Parylene Coatings:

Medical applications and R&D trends

EPHJ - Photonics 4 Luxury Coatings, June 2017

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Comelec SA, rue de la Paix 129, 2301 La Chaux de Fonds, Switzerland

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 :

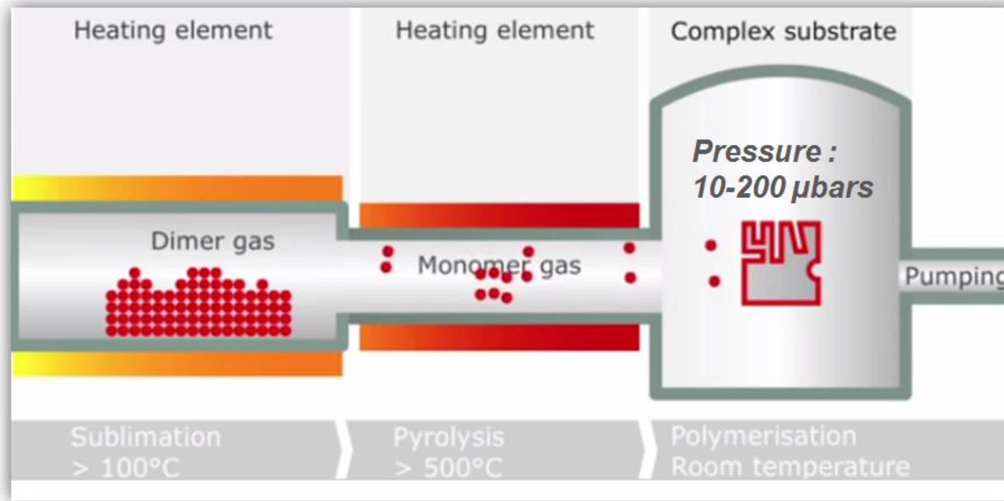
2007-2010 2010-2013 2015-2018

- ✓ CTI (Swiss funded projects)

Comelec SA, rue de la Paix 129, 2301 La Chaux de Fonds, Switzerland

❑ An unique polymer process…

- Process patented in 1967 (Gorham, USA) => first application : PCBs in 70's (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

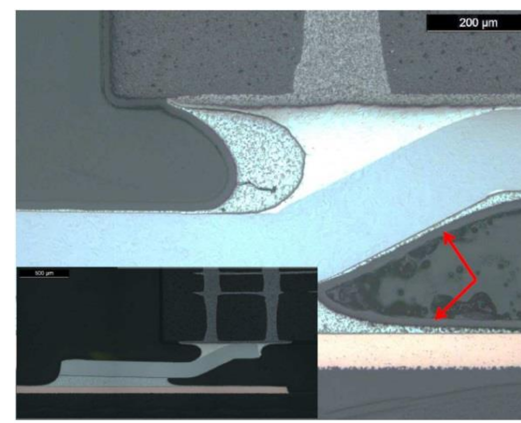
- ○ Very high **penetration ability** : near 100% conformal coating

  => *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)

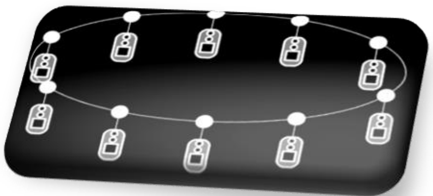


Parylene success is not only a question of material properties, this is also due to a unique process !

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 consumming)***

Tumble Coating

- ✓ ***No contact points***
- ✓ ***Very large volume production / very low cost***
- ✓ ***Limited by the size / shape / mechanical resitance***

- Some examples of standard coating equipements....

