VACUUM THIN FILM COATING ON PLASTIC SURFACES
MATERIALS, TECHNOLOGIES, APPLICATIONS

EuroNanoForum 2019, 13th June 2019, Bucharest, Romania

John Fahlteich
Cindy Steiner
Michiel Top
Matthias Fahland

Source: HIGHTEX GmbH
My Institute Fraunhofer FEP – Facts and Figures

- Employees: 174
- Total budget: 26.8 M€
- Industry returns: 11.5 M€
- Public funding: 7.82 M€
- Investments: 1.6 M€

(March 2019)

Director
- Prof. Dr. Volker Kirchhoff
Vacuum coated thin film nanomaterials in our daily life

- Optical filters (e.g. solar control films) for car windows
- Holographic images on banknotes
- Flexible circuit boards
- Food packaging
- Cell phone displays
- Architectural glass

Sources:
- Wikipedia
- Apple.com
What surface properties are we interested in?

- homogeneity, uniformity
- low defect rate, stability, low stress etc.
- maximized surface area for sensors
- (bio)polymer webs
- fabric and fibres
- ultra-thin glass
- polymer membranes
- thin metal foils
Vacuum Roll-to-Roll Coating and Surface Modification

- semi-continuous process
  - coating width up to 4.5 m
  - substrate lengths up to 100 km
  - process speed up to 20 m/s
Industry suited plasma processes for thin film nanomaterial deposition

**High-rate evaporation**
- Substrate
- Hollow cathode
- Neutral, excited particles
- Plasma activation

**Magnetron Sputtering**
- 
  - 
  - 
  - 
- 
  - 
  - 

**High-rate PECVD**
- Vacuum vessel
- Ar + O₂
- HMDSO inlet
- Power supply for hollow cathode

- Approx. 6000 nm·m/min highest productivity, low cost
- Approx. 100 nm·m/min wide material selection
- Approx. 100 … 1000 nm·m/min in-situ layer composition adjustment from SiO₂ to [Si(CH₃)₂-O]ₙ with HMDSO
Lab-2-Fab Facilities for Vacuum Roll-to-Roll Coating

lab-scale equipment (TRL 3 – 5)

- LB9
- labFlex® 200

pilot-scale equipment (TRL 5 – 7)

- coFlex® 600
- novoFlex® 600

process drum

dual magnetron

single magnetron
Application Example #1: Gas Permeation Barriers

- Water vapor
- Oxygen

Polymer web
- Permeation barrier
- Transparent electrode

Low defect single layers
Multi-layer stacks

Flexible solar cell
Sensitive food and drink
Flexible display

Sony 2009

500 nm
Gas Barrier Performance by Materials and Thickness

- ZTO
- SiO₂
- TiO₂

![Graph showing water vapor transmission rate at 38°C / 90% r.h. vs. layer thickness [nm]]

- Al₂O₃ - HAD on 12 µm PET
- SiCₓOᵧ - PECVD on PET
- TiO₂ on PET
- SiOₓNᵧ on PC
- SiO₂ on PC
- Al₂O₃ on PC
- Si₃N₄ on PC
- ZTO on PCS PET

Limit of detection
Application Example #3: Reactive plasma surface nano-structuring

- seed layer deposition
  - thin SiO₂ (< 10 nm)
- process drum
- top-coat deposition
  - thin SiO₂ layer (< 10 nm)
- oxygen plasma etching
- reactive oxygen plasma treatment
- single run roll-to-roll process
- 0.5 … 2 m/min run speed

PET surface before plasma etching
PET surface after plasma etching
Properties of nanostructured surfaces (Optical Anti-Reflection)

- broadband anti-reflective effect through “simulated” refractive index gradient
- maximum in transmittance:
  - untreated PET 89 %
  - single side treatment 93.7 %
  - double side treatment 98.5 %
Surface Energy | Wetting Behavior of Water

ETFE film surface $\Rightarrow 95^\circ$

nanostructured ETFE surface with 10 nm TiO$_2$ top coat $\Rightarrow 110^\circ$

nanostructured ETFE surface 10 nm SiO$_2$ top coat $\Rightarrow 30^\circ$

wings with anti-ice edge-protection polymers
Application Example #3: Flexible Organic Light Emitting Diodes

- **300 mm** web width
- additive surface structuring (flexo-printing) and substractive laser surface structuring
- thermal evaporation of organic semiconductors
- OLED layer thickness \( \leq 200 \) nm
Latest Research Topics: Thin-Film Nano-materials in Circular Economy of Plastics

- Novel flexible surfaces
- Nano-functionalisation
- Recyclable
- Degradable

Products:
- Degradable and recyclable packaging
- Degradable electronics
- Bio filter membranes
- Degradable security labels

Materials:
- BOPP
- PET
- HDPE
- PLA
- PBAT
- Paper
- PHBH

images provided by: I3Membrane, P&G, Capri-Sun, Hueck Folien
An Example: Towards Sustainable Packaging

- 13 µm PET
- 4 µm printing
- 7 µm PE
- 3 µm EVA
- 5 µm EVOH
- 3 µm EVA
- 15 µm PE
- 9 µm PP

- 15 µm polymer A
- 4 µm printed layer (biodegradable)
- 3 µm lamination adhesive
- 20 nm vacuum coated gas barrier
- 15 µm polymer A
Presented projects have received funding from the European Union with the 7th Framework and Horizon 2020 research and innovation programmes.

