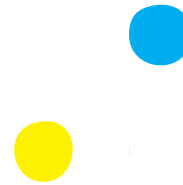


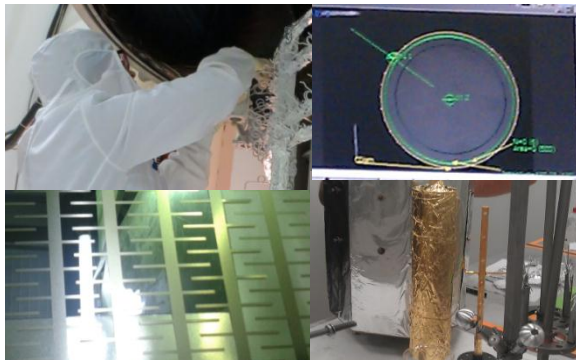


ireis

—
institut de recherches
en ingénierie des surfaces



EIROforum
Science-Business WAMAS
Workshop on Advanced Materials And Surfaces



Thin Film imbedded nanoparticles obtained in large size vacuum deposition system

L. Dubost, November 19th 2013

HEF Surface engineering



3 skills

Tribology

- Wear
- Friction



Thermochemistry & diffusion layers

- Nitriding
- Nitrocarburizing
- Molten salts
- Heat transfer salts



Thin films & plasma sources

- Sputtering
- PECVD
- Microwave plasma sources



3 business models

Jobbing

- Specific coatings on customers parts



Technology transfer

- Licencing
- Engineering
- Equipments
- Consumables



Products

- Bearing
- Bushing



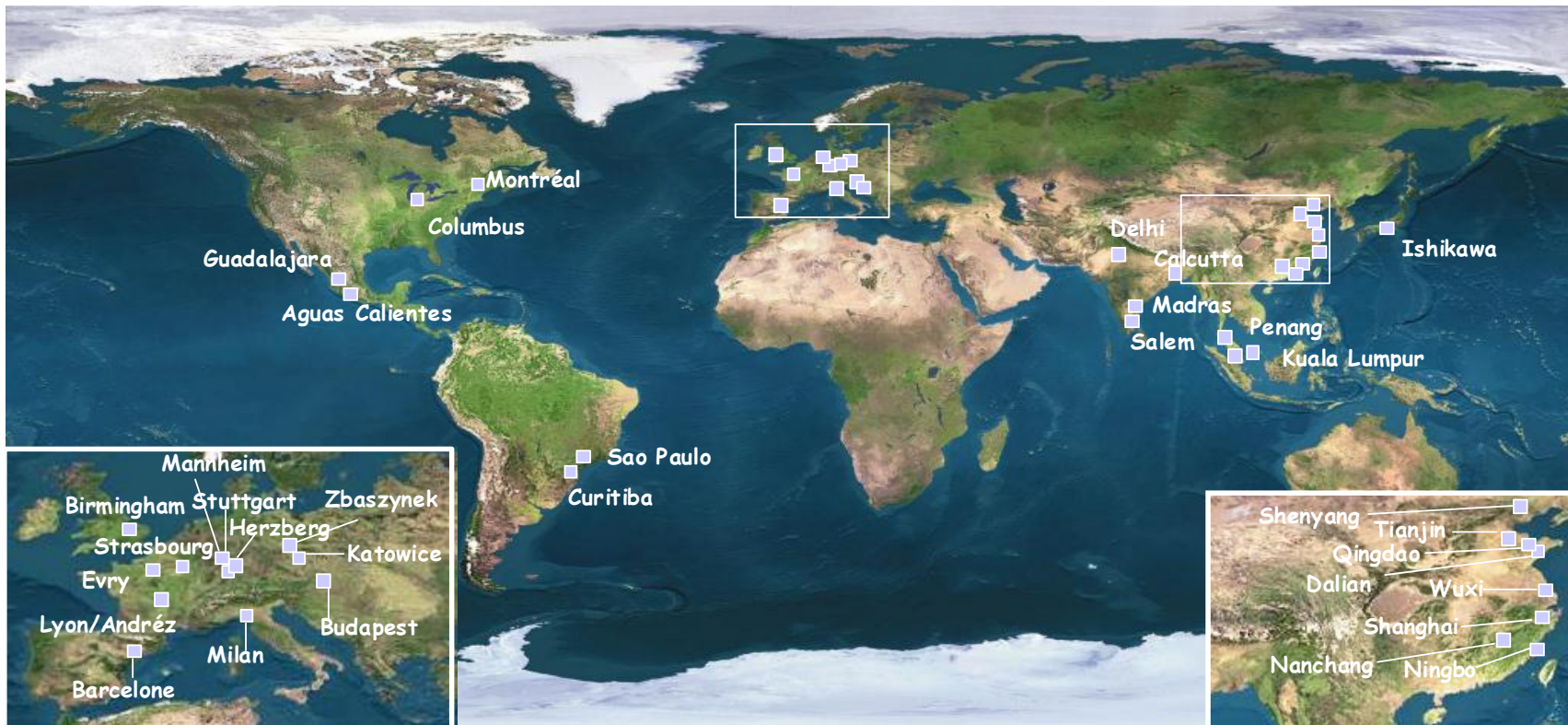
Worldwide activity



- Headquarters : Andrezieux
- 58 industrial sites
- Presence in 15 countries

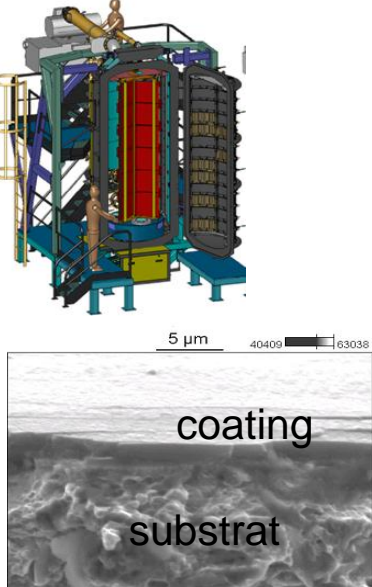

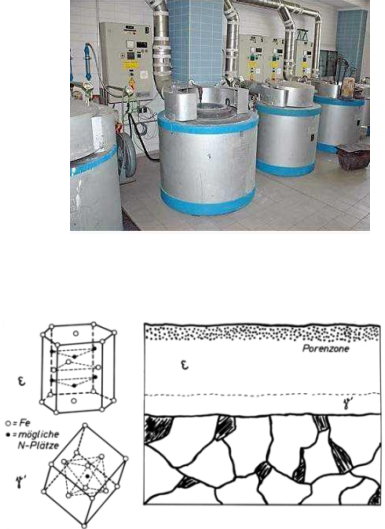
- 1400 employees
- 140 M€ sales
- Capital owned by the employees