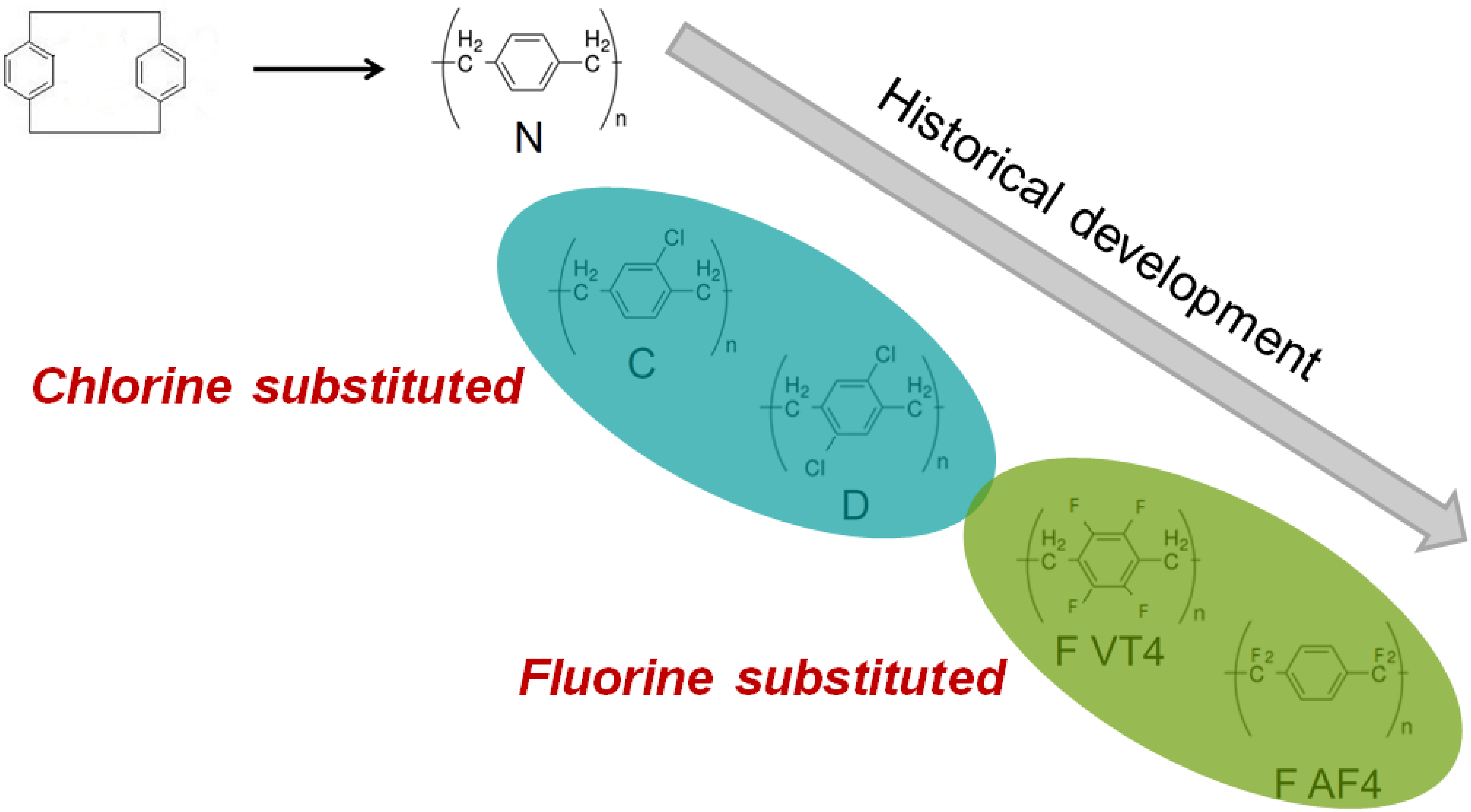
C-50S

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

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

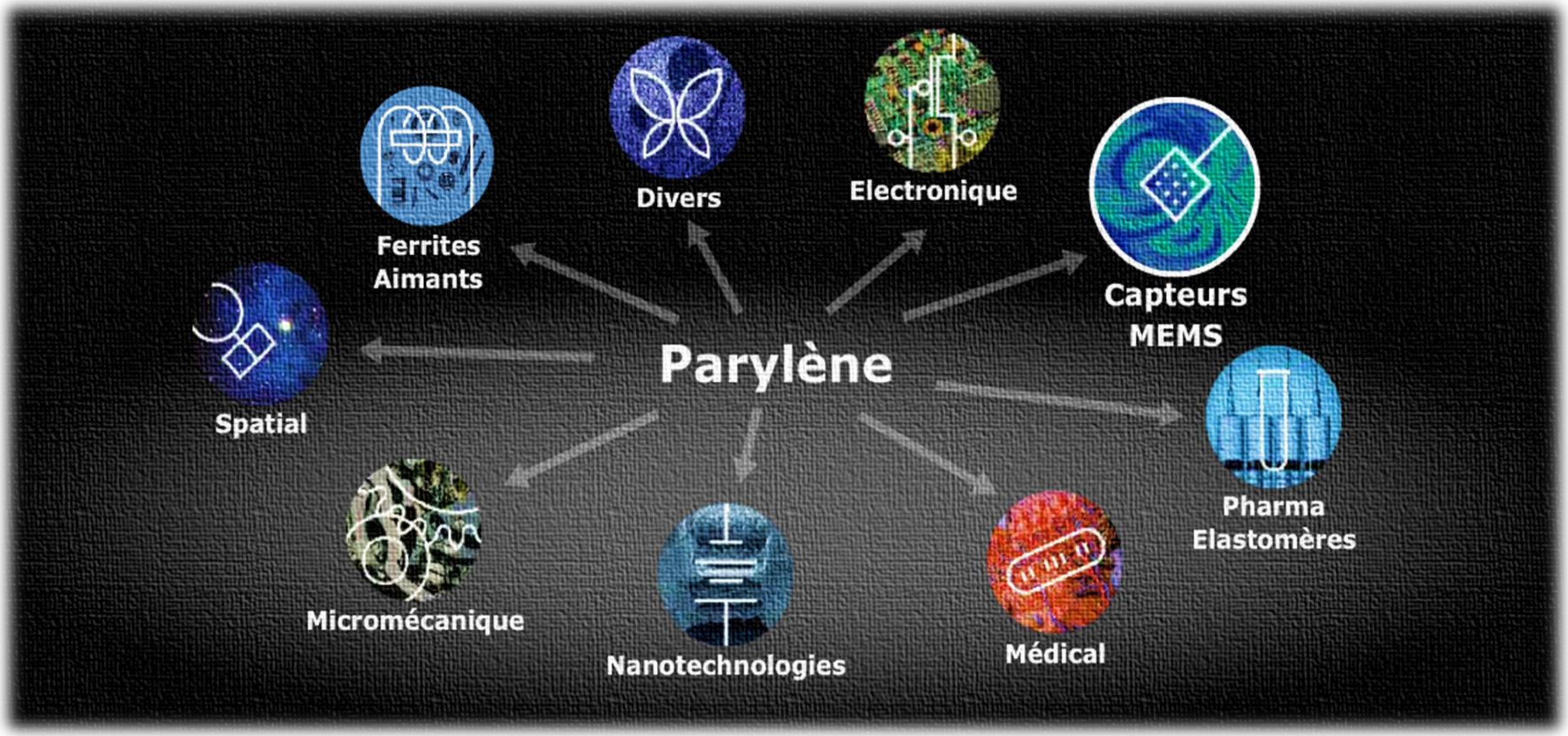


❑ Most popular properties leading to success of Parylene :

- Chemically neutral with most substances.
- Biocompatible, and biostable (FDA approved, USP Class VI).
- Very good dielelectric 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

REVÊTEMENT PARYLÈNE

3. Medical Applications



3. Medical applications

❑ Historical first Parylene application

✓ **PCB coating :**

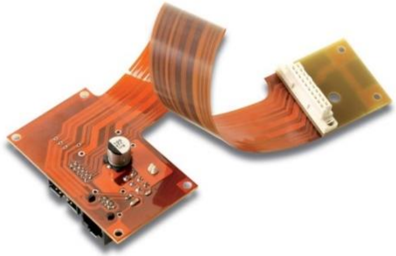
- **Protects against *moisture and oxygen.***
- **Protects against *corrosive agents.***
- **Avoids *electrical damage* of chips.**
- **Prevents from Tin whiskers related damages.**
- **Enhances mechanical reliability (vibration)**

=> Improved reliability in harsh environment

Especially for Milatary and aerospace applications.

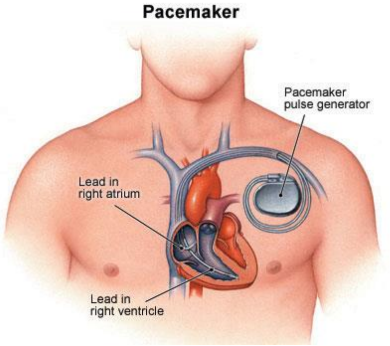
Evolution to flex PCBs (especially for medical applications) :

- **As substrate or packaging layer**

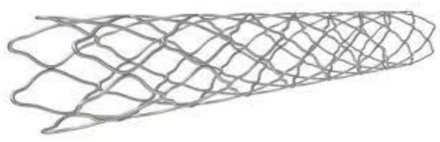


3. Medical applications

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



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

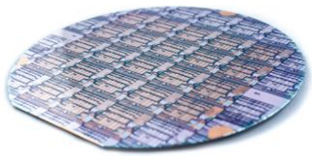


- ✓ **Rubbers seals / O-rings / silicones parts**
    - *Dry lubricity facilitates insertion / gliding*
    - *Hydrophobicity enhances performances (fluid management)*
    - *Brings chemical inertness to elastomers (prevents from elastomer damage or additives releases)*

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

- ✓ **Implantable glass tags :**
    - *improves and accelerates tissue adhesion*

