Multifunctional Protection of Material Surfaces
by Nano Textured Thin Films

Prof. Dr Eva Maria Moser

Outline

- Corrosion protection of metallic surfaces
  - Nano textured DLC layers
- Anti-fingerprint and germ inhibiting surfaces:
  - Photocatalytically active titania layers
- Nano-micro structuring of material surfaces
- Examples of applications

Lotus effect:
Transport of pollution

Smooth surface:
Gliding water drops

Structured surface:
Rolling water drops

www.botanik.uni-bonn.de et www.basf.de
Food Protection against Undesirable Interaction with Packaging

Environment: gases, vapour, germs, waste, information

Packaging: Plasticiser diethylhexyladipate (DEHA) or 2-ethylhexanacid (2-EHA)

Product: chem. and biol. contamination, taste, aroma, protection

10 of 11 Alu cans: Bisphenol A
Packaging: Plasticiser diethylhexyladipate (DEHA) or 2-ethylhexanacid (2-EHA)
Semicarbazide or epoxidised soja oil (ESBO)

Production of Thin Coatings using PVD and PE-MOCVD Processes at Ambient Temperatures

PVD: Reactive dc-sputtering of metallic particles at 10⁻² mbar
PE-MOCVD: Evaporation of metal containing precursor in plasma reactor at 10⁻² mbar

Upscaled plasma process: 30 cm
Production of titania coatings onto flat substrates at atmospheric pressure
Upscaled deposition of Thin Films

Linear microwave discharge and dc-magnetron sputtering discharge

Pilot R&D plasma web coater at EMPA

Sustainable Nano Texturing of DLC Layers:
- Durable encapsulation of metallic particles
- Tailoring of wettability

DLC matrix of 70 nm:
Diamond Like Carbon layer
Structure of the Plasma Polymer DLC (Diamond Like Carbon), a-C:H

Plasma polymer CH_x

Polyethylene (PE)

PET-film 12 µm, as received
Cluster size: 10 - 20 nm
RMS roughness: 0.8 nm

Plasma coating 76 nm on PET-film
Cluster size: 25 - 35 nm
RMS roughness: 2.0 nm

Topography of the PET surface
Sustainable Polymer-like DLC Layer as Diffusion Barrier

Coated PET / CPP O₂-Perm. 0% r.h. [ml/m²·dbar] O₂-Perm. 85% r.h. [ml/m²·dbar] H₂O-Permeability 90% r.h. [g/m²·d] Stretch failure [%]

PET: DC/RF /GHz
1.0 - 1.2 ± .2
PET: Web coater
0.8 - 2.1 ± .2

hydrophobe / PET
< 1.0 ± .2
< 0.8 ± .2
< 0.7 ± .2
< 0.8 ± .2
< 0.2 ± .2
< 0.2 ± .2
< 2.5 ± .2
< 4.7 ± .2

hydrophobe / CPP
40 ± .2
- 0.4 ± .2

Ref.: PET 12 μm
< 123.9 ± .3
< 93.0 ± .3
< 20.4 ± .3

Ref.: CPP 75 μm
1000 - 4000
- 4

Polymer-like diffusion barrier layer: Highly cross-linked and inherently flexible

Direct Contact of DLC with Food: No Interaction, no Migration

CPP/PET film plasma treated 3 wt% acetic acid (2h@90°C, 10d@40°C) 95 vol% ethanol (4h@60°C, 10d@40°C) isooctane (2h@60°C, 2d@20°C)

Ref: CPP/PET
< 1 mg/dm²
< 1 mg/dm²
< 4 mg/dm²

wincoat CPP
< 1 mg/dm²
< 1 mg/dm²
< 1 mg/dm²

phil /CPP
< 1 mg/dm²
< 1 mg/dm²
< 1 mg/dm²

phil /CPP
< 1 mg/dm²
< 1 mg/dm²
< 1 mg/dm²

phob /CPP
< 1 mg/dm²
< 1 mg/dm²
< 1 mg/dm²

Global Migration according to EU guidelines 2002/72/EG (detection limit: <1 mg/dm², tolerance limit: <10 mg/dm²)

ESR and fluorescence spectroscopy and polymer-like DLC food for germs (10²⁵ Spins/cm³, g-value: 2.0023 (11 Gauss):

→ no free radicals in DLC

Welding-peeling properties:

Hydrophobic DLC

Hydrophilic DLC
**Actual Project: DLC Layers and Active Corrosion Protection**

- Micro defect
- Adjustable wettability
- Plasma layer: 50 nm
- Metallic nano contacts (< 10 mg/m²)
- Anodic corrosion protection
- Reaction: \(2 \text{Me} + \text{O}_2 \rightarrow 2 \text{MeO}\)

