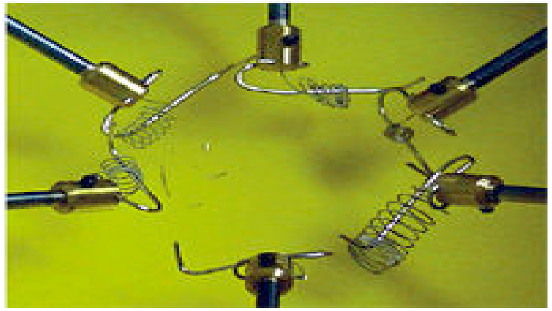
Nanocomposite and Nanolayered Coatings

Factors affecting the constitution, properties and performance of coatings:

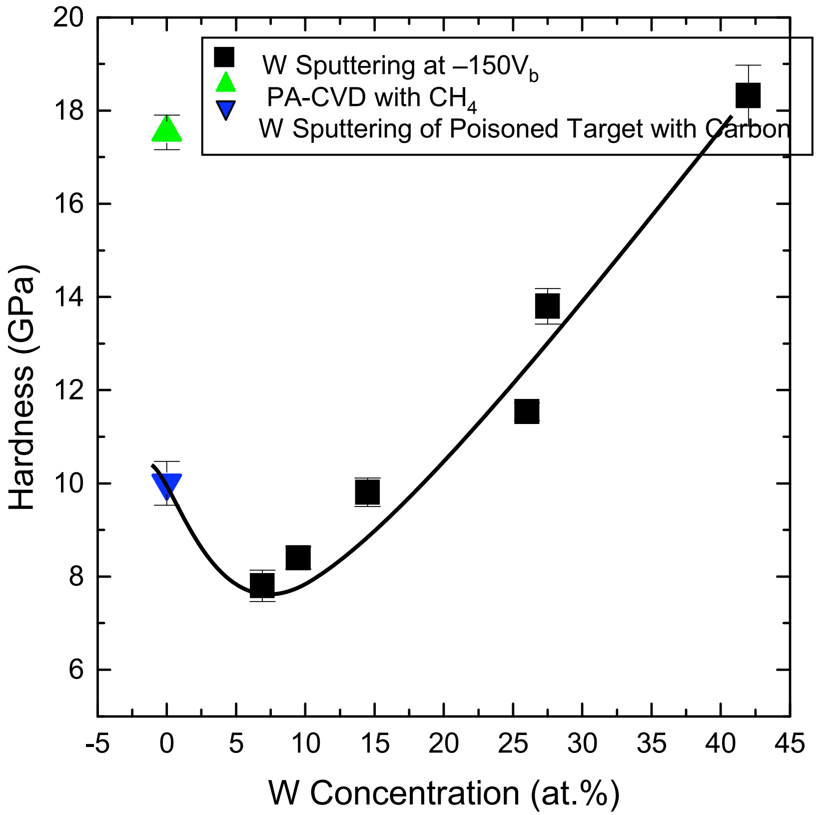
-material selection
-deposition characteristics

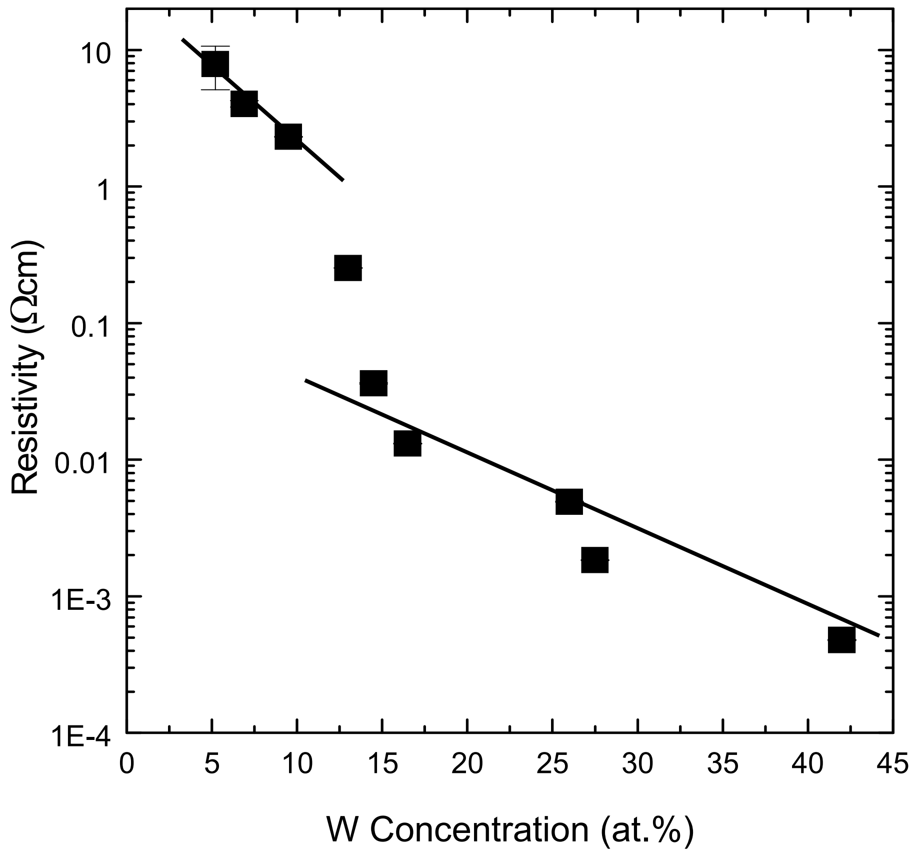
AND

-interface volume
-grain size,
-single layer thickness,
-surface and interface energy,
-texture
-epitaxial stress and strain



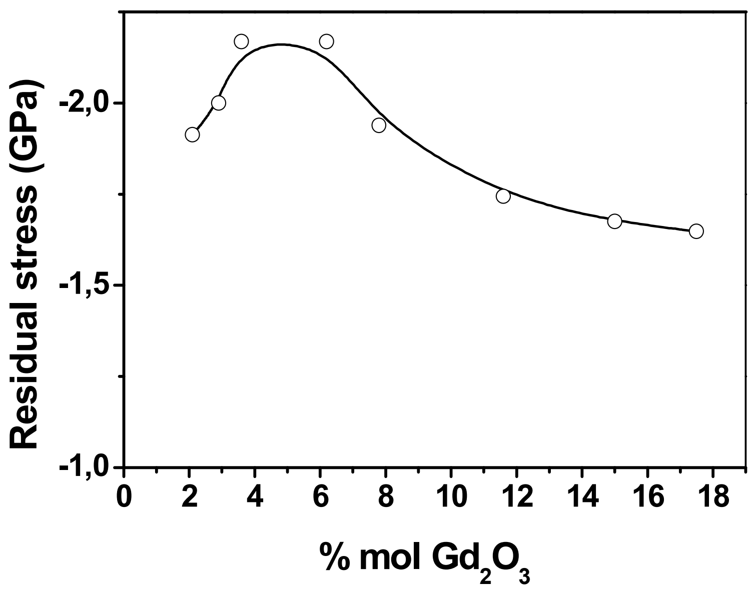
Examples of physical properties changes



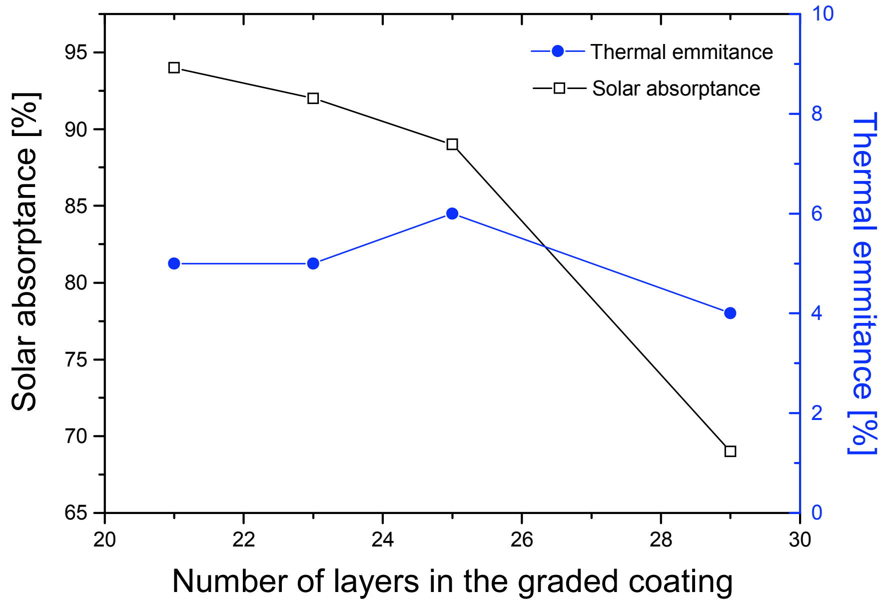


Hydrogenated WC-C nanocomposite coatings (metal containing DLC) by PA-PVD

Examples of physical properties changes



Influence of Gd_2O_3 content in the Residual stress of PVD ZrO_2-$Gd_2O_3Y_2O_3$ nanocomposite coatings