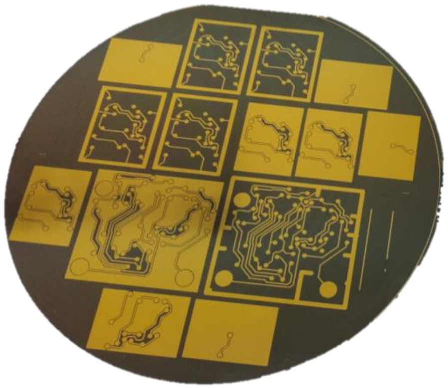
3. Medical applications

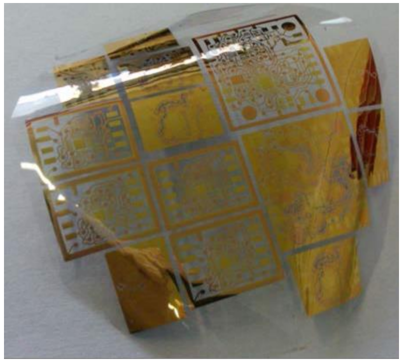


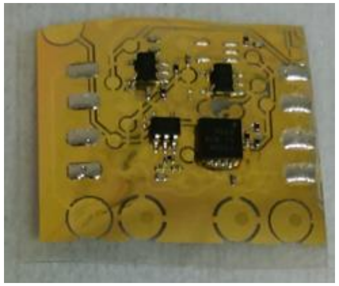
✓ **More and more Medtech devices built at the wafer scale, and so are deposited the Parylene layers.**

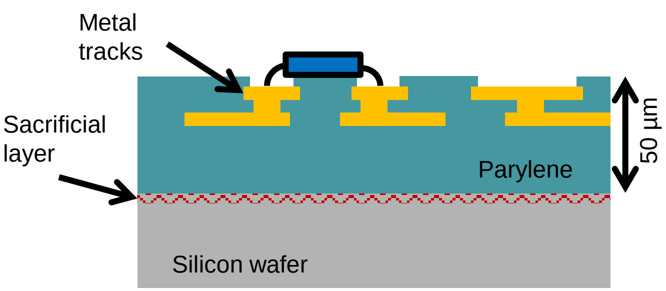
❑ European Project 2015-2018 : InForMed (ECSEL JU funding)

○ Smart Body Patches : electronics on flexible Parylene substrate



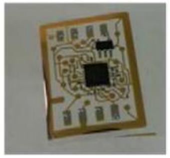


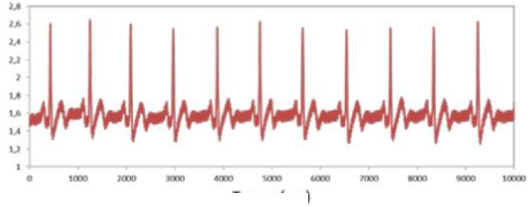




F. Bourgeois (Comelec SA), A.Bongrain (Bodycap), PA Chapon (Bodycap),G. Lissorgues (ESIEE), L. Rousseau (ESIEE)

- ❑ **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~ 50microns)**
- ❑ **First functional demonstrators (flexible ECG device)**

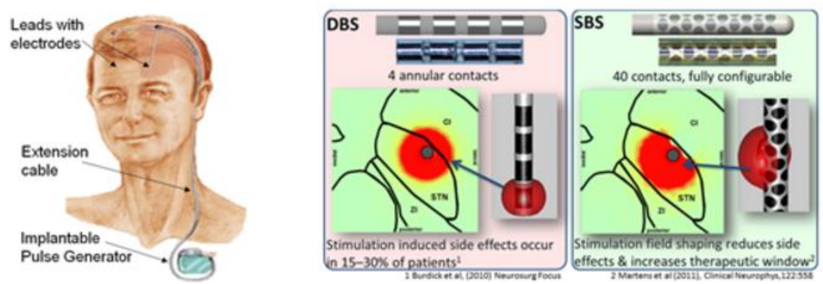




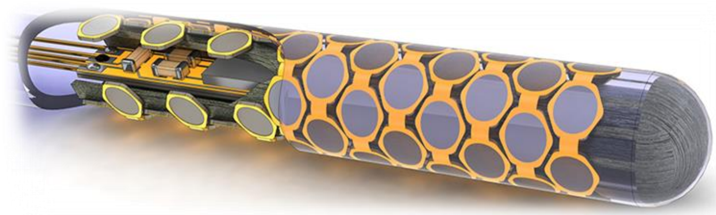
ECG on parylene

❑ 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.



Source: www.informed-project.eu

❑ 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)

comelec
REVÊTEMENT PARYLÈNE

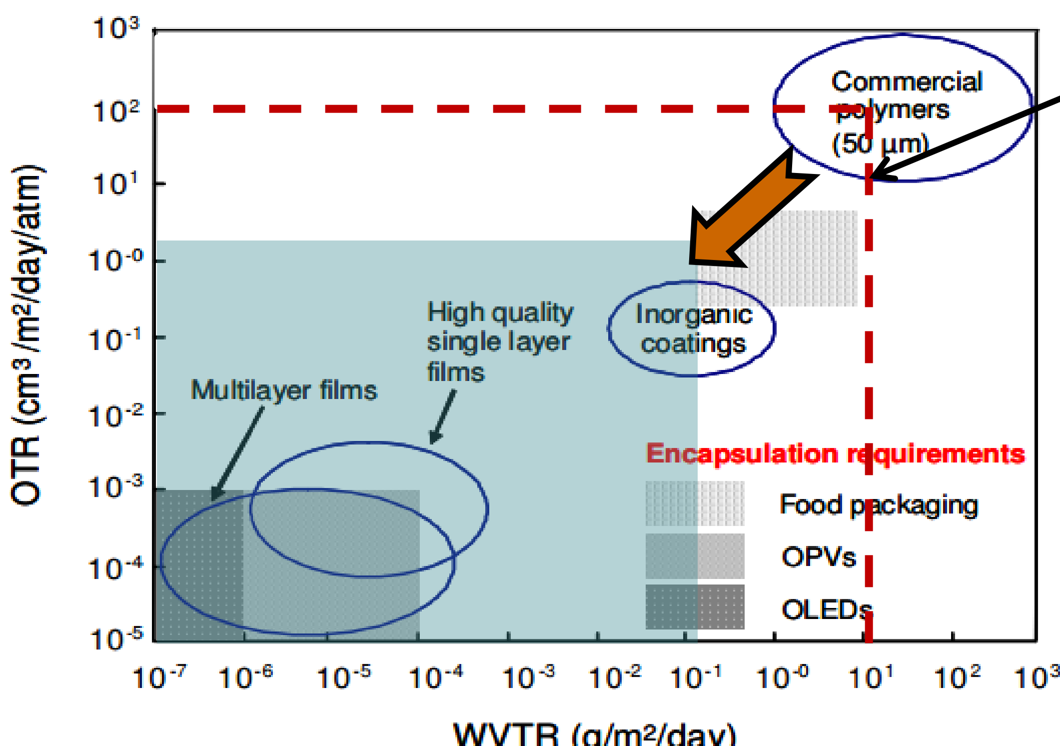
- **High Barrier Multilayer Coating**
- **Anti-microbial Parylene**
- **Parylene LASER ablation**
- **Development of Advanced Parylene Coaters for wafers processing in clean rooms**
- **Parylene adhesion reliability**
- **….**