**DLC: Diamond Like Carbon Plasma thin film (50 nm):**

- Highly crosslinked plasma polymer as durable matrix
- Metallic nano contacts: ∅ 5 nm
- Metallic substrate: Aluminium, steel,
Excellent Corrosion Protection by Metallic Nano Contacts

Corrosion tests performed at EMPA, Dr Markus Faller:
- Pore test according to Verpackungsrundschau 11/1976
- Determination of electrochemical parameters (impedance-spectroscopy)
- Salt spray test (DIN EN ISO 9227 NSS): Storage for 3 days at 35 °C
- Condensed water test climate (DIN EN ISO 6270-2 AHT: 7 days with 2 cycles at 100% rel. humidity (8 h at 40°C and 16 h at 23°C)

Pure DLC layer deposited onto Al-foil with poor protection; many pores are visible

Metal-doped DLC layer onto Al-foil with good protection; without pores

Al-foils after 27 days condensed water test:
left: Hydrophobic, metal-doped DLC
right: Chemically cleaned Al-foil, without coating

Corrosion tests performed at EMPA, Dr Markus Faller:
- Pore test according to Verpackungsrundschau 11/1976
- Determination of electrochemical parameters (impedance-spectroscopy)
- Salt spray test (DIN EN ISO 9227 NSS): Storage for 3 days at 35 °C
- Condensed water test climate (DIN EN ISO 6270-2 AHT: 7 days with 2 cycles at 100% rel. humidity (8 h at 40°C and 16 h at 23°C)
Corrosion protection of metallic surfaces

Anti-fingerprint and germ inhibiting surfaces:
- Photocatalytically active titania layers
- Nano-micro structuring of material surfaces
- Examples of applications

AFM images of E. coli on the TiO$_2$ surface:

Benefits of Photo-induced Titaniumdioxid (Titania, TiO$_2$)

- bioactivity
- biocompatibility
- disinfection
- detoxification
- decontamination
- selective diffusion barrier
- UV-protection
- anti-fogging
- active self-cleaning
Tests for Photo-induced Catalytic Activity at Humid Conditions

Activation of titania layers at 365 nm (UV light)*

Bleaching of a 0.05 mmol solution of methylene blue by titania

Activation of titania layers at 428 nm (visible blue light)

Activation of titania under visible light at 625 nm

*CIF = 1.0 corresponds to bleaching of 1.7 mmol/m² d of methylene blue by a PVD-TiO₂ ref. layer (50 nm, on a glass slide) according to ISO 10678:2010

Photocatalytic Reactions at Titania Surfaces

Photocatalyst reaction: TiO₂ → electron + hole

O₂ + e⁻ → O₂⁻

H₂O + h⁺ → OH⁻

Redox potential: 3.2 eV

Organic compound + Mineral acid → Titania TiO₂

hν ≥ E₁
Crystallinity of PVD Titania Layers

HRTEM-image of the 192 nm sputtered pure PVD TiO$_2$ layer, ref. A:
Crystalline domains of anatase (110) in amorphous matrix

Destruction of Stearic Acid: Fingerprints and Germs

<table>
<thead>
<tr>
<th>Concentration of stearic acid [mol/l]</th>
<th>Time of irradiation [h, @ 365 nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>0.9</td>
<td>5</td>
</tr>
<tr>
<td>0.6</td>
<td>10</td>
</tr>
<tr>
<td>0.3</td>
<td>15</td>
</tr>
<tr>
<td>0.1</td>
<td>20</td>
</tr>
<tr>
<td>0</td>
<td>25</td>
</tr>
</tbody>
</table>

Roughness (nm): 14.9, 7.2, 4.7, 5.4, 3.5

AFM-Images: 200 nm thick PVD-TiO$_2$
Inactivation of the Viability of Bacteria and their Destruction

* The destruction of Escherichia coli cells as well as the released endotoxin has been investigated using a modified form of the ISO/DIN 22196.

RODAC plates contaminated with E. coli → 428 nm for 16 h
- Red colour: No growth of bacteria (negative)
- Yellow colour: Colonies of bacteria (positive)

Germ-Inhibiting Features of Titania

Antibacterial activity under visible light

- Tests according to ISO 22196: Growth reduction efficacy (log cfu)

<table>
<thead>
<tr>
<th>Surface Type</th>
<th>E. coli</th>
<th>S. aureus</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVD TiO₂-b 13.8.3.0047-1</td>
<td>0.75 (slight)</td>
<td>0.62 (slight)</td>
</tr>
<tr>
<td>(300 nm, CIF = 7.0/1.7, RMS = 5.2 nm, hydrophilic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PE-MOCVD TiO₂-c 13.8.3.0047-2</td>
<td>2.35 (significant)</td>
<td>2.46 (significant)</td>
</tr>
<tr>
<td>(200 nm, CIF = 7.3/3.1, RMS = 1.0 nm, hydrophobic)</td>
<td>E. coli do not stick well to the titania surface and can be removed easily</td>
<td></td>
</tr>
<tr>
<td>PVD TiO₂ black 13.8.3.0047-3</td>
<td>&gt; 5.52 (strong)</td>
<td>&gt; 3.68 (strong)</td>
</tr>
<tr>
<td>(1.4 µm, CIF = 10.1/1.3, RMS = 5.0 nm, hydrophilic)</td>
<td>20 of 1 mio germs</td>
<td></td>
</tr>
</tbody>
</table>

