Nanocoatings and Nanofilms

Coatings have been used for centuries

Why?
Coating Uses
Uses

Optical properties
- No light scattering, color can be selected
- Adaptable refractive index (light curing adhesives)
- Photocatalysis, UV/IR protection with absorbing NP

Electrical properties
- Electrical conductive but transparent coatings
- Printable electronics

Magnetic properties
- Temperature increase in magnetic field (bond/disbond control)

Thermo-mechanical properties
- Scratch, anti-abrasion resistance
- Anti-friction, corrosion protection
- Hydrophobic coatings
Functional Coatings

* Functional coatings, tailored to all types of requirements are being developed with the application of chemical nanotechnology. This facilitates completely new product properties, which can be used for any industrial application. “Intelligent”, environmentally-friendly and cost-effective solutions are aimed at securing competitive advantages.

* At present nanograde is “on top” in three hi-tech application areas: permanent non-stick coatings on glass, ceramics, metals or polymers, non-scratch systems for plastics and anti-corrosion systems for light metals.

Wood Preservative

* The water droplets rest on the impregnated wood surface like mysterious blue pearls. But this is no conjuring trick: the wood has been treated with a BASF’s nanoparticulate surface coating, which has made its surface extremely water-repellent (superhydrophobic). This coating reduces the contact area between water and wood to a minimum. It also decreases the forces of adhesion, making the water droplets assume a globular form. Surfaces become self-cleaning and stay clean for a long time by applying nanostructures as they can be found on the leaves of the lotus plant.

One Step Paint

* Nanophase’s proprietary nanoparticles are now being used in Behr’s Premium Plus Ultra paint. Nanophase’s nanoparticles not only lend the paint improved adhesion and anti-mildew properties, but also allow users to forgo the normal two-step priming and coating process. The new paint reportedly does both in a single step.

Anti-Graffiti Paint

* Deletem 5000’s special ingredient is silica. It is loaded with particles of the stuff that are but a few nanometers across. These particles have both oil-repellent and water-repellent molecules attached to their surfaces. Both are necessary, since the materials used by graffiti artists may be oil-based or water based. However, if merely mixed together, the two would end up repelling each other, and thus separating. By attaching them to the silica, this mutual loathing can be overcome and, as the paint dries, the changes that take place force the oil-and-water-proofing to the surface. The result is that most agents used will not stick to that surface—and what does stick can be washed or brushed off easily.

Environmentally Safe Epoxy

* Advanced Nano-Coatings, Inc (“ANC”) is a producer of high performance, VOC compliant epoxy coatings.

* ANC’s products are based upon unique polymer chemistry combined with cutting edge Nano Technologies.

* ANC’s utilization of these technologies produces multi functional coating systems. These systems exhibit unique qualities, which now allow a coating system to solve more than one market need.

* Applications for these products include wood, steel and concrete protection, fire protection and retardancy, insulation of building materials and many other structural protection applications.

Construction Coatings

* The implementation of Nanotechnology components into wall and facade coatings created some products which architects and building owners have been waiting for.

* These high-tech products make it possible, by simply replacing conventional wall paints, to achieve better energy ratings for buildings, better indoor air quality and fewer allergy-related illnesses.
Smart Coatings™ Characteristics

**Smart Coatings™ Functions:**
- Preserve items from corrosion
- Incorporate nanomachines
- Self-heal
- Permit easy removal when given the proper “orders”
- Protect items from harsh environments endured because of mission requirements
- Alert sustainment community of potential coating/substrate problems

**Possible Coating Structure:**

[Diagram of coating structure]

**Useful nano coating properties**
Chemical and Physical vapour deposition

CVD & PVD

Evaporation PVD

1. Resistance heating is used to vapourise the metal to be deposited (High T)

2. Vacuum used so little contamination and collisions
**“LINE OF SIGHT”**

No surface diffusion  
Everything sticks where it hits (physical processes only)  
Poor surface coverage  
“Line of sight”

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**Sputtering**

The poor coverage problem in thermal evaporation was solved when sputtering emerged.

“Knocking-off” of the metal atoms from the metal material source by gas ions bombards the “knocked-off” ions on to the wafer.

Collision between the metal ions and the gas molecules produces more uniform coverage  
No longer purely “line of sight”

This grants sputtering a better coverage of deposition than thermal evaporation.

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**Comparison**

1. **Coverage Area**
   
   Sputtering has a wider range of choices for material than thermal evaporation.

2. **Deposition Rate Control Factors**

   In thermal evaporation, deposition rate can be controlled by the amount of heat supplied on the material (evaporation point). On the other hand, sputtering offers a way through gas pressure, temperature, the potential difference between the material, which acts as the cathode of anodes on the wafer placed on the substrate's anode.

