Vrije Universiteit Brussel

Comparison between wet deposition and plasma deposition of silane coatings on metals for surface passivation

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VUB-ULB-FUNDP-CoRI

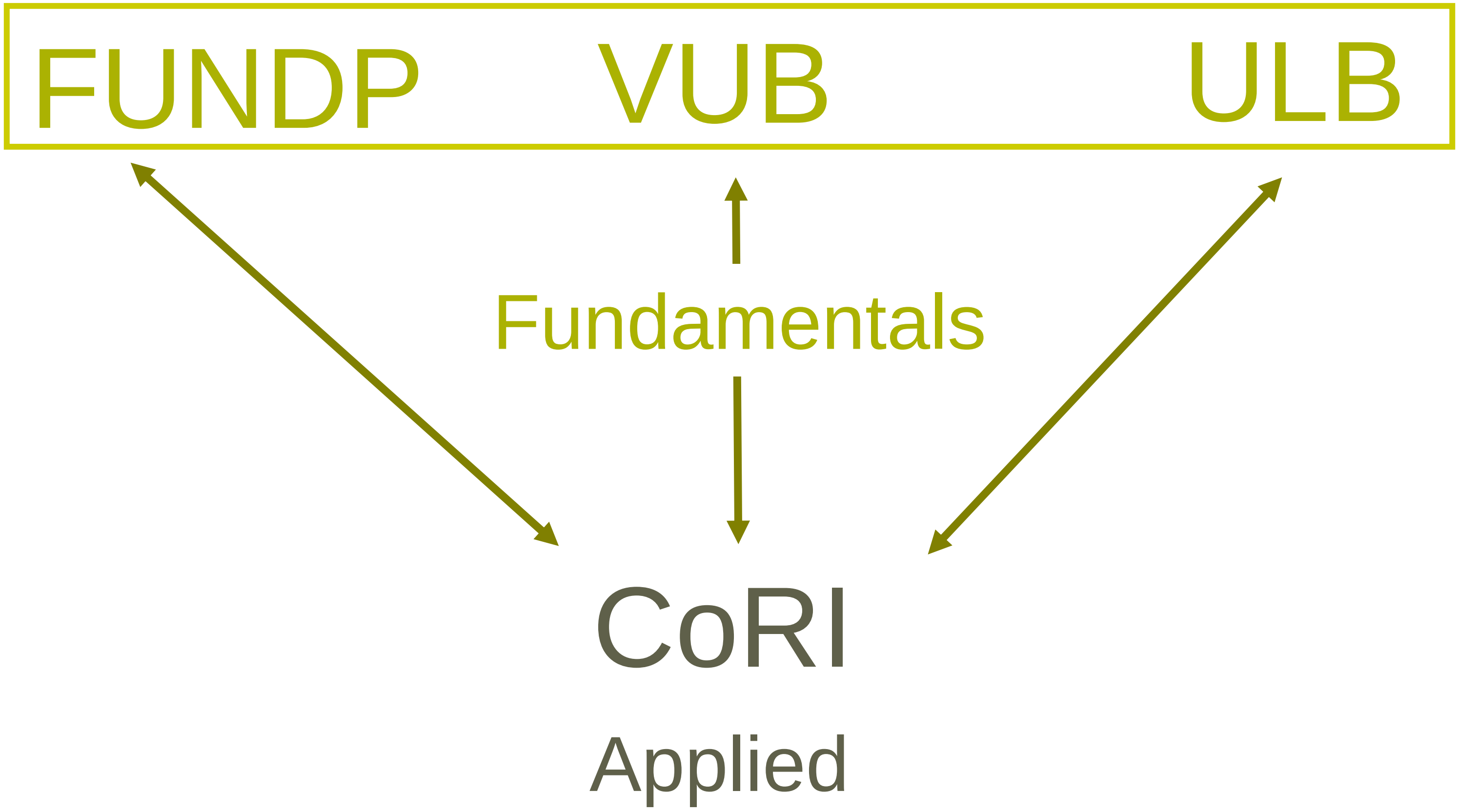
FOMOS project

Functional properties
by Mixed Nano Organic/Metal Oxide Systems

Acknowledgment for funding: Belgian Science Policy – Belspo

“Programme to stimulate knowledge transfer in areas of strategic importance”

Consortium



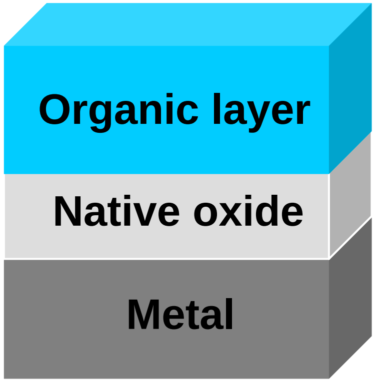
Users committee

- *Bekaert Technology Center*
- *Aleris Aluminium*
- *R&D Umicore*
- *OCAS-Arcelor Zelzate*
- *Arcelor Research Industry Liège*
- *Coil Landen*
- *Chemetall GmbH*
- *Akzo Nobel Decorative Coatings*
- *SIGMAKALON*
- *IWT*

Main question in the project

Starting point: concept of organic coating of metals

System 1: layered system of metal with native oxide and organic pretreatment coating (< 1µm)



System 1

Main question in FOMOS :
How to improve properties and/or create innovative properties?

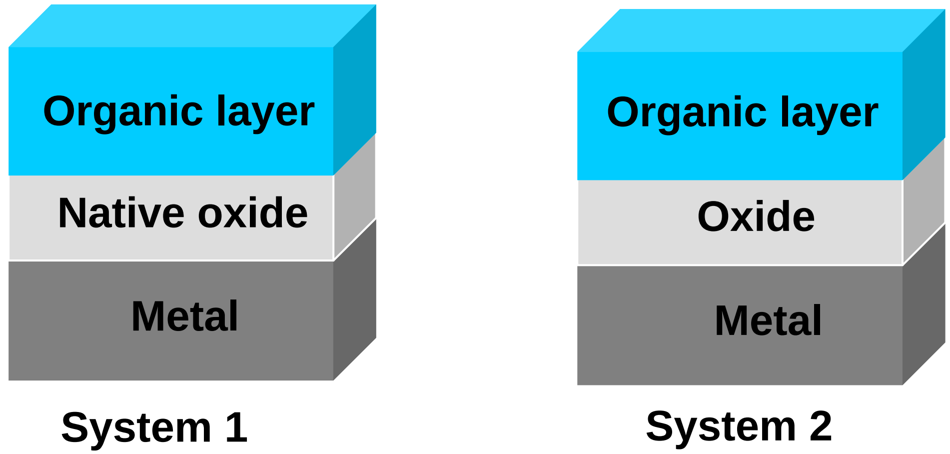
What properties ?

- Mechanical
  - Hardness
  - Tribological: friction, wear…
  - Thermomechanical

- Functional !!! >>> main focus of FOMOS
  - Corrosion: barrier, inhibitors, self-healing…
  - Adherence, interfacial bonding…
  - Optical: appearance, reflectance, colour...
  - Ageing and chemical stability…
  - Wettability, hydrophobic/hydrophilic…
  - Other innovative properties….

