Parylene Coatings:

Medical applications and R&D trends

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F. BOURGEOIS, PhD, R&D Project Manager
1. Comelec SA : Company Profile

2. Parylene Coatings main features

3. Medical applications

4. R&D projects

- High barrier multilayer coatings
- Anti-bacterial Parylene Coating
- Parylene LASER paterning
1. Company profile

- Founded in 1979, European leader in Parylene Coating.
- Coating service provider and equipment manufacturer
- 20 People
- 10 coaters at Comelec / 2000 batches deposited per year
- 55 equipments worldwide

- Strong involvement in R&D projects:
  - European projects:
    - 2007-2010
    - 2010-2013
    - 2015-2018
  - CTI (Swiss funded projects)
2. Parylene main features

An unique polymer process...

- Process patented in 1967 (Gorham, USA) => first application: PCBs in 70s (Union Carbide Corp.)
- Vacuum Process known as “Vapor Deposition Polymerization”, very similar to CVD.
- Typical thicknesses: 1-50 µm (control possible from 50 nm)

…with unique advantages

- Very high penetration ability: near 100% conformal coating => coating of very complex 3D items is possible
- Near room temperature process => stress free coating
  => no damage on heat sensitive parts (often at the very end of the manufacturing line)

Parylene success is not only a question of material properties, this is also due to a unique process!
2. Parylene main features

- 2 kinds of tools to deposit Parylene coatings:
  - **Static Coating**
    - Almost no size / shape limitation
    - Fragile parts handling
    - Manual disposal of the parts (time consuming)
  - **Tumble Coating**
    - No contact points
    - Very large volume production / very low cost
    - Limited by the size / shape / mechanical resistance

- Some examples of standard coating equipements:

- C-50S
- C-25S-Plasma
- C-22T

- Featured options:
  - In situ plasma process (ICP, CCP, MW)
  - Vaporization modules (adhesion promotor, etc…)
  - Chamber heating / cooling
  - Automated LN2 filling
2. Parylene main features

- 5 main chemistries of “PARYLENE”: poly(para-xylylene) polymers

- Chlorine substituted

- Fluorine substituted

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Most popular properties leading to success of Parylene:

- Chemically neutral with most substances.
- Biocompatible, and biostable (FDA approved, USP Class VI).
- Very good dielectric material.
- Solid lubricant (ease of slipping for medical devices)
- Hydrophobic
- Very good barrier properties among polymeric materials
- Almost 100% conformal coating, without pinholes.
- High to very high thermal stability (up to 450°C)
- Transparent film in the visible wavelengths
3. Medical Applications
3. Medical applications

Historical first Parylene application

- PCB coating:
  - Protects against *moisture and oxygen*.
  - Protects against *corrosive agents*.
  - Avoids *electrical damage* of chips.
  - Prevents from Tin whiskers related damages.
  - Enhances mechanical reliability (vibration)

=> *Improved reliability in harsh environment*

Especially for Military and aerospace applications.

Evolution to flex PCBs (especially for medical applications):
- As substrate or packaging layer
3. Medical applications

✓ Implantable electronic devices (Pacemakers, Micropumps, cochlear implants, sensors…)
  o Improves reliability. Used as a complement to Titanium housing (diffusion barrier layer, protection against dielectric breakdown, wiring mechanical reinforcement, etc.)
  o Passivates materials to prevent from allergen reactions

✓ Catheters, canulae, wirings, stents, etc…
  o Dry lubricity makes insertion easier

✓ Rubbers seals / O-rings / silicones parts
  o Dry lubricity facilitates insertion / gliding
  o Hydrophobicity enhances performances (fluid management)
  o Brings chemical inertness to elastomers (prevents from elastomer damage or additives releases)

✓ Polymers containers (pharmacology)
  o Brings chemical inertness and keep pharmaceutic fluids pure

✓ Implantable glass tags :
  o improves and accelerates tissue adhesion
More and more Medtech devices built at the wafer scale, and so are deposited the Parylene layers.

- European Project 2015-2018: InForMed (ECSEL JU funding)
  - Smart Body Patches: electronics on flexible Parylene substrate

- Manufacturing of free standing Parylene based PCBs

- Processing on Silicon wafers (100mm)
  - Up to 3 level of metals (Au) including interconnexions
  - ICs bonding / brazing
  - Parylene substrate release (overall thickness of ~50 microns)

- First functional demonstrators (flexible ECG device)
3. Medical applications

European Project 2015-2018: InForMed (ECSEL JU funding)

- Steering Deep Brain Stimulator

Left: State-of-the-art DBS system; Right: clinical trials have proven that the segmented steering probe of SAPIENS can prevent side effects normally associated with DBS.