Solar absorptance and thermal emittance in Mo-Al_2O_3 sputtered absorbers gradient coatings

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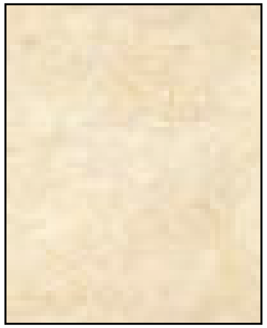
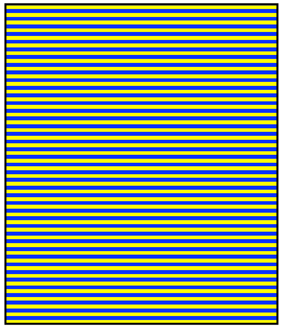
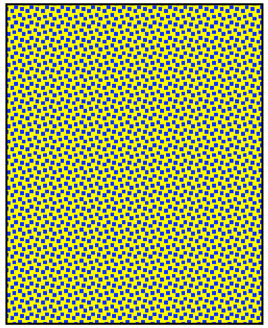
Alloyed, multilayered, isotropic multiphase coating

A composite coating usually consists of two or more phases combined either as different layers (multilayer or nanolaminate) or as homogeneous isotropic mixture of different phases (multiphase).







Alloyed multiphase

TiAlN
Si-DLC
$ZrO_2Y_2O_3$
NiCoCrAlY

Multilayered

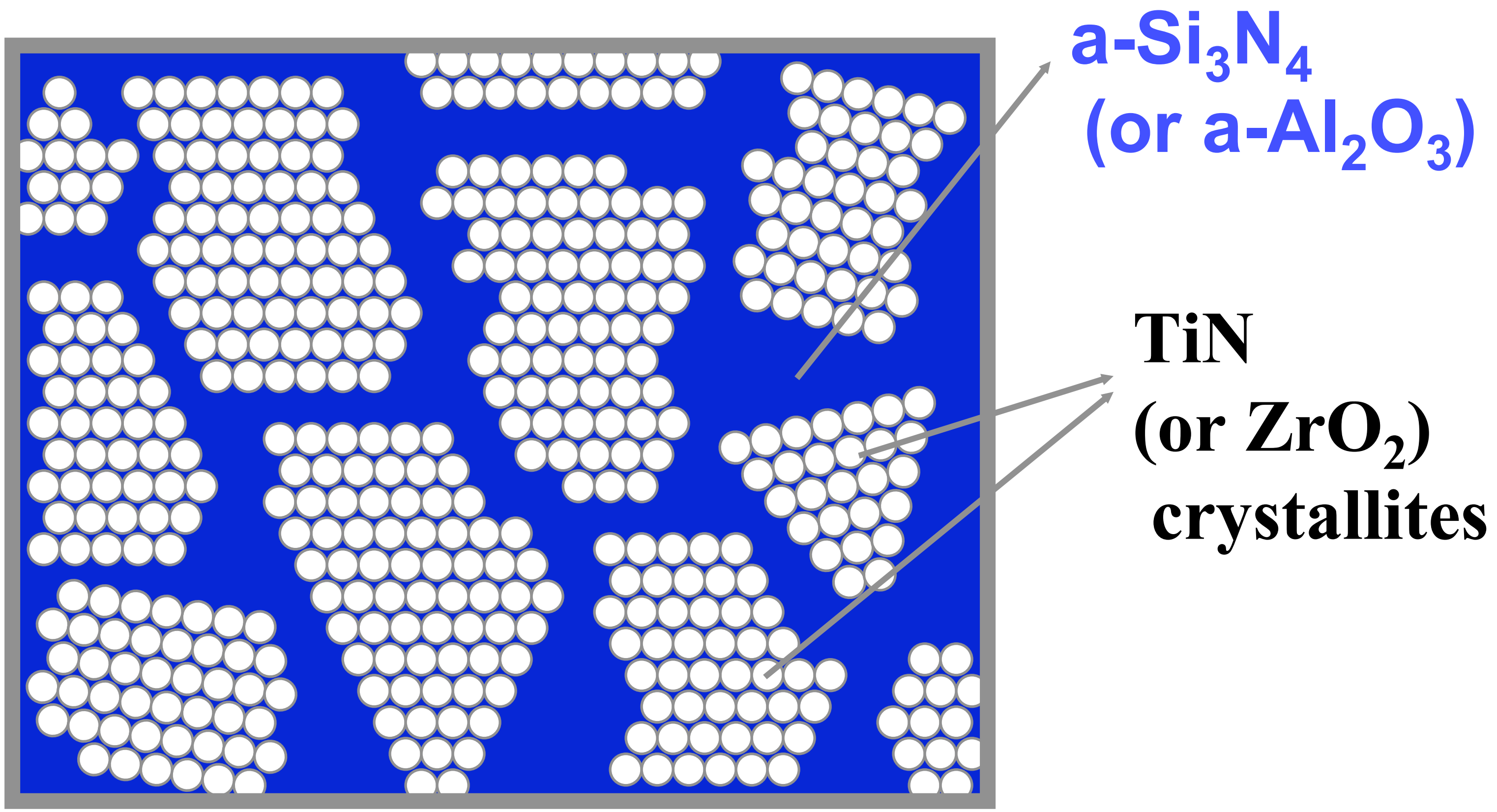
TiN-Mo
$TiN-Al_2O_3-TiC$
$ZrO_2-Al_2O_3$
$ZrO_2Y_2O_3-Al_2O_3$

Isotropic

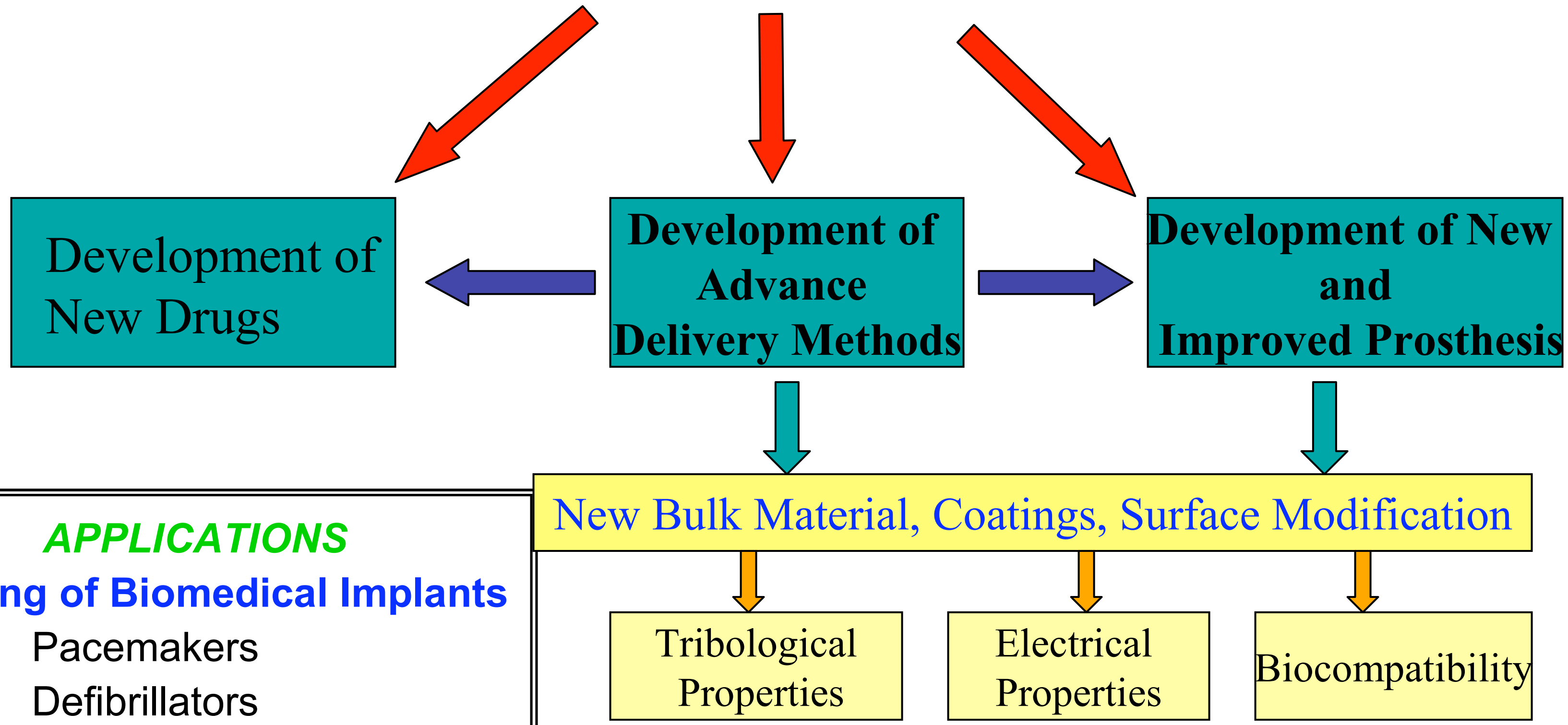
$TiN-Si_3N_4$
TiC-a-C
TiC-DLC
$ZrO_2-Al_2O_3$