- 3 research centers :
France, Germany,
Canada
- 50 FTE





Research contract services

Thin Films	Tribology	Thermochemistry
 <p>5 µm 40409 63038</p> <p>coating</p> <p>substrat</p>		 <p>Porenzone</p> <p>○ = Fe ● = mögliche N-Platze</p>

Surface engineering & Coatings fields :
Energy, optical, electrical devices
and chemistry, mechanic

B to B
Collaborative projects
National calls : ANR, FUI, ...
EU Calls : NMP, Energy, Space

R&D on industrial size coating machine standard line



TSD 400



TSD 550



TSD 800



TSD 850



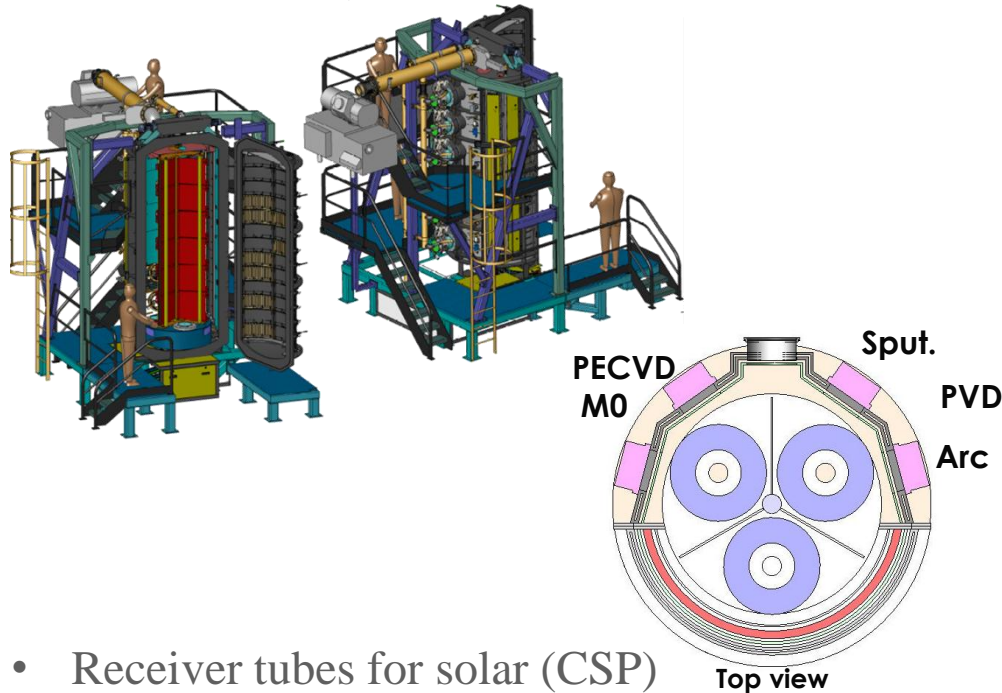
TSD 900



Special equipment



Pilot equipment TSD 2800 R



- **H = 2.8 m**
- **D = 1100 mm**
- **3.3 TONNES/POSITION**

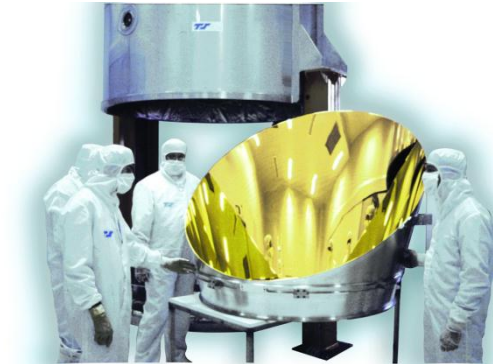
- Receiver tubes for solar (CSP)
- Rolling mills
- Aeronautic parts
- Large scientific instrument
- Chemical plant parts



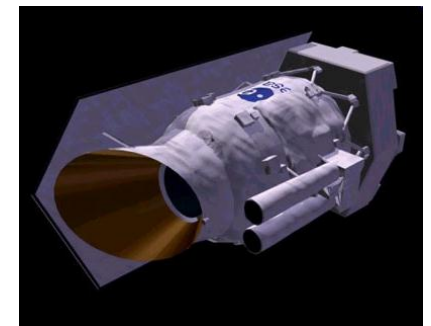
Equipment TSD 2200



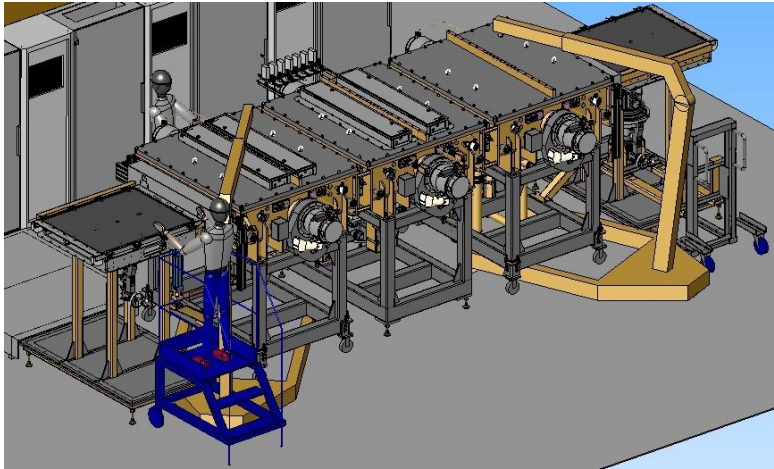
- **Coating height= 1,7 m**
- **Diameter = 1,5 to 2 m**
- **Internal mag. sputtering cathodes**