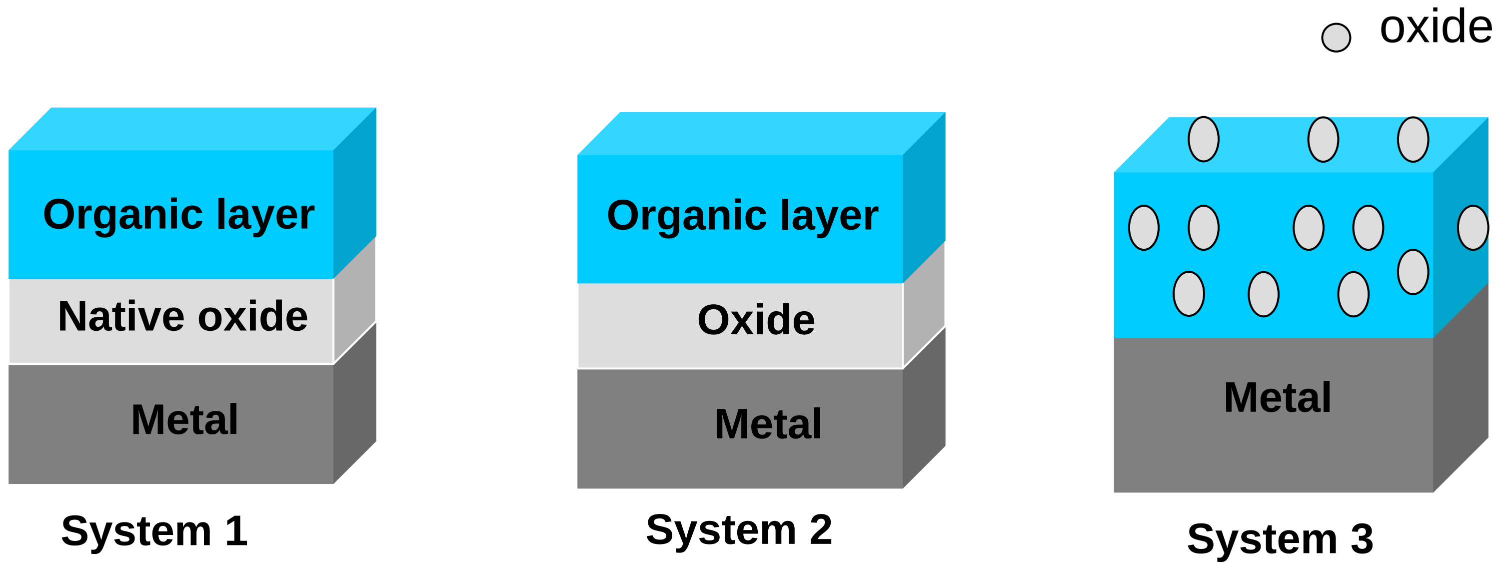
Approach in the project = Investigation of innovative systems (1)

System 2: layered system with tailored metal oxide layer

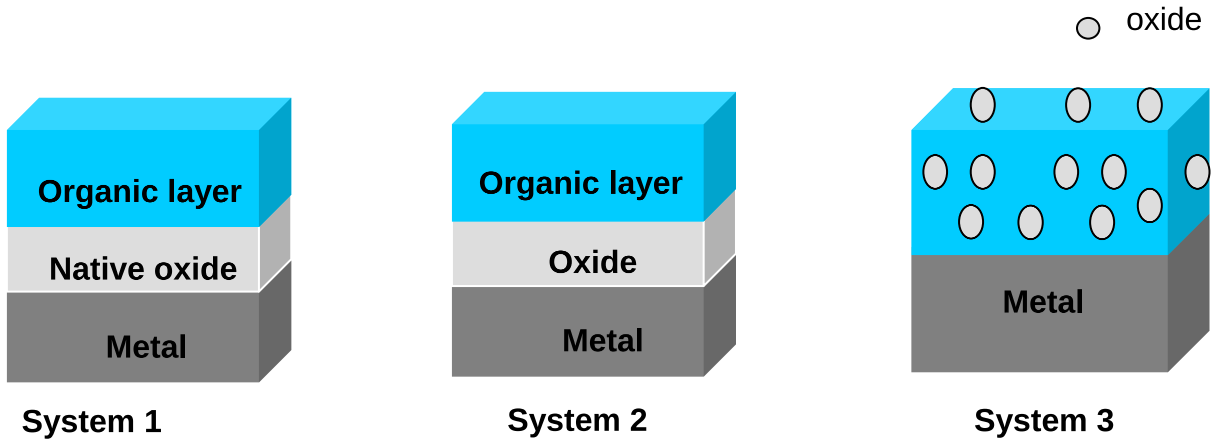


Approach in the project = Investigation of innovative systems (2)

System 3: hybrid system of mixed organic / metal oxide nanoparticle coating



Variables



Organic medium: silanes (multimetal ! hybrid organic- inorganic chemistry)

Metal oxide: Si-oxide, Ce-oxide

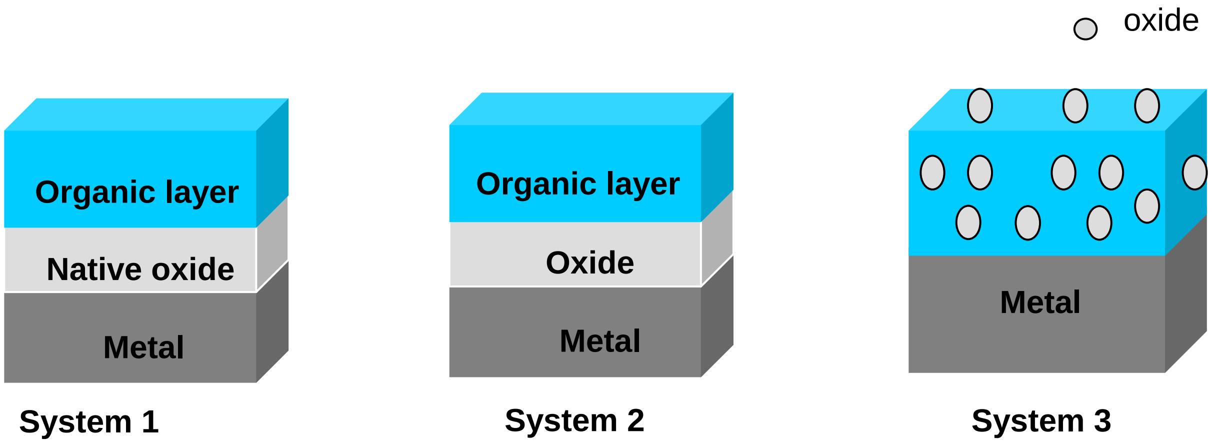
Coating deposition method !!!

- Wet deposition from solutions (water-based)
- Solvent free plasma deposition: vacuum and atmospheric

Substrate and pre - and post-treatments:

- Aluminium, steel
- Precleaning method (chemical or plasma)
- Curing of the organic system (thermally induced or during plasma deposition)

Critical focus points



- Compatibility between inherently very different media

>>> Organic molecules versus inorganic metal oxide: interfacial bonding?

- Film formation mechanisms using the various deposition methods? …resulting properties?

Characterisation Tools

Organic solution characterisation

>>> DLS, NMR

Coating characterisation

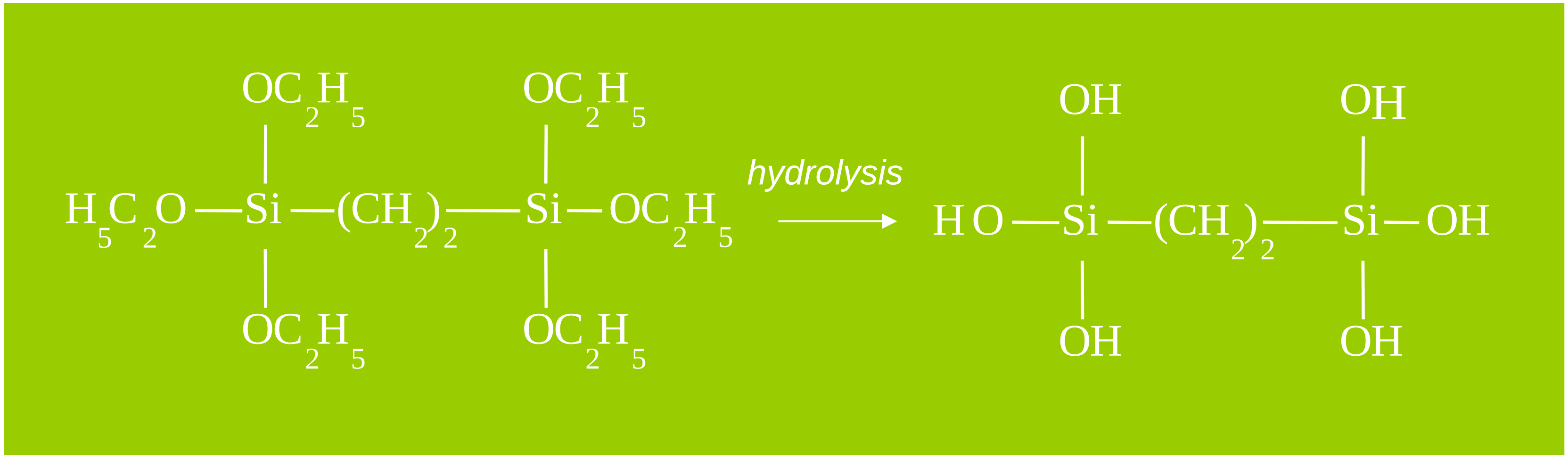
>>> FEG-SEM, FEG-AES, XPS, Tof-SIMS, GDOES, FIB TEM... Vis & IR-SE, Raman,…

Properties characterisation

>>> Corrosion standard tests, EIS,… thermomechanical DSC, TGA, DMA…adherence…optical TIS … wettability contact angle...