EU Horizon 2020 – „PI-SCALE“ GA no. 688093
EU FP7 SMARTONICS: GA no. 310229
EU Horizon 2020 – „Smart2Go“: GA no: 825143
Fraunhofer FEP – core competencies

- Electron Beam Technologies
- Plasma-Activated Large Area and Precision Coating
- Organic Electronics
- Roll-to-Roll Technology
- Technological Key Components
- IC Design
Application Example #2: Adjust optical properties with thin film nano-laminates

9 layers
30 ... 100 nm each

PET substrate

SiO₂ (n = 1.47)

SiO₂ (n = 2.45)

TiO₂

SiO₂ sputtered

SiO₂ made with PECVD

Reflectance [%]

0  20  40  60  80  100

900 1200 1500 1800 2100

sputtered SiO₂

PECVD SiO₂
Gas Permability

- HAD-AlO\textsubscript{x} 1
- Single layer sputtering 0.0005
- High-rate PECVD barrier layers 0.05
- Multilayer: sputtering + wet coating 0.0001
- Multilayer: one-pass-process 0.001

Wide material selection
Mechanical performance
• Substrate independence
• Robustness

High-performance functional films

R&D
Pilot
Industrial

WVTR [g/m\textsuperscript{2}d] @ 38°C / 90% r.h.
### Materials

<table>
<thead>
<tr>
<th>Group</th>
<th>Period</th>
<th>Element</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>IA</td>
<td>1</td>
<td>Hydrogen</td>
<td>H</td>
</tr>
<tr>
<td>IIA</td>
<td>2</td>
<td>Lithium</td>
<td>Li</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Sodium</td>
<td>Na</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Magnesium</td>
<td>Mg</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>Aluminum</td>
<td>Al</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Silicon</td>
<td>Si</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>Phosphorus</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>Sulfur</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>Chlorine</td>
<td>Cl</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>Argon</td>
<td>Ar</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>Potassium</td>
<td>K</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>Calcium</td>
<td>Ca</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>Scandium</td>
<td>Sc</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>Titanium</td>
<td>Ti</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>Vanadium</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>Chromium</td>
<td>Cr</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>Manganese</td>
<td>Mn</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>Iron</td>
<td>Fe</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>Nickel</td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>Copper</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>Zinc</td>
<td>Zn</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>Gallium</td>
<td>Ga</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>Germanium</td>
<td>Ge</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>Arsenic</td>
<td>As</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>Selenium</td>
<td>Se</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>Bromine</td>
<td>Br</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>Krypton</td>
<td>Kr</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>Rubidium</td>
<td>Rb</td>
</tr>
<tr>
<td></td>
<td>29</td>
<td>Strontium</td>
<td>Sr</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>Yttrium</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>31</td>
<td>Zirconium</td>
<td>Zr</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>Niobium</td>
<td>Nb</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>Molybdenum</td>
<td>Mo</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>Technetium</td>
<td>Tc</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>Ruthenium</td>
<td>Ru</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>Rhodium</td>
<td>Rh</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>Palladium</td>
<td>Pd</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>Silver</td>
<td>Ag</td>
</tr>
<tr>
<td></td>
<td>39</td>
<td>Cadmium</td>
<td>Cd</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>Indium</td>
<td>In</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>Tin</td>
<td>Sn</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>Antimony</td>
<td>Sb</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>Tellurium</td>
<td>Te</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>Iodine</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>Xenon</td>
<td>Xe</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>Rhenium</td>
<td>Re</td>
</tr>
<tr>
<td></td>
<td>47</td>
<td>Osmium</td>
<td>Os</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>Iridium</td>
<td>Ir</td>
</tr>
<tr>
<td></td>
<td>49</td>
<td>Platinum</td>
<td>Pt</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>Mercury</td>
<td>Hg</td>
</tr>
<tr>
<td></td>
<td>51</td>
<td>Thallium</td>
<td>Th</td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>Lead</td>
<td>Pb</td>
</tr>
<tr>
<td></td>
<td>53</td>
<td>Bismuth</td>
<td>Bi</td>
</tr>
<tr>
<td></td>
<td>54</td>
<td>Polonium</td>
<td>Po</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>Astatine</td>
<td>At</td>
</tr>
<tr>
<td></td>
<td>56</td>
<td>Radium</td>
<td>Ra</td>
</tr>
<tr>
<td></td>
<td>57</td>
<td>Actinium</td>
<td>Ac</td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>Thorium</td>
<td>Th</td>
</tr>
<tr>
<td></td>
<td>59</td>
<td>Protactinium</td>
<td>Pa</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>Uranium</td>
<td>U</td>
</tr>
<tr>
<td></td>
<td>61</td>
<td>Neptunium</td>
<td>Np</td>
</tr>
<tr>
<td></td>
<td>62</td>
<td>Plutonium</td>
<td>Pu</td>
</tr>
<tr>
<td></td>
<td>63</td>
<td>Americium</td>
<td>Am</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>Curium</td>
<td>Cm</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>Berkelium</td>
<td>Bk</td>
</tr>
<tr>
<td></td>
<td>66</td>
<td>Californium</td>
<td>Cf</td>
</tr>
<tr>
<td></td>
<td>67</td>
<td>Einsteinium</td>
<td>Es</td>
</tr>
<tr>
<td></td>
<td>68</td>
<td>Fermium</td>
<td>Fm</td>
</tr>
<tr>
<td></td>
<td>69</td>
<td>Mendelevium</td>
<td>Md</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>Nobelium</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>Lawrencium</td>
<td>Lr</td>
</tr>
</tbody>
</table>

*process or reactive gas*

*coating material*