Comelec SA, rue de la Paix 129, 2301 La Chaux de Fonds, Switzerland

❑ 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

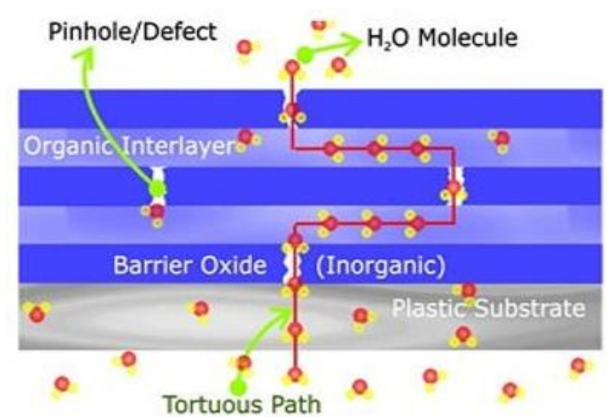


G. Dennler,et. al., J. Mater. Res., Vol. 20, No. 12, Dec 2005. Vol.20, 3224

Par.C 25µm :

WVTR => ~ 4 $g/m^2/day$

O2TR=> ~ 120 $cm^3/m^2/day$



High Barrier Multilayer Coating

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

Producer	Encapsulation Structure	Number of layers	W V T R 23°C, 50% RH ($g.m^{-2}.day^{-1}$)	Strain at failure (%)
Vitex (Barix)	[acrylate/Al_2O_3]$_4$	7 + planarization	~ 1×10^{-6}	0.8
Philips (NONON)	[SiN_x/SiO_x]$_n$	'12' + topcoat	3.6×10^{-6}	1.0
GE (graded UHB)	[SiN_x/SiO_x]$_n$	'5'	8.6×10^{-6}	?
Applied Materials	[SiN/lacquer]$_2$	4 + planarization	~ 10×10^{-6}	1.0
3M	[oxide/polymer]$_2$	4 + planarization	~ 0.5×10^{-6}	?
Picosun	ALD (batch)	1	~ 1×10^{-6}	?
Tera-Barrier	[nanocompos./oxide]$_2$	5 + planarization	~ 1×10^{-6}	?
Rolic	[SiN_x/polym nanocomp.]$_{1,2}$	2 or 4	~ 10^{-5} – ~ 10^{-6}	?
Fraunhofer	[ormocer/ZTO]$_2$	4 + planarization	70×10^{-6}	?

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

Comelec goals :

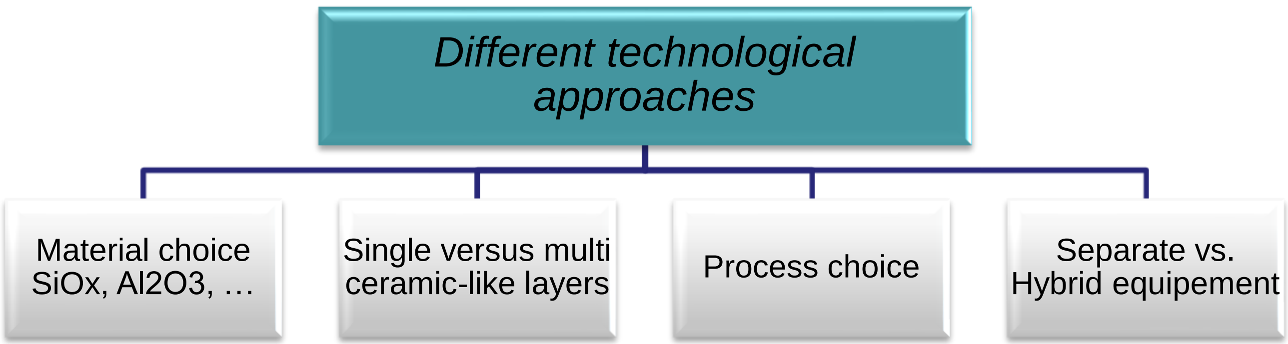
- ✓ WVTR < 10^{-2} g/(m^2.day) for a 10µm multilayer coating (x 100)
- ✓ Strain at failure > 2%
- ✓ Industrial scale process for 2D and 3D parts (large reactors)
- ✓ Low temperature process (<100°C)

4. High Barrier Multilayer Coating

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.*



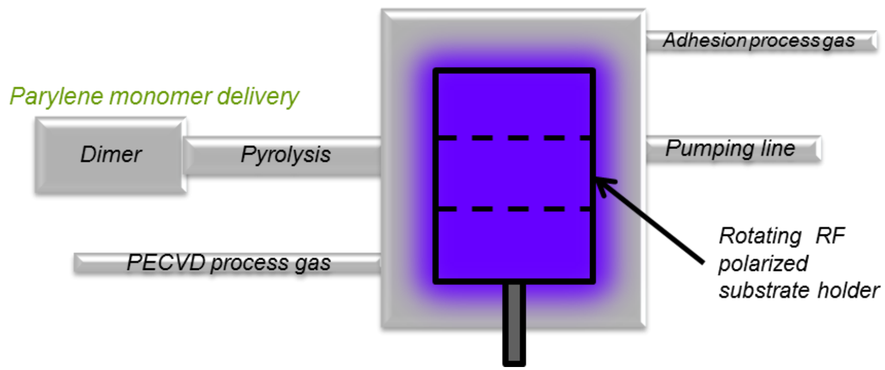
No universal choice for all applications => Comelec develops different approaches

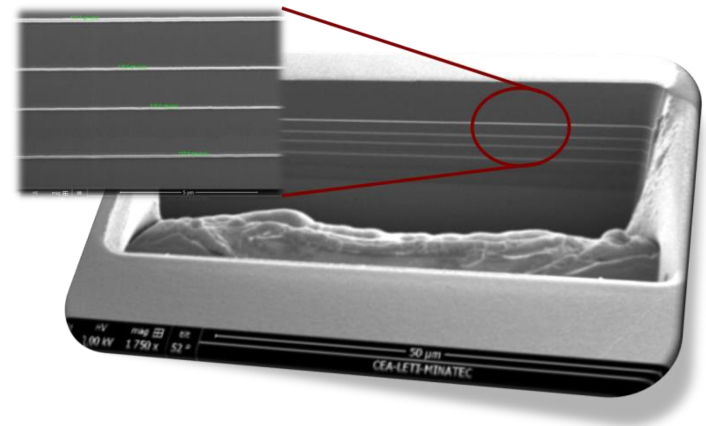
Advantages of Parylene:

- 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

❑ High Barrier Multilayer Coating: results / status

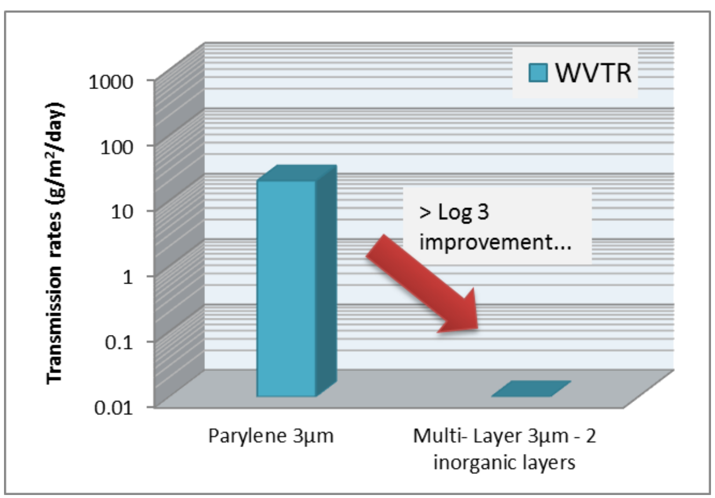
- Hybrid equipment including Capacitive Coupled Plasma (CCP) :