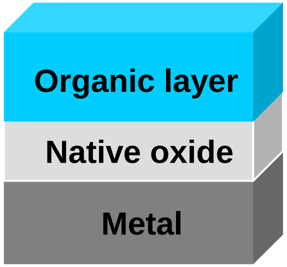
What are silanes ?

- Alternative to CrVI+ surface treatments for corrosion protection
- Multimetal process on aluminium, steel, magnesium, zinc …
- Silanes = hybrid organic-inorganic molecules



BTSE = bis-1,2-(triethoxysilyl)ethane

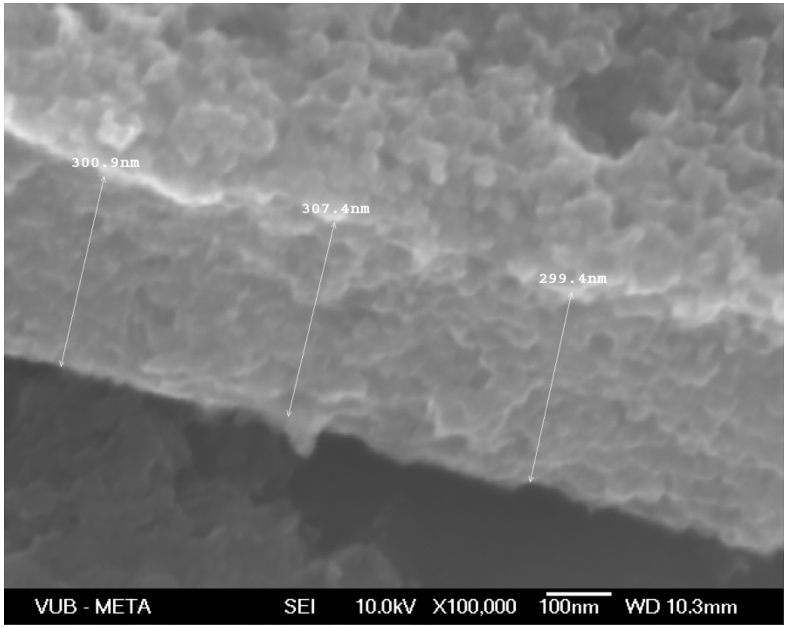
= Very reactive towards metal-film bonding and crosslinking



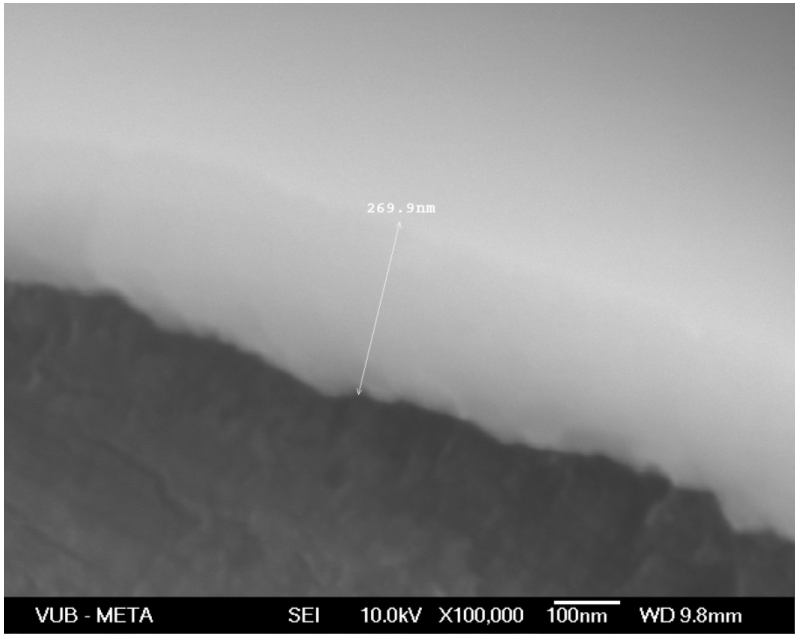
System 1

Part 1: Wet deposition of silane

FEG-SEM secondary electron images roll-coated layers on aluminium

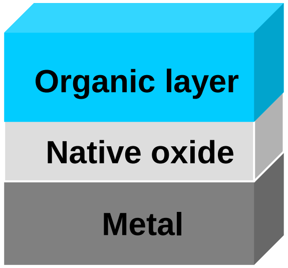


0.5 wt% BTSE



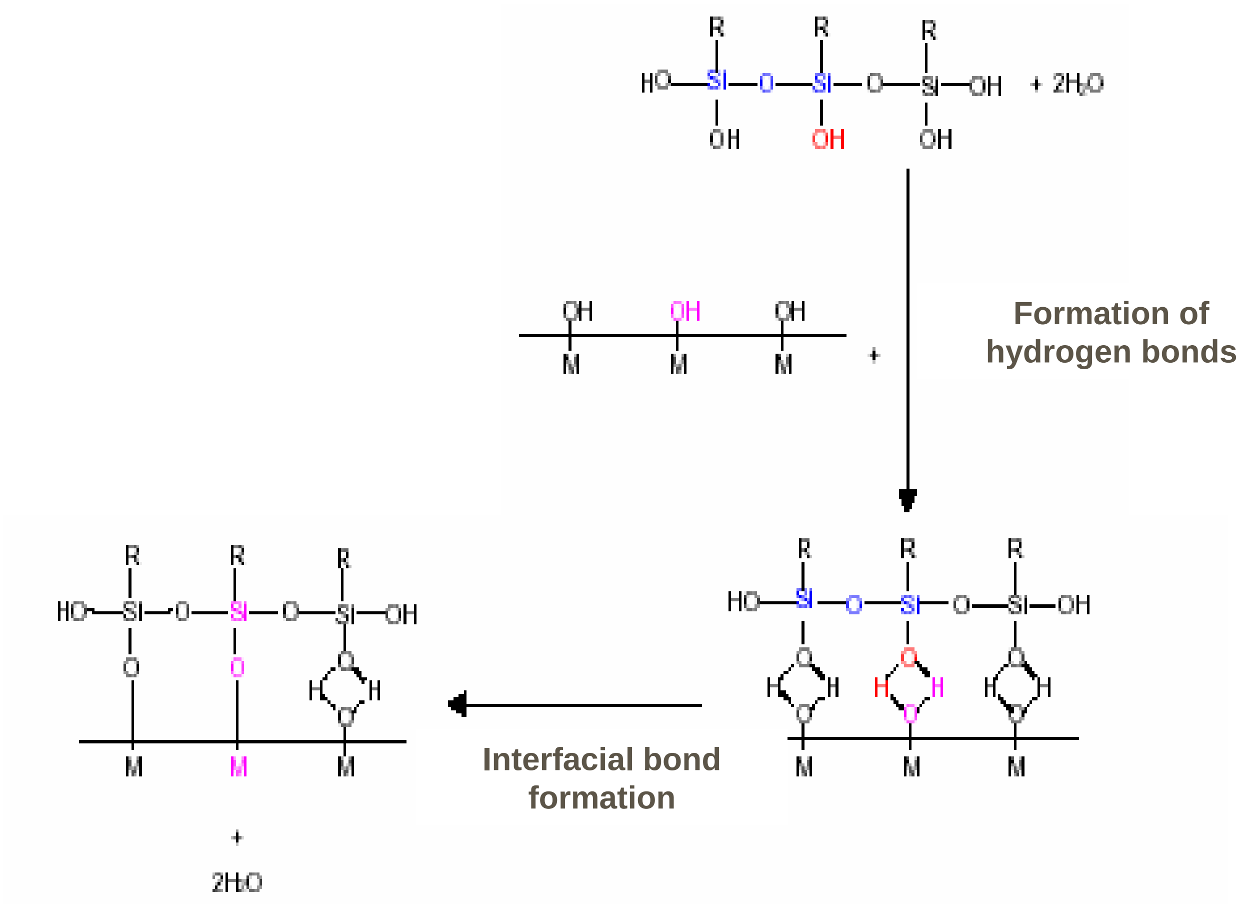
2.5 wt% BTSE

⇒ Film morphology depending on solution concentration and wet deposition method (roll-coating vs dipcoating)

