Choice of a Suitable Coating Method

- Requirements to the coating material (chemical composition, purity, crystallinity, materials properties)
- Thermal stability of the substrate material
- Adhesion of the coating under certain conditions (temperature, humidity, sunlight, etc.)
- Throughput
- Costs for investments, running costs
- Environmental aspects
### Comparison Sol-Gel Processing / CVD

<table>
<thead>
<tr>
<th>Sol-Gel Processing</th>
<th>CVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>• larger variety of precursors</td>
<td>• non-oxidic materials can also be deposited</td>
</tr>
<tr>
<td>• many processing options</td>
<td>• no shrinkage during annealing</td>
</tr>
<tr>
<td>• preparation of inorganic-organic hybrid materials possible</td>
<td>• epitactic growth and selective deposition possible</td>
</tr>
<tr>
<td>• generation of complex micro- and nanostructures (incl. porosity) possible</td>
<td>• better control of film growth</td>
</tr>
<tr>
<td>• low thermal stress of the substrat</td>
<td>• simple coating techniques</td>
</tr>
</tbody>
</table>

### Preparation of Lead Zirconate Titanate (PZT) – A Comparison

**Solid state reaction**

\[
PbO + TiO_2 + ZrO_2 \quad \text{750 - 1100 °C several h}
\]

**Sol-gel processing**

\[
Pb(OAc)_2 \cdot 3 \text{H}_2\text{O} + \text{Ti(OPr)}_4 + \text{Zr(OPr)}_4 + \text{acetylacetone} \quad \text{700 °C / 2 min}
\]

\[
Pb(Zr_{0.53}Ti_{0.47})O_3
\]
**Sol-Gel Processing Scheme**

- **Sol**
- **Sol Evaporation**
- **Gel**
- **Solvent Evaporation**
- **Supercritical Extraction**
- **Xerogel**
- **Aerogel**

**Materials costs no big issue**

**Shrinkage can be controlled (< ca. 5 μm)**

---

**Application of Sol-Gel Coatings**

- **Precursors**
  - Metal Alkoxides
  - Metal Salts
  - + water (ev. catalyst or additives)
  - - alcohol

- **Hydrolysis Condensation**

- **Coating**

- **Wet film**

- **Drying, Hardening (thermal or uv)**

- **Coating**

---
Coating materials
- inorganic (ceramic materials)
- inorganic-organic hybrid materials
- nanoparticles

Variation of the film properties
- Chemical composition
- Porosity
- Micro-/Nanostructure (texture)

Coating techniques
- Dipping
- Spraying
- Doctor blading
- Painting
- Rolling
- Flow coating

Curing methods
- Thermal
- Photochemical

Which materials can be coated
- Glasses
- Ceramics
- Metals
- Polymers

Application of the coating solution
- Spreading of the film
- Solvent evaporation

Spray coating
Spin coating
Coating Techniques

Dip coating

Flow coating

Industrial dip coating plant
(up to 1.15 x 1.60 m²)
(Prinz Optics GmbH)

Tailoring of Sol-Gel Coatings

An example for a deliberate tailoring of the materials properties

\[(\text{RO})_3\text{Si}\] Formation of a dual inorganic-organic network

\[(\text{Bu'O})_3\text{Al}\] Hardness

\[(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_3\] Reduction of brittleness

\[\downarrow\] Addition of solvents (alcohol) and lacquer additives

Sol

\[\downarrow\] 1) Conventional coating techniques

2) Curing (130°C, 45 min)

Scratch-resistant and corrosion-protecting coating for brass
**Crackability**
- stresses develop during drying due to shrinkage
- thermal expansion mismatches
- plastic deformation of substrate

**Thickness limits**
(Thick films required for thermal barriers, and abrasion and wear protection)

**Reasons:**
Cracks develop during drying more likely in thicker films

**Possible solutions:**
- multilayer deposition
- use of fillers to reduce shrinkage
Scratch-resistant coatings for polycarbonate lenses

Most successful material for optical lenses: CR39® (PPG Industries).

$n_0$ 1.498, Abbé number 59, density 1.31 g/cm³, luminous transmittance 91%.