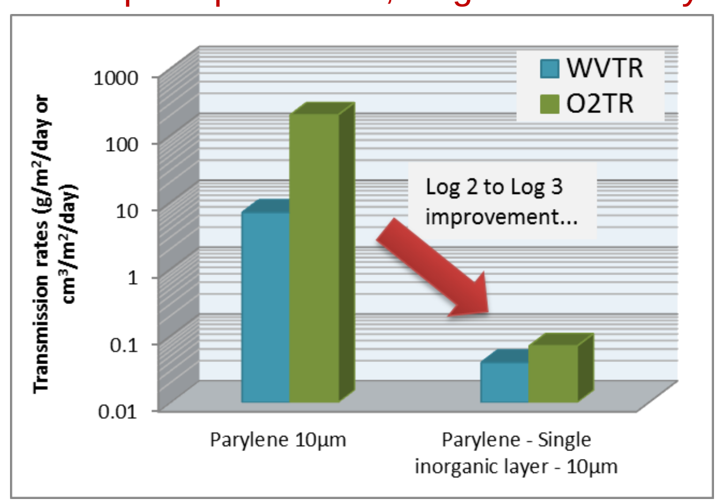


- Proof of concept validated, first Parylene based multilayer with enhanced WVTR (3 logs !!)

Hybrid process



Subsequent processes, single ceramic layer

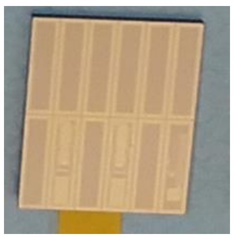


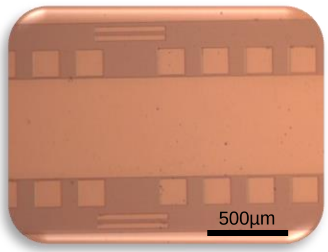
4. High Barrier Multilayer Coating

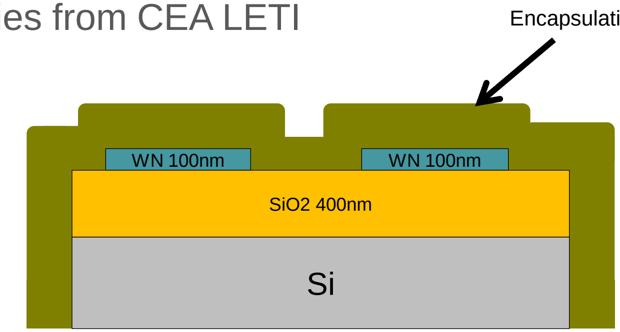
❑ High Barrier Multilayer Coating: results / status

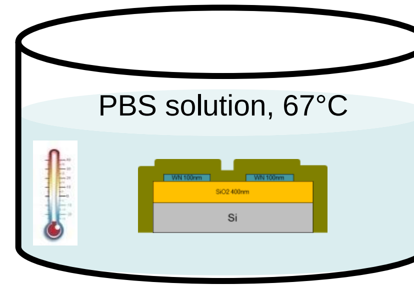
F. Bourgeois (Comelec SA),
JC. Souriau (CEA-LETI),
C. Quiniou (CEA-LETI)

- Hybrid equipment – several SiOx layers approach:
  - ✓ Demonstration on silicon dies from CEA LETI



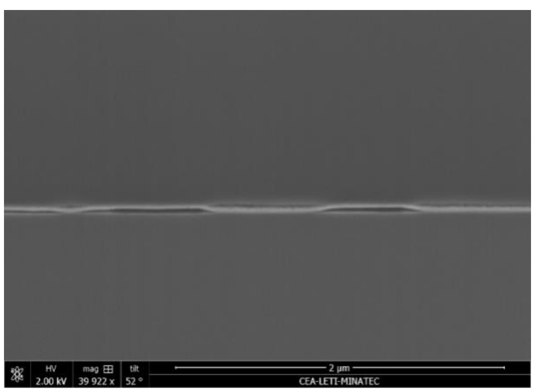


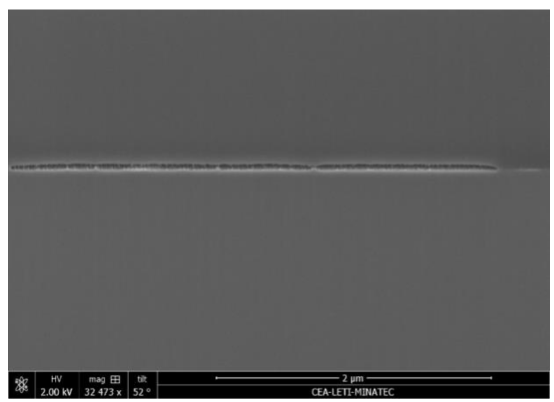


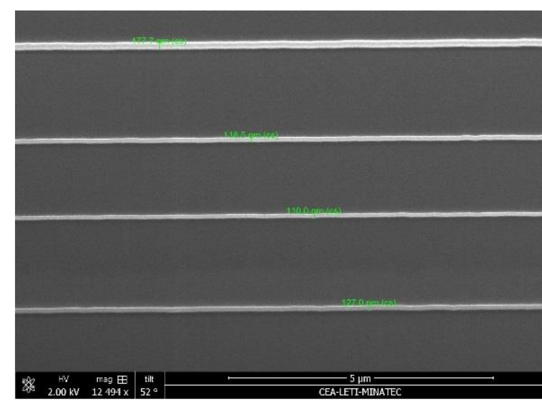


➡ Results after 4 months soaking:

Par. AF4 – 15 µm	*Par. C – 15 µm*	*SiOx/ParC Multilayer– 15 µm*







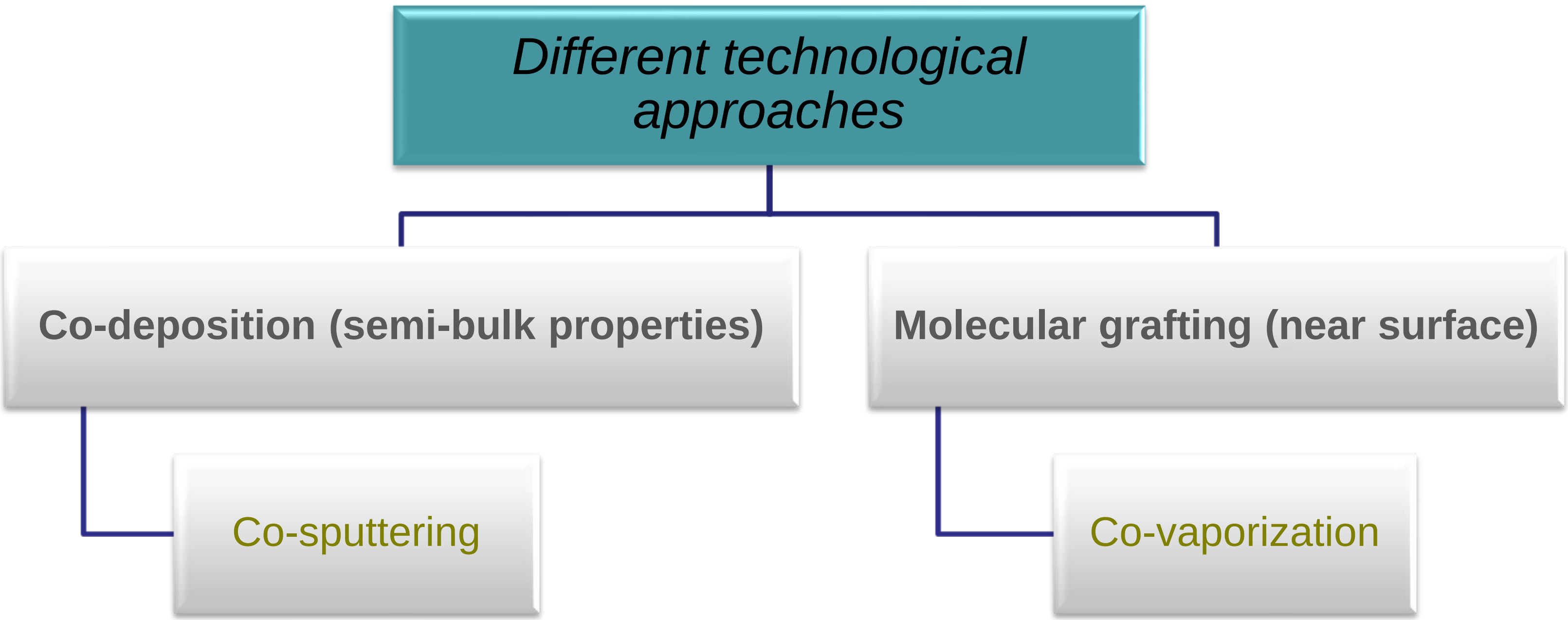
Par. AF4 – 15 µm
- ✓ WN not dissolved
- ✓ Adhesion NOK

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

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

❑ Anti-microbial Parylene

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



Challenges:

- control anti-microbial efficiency over time and biocompatibility

- develop a scalable industrial process

4. Anti-microbial Parylene

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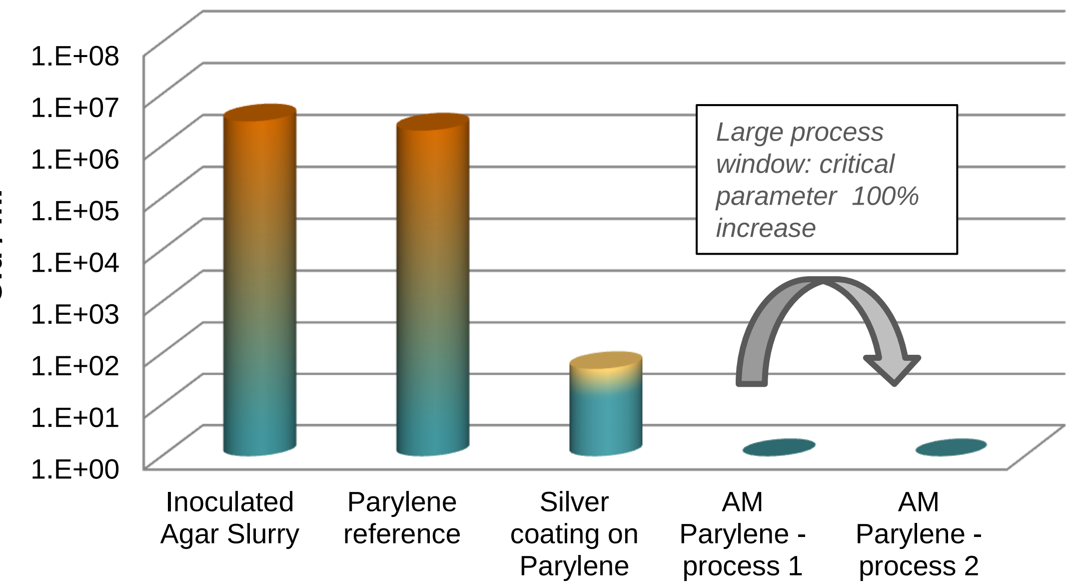
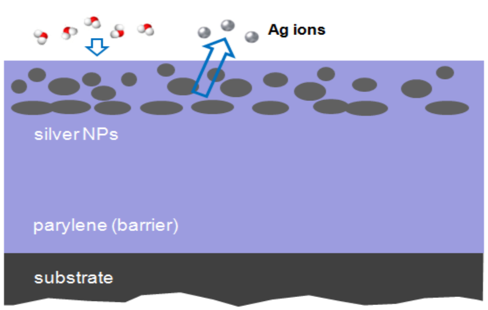
❑ Co-sputtering approach – Silver / Parylene composite