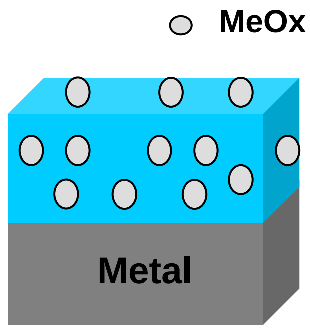


System 1

Part 1: Wet deposition of silane



⇒ Strong covalent metal-film bonding; good adhesion



System 3

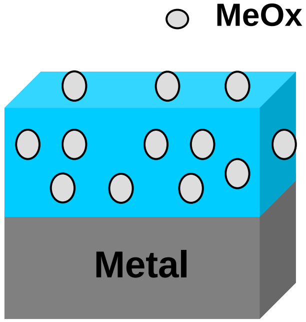
Part 1: Wet deposition of silane + nanoparticles

- **CeO_2 nanoparticles** (10-20nm) for barrier properties and as nano-carriers for corrosion inhibitors
- **$Ce(NO_3)_3$** for self-healing properties

In collaboration with:

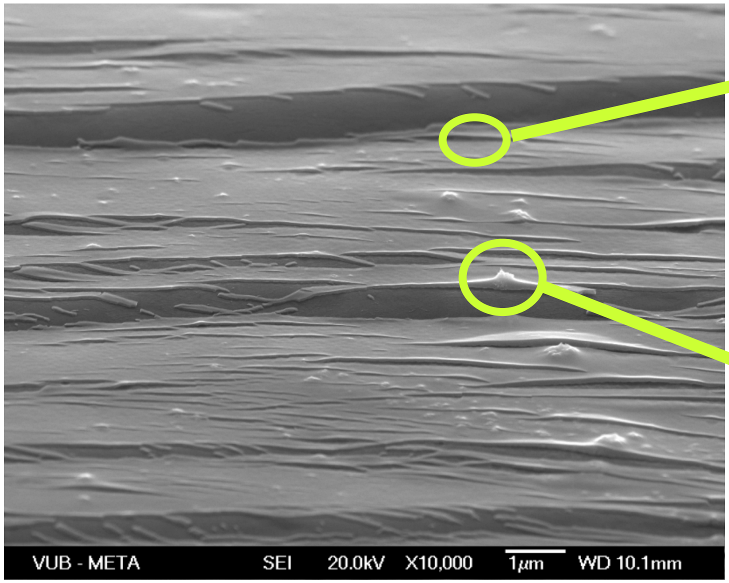
- Instituto Superior Técnico, ICEMS, Lisboa (Fatima Montemor)
- Centre de Recherche Public Henri Tudor (CRP-HT), Luxembourg
- Umicore

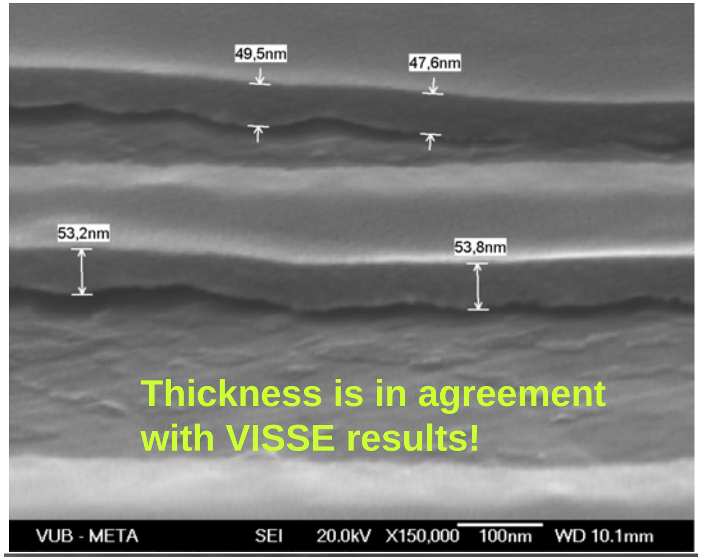
FEG-SEM / EDX

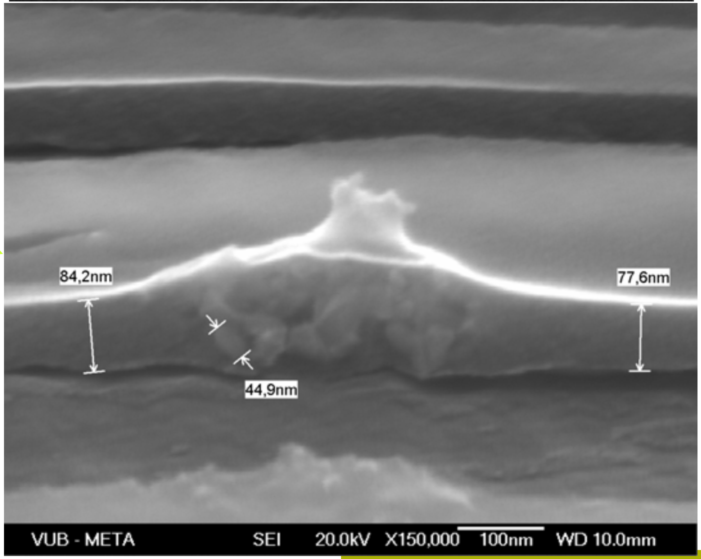


System 3

Al 99.99% electropolished
Spin/dip Coated with BTSE 5 wt%
+ 250ppm CeO_2+ 250ppm $Ce(NO_3)_3$