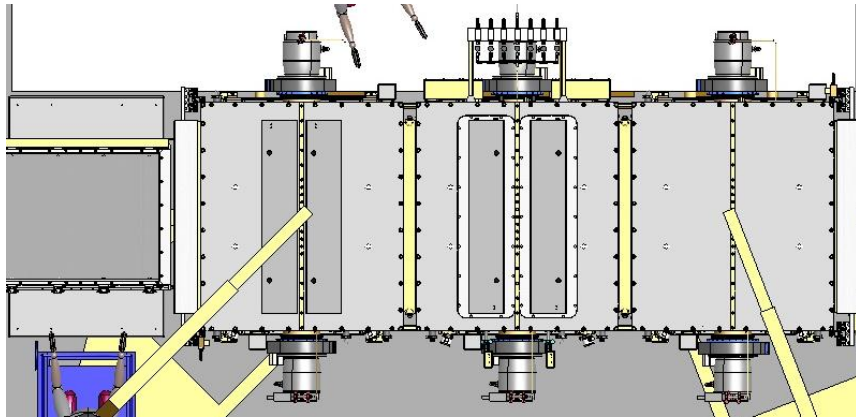
Sun screen ISO satellite
Aluminium structure
5 mm thick
Diameter : 2 m
Gold coating of internal
conical shape



Equipment HPL 800-3



- Coating area = 1 m x 0,8 m
Up to 1 m²
- In line deposition chambers
- Magnetron sputtering
- PECVD : microwave



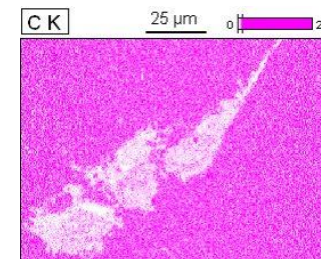
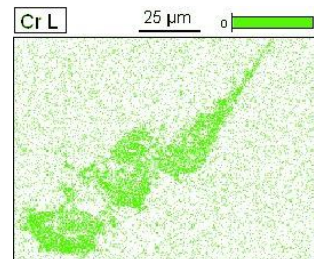
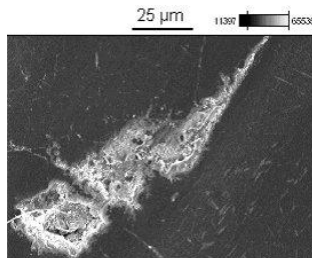
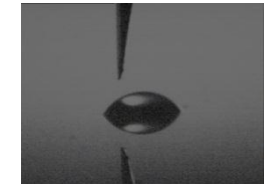
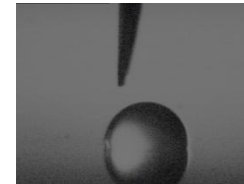
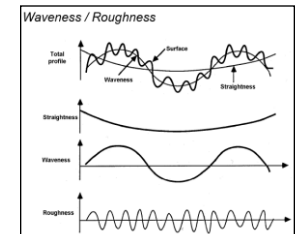
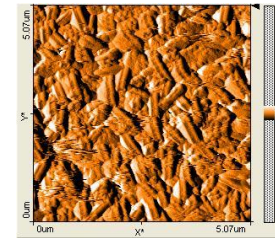
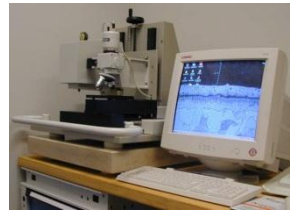
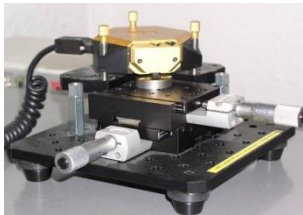
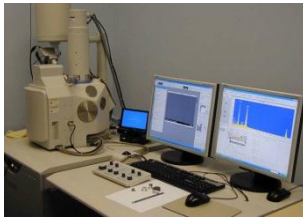
ISO 6		
Part/m ³	0.3 μm	102000
	0.5 μm	3520
	5 μm	29

Characterisation and material analysis



Optical microscope,
Spectrophotometer UV Vis / Integration sphere
SEM
AFM, Profilometry, Roughness 2D et 3D
EDX analysis Metallographic analysis

Nano indentation
Hardness(Rockwell → Nano)
Surface tension
Scratch test



Large panel of applications in various fields




Functions	Tribological Coatings		Electrically conductive coatings		Gas barrier coatings	
	Hard coatings		Transparent and conductive		Membranes	
	Corrosion resistant coatings		IR filtration coatings		Hydrophilic or hydrophobic	
	Decorative coatings		Reflective coatings		Catalytic or Biostatic	
Systems	Microbatteries		Electrochromic systems		Outside mirrors	
	Li-Metal thin films batteries			Electrochromic film on flexible substrates	Heating coating + Reflective coating	

Nanoparticles imbedded in thin films



Nanoparticles developed for various applications at HEF :