- Coating for long term implantable devices.
- Development of adhesion strategies on a single device combining “critical” materials (PI, noble metals, …)
  - Adhesion evaluation using delamination tests or IDE. Before/After PBS soaking or during PBS soaking
  - Interface control using plasma and plasma polymers process and / or adhesion promotors
- Toward a Flex-2-Rigid technology with Parylene (instead of Polyimide)
4. R&D Projects

- High Barrier Multilayer Coating
- Anti-microbial Parylene
- Parylene LASER ablation
  - Development of Advanced Parylene Coaters for wafers processing in clean rooms
  - Parylene adhesion reliability
- ....
4. High Barrier Multilayer Coating

Goal: Develop a parylene based multilayer coating with enhanced barrier properties

General approach: combine ceramic-like layer(s) with tight structures and Parylene

4. High Barrier Multilayer Coating

State of the art: process often developed on silicon wafers or on free standing packaging films

<table>
<thead>
<tr>
<th>Producer</th>
<th>Encapsulation Structure</th>
<th>Number of layers</th>
<th>WVTR 23°C, 50% RH (g.m².day⁻¹)</th>
<th>Strain at failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitex (Barix)</td>
<td>[acrylate/Al₂O₃]₄</td>
<td>7 + planarization</td>
<td>~ 1 x 10⁻⁶</td>
<td>0.8</td>
</tr>
<tr>
<td>Philips (NONON)</td>
<td>[SiNₓ/SiOₓ]ₙ</td>
<td>‘12’ + topcoat</td>
<td>3.6 x 10⁻⁶</td>
<td>1.0</td>
</tr>
<tr>
<td>GE (graded UHB)</td>
<td>[SiNₓ/SiOₓ]ₙ</td>
<td>‘5’</td>
<td>8.6 x 10⁻⁶</td>
<td>?</td>
</tr>
<tr>
<td>Applied Materials</td>
<td>[SiN/lacquer]₂</td>
<td>4 + planarization</td>
<td>~ 10 x 10⁻⁶</td>
<td>1.0</td>
</tr>
<tr>
<td>3M</td>
<td>[oxide/polymer]₂</td>
<td>4 + planarization</td>
<td>~ 0.5 x 10⁻⁶</td>
<td>?</td>
</tr>
<tr>
<td>Picosun</td>
<td>ALD (batch)</td>
<td>1</td>
<td>~ 1 x 10⁻⁶</td>
<td>?</td>
</tr>
<tr>
<td>Tera-Barrier</td>
<td>[nanocompos./oxide]₂</td>
<td>5 + planarization</td>
<td>~ 1 x 10⁻⁶</td>
<td>?</td>
</tr>
<tr>
<td>Rolic</td>
<td>[SiNₓ/polym nanocomp.]₁,₂</td>
<td>2 or 4</td>
<td>~ 10⁻⁵ – ~ 10⁻⁶</td>
<td>?</td>
</tr>
<tr>
<td>Fraunhofer</td>
<td>[ormocer/ZTO]₂</td>
<td>4 + planarization</td>
<td>70 x 10⁻⁶</td>
<td>?</td>
</tr>
</tbody>
</table>

Trade-off between barrier ultimate barrier properties and strain at failure!

Comelec goals:

- WVTR < 10⁻² g/(m².day) for a 10µm multilayer coating (x 100)
- Strain at failure > 2%
- Industrial scale process for 2D and 3D parts (large reactors)
- Low temperature process (<100°C)
4. High Barrier Multilayer Coating

Key Factors:
- Statistics of defects and configuration to hinder related effects (cracks, particles, …)
- Materials quality: intrinsic diffusion
- Interface control: stress, adhesion.

Different technological approaches

Material choice
SiOx, Al2O3, …

Single versus multi-ceramic-like layers

Process choice

Separate vs. Hybrid equipment

No universal choice for all applications => Comelec develops different approaches

Advantages of Parylene:

- Ability to «heal» defects thanks to exceptional conformality:
  - Particles immobilization
  - Cracks / pinholes penetration

- Low stress coating thanks to low temperature process (20-50°C) / no shrinkage
4. High Barrier Multilayer Coating

- **High Barrier Multilayer Coating: results / status**
  - Hybrid equipment including Capacitive Coupled Plasma (CCP):
    - Proof of concept validated, first Parylene based multilayer with enhanced WVTR (3 logs !!)

**Hybrid process**

![Graph showing WVTR comparison between Parylene and Multi-Layer systems](image1)

- Log 3 improvement...

**Subsequent processes, single ceramic layer**

![Graph showing WVTR and O2TR comparison between Parylene and Single inorganic systems](image2)

- Log 2 to Log 3 improvement...