Scratch-resistant coating:

1. Sol-gel processing of Si(OMe)$_4$, Ti(OEt)$_4$ and (RO)$_3$Si

2. Spin coating on CR39 lenses

3. Thermal curing at 110°C for several h

High scratch and abrasion resistance due to the formation of titanium oxo clusters and high degree of organic crosslinking (polymerization of the epoxy groups)

Subsequent improvements of scratch resistant coatings on polycarbonate

by replacement of Ti(OEt)$_4$ for Zr(OR)$_4$ or Al(OR)$_3$, or by addition of boehmite (AlOOH) nanoparticles

Increase of haze during abrasive treatment (Tumble test): × noncoated CR39, + titanium containing coating, ○ coating containing AlOOH nanoparticles.
Surface Protection

UV curable hard coatings based on

\[
\text{Si} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{Si} \quad \text{O} 
\]

⇒ high throughput and short processing times

Increase of \(n_d\) (1.49 to 1.52) by addition of 12 mol% methacrylate-substituted Zr(OPr)\(_4\)

magnifying PMMA lenses with scratch-resistant sol-gel coating

scratch-resistant and easy-to-clean coating for PMMA earmoulds

Bressanone Sept. 2006 Coatings 15

Surface Protection

Optical fibers coatings for protection against scratching

Tailoring the organic spacer between the inorganic species allows tailoring both the refractive index and Young’s modulus in a wide range

<table>
<thead>
<tr>
<th>Refractive index</th>
<th>Young’s modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.56 – 1.60</td>
<td>0 – 20 MPa</td>
</tr>
<tr>
<td>1.52</td>
<td>1400 MPa</td>
</tr>
</tbody>
</table>

Bressanone Sept. 2006 Coatings 16
Thin (≤ 4 μm) inorganic-organic hybrid coating:

- natural, optical and haptic properties are preserved
- high hydrophobicity
- high water vapour permeability and water vapor up-take
- very good scratch resistancy and improved wear properties
- good temperature- and light-proof

Protection of sensitive surfaces

Coatings with optical properties
- Decorative (colored) coatings
- Photochromic coatings
- Interference layers
- Antireflective coatings
- Reflective coatings
- Optoelectronic components
- Photocatalysis

Coatings with barrier properties
- Modification of surface polarity
- Electroactive layers
- Sensor layers
Coatings with Optical Properties

Decorative coatings

\[
\text{Si(OMe)}_3 + \text{Ti(OEt)}_4 + (\text{EtO})_3\text{Si-CH=CH}_2 + (\text{RO})_3\text{Si-O} \rightarrow 
\]

addition of **organic dye**

UV and/or thermal curing

- wide variety of colours
- improved mechanical properties of the glass
- as easy to recycle as uncoloured glass
- dishwasher-safe

Research Laboratory for Packaging, Japan

Bressanone Sept. 2006 Coatings 19

---

Coatings with Optical Properties

Decorative coatings on glass

Bressanone Sept. 2006 Coatings 20
Wavelength-selective absorption films

to raise the color purity of luminiscence and improve contrast in high-performance cathode ray glass tubes

Rhodamine B is soluble in water and alcohols
⇒ dye seeps out when film is wiped
⇒ chemical bonding of the dye to the SiO2 network

---

**Photochromism:** fast for optical switches, for eye protection, privacy shields
slow for optical data storage, energy conserving coatings, etc...

**Example:** Spirooxazine derivative

Embedding in sol-gel coatings:
For sufficient photochromism: dye concentration > 25 wt% → mechanical stability of sol-gel film is deteriorated.

Grafting of the dye to the sol-gel matrix → higher chromophore concentrations can be achieved without affecting the mechanical integrity of the sol-gel matrix
Antireflexion Layers on Glass

Requirements

- improved transmission
- high band width
- low angle dependence
  - colorless residual reflexion
- high mechanical stability

Materials and microstructures

- gradient layers (index)
- interference layers (\(\lambda/4\) single layers)
- interference multiple layers (\(\text{SiO}_2\)-\(\text{TiO}_2\))

Anwendungen

Architectural glass, displays, solar cells, optical components

Bressanone Sept. 2006 | Coatings | 23
Porous anti-reflection sol-gel coatings on glass

No reflexions for a given $\lambda$, if optical thickness $= \lambda/4$

$n_{\text{film}} = \sqrt{n_0 \cdot n_{\text{glass}}} \approx 1.22$

Coatings with Optical Properties

Antireflective coating: Structuring by deposition of small particles

Si(OR)$_4$ (TMOS, TEOS) Hydrolysis/Condensation

EtOH, MeOH

H$_2$O

NH$_3$

Stöber particles

Nanoporous SiO$_2$ layer

Thermal toughening (400-550°C ⇒ wipe-proof, weather-resistance porous SiO$_2$ layer

Bressanone Sept. 2006 Coatings 25

Bressanone Sept. 2006 Coatings 26
Interference Filter

Alternating SiO₂ and TiO₂ layers

Increasing withdrawal speed during dip coating:
- increasing film thickness (60 nm → 120 nm)
- change of optical properties
- color effect filter

Structuring by embossing (gradient layers)