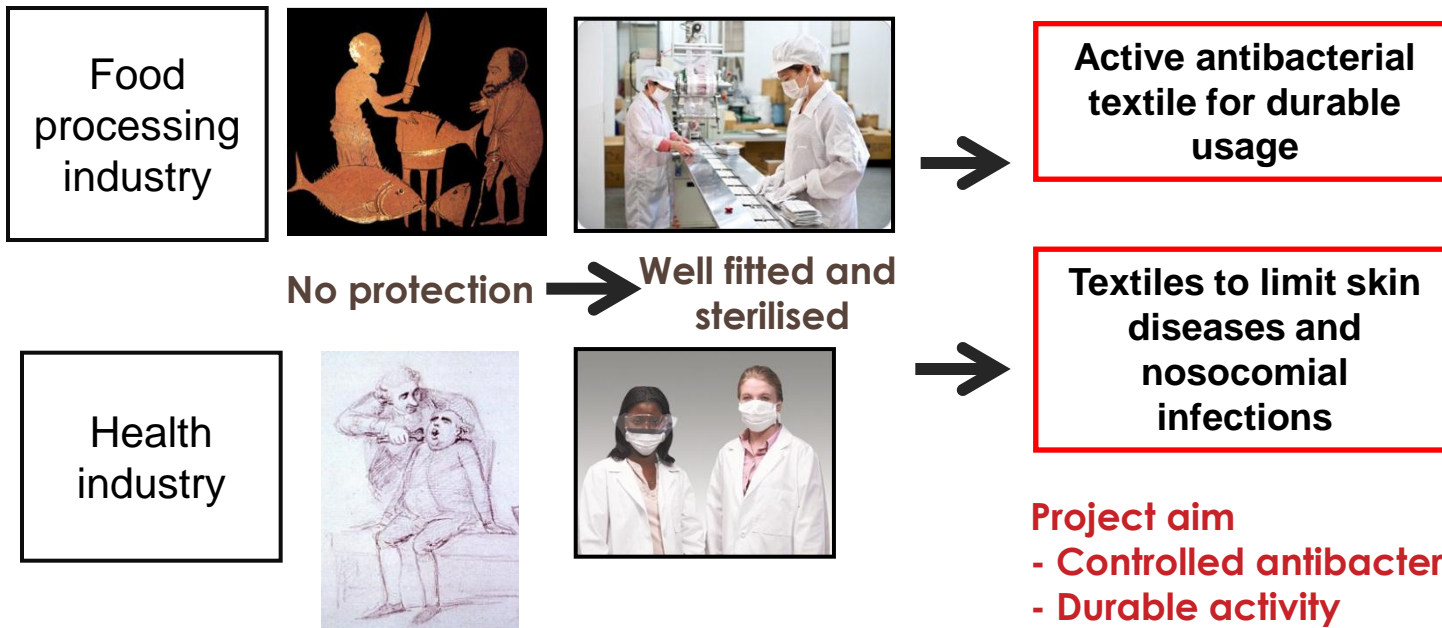
- Al_2O_3 / Pt Cermet
- SiOCH / Ag Antibacterial  Actiprotex
- TiO_2 / Ag Photochromism
- CrN / Ag XX
- TiN / Ag XX
- DLC / Ag XX

Actiprotex project context & objectives

Silver nanoparticles in SiOCH films



Antibacterial protective tissues



- Project aim**
- **Controlled antibacterial activity**
 - **Durable activity**
 - **Transparent**

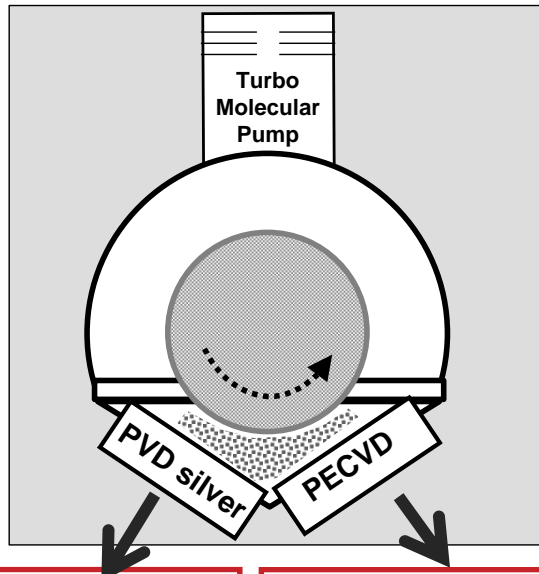
Collaborative Project Actiprotex supported by Techtera, the competitiveness cluster in Rhône-Alpes (France) and CG 42

IREIS :
Silver based coating

Plasma deposition tool



TSD 700 / top view



TSD 700 / side view



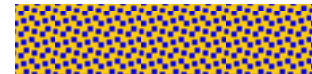
Magnetron sputtered Silver

Pressure : $3 \cdot 10^{-3}$ to $3 \cdot 10^{-2}$ mbar
Power : pulsed DC
 100- 2000 W
Gas : Ar

PECVD SiOCH

Pressure : $3 \cdot 10^{-2}$ mbar
Power : Radiofrequency capacitive coupling
 @13,56 Mhz 100W
Gas : HMDSO + O₂ + Ar

Simultaneous



Alternate



Material deposition and characterization

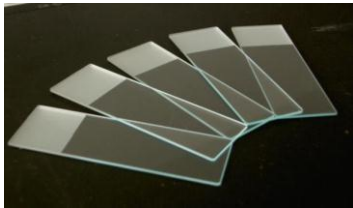


Glass slides

Characterisation



Silver composite
obtained from
plasma process



Analytical
TEM, SEM, XPS, ToFSIMS



&



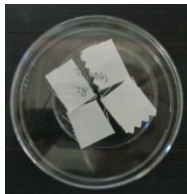
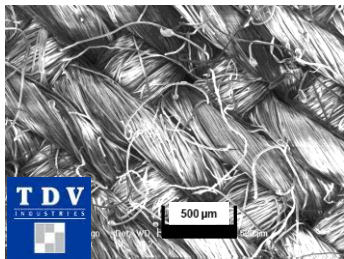
Optical