3. **Deposition Rate**

   When talking about deposition rate, the more controlled the rate is (lower number of atoms/second), the better. Sputtering can trim down its deployment of metal layers up to one atomic layer per second, whereas thermal evaporation can only control it to hundreds or thousands of atomic layers per second.

4. **Choice of Material**

   Sputtering has a wider range of choices for material than thermal evaporation.

5. **Decomposition of Material**

   The uniformity of decomposition and erosion of the material in sputtering makes it more efficient than thermal evaporation.

6. **Equipment Cost**

   Operating using sputtering will cost more than thermal evaporation because the latter only needs a vacuum chamber with precision thermometers, while the former requires twice or thrice of the energy used in thermal deposition to excite the ion of the material.

7. **Surface Damage**

   Surface damage has higher possibility in sputtering, its ion particle bombardment can induce damage in the substrate.
Chemical Vapour Deposition (CVD)

The substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit.

**Advantages:**
- high growth rates possible
- can deposit materials which are hard to evaporate
- good reproducibility
- can grow epitaxial films
- Can grow nanotubes

**Disadvantages**
- high temperatures
- complex processes
- toxic and corrosive gases
Example: Silicon dioxide

Common source gases include:
- silane and oxygen,
- dichlorosilane (SiCl₂H₂) and nitrous oxide (N₂O), or
- tetraethylorthosilicate (TEOS; Si(OC₂H₅)₄). The reactions are as follows:

Reactions:

\[
\begin{align*}
\text{SiH}_4 + O_2 & \rightarrow \text{SiO}_2 + 2 \text{H}_2 \\
\text{SiCl}_2\text{H}_2 + 2 \text{N}_2\text{O} & \rightarrow \text{SiO}_2 + 2 \text{N}_2 + 2 \text{HCl} \\
\text{Si}[\text{OC}_2\text{H}_5]_4 & \rightarrow \text{SiO}_2 + \text{byproducts}
\end{align*}
\]

Oxide may also be grown with impurities (alloying or "doping")
Metal CVD processes

Mo, Ta, Ti, Ni, and W are widely used.

• These metals can form useful silicides when deposited onto silicon.

Mo, Ta and Ti are deposited by LPCVD, from their pentachlorides.

Ni, Mo, and W can be deposited at low temperatures from their carbonyl precursors.

In general, for an arbitrary metal M, the reaction is as follows:

\[ 2 \text{MCl}_5 + 5 \text{H}_2 \rightarrow 2 \text{M} + 10 \text{HCl} \]

The usual source for tungsten is tungsten hexafluoride, which may be deposited in two ways:

\[ \text{WF}_6 \rightarrow \text{W} + 3 \text{F}_2 \]
\[ \text{WF}_6 + 3 \text{H}_2 \rightarrow \text{W} + 6 \text{HF} \]
Testing

Some of the techniques used to measure the physical properties of PVD/CVD coatings are:

- **Calo tester**: coating thickness test
- **Scratch tester**: coating adhesion test
- **Pin on disc tester**: wear and friction coefficient test
- **Nano-indentation**

Atomic layer deposition (ALD)

- Coat complex, 3-dimensional objects with precise, conformal layers
- ALD uses alternating, saturating reactions between gaseous precursor molecules and a substrate to deposit films in a layer-by-layer fashion.
- By repeating this reaction sequence in an ABAB... fashion, films of virtually any thickness, from atomic monolayers to micrometer dimensions, can be deposited with atomic layer precision.

![Atomic layer deposition](image)

Reaction A, the substrate surface is initially covered with hydroxyl (OH) groups. The hydroxyl groups react with trimethyl aluminum (TMA) to deposit a monolayer of aluminum-methyl groups and give off methane (CH₄) as a byproduct.

Because TMA is inert to the methyl-terminated surface, further exposure to TMA yields no additional growth beyond one monolayer.
Atomic layer deposition (ALD)

Reaction B, this new surface is exposed to water regenerating the initial hydroxyl-terminated surface and again releasing methane. The net effect of one AB cycle is to deposit one monolayer of Al₂O₃ on the surface.

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Case Study:

Development of High Performance “Nanostructured” Ternary Nitride Coatings, and Assessment and Modelling of Their Performance

Strategy: Formation of Nanostructured Coatings
To Increase Nucleation for Grain Refinement
by increasing the number and energies of atoms/molecules arriving the substrate

Control Parameters:
- Bias Voltage
- Substrate Temperature
- Magnetron Configuration
- Nitrogen Deposition Pressure
- Magnetron Discharge Power
Coatings were deposited in a Varian 3120 deposition unit.
Pirrani gauges and Tylan mass flow controllers were used to monitor pressures and flow rates of reactive gas.
Coatings with multiple-layers of Ti/TiAl/TiAlN or Cr/CrAl/CrAlN were produced.

Ternary nitride coatings with nanograin size were produced by magnetron co-sputter deposition.