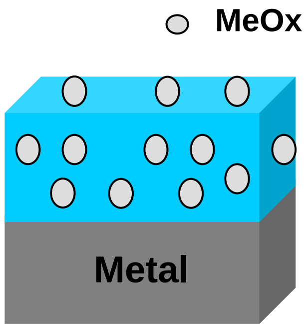




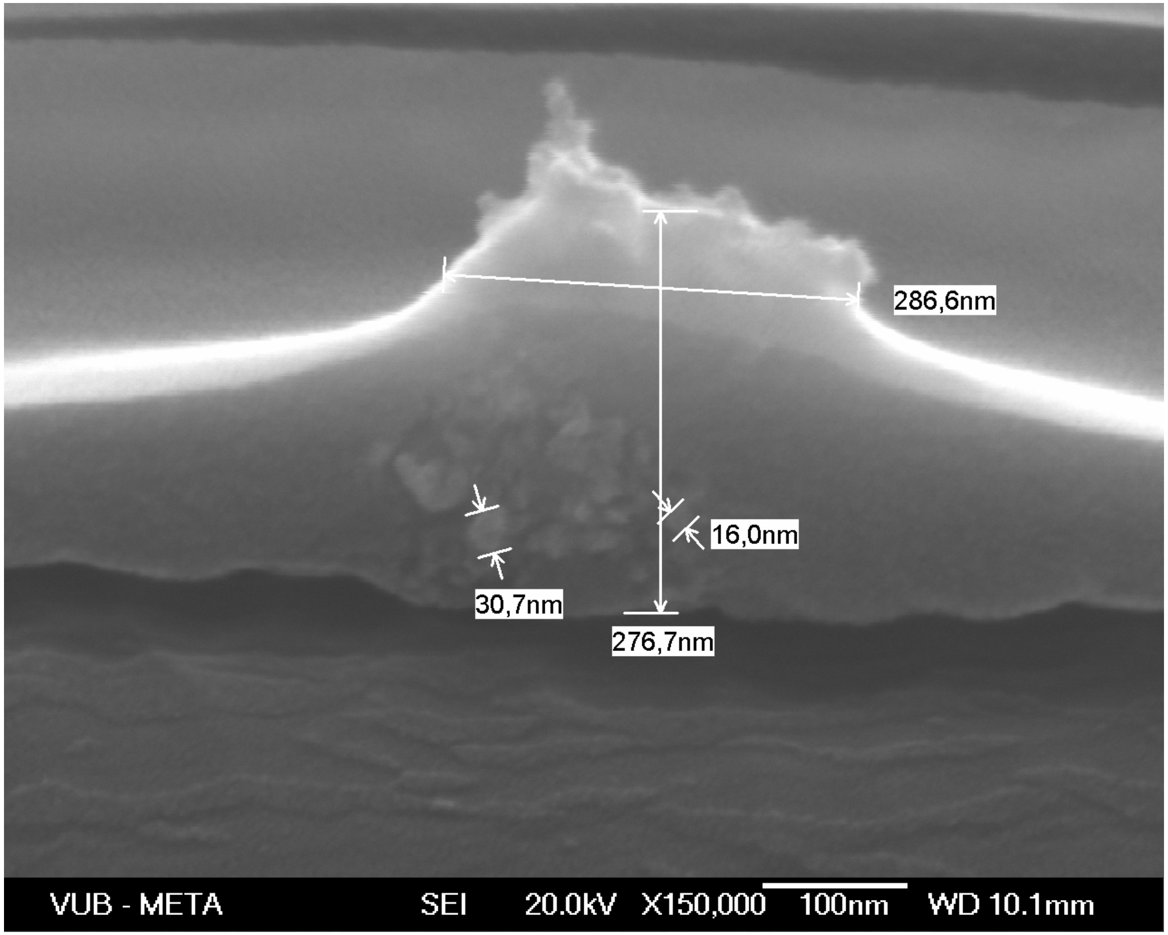


⇒ Agglomeration of nanoparticles

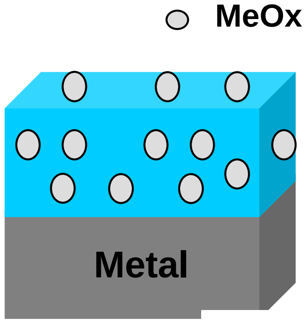
FEG-SEM / EDX



System 3



⇒ Agglomeration should be avoided by improved solution preparation

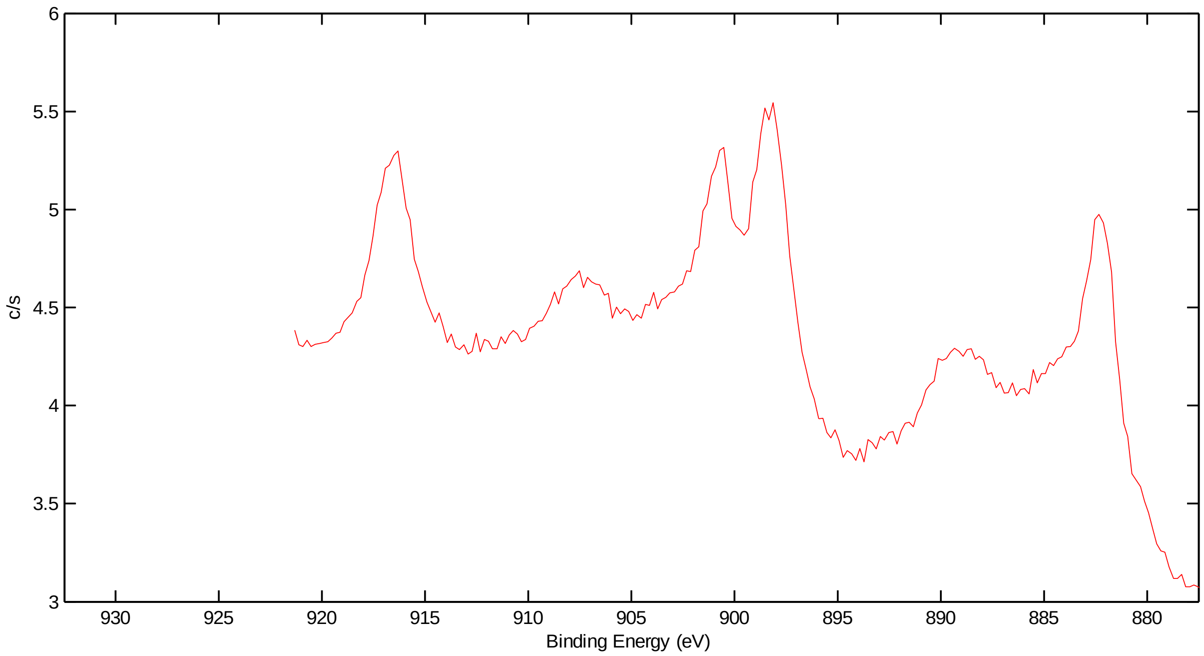


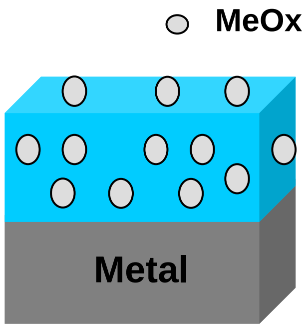
System 3

XPS: bonding between silane and MeOx nanoparticle?

Experiment: XPS on CeO_2 powder pellet

Ce XPS signals



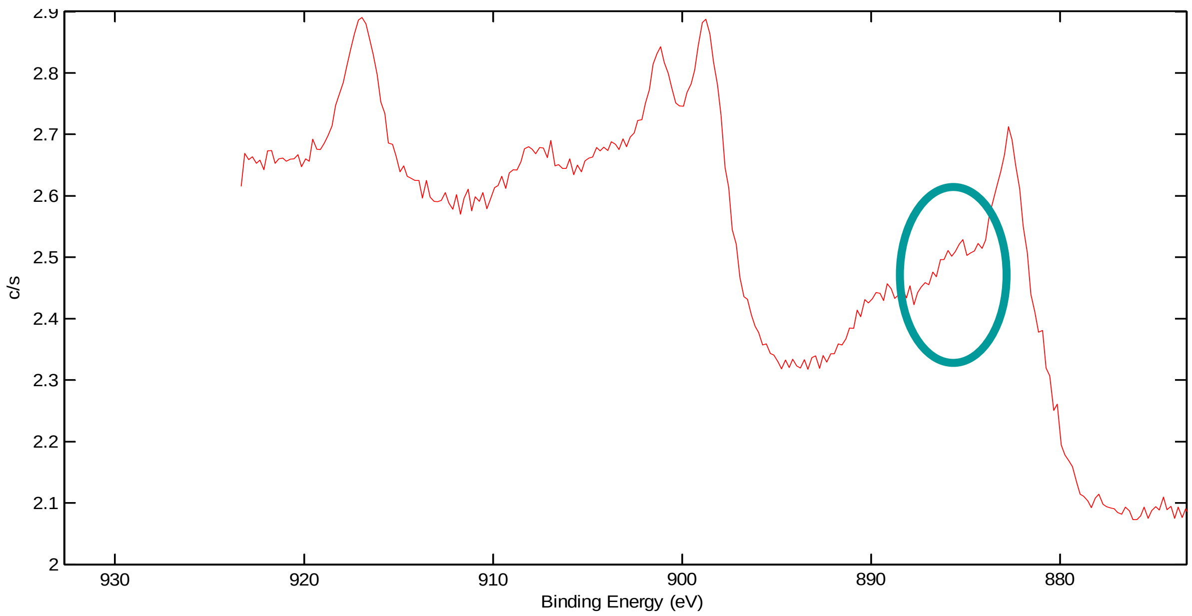


System 3

XPS: bonding between silane and MeOx nanoparticle?

Experiment: XPS on CeO_2 powder pellet + drop of BTSE

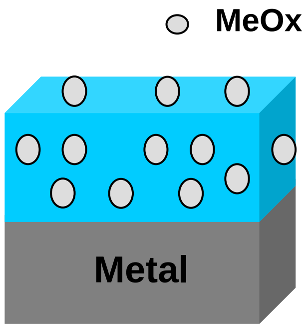
Ce XPS signals



⇒ Indication of additional type of Ce environment

⇒ Possible evidence of silane bond formation on Ce-oxide pellet

Wet deposition of silane + nanoparticles



System 3

Film properties ? Effect of wet deposition process conditions on properties ?

Ongoing work….