Antireflective coating
1. Polysiloxane chains from

2. Embossing
3. UV curing = fixing the imprinted structure

Optoelectronic components
Reflective coatings

ZrO\textsubscript{2} / PVP

\ldots

210 nm SiO\textsubscript{2}

ZrO\textsubscript{2} / PVP

210 nm SiO\textsubscript{2}

substrate

15 nm ZrO\textsubscript{2} particles (from ZrOCl\textsubscript{2}) in PVP binder (15 wt%), \( n_\text{o} = 1.70 \)

SiO\textsubscript{2} from Si(OEt)\textsubscript{4}, \( n_\text{o} = 1.22 \)

20 layers SiO\textsubscript{2} / ZrO\textsubscript{2}

a: theoretical, b: experimental

Optical Waveguides

Hybrid materials from Ph\textsubscript{2}Si(OH)\textsubscript{2} and CH\textsubscript{2}=C(\text{Me})OC(O)(\text{CH}_2)\textsubscript{3}Si(\text{OMe})\textsubscript{3}

photopatternable core layer (high refractive index)

buffer layer (lower refractive index)

cladding (lower refractive index)
**TiO₂ photocatalysis**

- UV irradiation (λ < 388 nm)
  - Promotes degradation of organic compounds
  - Alters the polarity of the surface ("photoinduced super-hydrophilicity")

Creation of porosity (high surface area) by embossing or by deposition of particles.

**Coatings with Optical Properties**

**Anti-fogging**

A TiO₂-coated surface is rendered more hydrophilic by UV irradiation (right).

**Self-cleaning**

Bressanone Sept. 2006 Coatings 31
Protection of sensitive surfaces
Coatings with optical properties
Coatings with barrier properties
   Corrosion protection (water and oxygen barriers)
   Barrier against diffusion of organic compounds
Modification of surface polarity
Electroactive layers
Sensor layers

Uncoated Al pigments
After sol-gel hybrid coating

Immediate reaction
2Al + 6H₂O → 2Al(OH)₃ + 3H₂

Neutral water test: <1 ml H₂ from 3g Al in 3 days
Boiling test (time to react 50% of the Al in boiling water): 13h
Not stable at pH 9
Coatings on Metals

- Corrosion protection
- Abrasion resistance
- Adhesion promotion for paints

Replacement of conversion coatings (especially chromating)

AIMg1 alloy

Top: wet coating system (poxy primer and polyurethane top layer) after 1000 h ESS test.

Bottom: sol-gel inorganic-organic hybrid coating
**Corrosion protection of silver reflector in laser cavities**

- Protection against oxidation to preserve the high reflectivity
- Protection against mechanical and chemical attack during handling, cleaning or weathering

10-50 nm dense, hydrophobic or hydrophilic films from Si(OEt)₄ / RSi(OR)₃ at pH 2. \( n_D 1.445-1.449 \)

---

**Passivation layers in electronic devices**

1. One or two silanes with epoxy and methacrylate groups → adhesion to polymeric substrates, curing at low temperatures or by UV.
2. Tri- or tetraethoxysilane for high inorganic crosslinking → reduction of water vapor permeation, adhesion to metallic substrates.
3. Diorganosilane (e.g. \( \text{Ph}_2\text{Si(OH)}_2 \)) → modification of Young's modulus, improvement of dielectric properties, influence on hydrophobicity and solubility of water in the material.
Barrier Coatings

High- and ultra-barrier coatings

State-of-the-art with ORMOCER® coatings

Requirements

- Flexible OLEDs
- Organic solar cells
- Encapsulation of solar cells
- Flexible LCDs
- Food packaging foils
- Packaging of technical products

Barrier properties

- Oxygen permeability \( \text{cm}^3/\text{m}^2\text{dbar} \)
- Water vapor permeability \( \text{g/m}^2\text{d} \)

Barrier Coatings

Barrier layers on plastics

<table>
<thead>
<tr>
<th>Type 1</th>
<th>Type 2</th>
<th>Type 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (\text{RO})_3\text{Si} )</td>
<td>( \text{Zr(OPr)}_4 )</td>
<td>( \text{Al(OtBu)}_3 )</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{C(Me)}\text{COOH} )</td>
<td>( \text{N(CH}_2\text{CH}_2\text{OH})_3 )</td>
<td>( \text{(MeO)}_3\text{Si(CH}_2\text{)}_2\text{NMMe}_3^+\text{Cl}^- )</td>
</tr>
<tr>
<td>( \text{a} ), ( \text{b} )</td>
<td>( \text{a} ), ( \text{b} ), ( \text{c} )</td>
<td>( \text{a} )</td>
</tr>
<tr>
<td>4, 4</td>
<td>4, 7, 3, 2</td>
<td>2</td>
</tr>
<tr>
<td>1, 1</td>
<td>1, 3, 2, 1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1, 3</td>
<td>1</td>
</tr>
</tbody>
</table>
Barrier layers on plastics