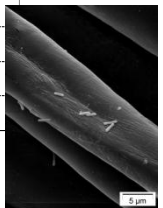
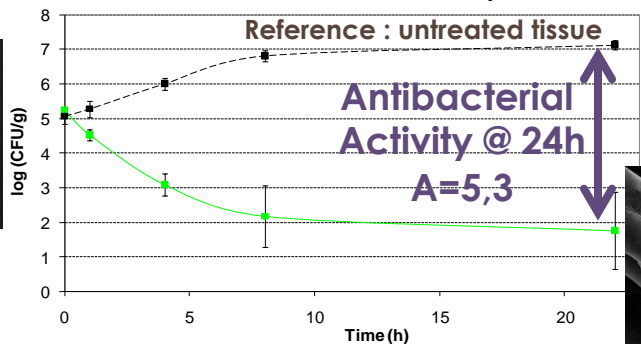
Microbiological

5 log CFU/mL

65% polyester / 35%
cotton (P/C) white



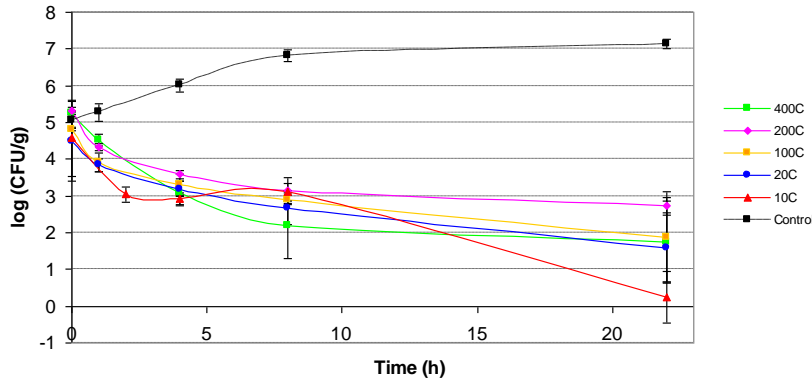
Listeria innocua LRGI A 01 (and *E. Coli*)



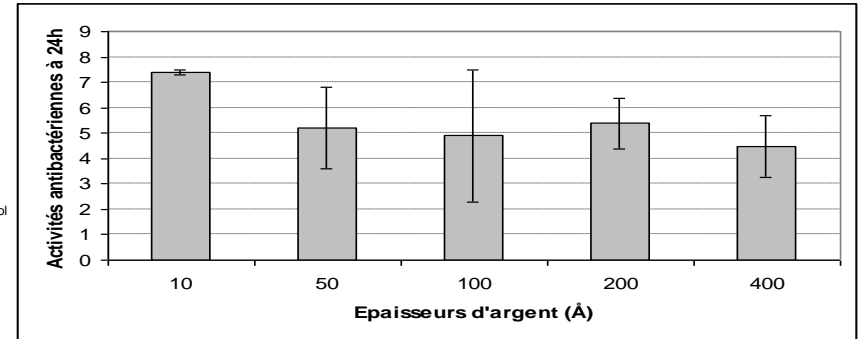
Silver single layers 10 to 400 nm thick



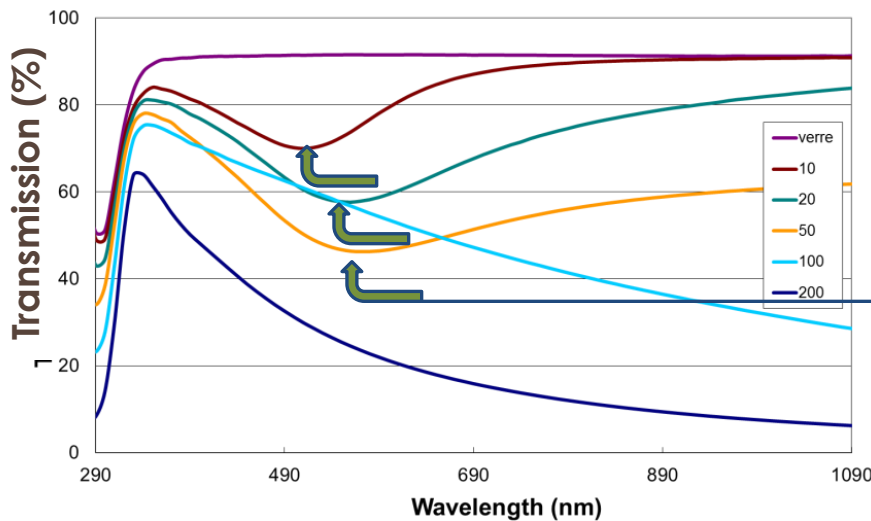
Listeria innocua count



Antibacterial activity



- Strong antibacterial activity
- Colored tissues
- Almost transparent films with 10 nm silver coating