NANOCOMPOSITE COATING

Nanocrystalline phase embedded is an amorphous matrix,eg. TiN/a-Si_3N_4 or ZrO_2/a-Al_2O_3



Advances in Medical Field

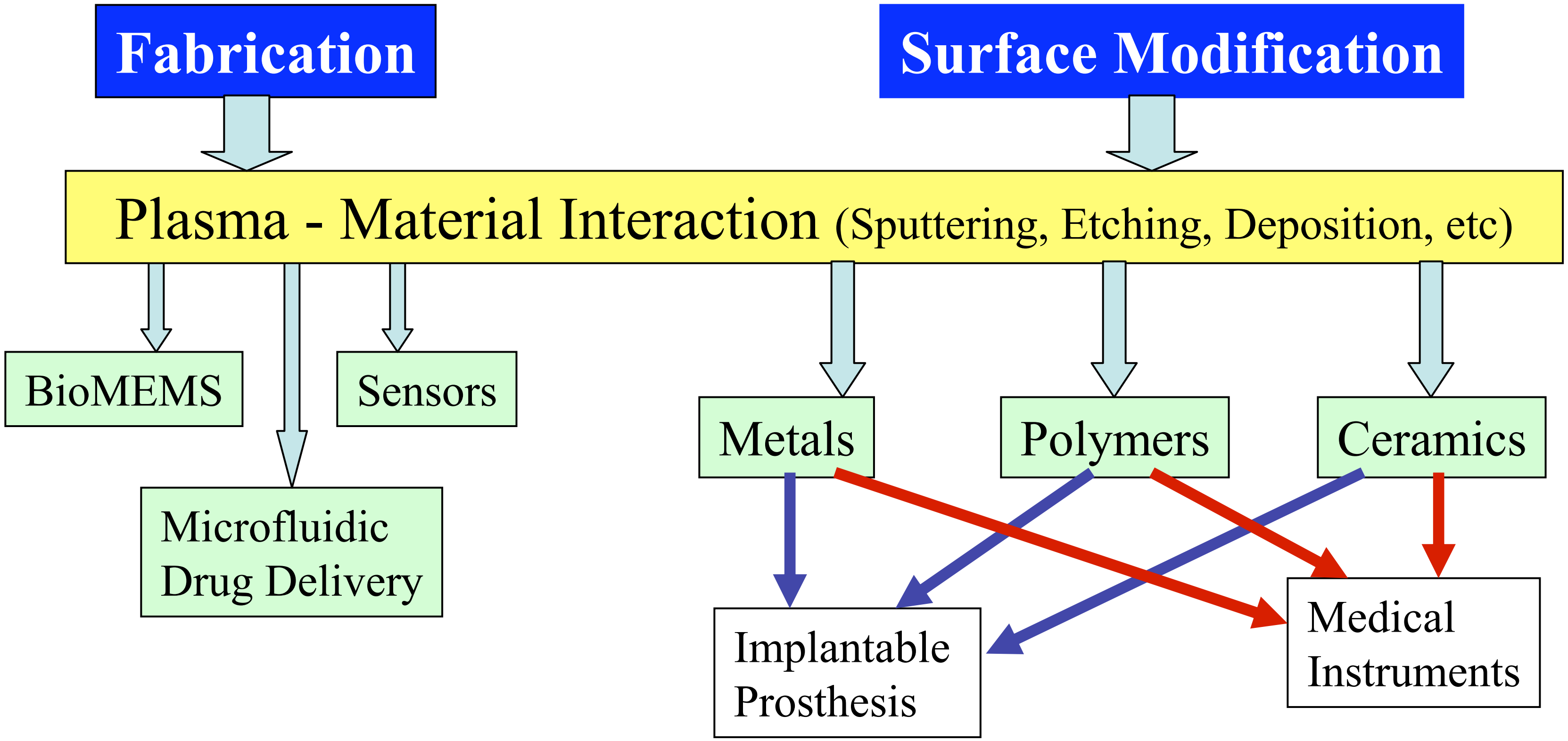


APPLICATIONS

- **Coating of Biomedical Implants**
  – Pacemakers
  – Defibrillators
- **Medical Devices**
  – Forming Mandrels,
  – Catheters and Guide Wires
  – Sensors and Transducers
  – Stents
  – Probes and Electrodes

Most medical prosthesis require surface properties that differ from bulk properties

Role of Plasma-Based Processes in Biomedical Applications



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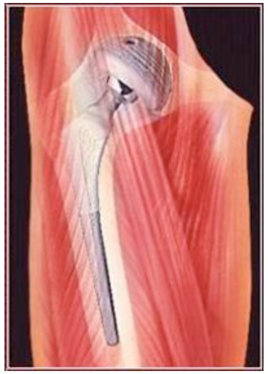
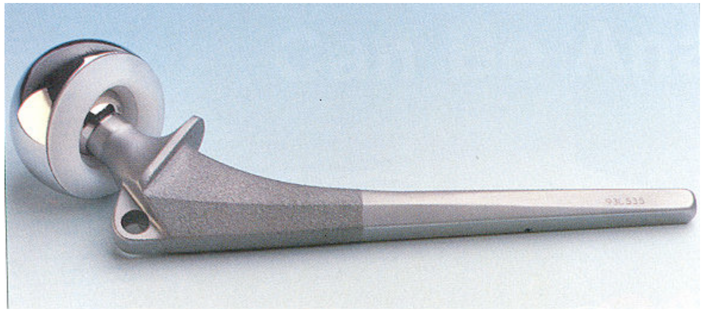
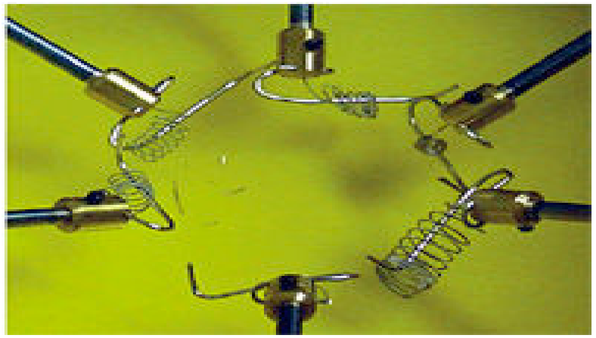
Biomedical applications

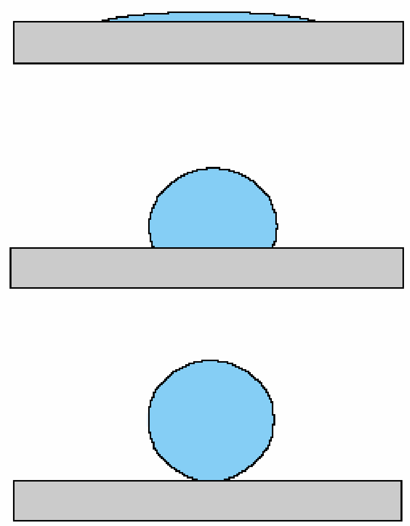






Smart nanocoatings – Self-cleaning and anti-dirt surfaces

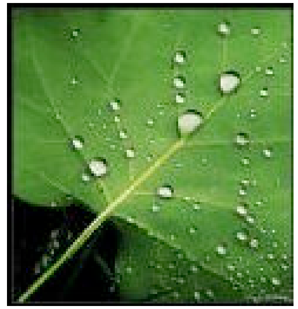
Water droplets at surfaces: contact angle