Experimental Details

Process Flowchart:

1. Sample inserted in deposition unit and placed under high vacuum
2. Deposition parameters adjusted
3. Deposition of first layer (interlayer)
4. Deposition of second layer (interlayer)
5. Introduction of nitrogen gas and deposition of ternary nitride
6. Chamber opened and sample removed
Effect of Bias Voltage: Case Study - TiAlN

Effect of substrate bias voltage on elemental composition of the coatings:

- Nitrogen content almost unchanged
- Titanium and aluminium contents slightly changed

![Graph showing elemental composition (at%) vs. Substrate Bias Voltage (-Volts)](image)

Effect of Bias Voltage: TiAlN

Micrographs showing surface morphology of coatings produced at -100V, (a) SEM and (b) AFM images

![Micrographs (SEM and AFM)](image)

Effect of Nitrogen Pressure: TiAlN

A schematic diagram of the two dimensional structure zone model showing the effect of nitrogen pressure on the microstructure and morphology of (Ti,Al)N coatings can be established:

![Schematic diagram showing effect of nitrogen pressure](image)
Coating Structures

Nitrogen Pressure: 0.2 mTorr

Coating Structures

Nitrogen Pressure: 0.65 mTorr

Coating Structures

Cross-sections
**Grain Size Development**

Grain size: ~90 nm at 0.2 mTorr; 170 nm at 2.4 mTorr

**Coating Compositions**

As nitrogen pressure increased, nitrogen & titanium contents increased, aluminium content decreased

**Phase Development**

As nitrogen pressure increased, TiN/TiAlN (200) and AlN (101) components were weakened; TiN/TiAlN (111) components developed
Coating Hardness

Coating Hardness: ~2100 HV at 0.2 mTorr; 1000 HV at 2.4 mTorr

Nanoindentation Properties

Nanoindentation load-displacement curves of (Ti,Al)N coatings

Nanoindentation Properties

Mechanical properties of the coatings determined by nanoindentation

<table>
<thead>
<tr>
<th>Nitrogen Pressure (mTorr)</th>
<th>0.40</th>
<th>0.96</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness, H (GPa)</td>
<td>18.6 (1711)</td>
<td>13.6 (1251)</td>
</tr>
<tr>
<td>Elastic Modulus, E (GPa)</td>
<td>264</td>
<td>196</td>
</tr>
<tr>
<td>Plasticity Parameter, δp = εp/ε</td>
<td>0.53</td>
<td>0.51</td>
</tr>
</tbody>
</table>
Coating on Drills

Sol Gel

limitations
Spin coating

Dip Coating

SiO$_2$ coated with AIOOH

Corrosion Protection

a) Nanocomposite Coated Aluminium surface AFTER Corrosion Test
b) Uncocated Aluminium BEFORE Corrosion Test
c) Uncocated Aluminium AFTER Corrosion Test

(Chloroform Test: 60°C, 3.6 NaCl, pH 3.5)
Fracture Toughness of Nanoscale Hydroxyapatite Coatings on Titanium Substrates

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The Material

The titanium samples, commercially pure (CP), were anodised in a mixed H3PO4-H2SO4 solution. Three voltages were used,
- 25 volts,
- 50 volts and
- 75 volts

These voltages were based on the work of previous workers.

The anodization of the titanium samples produced

Oxide film thicknesses showing a linear growth of 2nm per volt.
- Anodised layers thus varied from 50-150nm
dilute anodizing solution
- a more porous oxide film
concentrated anodizing solution
- relatively porosity free at all voltages
Material system in this study

![Material system diagram]

Sol gel coating flow chart

![Sol gel coating flow chart]

Specimen Shape and Size

![Specimen shape and size diagram]
XRD patterns for the three HAp coated films.

Any differences in film property cannot be attributed to differences in the film chemistry and-or structure.
Uniform HAp coating

Effect of anodising & phosphating on the interfacial fracture energy

Anodising Voltage (V)
WHAT IF?
…you could have a fish tank which is self cleaning?

WHAT IF?
…you could see what was in the fridge without opening it?
HYDROPHILIC = WATER LOVING

When water hits a hydrophilic surface, it flattens and spreads out to form a thin sheet.

HYDROPHOBIC = WATER HATING

When water hits a hydrophobic surface, it beads.

WETTING & BEADING

<table>
<thead>
<tr>
<th>Poor wetting (beading)</th>
<th>Good wetting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle &gt; 90°</td>
<td>Contact angle &lt; 90°</td>
</tr>
</tbody>
</table>

Contact angles below 90° indicate good wetting, while contact angles above 90° indicate poor wetting (beading).
The leaves of Lotus plants have the unique ability to avoid getting dirty. They are coated with wax crystals around 1 nanometre in diameter and have a special rough surface. Droplets falling onto the leaves form beads and roll off taking dirt with them, meaning the leaves are self-cleaning. Sometimes referred to as "The Lotus Leaf Effect"
SELF CLEANING GLASS

Scientists have mimicked nature at the nanoscale to create glass surfaces that are 'self-cleaning' like the Lotus leaf.