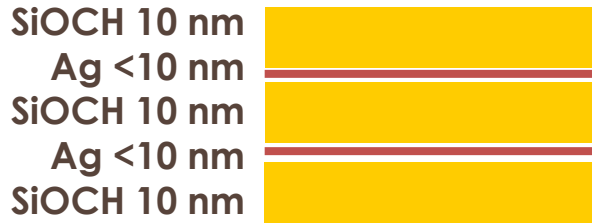


Plasmon absorption

Alternate deposition SiOCH / Ag

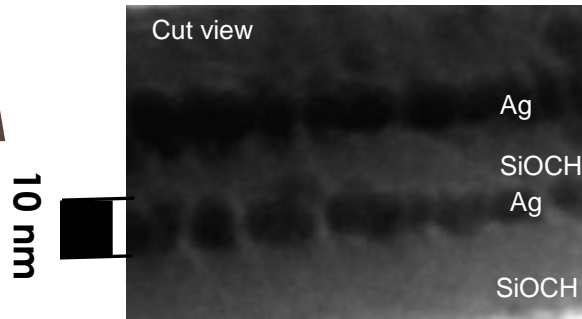


Film stack

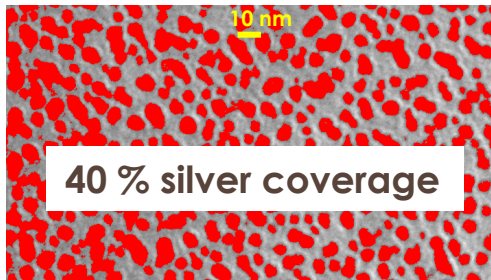


- 1) Average deposition rate measurement
- 2) Time control deposition

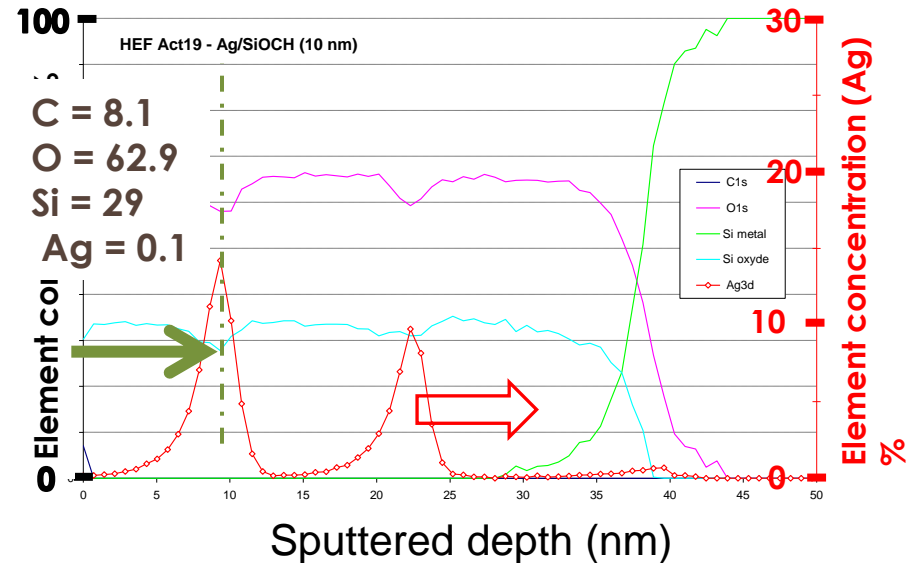
TEM



Top view optical Analysis Image J

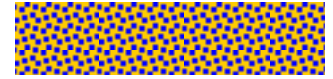


XPS Depth profile



Route not followed for antibacterial treatment

SiOCH Silver nano composite material simultaneous PECVD & PVD process

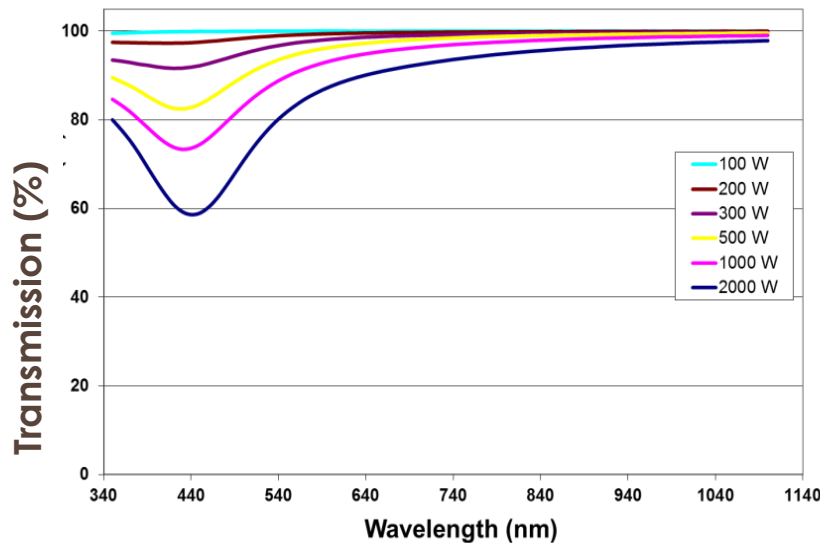


Vs PVD power

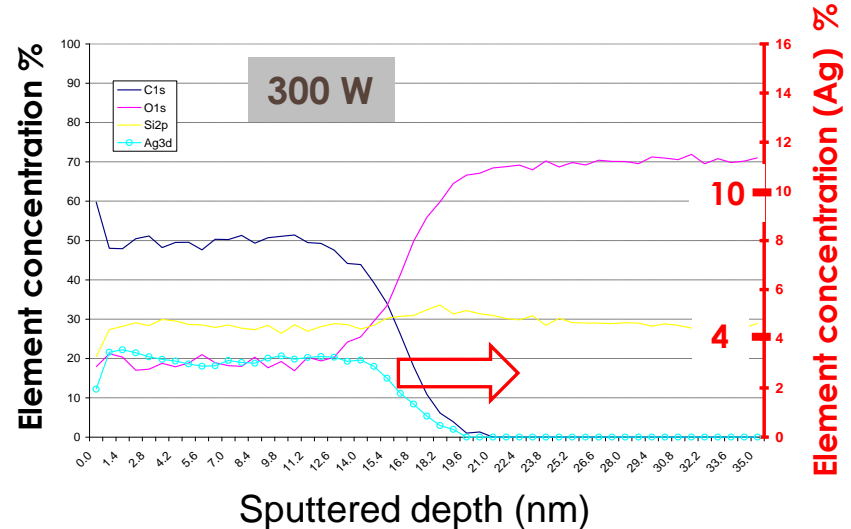
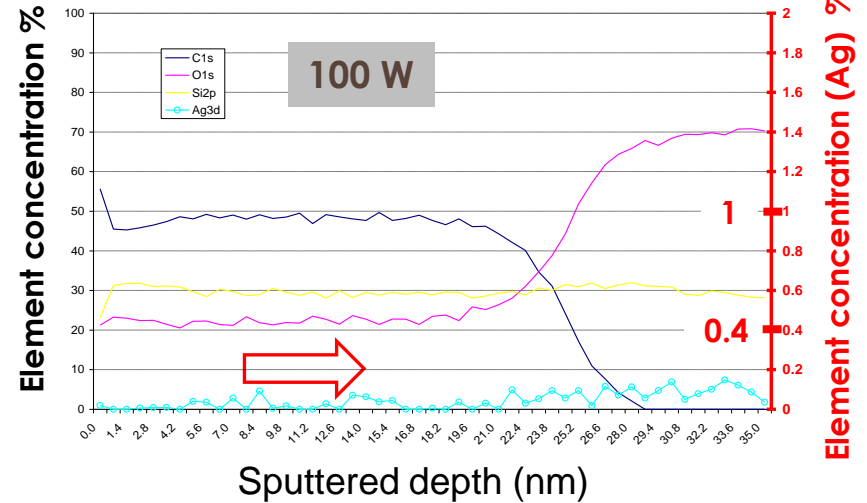
Gas : Ar + HMDSO + O₂