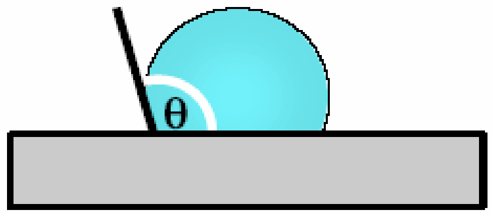
θ << 90° ***hydrophilic surface***

θ= 120° ***hydrophobic surface*** (e.g. Teflon)
sliding drops, no roll off

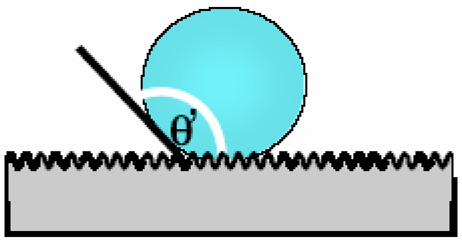
θ → 180° ***ultra-hydrophobic surface***
roll off angle → 0°



Ultra-hydrophobic surfaces: "Self-cleaning effect"

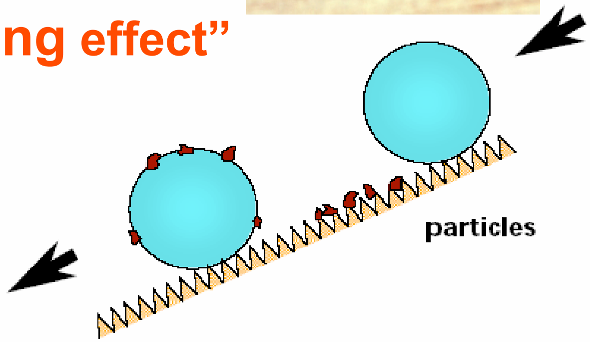


(flat) hydrophobic surface
90° <= intrinsic contact angle θi <=120°



hydrophobic surface combined
with specific surface nano-roughness

contact angle θ →180°



-Rolling water drops
act as "mini-wipers"
-no adhering water drops => no
evaporation residues, "spots"
-self-cleaning

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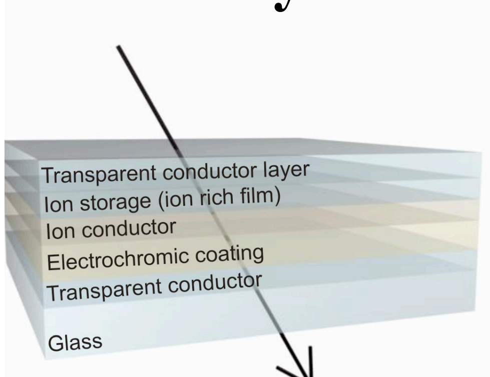
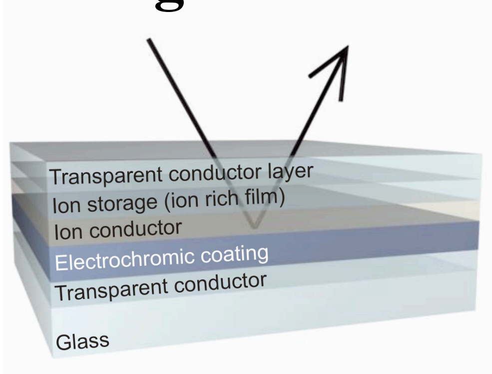
Active nanocoatings

Smart multilayered nanocoatings – smart windows and smart labels

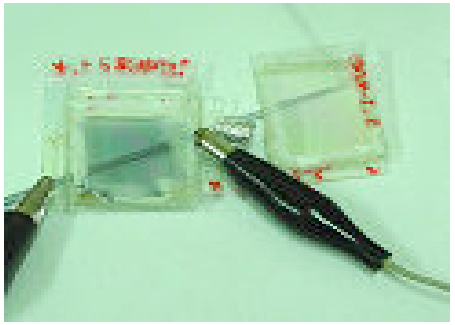




Carl M. Lampert, Materials Today, March 2004 p.28-35

Electrochromic materials change their optical properties persistently and reversibly under the action of voltage pulses. By sandwiching the electrochromic material and an ion rich transparent solid between a layer of a transparent conductor, a very small potential can induce an electric field that causes ions to cross to the electrochromic layer and change its colour state.

$$xM^{+} + xe^{-} + WO_3 \underset{\text{bleach}}{\overset{\text{colour}}{\rightleftarrows}} M_xO_3$$



Courtesy: C. Granqvist, ChromoGenics

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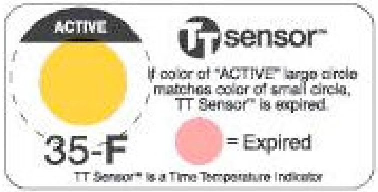
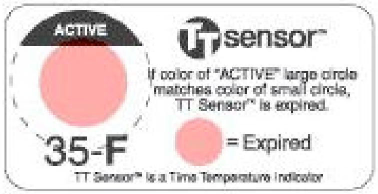
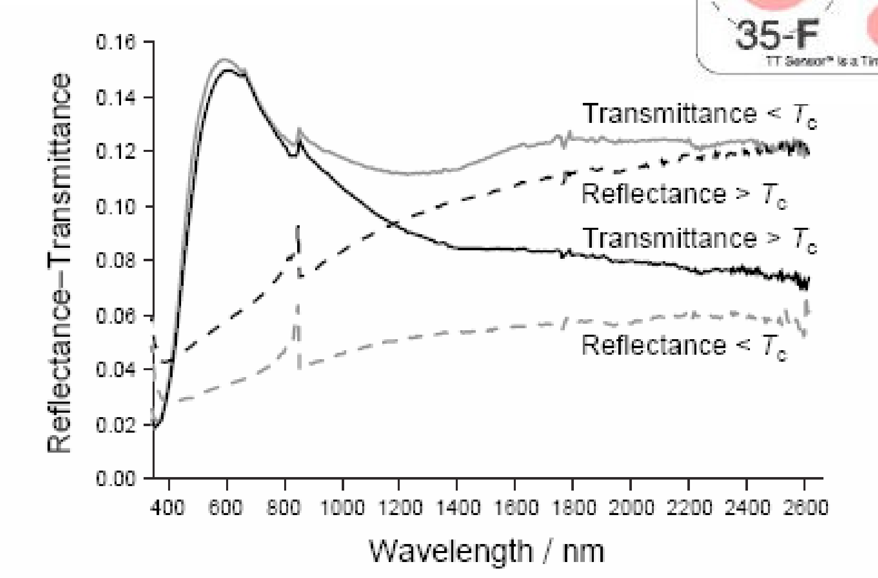
Active nanocoatings

THERMOCHROMIC COATINGS

Thermochromic materials such as vanadium oxide are used in devices with color change activated by temperature changes







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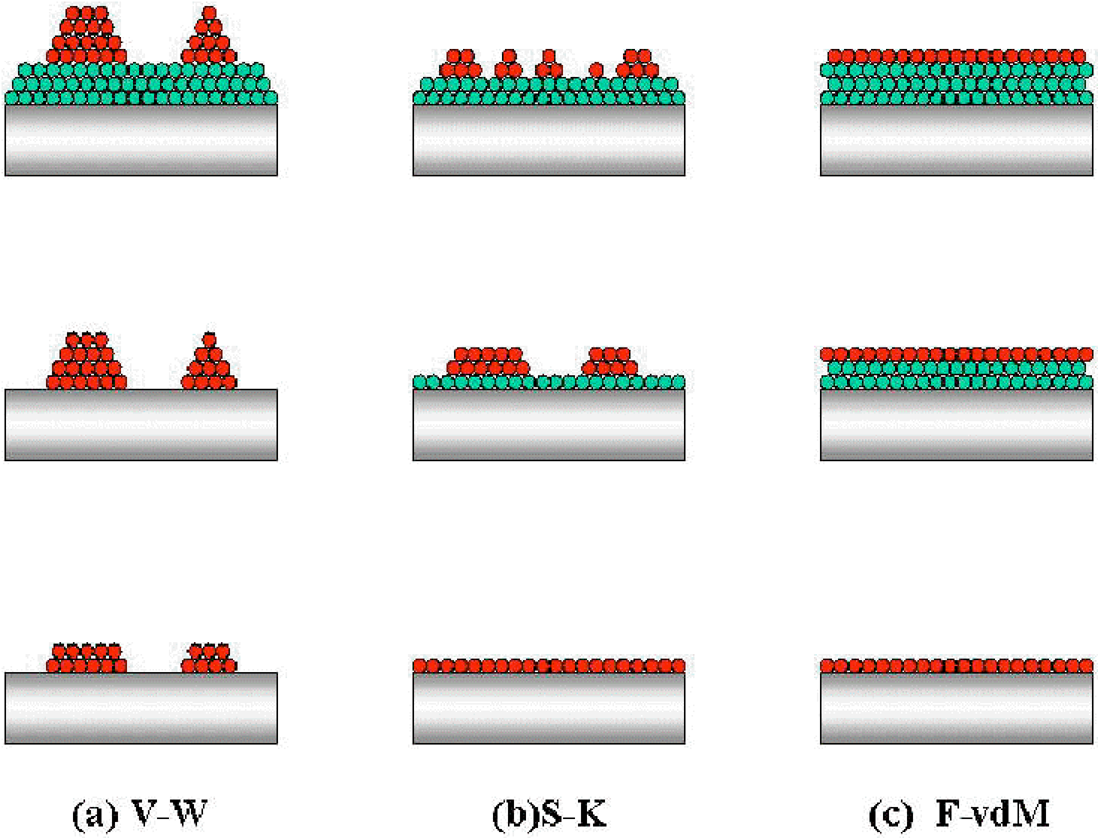
Growth Modes for Ultrathin Films



- The growing film surface can exhibit different behaviors depending on substrate temperature, interfacial strain, and alloy miscibility.