SELF CLEANING GLASS

HOW DOES IT WORK?

Glass is coated with a layer of nanocrystalline titanium dioxide (TiO₂). The titanium dioxide reacts to the ultraviolet (UV) component of sunlight causing a gradual break down and loosening of dirt.

This is known as the 'photocatalytic' stage.
SELF CLEANING GLASS

HOW DOES IT WORK?

The reaction also causes the glass surface to become super hydrophilic. This forces water to spread across the surface like a sheet, rather than beading, thereby washing away the loosened debris on the surface of the glass as it falls.

This is the ‘hydrophilic’ stage.

Photocatalytic TiO₂ Nanoparticles

SO CAN A FISH TANK BE SELF-CLEANING?

Australian company Diamond Shell has made self cleaning aquarium glass called ‘Barracouta Glass’ based on the photocatalytic and hydrophilic process.
SELF CLEANING GLASS

HOW DOES IT WORK?

Another type of self cleaning glass uses hydrophobicity, not hydrophilicity.

This type of glass is given a coating which makes it super hydrophobic, meaning water forms beads and runs off the glass.

This type of glass is used indoors, such as in shower screens, where there is no sunlight to enable use of the other type of glass.

Optical nanocoatings

Thin films are used commercially in anti-reflection coatings, mirrors, and optical filters.

They can be engineered to control the amount of light reflected or transmitted at a surface for a given wavelength.

Takes advantage of thin film interference to selectively choose which wavelengths of light are allowed to transmit through the device.

Manufacture of coatings

- apply by physical vapour deposition (PVD)
- chemical vapour deposition (CVD)
- magnetron sputtering
- thermal evaporation

need for a vacuum chamber

multiple layers
Application areas

coatings on windows
spectacles and sun glasses
narrowband filters for optics
lenses and optical elements
decorative
electron conduction plus transmission
polarization control
dichroic beam splitters
cold mirrors (transmit IR, reflect visible)

Antireflective Coatings

Eliminates reflected light and maximizes transmitted light

A film is designed such that reflected light produces destructive interference and transmitted light produces constructive interference for a given wavelength of light.

- \( d_{\text{coating}} \) is a quarter-wavelength of the incident light and its refractive index is greater than the index of air and less than the index of glass.

\[
\frac{n_{\text{air}}}{n_{\text{coating}}} < \frac{n_{\text{coating}}}{n_{\text{glass}}}
\]

\[
d = \lambda / (4n_{\text{coating}})
\]
GLASS NANO-COATINGS

ANTI-REFLECTIVE GLASS

Type 1

Glass is coated with multiple layers of metal oxides such as TiO₂ which have a high refractive index, meaning light passes through them very quickly.

The thickness of the layers is related to the wavelength of light, resulting in destructive interference of light reflected off the surfaces, making the glass non-reflective.

Reflection and interference

Reflection and interference

Reflection and interference

Reflection and interference

If \( m = 1 \)

Destructive interference for

\[ d = \frac{\lambda}{4n} \]

“\( \frac{\lambda}{4} \) wavelength coating”
GLASS NANO-COATINGS

ANTI-REFLECTIVE GLASS

Type 2

Another method of producing anti-reflective glass is to coat it with a single layer of nanoporous SiO$_2$. The refractive index of the porous coating is between that of the glass surface and air, thereby reducing the reflectivity and increasing the transmission of light at the glass surface.

What about heat?

Cutting out infrared

Umisol installs Infrared Blocking window filters at Coca-Cola

Cost: €93k
Saving p.a.: €14/m$^2$/year
Area: 510 windows x 1.66m$^2$ = €11.9k

Oh Dear!

Reflect the heat (IR), right?

08 Nanocoatings and films/BBC News - 'Walkie-Talkie skyscraper melts Jaguar car parts.htm
One structure

Doing calculations

- e.g. OpenFilters, by S. Larouche
- www.polymtl.ca/larfis

SWITCHABLE GLASS

Switchable glass has applications in car sun roofs, office buildings, and residential apartments. Skydeck 88 in the Eureka Tower in Melbourne is the only observation deck in the world that can thrill you with ‘The Edge’ - a glass cube made of switchable glass, which projects 3 metres out from the building and suspended almost 300 metres above the ground, with you in it!
Nano-Particless in Coatings:

Challenges
- Dispersion and Dispersant Demand
- Rheology
- Functionalization
  - Application Specific?

Characterization
- Cost/Performance Balance

Health Effects
- Nanosafe2.org
- "Nanoscience and nanotechnologies: opportunities and uncertainties",