*Tests were performed according to ISO 22196: Sterilisation if <1 of 1 mio germs after 24 hours
Nano Hardness of Titania Monolayers

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PVD titania invisible 2012</td>
<td>2.8</td>
<td>86.2</td>
<td>265</td>
</tr>
<tr>
<td>PVD titania black 2012</td>
<td>3.4</td>
<td>29.5</td>
<td>321</td>
</tr>
<tr>
<td>PE-MOCVD titania invisible 2012</td>
<td>1.5</td>
<td>42.4</td>
<td>142</td>
</tr>
</tbody>
</table>

Nano hardness of titania layers has been improved up to > 15 GPa!

Hardness testing results are en route!

Tests have been performed according to ISO 14577 at CSEM Neuchâtel

- VH = 0.0945 MPa

Corrosion protection of metallic surfaces
- Nano textured DLC layers

Anti-fingerprint and germ inhibiting surfaces:
- Photocatalytically active titania layers

Nano-micro structuring of material surfaces

Examples of applications

- Anti-fogging effect
- Easy-to-clean effect

Adhesion Improvement and Anti-fogging Effect
Micro Structuring of Polymeric Surfaces at PSI

PSI: HEX03 technical data:
- Max. Press force 200 kN
- Permissible thickness of the emboss sandwich max. 20 mm
- Vacuum / chamber <1 mbar
- Max. embossing area 120 mm
- Max. temperature 320° C

PSI: Specac technical data:
- Max. Press force 40 kN
- Permissible thickness of the emboss sandwich max. 80 mm
- Vacuum / chamber none
- Max. embossing area 100 mm
- Max. temperature 280° C

The hot embossed CPP film is lifted from the structured master wafer.

Sustainable Nano – Micro Structures on Polyolephins

Hydrophilic surfaces
- Sustainable (no interaction)
- Super-polar, anti-fogging
- Stretchable
- Chemically resistant
- Printable, good adhesion
- Weldable

Hydrophobic surfaces
- Sustainable (no fluor)
- Super-hydrophobic
- Stretchable
- Water repellent, „LOTUS”
- Chemically resistant
- Weldable

Controlled Condensation of Water due to Plasma Treatment of Polymeric Surfaces

→ “Easy-to-clean” surfaces
→ Complete emptying of content (packaging)

Untreated surface: Cast-polypropylene: 97°

wincoat® treated surface: 6°
Anti-fogging effect

wincoat® treated surface: 146°
Water repellency

The surfaces “easy-to-clean” are distinguished by their surface energies and the micro-nano structures of the surfaces. ($\Theta =$ water contact angle)

<table>
<thead>
<tr>
<th>Active, interacting surfaces</th>
<th>Passive, not interacting surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ and micro structure</td>
<td>super-hydrophobic: $\Theta &gt; 120^\circ$</td>
</tr>
<tr>
<td>TiO$_2$ flat or with micro structure</td>
<td>hydrophobic: $80^\circ &lt; \Theta &lt; 120^\circ$</td>
</tr>
<tr>
<td>TiO$_2$ smooth or nano structure</td>
<td>hydrophilic: $10^\circ &lt; \Theta &lt; 80^\circ$</td>
</tr>
<tr>
<td>TiO$_2$ smooth or nano structure</td>
<td>super-hydrophilic: $\Theta &lt; 10^\circ$</td>
</tr>
</tbody>
</table>

The surfaces “easy-to-clean” are distinguished by their surface energies and the micro-nano structures of the surfaces. ($\Theta =$ water contact angle)
Functionalisation
Structuring
Doping
Tailored manipulation at material surfaces using plasma technology
The human tendency to regard little things as important has produced very many great things.

Georg Christoph Lichtenberg (1742-1799)

R&D projects Nr. 7960.2, 10778.1, 10747.2 PFNM-NM have been funded by CTI

Several patents are hold for the presented thin films and deposition processes.

Meri – Grazie – Danke - Thank you

Dr Eva Maria Moser
HESSO hepia
eva.moser@sunrise.ch
+41 76 321 21 59

Die Neigung des Menschen, kleine Dinge wichtig zu nehmen, hat sehr viel Grosses hervorgebracht.

The human tendency to regard little things as important has produced very many great things.

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