(a) Volmer-Weber (island growth) mode $\gamma_s < \gamma_f + \gamma_{sf}$

(b) Stranski-Krastanov (layer plus island growth) mode $\gamma_s > \gamma_f + \gamma_{sf}$ with misfit

(c) Frank van der Merwe (layer by layer) mode $\gamma_s > \gamma_f + \gamma_{sf}$

γ_s: surface energy of substrate γ_f: surface energy of film
γ_{sf}: interface energy of substrate-film

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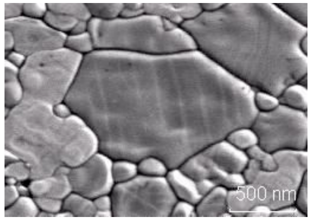
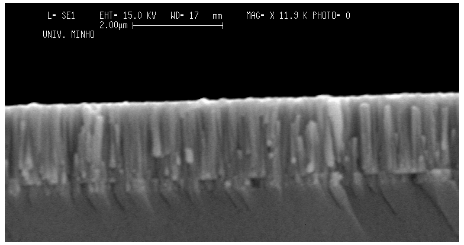
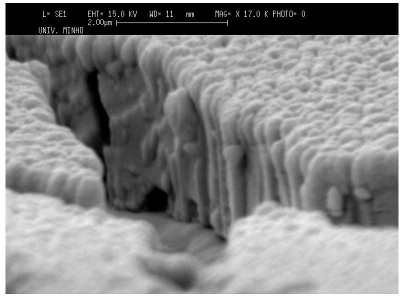
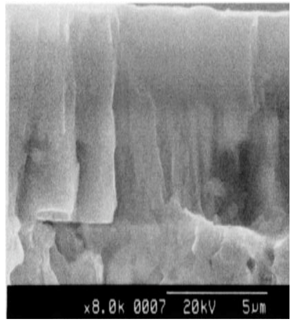
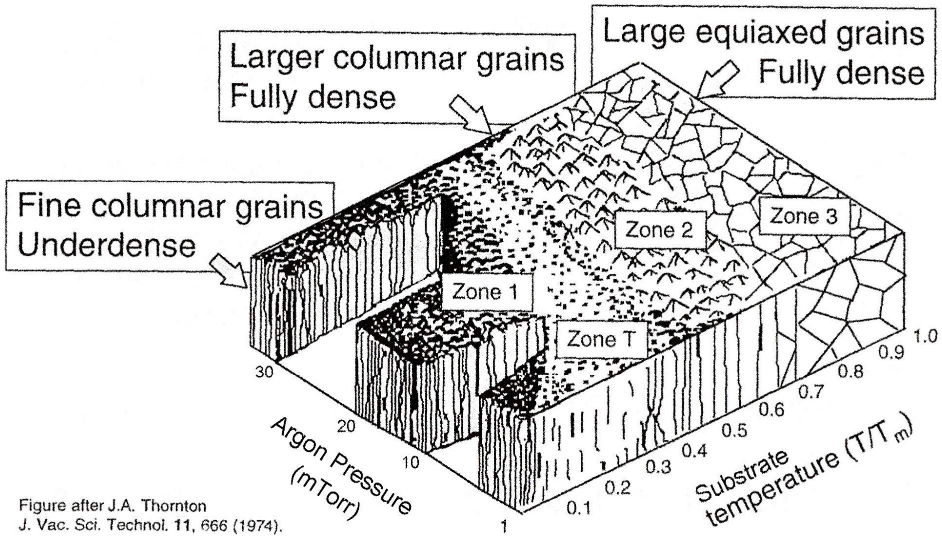
Coating Microstructure



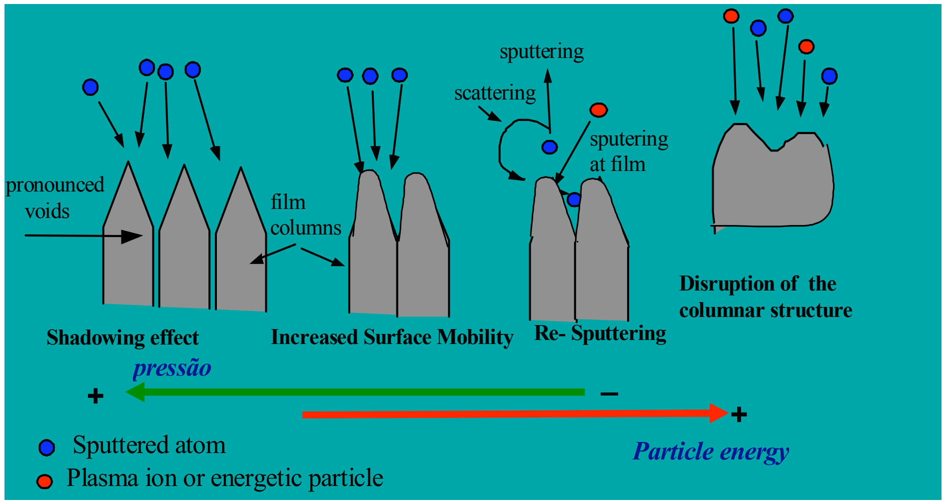








Thornton Diagram



Model for Coating Densification

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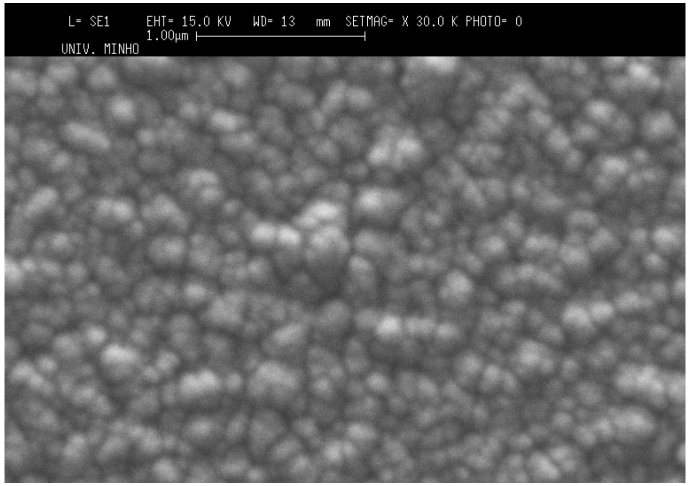
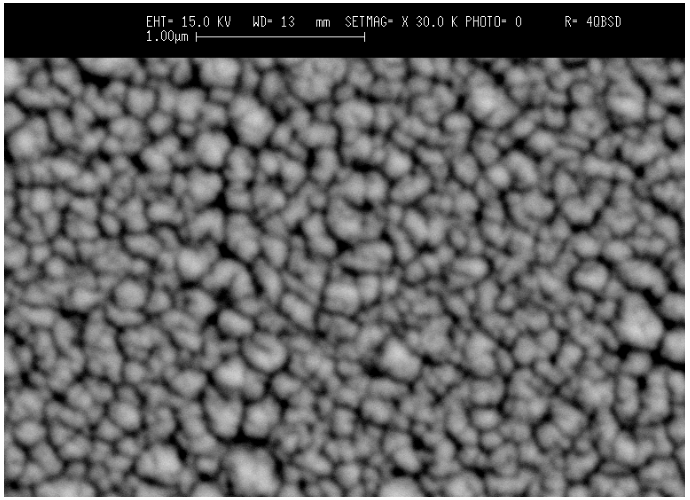
Parameters affecting film structure

- Some parameters that control grain structure are:
  - Substrate material and surface finishing
  - Base pressure (or contamination level)
  - Deposition temperature
  - Deposition rate
  - Later processing temperature
  - Process pressure (particle bombardment)
  - Ion beam bombardment

Parameters affecting film structure



SEM micrograph of a selective absorber Cr-Cr_2O_3 deposited by sputtering at $P=5x10^{-3}$ mbar



SEM micrograph Cr-Cr_2O_3 at $P=10x10^{-3}$ mbar

Smart Packaging

Packaging can be broadly categorized into the following types:

passive, active, intelligent, and smart.