Barrier properties of the barrier systems produced by roll-to-roll processes (OR: ORMOCER®, OTR = Oxygen Transmission Rate, WTR = Water Vapor Transmission Rate)

10 µm

PET / SiOx / hybrid polymer / PET

Hybrid polymer on SiOx-coated foils for food packaging

Oxygen permeability

Water vapor permeability

Bressanone Sept. 2006 Coatings 41

Bressanone Sept. 2006 Coatings 42
Barrier Coatings

Hybrid polymer on SiO₂-coated foils for food packaging

Flexible polymer barrier films for the encapsulation of solar cells

Encapsulation system for solar modules:
- a) the front side
- b) the rear side of the solar cell
Protection of sensitive surfaces
Coatings with optical properties
Coatings with barrier properties

Modification of surface polarity
Antigrafiti / antisoiling coatings
Hydrophilic / hydrophobic coatings

Electroactive layers
Sensor layers

Wetting of inorganic-organic hybrid coatings of varying polarity by water droplets

```
\gamma_{LV} \cdot \cos(\theta) = \gamma_{SV} \cdot \gamma_{LV}
```

“superhydrophobic”: $\theta > 150^\circ$; “superhydrophilic”: $\theta = 0^\circ$
While alkyl chains provide hydrophobicity, fluoroalkyl chains also provide oleophobicity.

Examples for fluorinated silanes:

\[(\text{RO})_3\text{Si}\left(CH_2\left(CH_2\left(CH_2\right)\left(CH_3\right)\left(CH_2\right)\text{O}\right)\text{Si}(\text{RO})_3\right)\]

Superhydrophobicity: + nanostructured surface

(Bressanone Sept. 2006 Coatings 47)

**Modification of Surface Polarity**

Superhydrophobic Coatings:

- Gel from Si(OMe)₄
- Apply 10 PSI pressure and allow to gel
- Remove the mold
- Anneal at 1100 °C
- Hydrophobization by a monolayer of Cl₃SiCH₂CH₂(CF₂)₉CF₃

Contact angle before: 118°, after: 170°

G. M. Whitesides et al., 1998

J. Bico et al., 1999

(Bressanone Sept. 2006 Coatings 48)
Modification of Surface Polarity

Hydrophobic or Oleophobic Coatings

- less adhesion of dust particles
- easier to clean
- anti-wetting behavior of paints = anti-graffiti coatings

Protection of sensitive surfaces
Coatings with optical properties
Coatings with barrier properties
Modification of surface polarity

Electroactive layers
- Antistatic coatings
- Transparent conducting coatings
- Dielectric layers
- Piezoelectric layers
- Electrochromic layers

Sensor layers
Antistatic Coatings

Antistatic properties can be obtained by:
- increasing the proportion of polar groups
- incorporating ionic compounds

Best results for:

Antistatic Coatings

Electroactive Layers

Transparent conducting coatings on glass

Sheet resistance vs. sintering temperature of dip-coated SnO$_2$:Sb (ATO, 10 layers), In$_2$O$_3$ (ITO, 2 layers) and ZnO:Al (AZO, 10 layers) on silica glass $\rightarrow$ adjustable sheet resistance

Transmission (→) and reflectance spectra (-) of dip-coated ATO and AZO (layer on both sides) and ITO coatings (layer on one side)
Inorganic-organic hybrid materials as dielectric layers in microelectronics

Good adhesion to various substrates
Patternable by direct laser-writing or laser ablation

Manufacturing stages (bottom to top) for one of the smallest Pentium® Multichip Modules (MCM-L/D, 40 x 40 x 1.2 mm) by multilayers of inorganic-organic hybrid materials

Electroactive Layers

Piezoelectric Layers

Film thickness on a metal substrate about 0.8 μm. Piezoelectric charge:

charge per area in mC/cm²

- 500
- 400
- 300
- 200
- 100

unidirectional strain: 0.12 %
bidirectional stress and strain: 0.06 %
unidirectional stress: 0.12 %

number of cycles

10^0 10^1 10^2 10^3 10^4 10^5 10^6 10^7 10^8 10^9
Electrochromic Devices

Applications
• "Smart Windows"
• Automotive glazing and sunroofs
• Active and passive displays

ITO = indium tin oxide
FTO = fluorine-doped tin oxide
tungsten trioxide
inorganic-organic hybrid polymer
CeO₂/TiO₂

Protection of sensitive surfaces
Coatings with optical properties
Coatings with barrier properties
Modification of surface polarity
Electroactive layers
Sensor layers
Fiber-optical sensors

Sensor fiber in a CFK-composite (photo: DaimlerChrysler AG)

Signal of an optical sensor with CO$_2$-sensitive ORMOCER® layer at different humidities