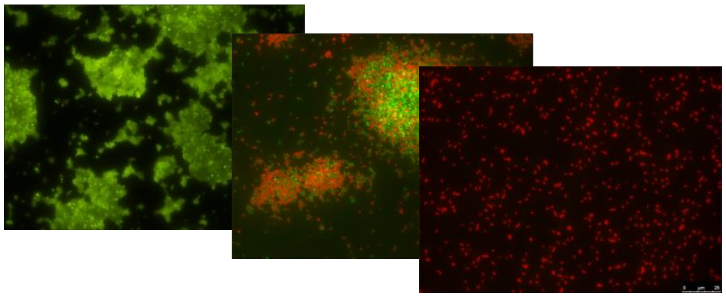
ASTM Standard Test Method

- ***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)*

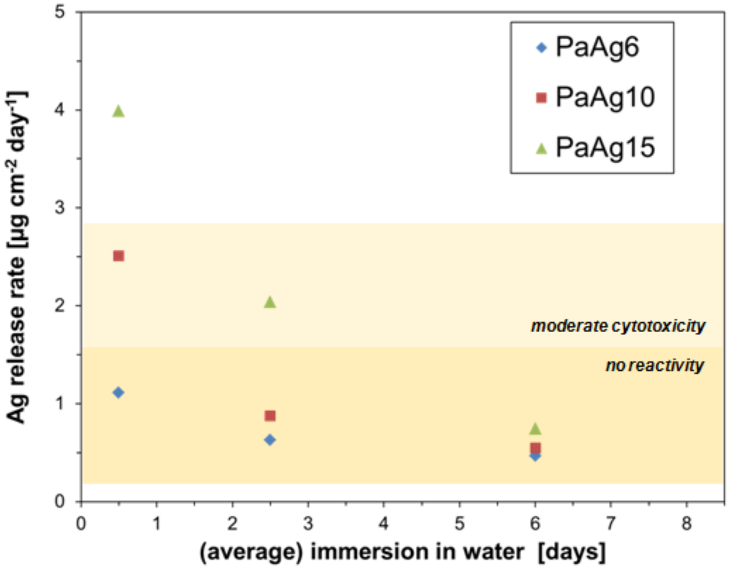




LIVE / DEAD staining tests



Ag release versus time



4. Anti-microbial Parylene

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

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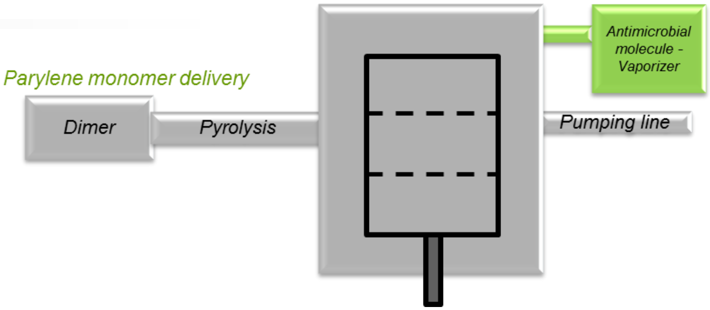
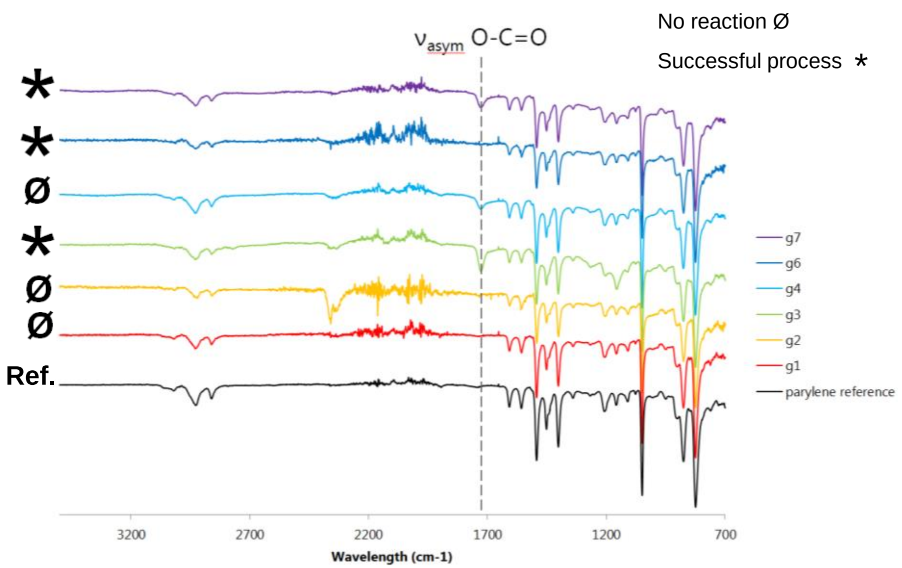


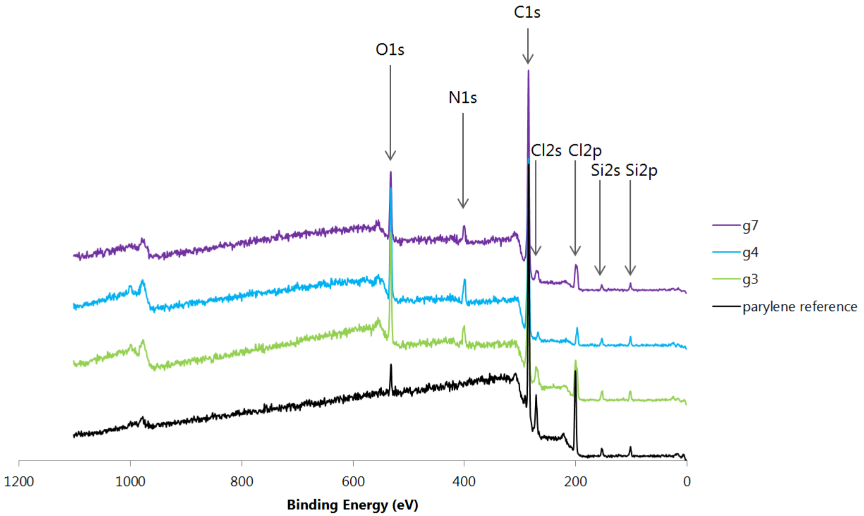
FTIR analysis :

- *O-C=O signature indicates presence of the antimicrobial molecule in the coating*



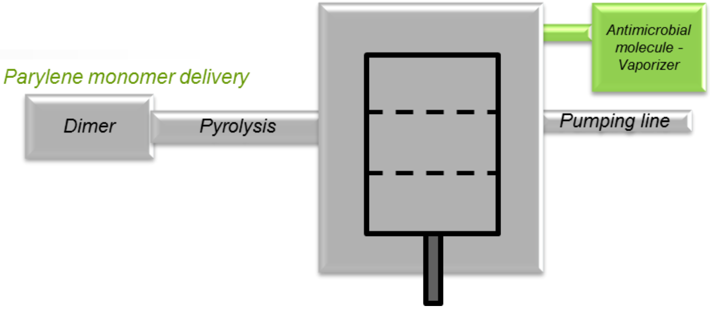
XPS analysis :

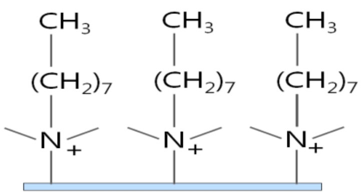
- *N presence indicates presence of antimicrobial compound at the parylene surface*



4. Anti-microbial Parylene

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





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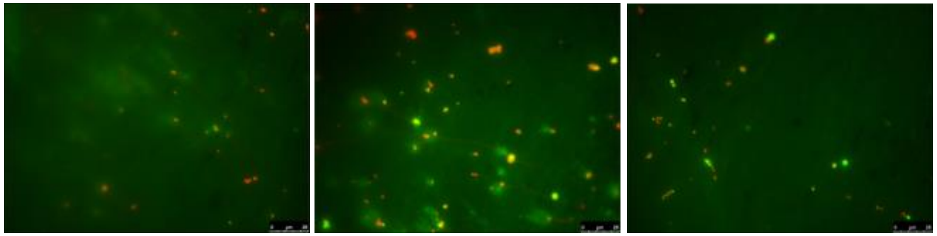
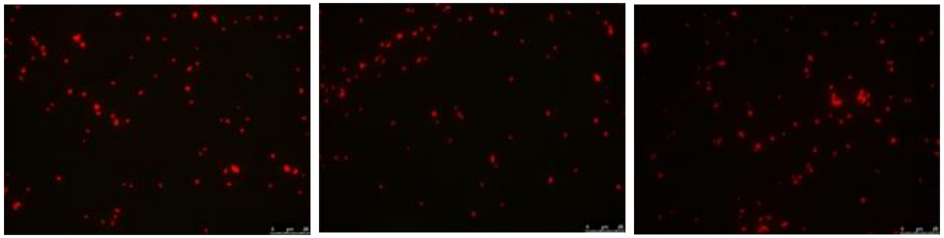


Parylene reference



"Ammonium" grafted Parylene

- ❑ **Promising process allowing combination of antimicrobial molecule with Parylene**
- ❑ **Antimicrobial activity demonstrated**
- ❑ **Next steps :**
  - Process industrialization
  - Applications demo