Passive packaging refers to the traditional packaging that involves the use of a covering material, characterized by some inherent insulating, protective or ease-of-handling qualities.

Active packaging entails the concept of the package reacting to various stimuli – to keep the internal environment favorable for the products. A typical example would be a packaging with oxygen scavenger (an oxygen scavenger can absorb oxygen inside a package to increase the shelf-life of the item).

Intelligent packaging refers to the concept of making innovations in the design of packaging that renders it more useful for the consumer. E.g., intelligent packaging would include the packaging of automobile oil, where the very packaging structure makes it convenient for the user to pour oil into his automobile without getting his hands dirty.

Smart packaging refers to packaging that is made much more functional and useful; it involves the use of technology that adds features such that packaging becomes an irreplaceable part of the whole product. Smart packaging performs additional functions, responds to stimuli generated by the environment or from the product being packaged, and reflects the change in a manner that makes the product more convenient and useful for the consumer or firms in the supply chain. Smart packaging relies on the use of chemical, electrical, electronic, or mechanical technology, or any combination of them.

Metallized film

Al thickness ranging from 40 nm to 50 nm

Primarily for appearance

-Glossy look of metal

Replacement for aluminum foil laminations

-Provides barrier, especially to oxygen

-Permits downgauging of films

-Limits disposal impact

-Saves money

Metallized film can also be used for appearance

Nanocomposite coating process to improve food packaging

- Recent technological developments have enabled the food industry to create active packaging that prolongs food quality and shelf life.
- Active packaging interacts with food to reduce oxygen levels, or add flavourings or preservatives. Intelligent packaging can monitor the food and transmit information on its quality.
- A few commercial products exist today because it is difficult to produce a safe and effective packaging material at reasonable cost.

SOLPLAS

- Organic/inorganic coatings
- Plasma-assisted deposition
- Barrier and antimicrobial layers

Gas barriers

Nanocomposite packaging applications

- The gaseous barrier property improvement that can result from incorporation of relatively small quantities of nanoclay materials is shown to be substantial.
- Further data reveals the extent to which both the amount of clay incorporated in the polymer, and the aspect ratio of the filler contributes to overall barrier performance.

Table 1 Nanocomposite packaging applications

Supplier	Matrix resin	Nano filler	Use
Bayer AG	Nylon 6 (Durethan LPDU)	Organo clay	Barrier film
Clairant	PP	Organo clay	Packaging
Nanocor	Nylon MDX6	Organo clay	PET beer bottles

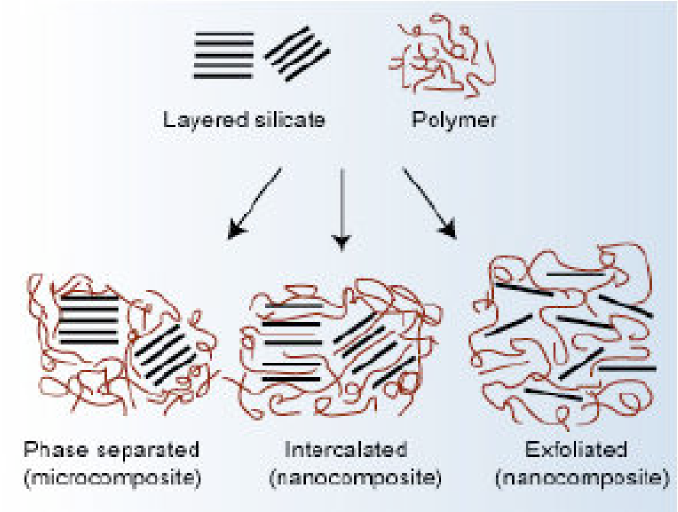
Source: Imperm

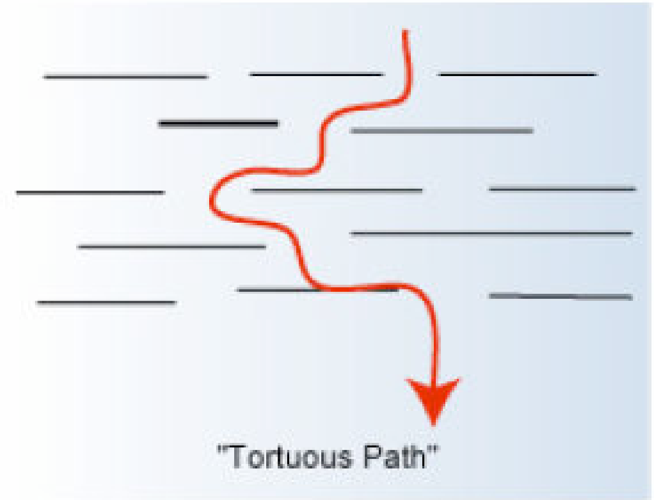
Other barrier materials include SiO_x and Aluminium oxide

Nanoclay composites in food packaging applications

•Such excellent barrier characteristics have resulted in considerable interest in nanoclay composites (Montmorillonite, usually) in food packaging applications, both flexible and rigid.

•Specific examples include: packaging for processed meats, cheese, confectionery, cereals and boil-in-thebag foods, also extrusion-coating applications in association with paperboard for fruit juice and dairy products, together with co-extrusion processes for the manufacture of beer and carbonated drinks bottles.





Vasco Teixeira

Nanoclay in PET Bottles

Nanocor

- Nanoclay with MXD6 nylon as component in barrier layer in beer bottles

- Plates are nanometers thick, aspect ratio above 200:1

Security and Sensory Packaging

- One of the problems that the food industry and retailers face is how to tell whether a food package has been opened or tampered with.

- One solution that has been proposed is the application of a novel **nanocrystalline indicator in the form of an oxygen intelligence ink** that is printable on most surfaces.

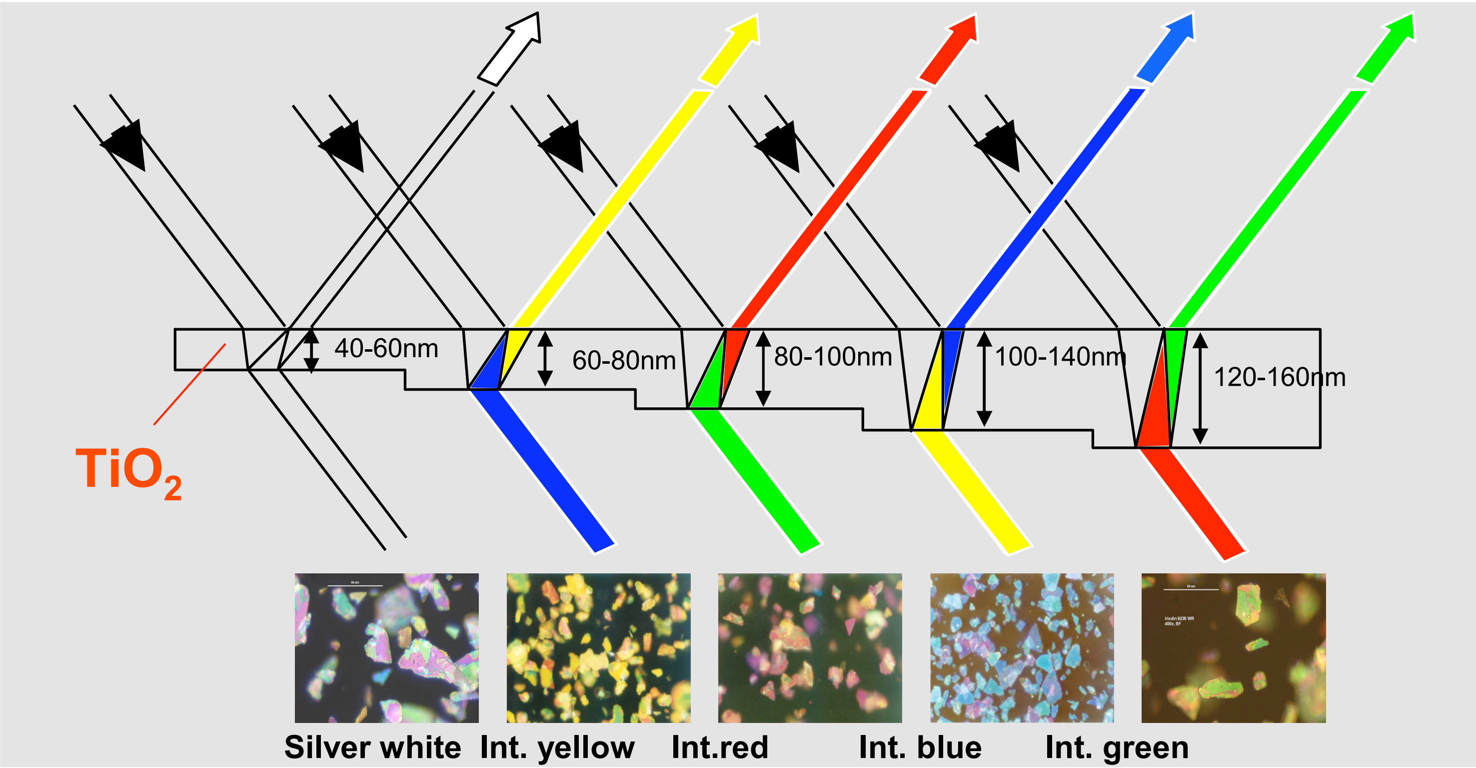
- Such ink can be composed as (besides others):

  UV light activated nanocrystalline particles of a semiconductor (usually titanium dioxide)

- Another security application is the use of **nanophosphorous particles which will appear white in daylight** but will fluoresce when exposed to light of certain wavelengths. Thus objects marked with nanophosphorous obtain an invisible and non-removable protection against counterfeiting.