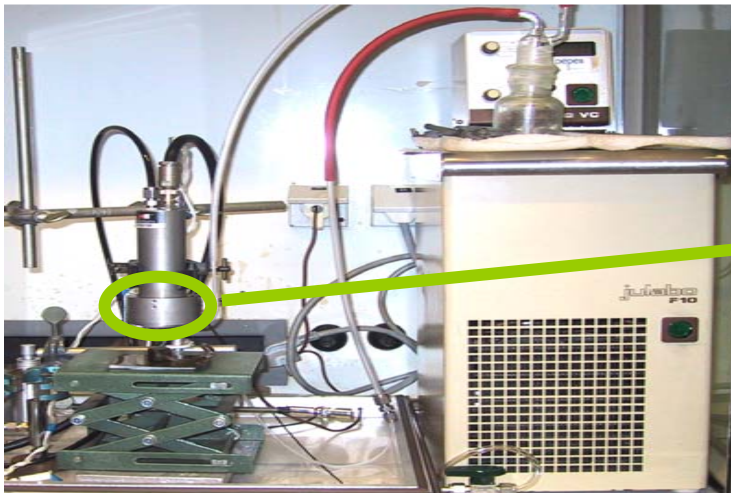
Part 2: Plasma deposition

Differences with wet deposition?

- Silane vapour is carried by argon gas into the plasma
- Silane is (partially?) decomposed by collision with plasma components
- What is being deposited???

Part 2 .1: Atmospheric plasma deposition

Plasma source Chemical bubbler



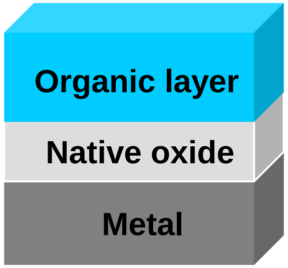
Sample support Thermostat

Precursor Inlet

Showerhead
25 mm of diameter

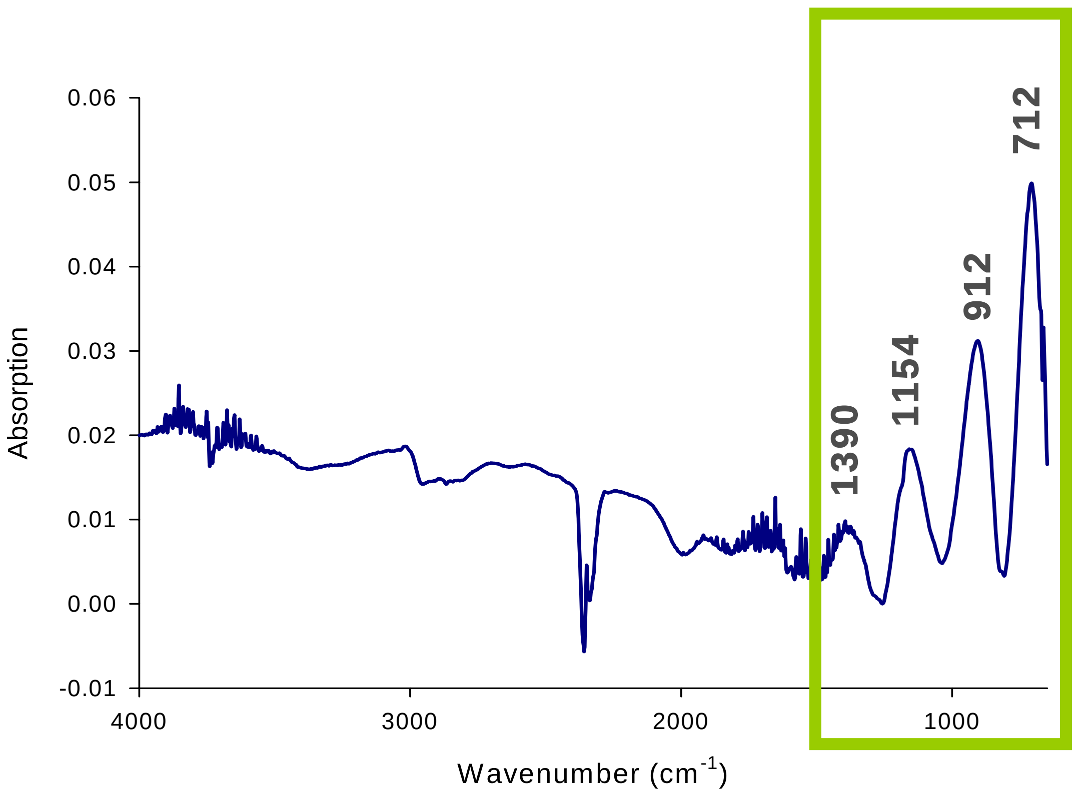
Coating material	**BTSE vapour at 100°C (from concentrated solution)**
Gas discharge	**Argon**
Substrate to showerhead distance	**5 mm**
Power	**40 to 80 W**
Argon flow	**23.9 l/min**
Deposition time	**30 to 300 s**

Part 2.1: Atmospheric plasma deposition



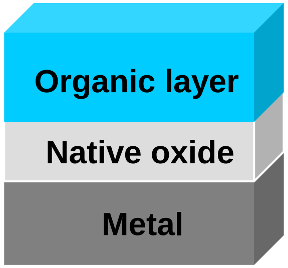
System 1

IR analysis of atmospheric plasma polymerised BTSE at 50W, 10 min



Peak position (cm^{-1})	Assignement
1390	C-H symmetric bending ($-CH_3$)
1154	Si-O-C ($-SiOCH_2CH_3$)
912	Si-O-C symmetric stretching ($-SiOCH_2CH_3$)
712	C-H rocking

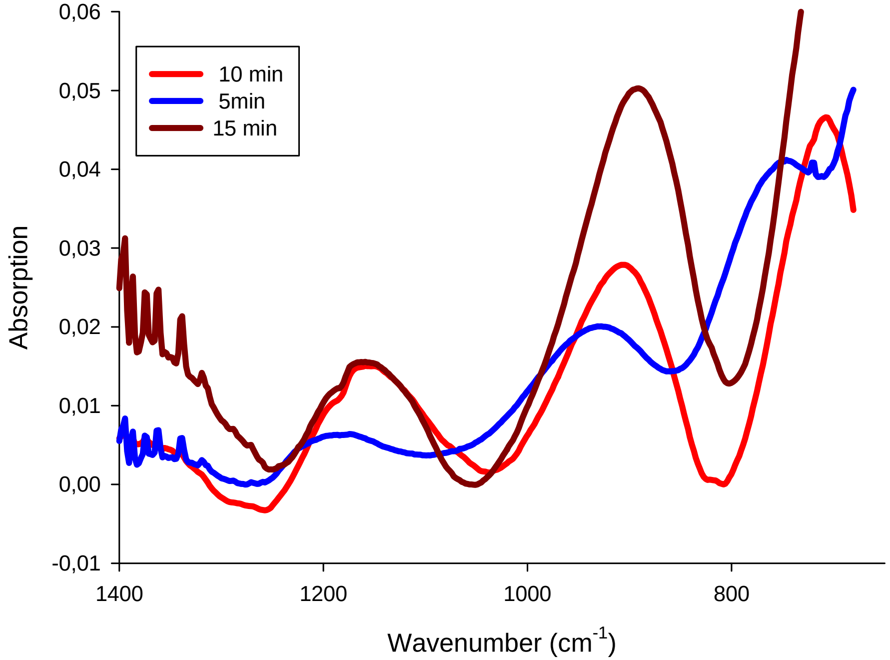
⇒ Film contains organic groups



Part 2.1: Atmospheric plasma deposition

System 1

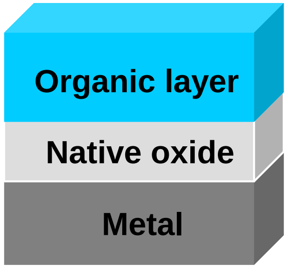
Influence of deposition time



(50 W)

Peak position (cm^{-1})	Assignement
1154	Si-O-C ($-SiOCH_2CH_3$)
912	Si-O-C symmetric stretching ($-SiOCH_2CH_3$)
712	C-H rocking