PECVD : 100 W

PVD : 100, 200, 300, 500, 1000, 2000 W



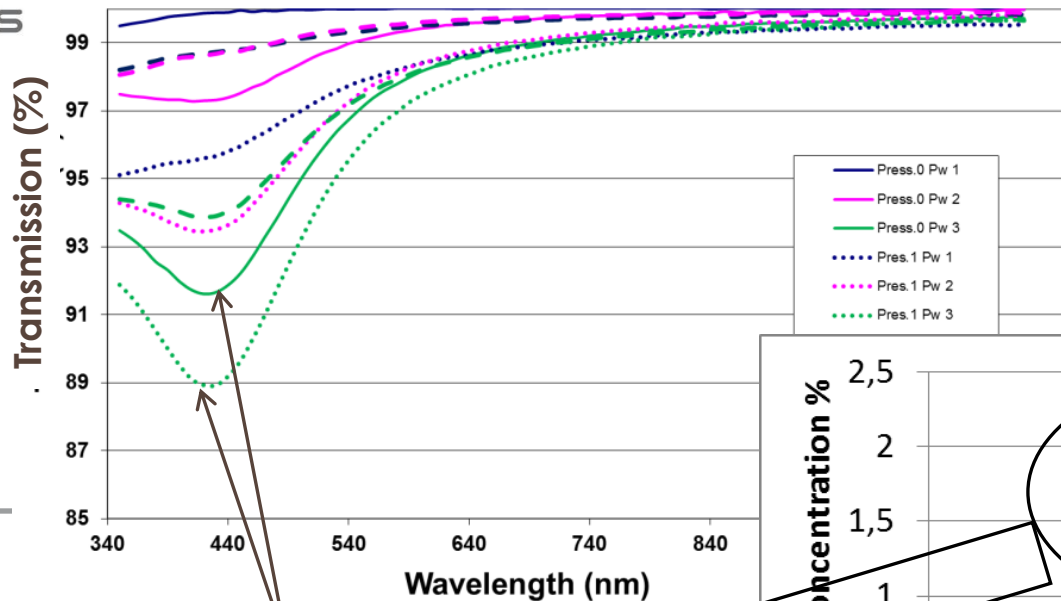
XPS Depth profile Press. 0



SiOCH Silver nano composite material simultaneous PECVD & PVD process



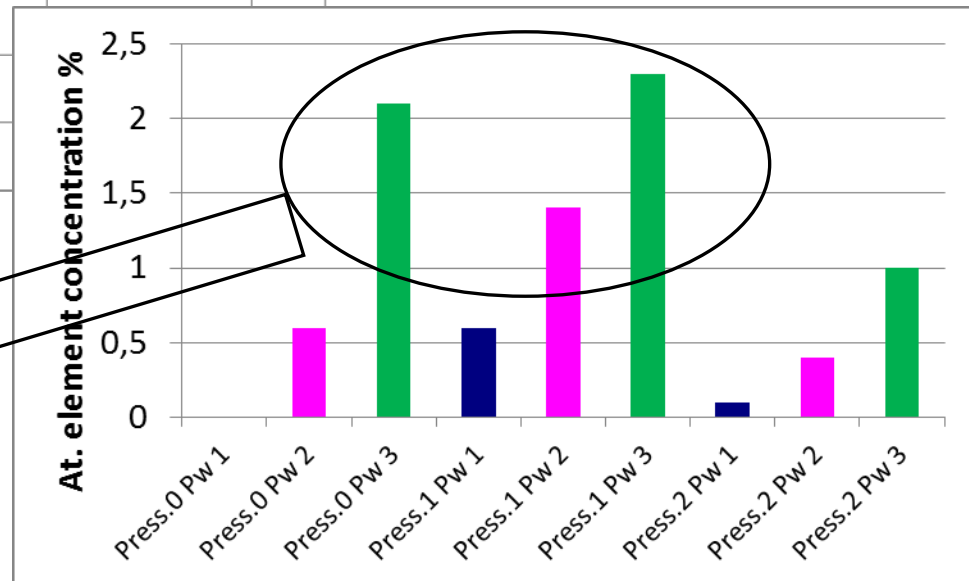
ireis



Similar Silver content
Different Plasmon absorption

Silver appears as AgO

XPS surface analysis

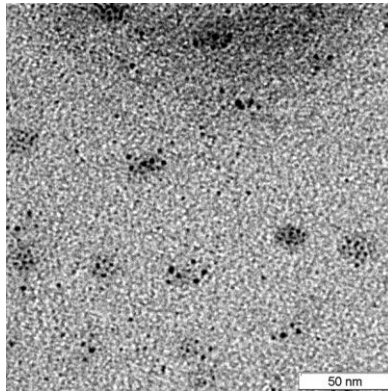


SiOCH Silver nano composite material



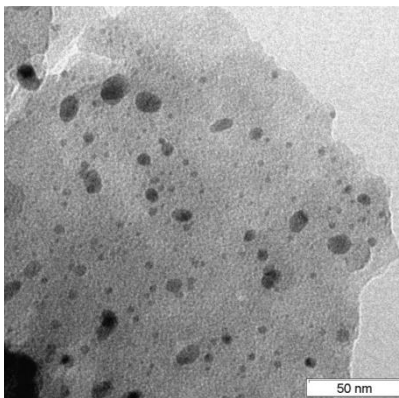
TEM

100 W



50 nm