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4. High Barrier Multilayer Coating

- High Barrier Multilayer Coating: results / status
  - Hybrid equipment – several SiOx layers approach:
    - Demonstration on silicon dies from CEA LETI

  ![Image of demonstration on silicon dies from CEA LETI]

  Results after 4 months soaking:

  - Par. AF4 – 15 µm
    - WN not dissolved
    - Adhesion NOK

  - Par. C – 15 µm
    - WN not dissolved
    - Adhesion NOK

  - SiOx/ParC Multilayer – 15 µm
    - WN not dissolved
    - Adhesion OK

  ![Diagram of encapsulation coating and PBS solution at 67°C]

  Encapsulation coating

  PBS solution, 67°C

F. Bourgeois (Comelec SA), JC. Souriau (CEA-LETI), C. Quiniou (CEA-LETI)
4. Anti-microbial Parylene

Goal: bring an anti-bacterial functionality to the parylene coating

Different technological approaches

- Co-deposition (semi-bulk properties)
  - Co-sputtering
- Molecular grafting (near surface)
  - Co-vaporization

Challenges:
- control anti-microbial efficiency over time and biocompatibility
- develop a scalable industrial process
4. Anti-microbial Parylene

Co-sputtering approach – Silver / Parylene composite

ASTM Standard Test Method

- **Staphylococcus aureus** (DSMZ No. 20231) suspension in agar slurry
  => $10^6$ colony forming units (cfu)/ml

- **Incubation at 37°C, non-shaking, 24 hours**

- **Compare activity value** (Control to test count)

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LIVE / DEAD staining tests

**Ag release versus time**

- Large process window: critical parameter 100% increase

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**Inoculated Agar Slurry**

- **Parylene reference**
- **Silver coating on Parylene**
- **AM Parylene - process 1**
- **AM Parylene - process 2**
4. Anti-microbial Parylene

Grafting of anti-microbial molecules (e.g. ammonium compounds)

FTIR analysis:
- O-C=O signature indicates presence of the antimicrobial molecule in the coating

No reaction Ø
Successful process *

XPS analysis:
- N presence indicates presence of antimicrobial compound at the parylene surface

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4. Anti-microbial Parylene

- Grafting of anti-microbial molecules (e.g. ammonium compounds)

LIVE / DEAD staining tests

- Promising process allowing combination of antimicrobial molecule with Parylene
- Antimicrobial activity demonstrated

Next steps:
- Process industrialization
- Applications demo
4. Parylene LASER patterning

- Development of Parylene LASER Ablation / patterning

**Goal**: replace and going further than manual masking

- Increase production yields: decrease costs
- Less mechanical solicitation: better quality
- Fullfill miniaturization requirements: no design trade-off

**Experimental set-up:**

- **KrF Excimer LASER, 248nm** => *Photo-chemical ablation (instead of photo-thermal ablation)*
- Beam homogenizer
- Mask projection system => very high productivity possible for large surfaces / high volume production
- Fluences: 200-500 mJ/cm²
- Repetition rate (frequency): 1-50 Hz

**Samples:**

- Parylene AF4 12µm on Si wafer
- Parylene AF4 12µm on glass
- Parylene C 6µm on Si wafer

Source: P. Hoffmann, Empa Thun
4. Parylene LASER patterning

Development of Parylene LASER Ablation / patterning

Characterization:

Par. C - 6µm - on Si

SEM

Par. AF4 - 12µm - on Si

Standard microscopy

EDX

Optical profilometry
Development of Parylene LASER Ablation / patterning

**Promising results:**

- The Excimer laser repetition rate (frequency) does not change the ablation behaviour between 1Hz to 50 Hz. This indicates no strong thermal accumulation effect.
- No delamination of the Parylene film (typical failure when high thermal load or «burning»)
- No ablation of Silicon and glass wafers, even for large thickness (12 µm)
- Ablation leads to pattern resolution below 3 micrometers.
- High ablation rate in the range of ~ µm/sec

**Observations to work on:**

- Brown debris is deposited around the ablation regions. Can be removed largely in isopropanol ultrasonication.
- Residues on the Si substrate on the ablated floor remains in all cases even with very large number of shots.
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3. Electronic applications

PCB coating:

- Protects against moisture and oxygen.
- Protects against corrosive agents.
- Avoids electrical damage of chips.
- Prevents from Tin whiskers related damages.
- Enhances mechanical reliability (vibration)

=> Improved reliability in harsh environment

Especially for Military and aerospace applications.

Coil / Cores insulating:

- Dielectric layer.

Flex PCBs:

- As substrate or packaging layer
3. Mechanical / Micromechanical industry

- Solid lubricant:
  - reducing the wear of parts in friction
    (only with relatively small stress)

- Anti-tarnishing:
  - avoiding corrosion related damages
    (silver tarnishing, ...)

- Cohesion media for sintered parts:
  - sealing porosities, reducing brittleness
  - particle immobilization

- Elastomer lubrication / protection:
  - reduce friction
  - protect against chemical damages