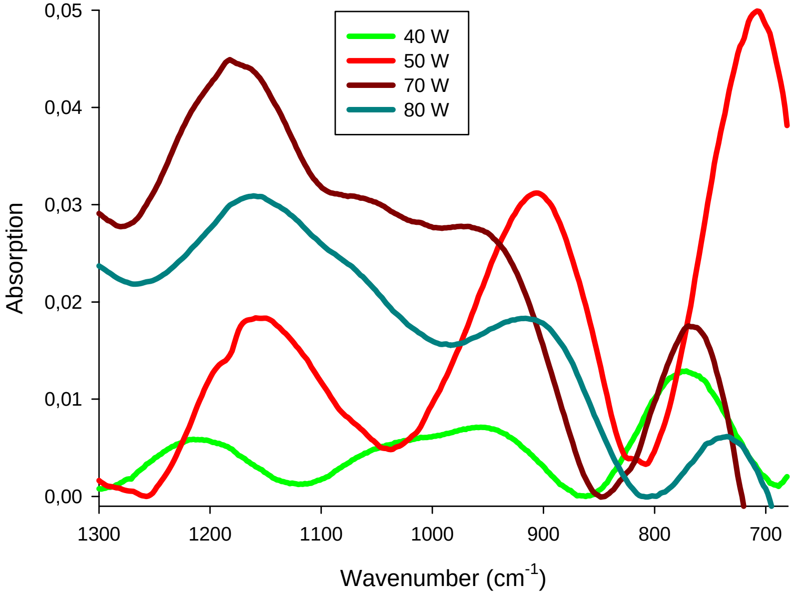
⇒ Increasing deposition time results in thicker layers



Part 2.1: Atmospheric plasma deposition

System 1

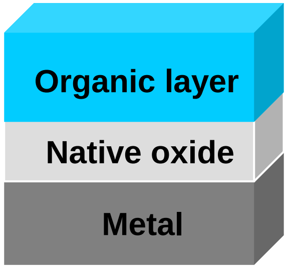
Influence
of input power



(10 min)

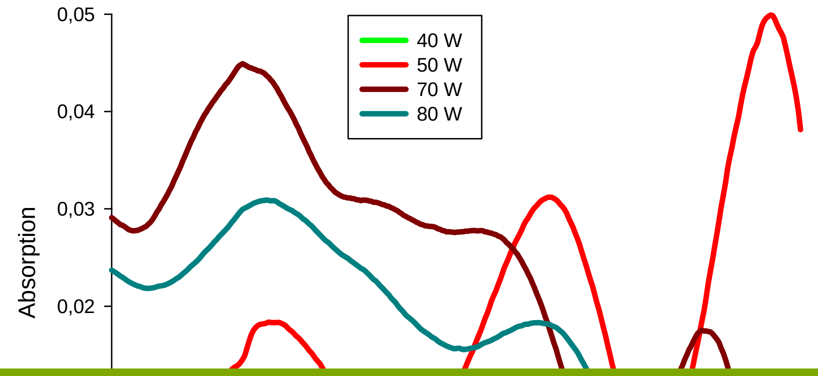
Peak position (cm^{-1})	Assignement
1154	Si-O-C (-$SiOCH_2CH_3$)
912	Si-O-C symmetric stretching (-$SiOCH_2CH_3$)
712	C-H rocking

⇒ Input power changes the amount of bonds and the chemical environment in the film



System 1

Influence
of input power



Film properties ? Effect of plasma conditions on properties ?

Ongoing work….

Peak position (cm^{-1})	Assignement
1154	Si-O-C ($-SiOCH_2CH_3$)
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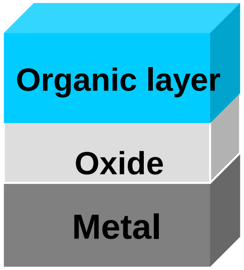
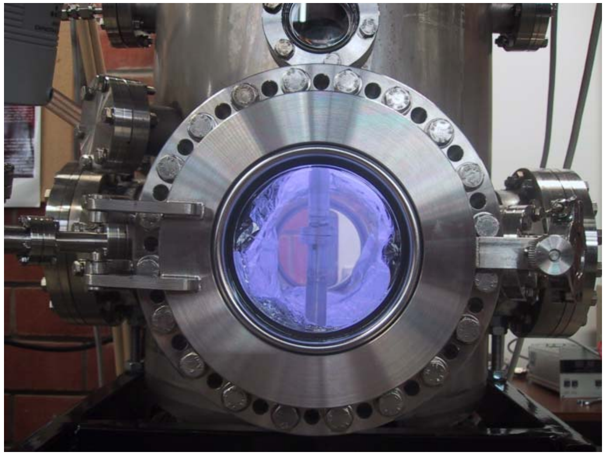


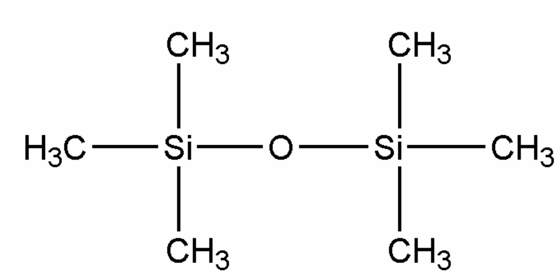
Part 2.2: Vacuum plasma deposition

System 2

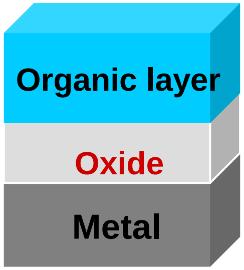


Aim:

- Step 1: Deposition of Si-oxide from hexamethyldisiloxane HMDSO



- Step 2: Deposition of organic layer of BTSE (similar to atmospheric plasma results; not shown)

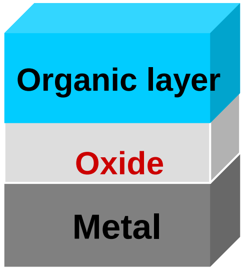


Part 2.2: Vacuum plasma deposition

System 2

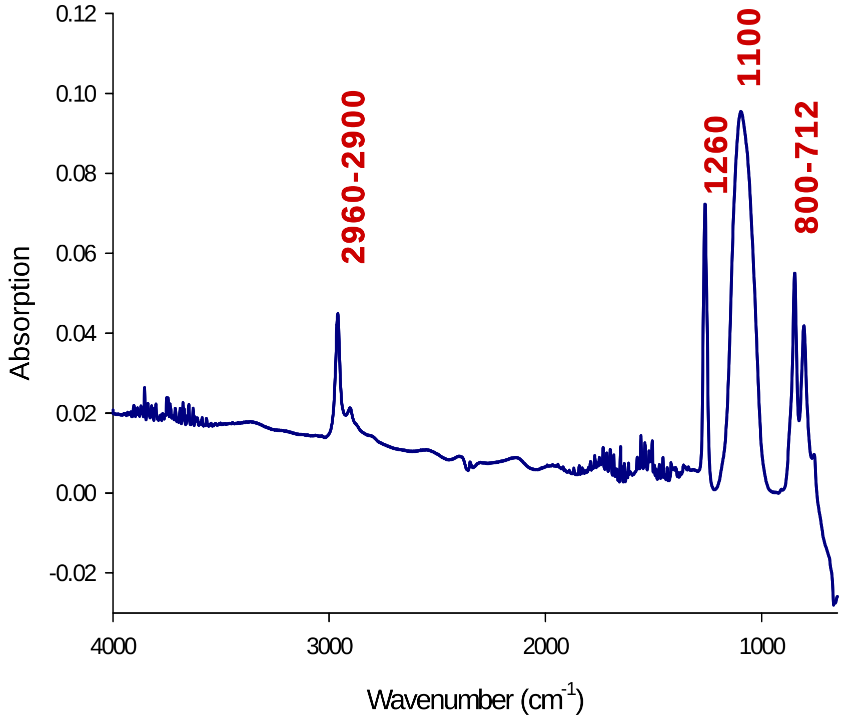
Coating material	Hexamethyldisiloxane (HMDSO) solution
Gas discharge	HMDSO or HMDSO+O_2
Power	50 to 300 W
Deposition time	300 s, 600 s

Part 2.2: Vacuum plasma deposition



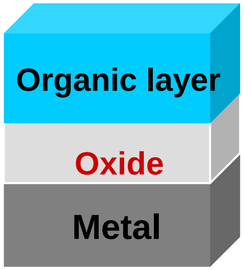
System 2

IR analysis of vacuum plasma polymerized coating from HMDSO
(300 W, 300 mT, 10 min)



Peak position (cm^{-1})	Assignement
2900-2960	C-H symmetric and asymmetric stretching (-CH_3-)
1260	CH_3 symmetric bending (-Si(CH_3)$_x$)
1100	Si-O / -Si-O-Si- stretching
790-800	-Si(CH_3)$_n$ rocking