Color pigments – Micro-colour codes in packaging and labelling applications

- Example of optically variable pigments that provide a strong overt feature
- Colour of interference pigments depends on the thickness of the coating



Source:Nicole Golomb-Simons Druck, ***ECpack25,*** *MERCK*

Security and Sensory Packaging

- Researchers hope to use the changing molecular composition of milk that is beginning to spoil to bring about a reaction with **nanoparticles embedded in the packaging**, causing the colour of the packaging to change.

- The advantage of such a technology is that store owners and consumers alike could easily tell if the product's quality had declined.

Sensory and Smart labels in packaging

- Electronics built on thin film laminate substrates that could be used in future sensory packaging applications.

- The development of sensory packaging that can monitor the conditions of pharmaceuticals and foods that are affected by changes in temperature, humidity and shock.

- Nano barcodes are being developed by Nanoplex, a spin-off from Surramed.

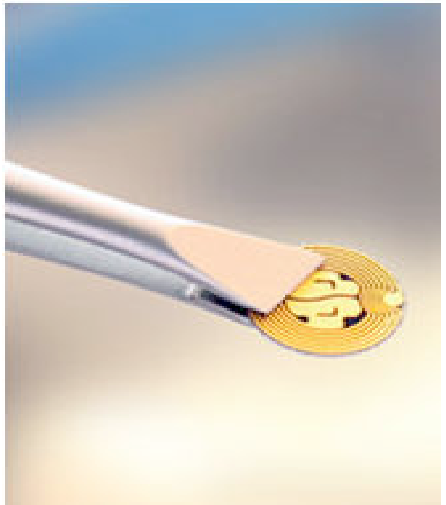
- When applied to products, the barcodes give each their own unique identities. The treated product can then be tracked.

Smart labels in packaging

- RFID or Radio Frequency IDentification is sometimes known as 'radio bar codes'. Usually, it takes the form of a small label. The information on this label can be 'read' electronically even when it is hidden within packaging.

- RFID works in almost any orientation so scanning is much easier than with the traditional barcode.

- RFID labels tend to be a silicon chip and a metal or printed ink antenna in a plastic label.



Coatings on PET Bottles

PET bottle began expanding to the packaging of sensitive beverages such as juices or beer.

The market requires the packaging industry to provide a technically and commercially convincing barrier solution for this purpose.

•Gases such as oxygen (O_2) and carbon dioxide (CO_2) are able to permeate the microstructure of the bottle wall.

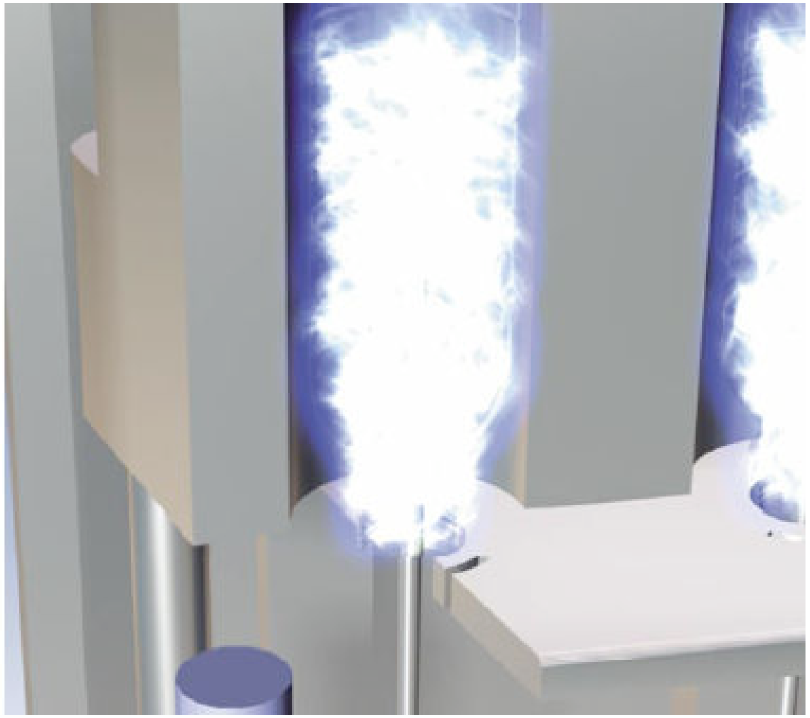
•In juices, for example, vitamins, flavorings and colorings are impaired significantly during storage as a result of this permeation, leading to a reduction of shelf life.

Coatings on PET Bottles

- PET bottles featuring SiOx coating are completely transparent and clear as glass.
- The inner glass coating is suitable for foodstuff, safe and has no interaction with products. Glass is used as standard in packaging!
- The inner coating of the bottle prevents contact between PET and the product, and thus impedes, for example, a change in taste due to flavor transfer.