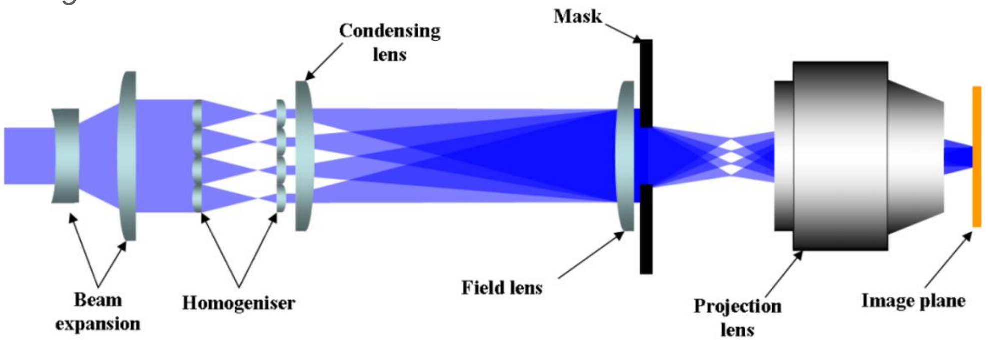
4. Parylene LASER patterning

❑ Development of Parylene LASER Ablation / patterning

<u>Goal</u> : replace and going further than manual masking

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

Source: P. Hoffmann, Empa Thun



<u>Experimental set-up:</u>

- *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/cm^2*
- *Repetition rate (frequency): 1-50 Hz*

<u>Samples :</u>

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

4. Parylene LASER patterning

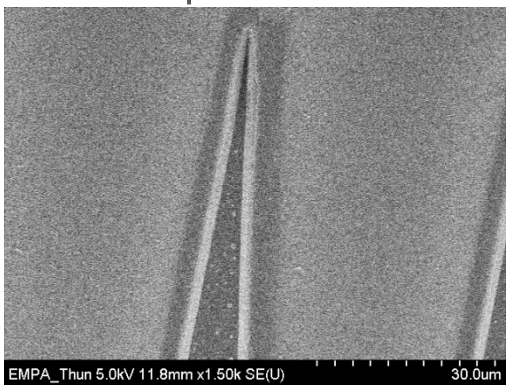
Materials Science & Technology

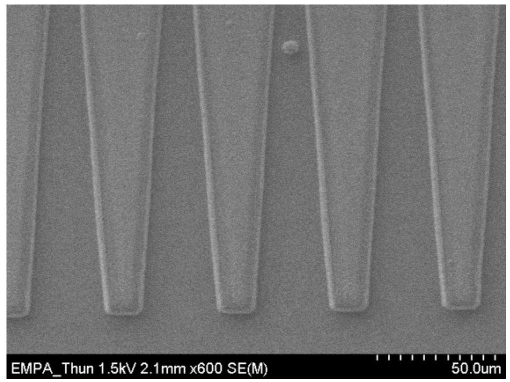
❑ Development of Parylene LASER Ablation / patterning

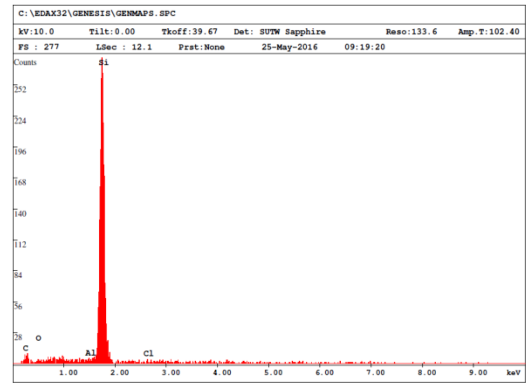
Characterization:

Par. C - 6µm - on Si

SEM

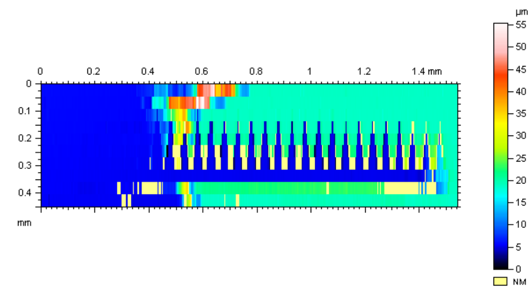






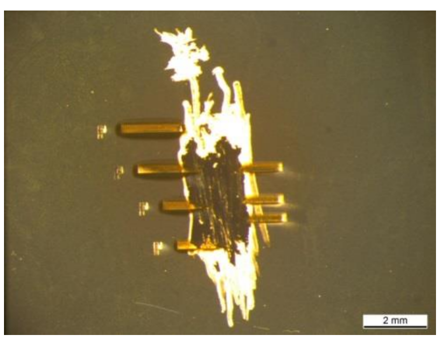
EDX

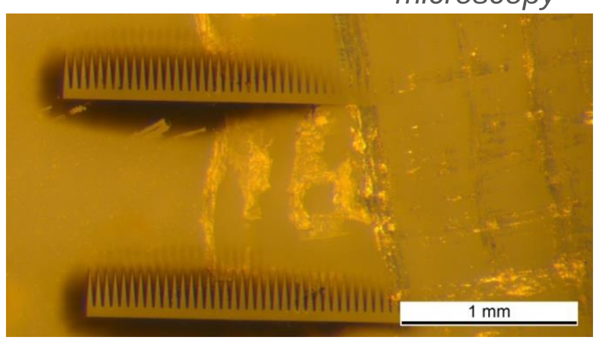
Optical profilometry

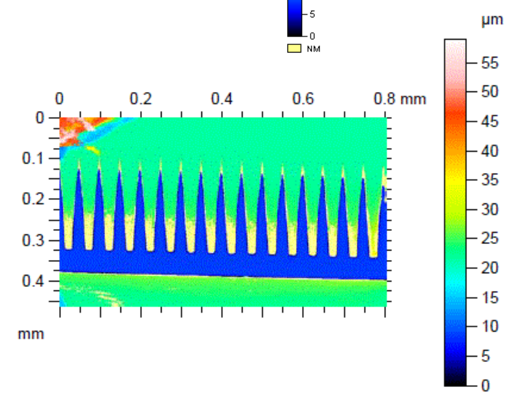


Par. AF4 - 12µm - on Si

Standard microscopy







4. Parylene LASER patterning

EMPA
Materials Science & Technology

❑ 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

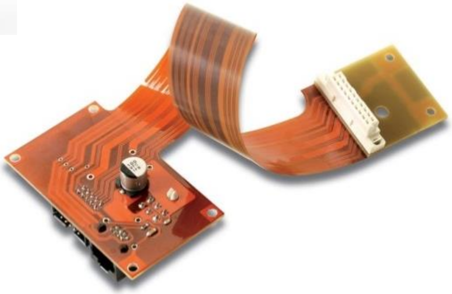
- ✓ **PCB coating :**
  - Protects against *moisture and oxygen.*
  - Protects against *corrosive agents.*
  - Avoids ***electrical damage*** of chips.
  - Prevents from Tin whiskers related damages.
  - Enhances mechanical reliability (vibration)

=> Improved reliability in harsh environment

Especially for Milatary 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 whith relatively small stress)

- ✓ **Anti-tarnishing:**
  - avoiding corrosion related damages (silver tarnishing, …)

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

- ✓ **Elastomer lubrification / protection:**
  - reduce friction
  - protect against chemical damages