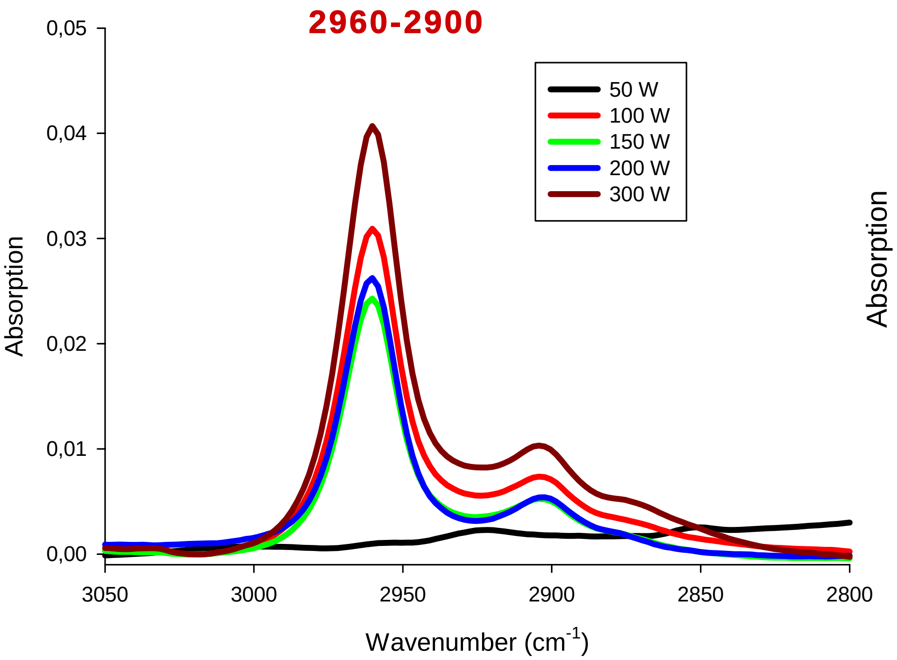
⇒ 'oxide' layer contains carbon groups

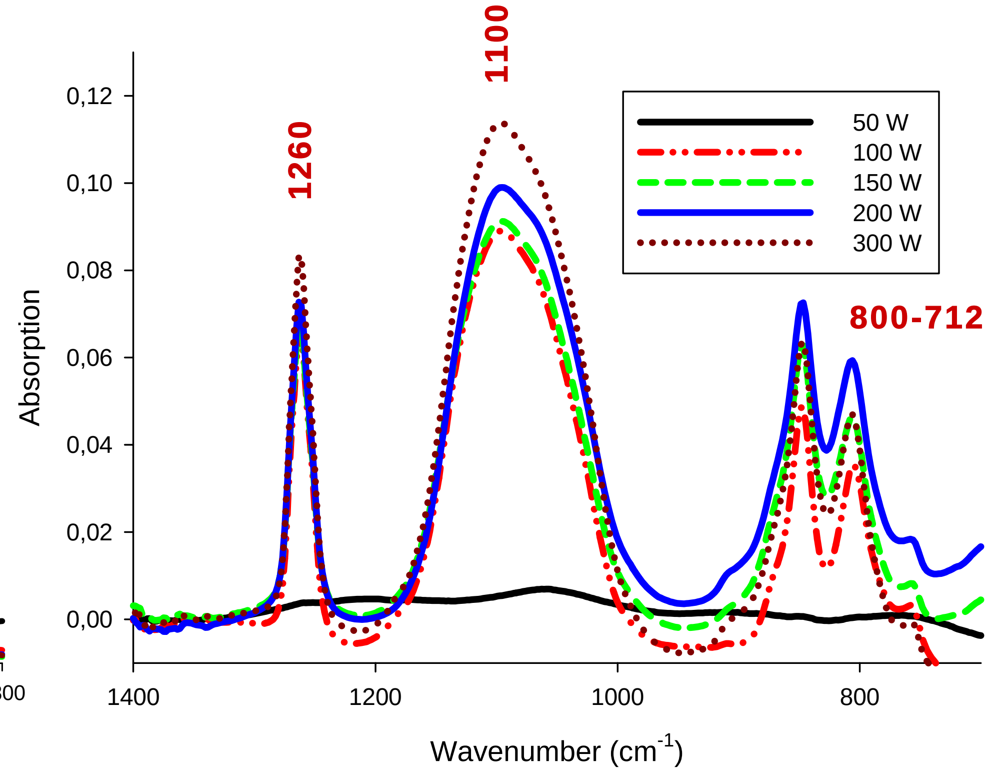


Part 2.2: Vacuum plasma deposition

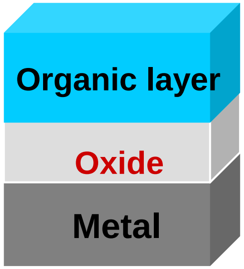
System 2

Influence of input power





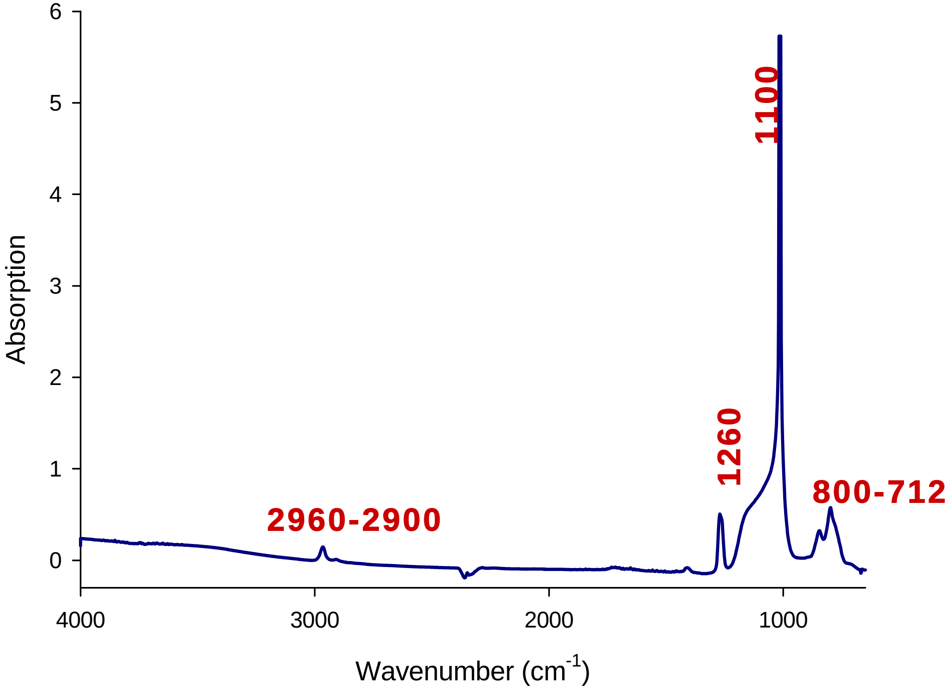
⇒ Increased input power results in thicker deposition



Part 2.2: Vacuum plasma deposition

System 2

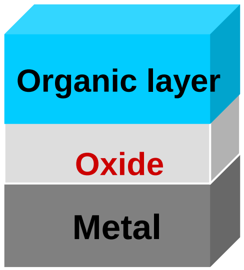
Influence of oxygen addition to HMDSO plasma :
20% HMDSO / 80% O_2
(200 W, 300 mT, 10 min)



Peak position (cm^{-1})	Assignement
2900-2960	C-H symmetric and asymmetric stretching ($-CH_3-$)
1260	CH_3 symmetric bending ($-Si(CH_3)_x$)
1100	Si-O / -Si-O-Si- stretching
790-800	$-Si(CH_3)_n$ rocking

⇒ Less carbon groups; more Si-O formation

⇒ Confirmed with XPS



System 2

Part 2.2: Vacuum plasma deposition

⇒ Oxygen addition favours decomposition of the HMDSO in the plasma and the deposition of a purer, inorganic layer of Si-oxide

⇒ x% HM

= variable for

Film properties ? Effect of plasma conditions on properties ?

Ongoing work….

= formation of layers with variable level of carbon groups and inorganic species resulting in different (???) film properties

Conclusions

⇒ different deposition methods and deposition conditions result in different types of films in terms of morphology and composition (organic, inorganic or mixed)

Film properties ?

Effect of processing conditions on properties ?

Ongoing work….