Coatings on PET Bottles

Plasma coating on the inside of a PET bottle

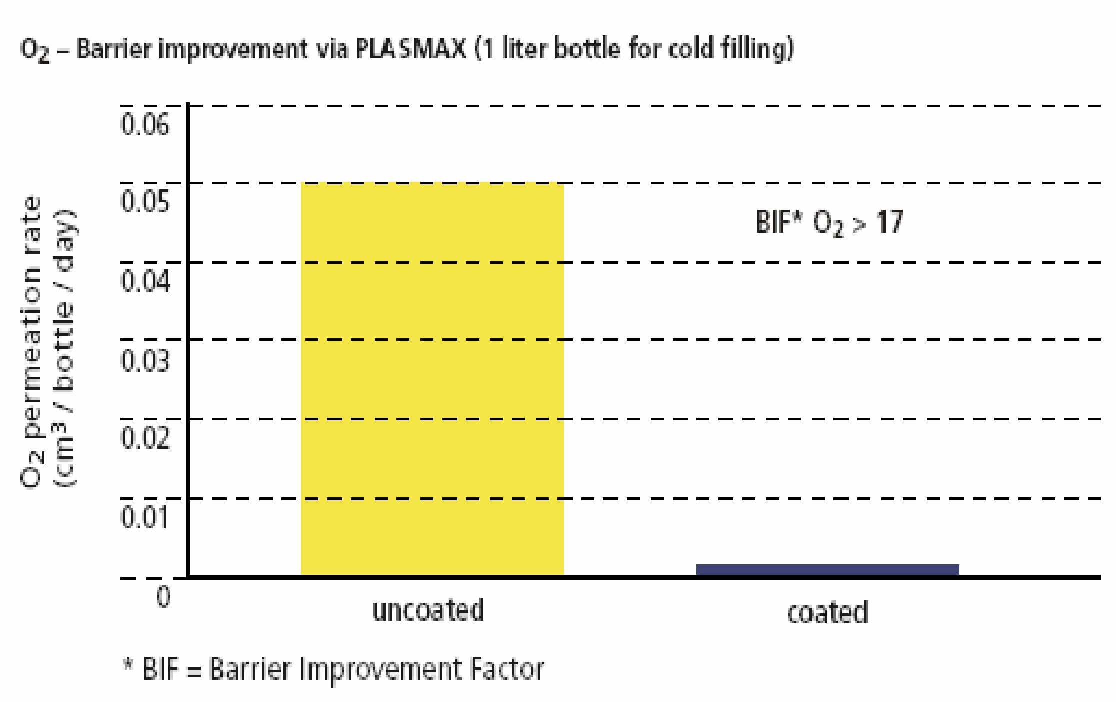


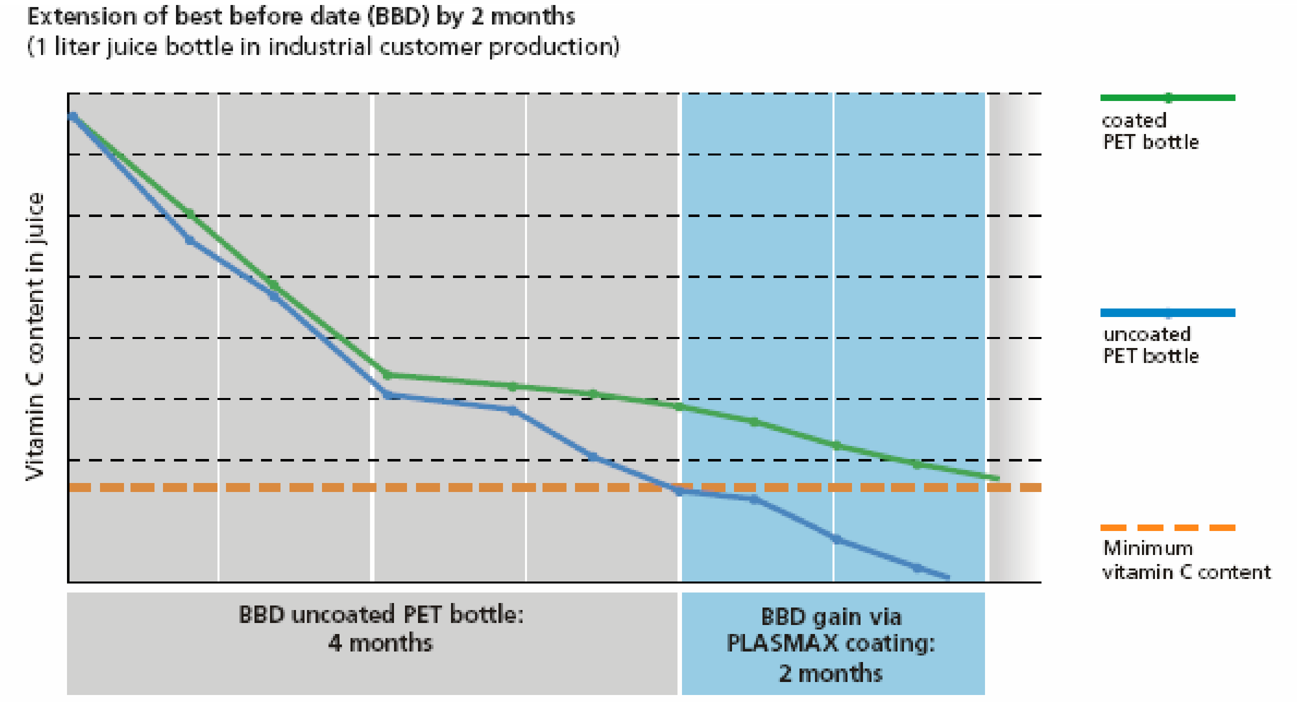
SiOx – like barrier deposited by **Plasma Enhanced Chemical Vapour Deposition** (PECVD)

PECVD allows industrial scale deposition os high quality barrier coatings with good uniformity and adherence to the substrate

Source: SIG PLASMAX GmbH

Results





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Nanocomposites on plastic bottles

- Nanocor, a subsidiary of Amcol International Corp., is a world leader in the production of nanocomposites, which are polymers bonded with nanocrystals to provide the materials with enhanced properties.

- The company is currently producing nanocomposites for use in plastic beer bottles that give the contents a six-month shelf- life.

- The material works by introducing nanocrystals into the plastic that essentially create a maze from which oxygen molecules find it difficult to escape.

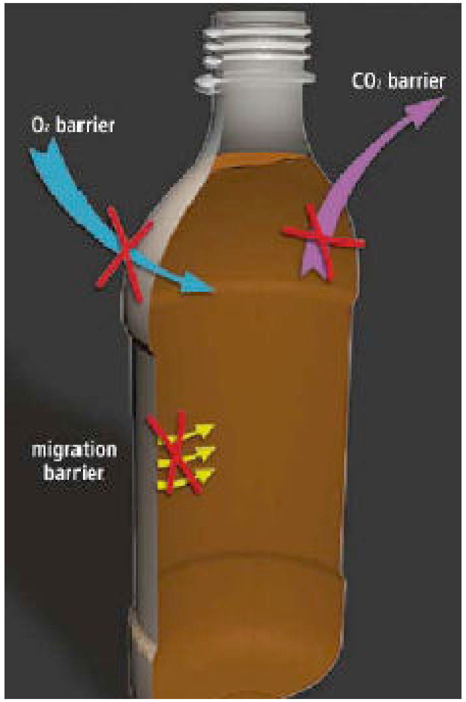
Amorphous carbon as barrier layer

Sidel – tradename Actis

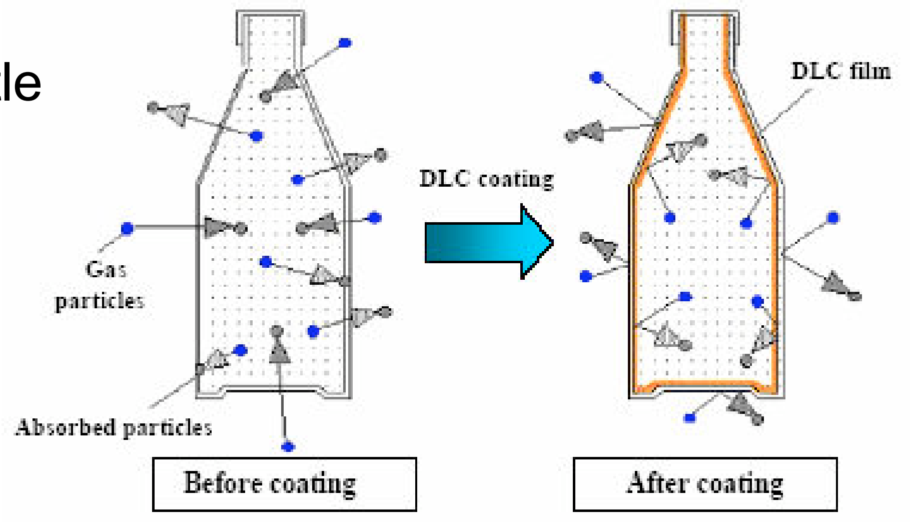
Uses a coating of about 200 nm thick

Coating on inside of bottle

Plasma Nano Shield
-Ionizes gas
- 20-40 nm thick



Sidel system:
Uses acetylene gas introduced into bottle
Excited to plasma state
Bonds to PET bottle wall on contact
Actis Lite
-Thinner layer for less sensitive foods



Antimicrobial nanoparticles for food packaging

•Most foods deteriorate in quality during transport, processing, and storage through contamination, which occurs by growth of microorganisms, enzymatic or nonenzymatic chemical reactions, and from physical changes

•Antimicrobial packaging can inhibit the growth of pathogenic or spoilage organisms on food surfaces, and thus, can contribute to extending the shelf life of packaged foods.

•Nanoparticles of zinc oxide and magnesium oxide have been shown to be effective in killing microorganisms*.

•This could provide a cheap, safe alternative to nano-sized silver, which has good antimicrobial properties, but is expensive and as a heavy metal, is not suitable for human contact.

•Ohters authors** have concluded that a combination of nisin and $\alpha-$tocopherol in a 3 mm thick coating conferred both antimicrobial and antioxidative properties.

•Yulan Ding & Malcolm Povey
** Chan Ho Lee et al., *Journal of Food Engineering* 62 (2004) 323–329

Bioactive packaging concepts

(i) integration and controlled release of bioactive components or nanocomponents from biodegradable and/or sustainable packaging systems,

(ii) micro- and nanoencapsulation of these active substances either in the packaging and/or within foods

and

(iii) packaging provided with enzymatic activity exerting a health-promoting benefit through transformation of specific food-borne components.

The development of such novel functional hybrid food/ packaging systems (the functional concept including prebiotics, probiotics, phytochemicals, marine oils, lactosefree foods, encapsulated vitamins, bioavailable flavonoids, etc.) will provide alternative, more efficient and, in some cases, unique industrial means to provide foods with improved impact on human health upon consumption.

Conclusions

- **Novel nanocomposite and nanolayered coatings are good candidates to be used in food and medical industries.**

- **The application of nanotechnology has the potential to improve food quality and safety significantly.and it will add value by reducing manufacturing costs in food industry.**

- **The excellent barrier characteristics of nanoclay composites in food packaging applications, both flexible and rigid, have resulted in considerable interest.**

- **Another window of opportunity for nanoparticles is represented by food safety applications. Anti-microbial packaging materials are one of the most promising active food packaging applications**.

- **Inclusion of high technology into packaging, e.g. RFID, smart labels, sensors etc.**

- **For brand security and/or supply chain tracking applications, the development of nanobarcodes and RFID tags offers a number of competitive advantages.**