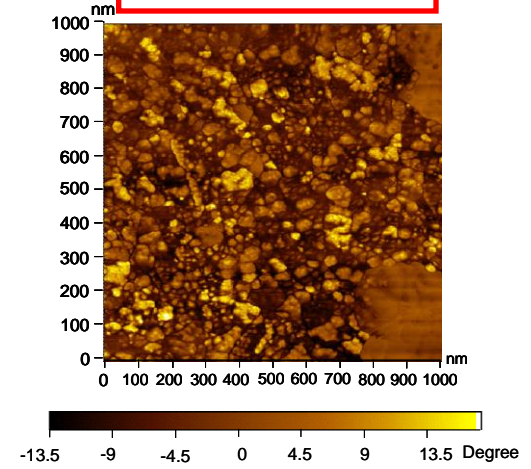
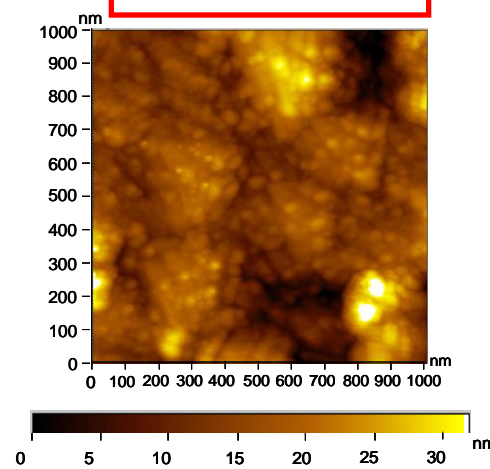
300 W



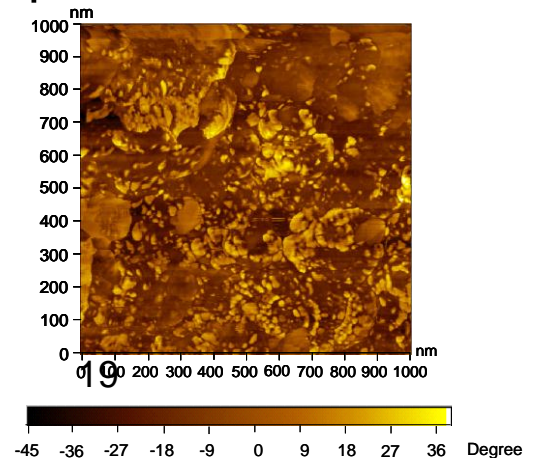
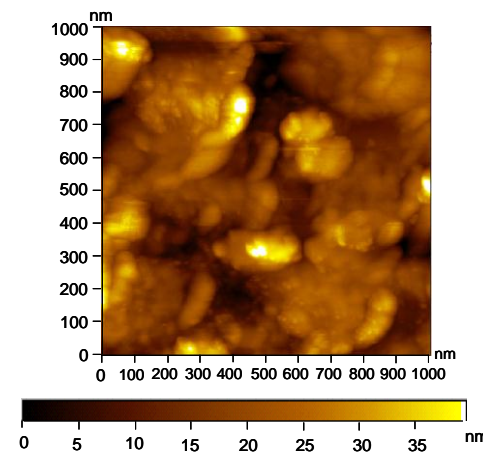
Morphology

AFM

Phase



Scan size = 1 μ m



SiOCH Silver nano composite material

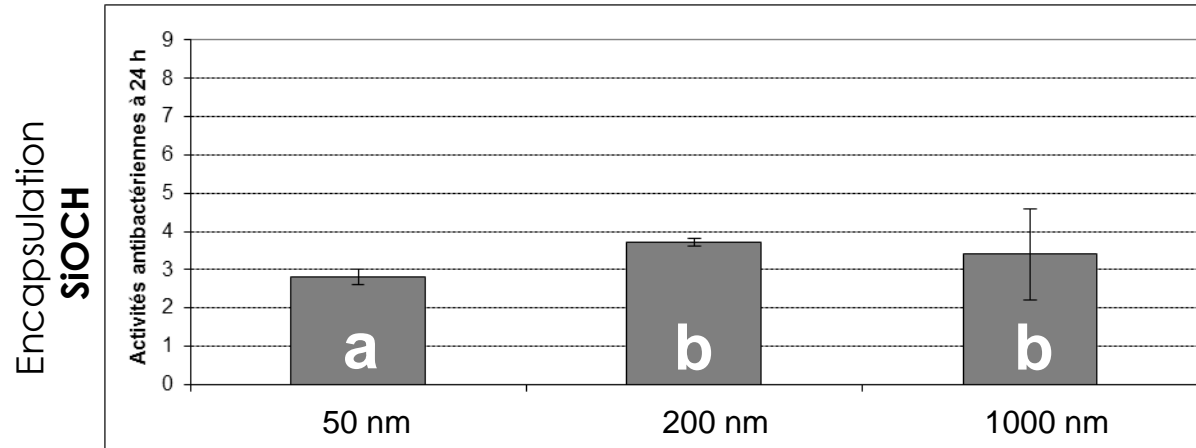


	PW 1			PW 2			PW 3			PW 4			PW 5		
							Ref	%T @440 nm	Acti						
Press.2							ACTI906	94,05	7,2						
Press.1							AC907	89,2	7,3						
Press.0	AC903	99,9	3	AC904	97,4	4	AC905	91,9	7,1	AC902	82,8	7	AC901	73,6	7



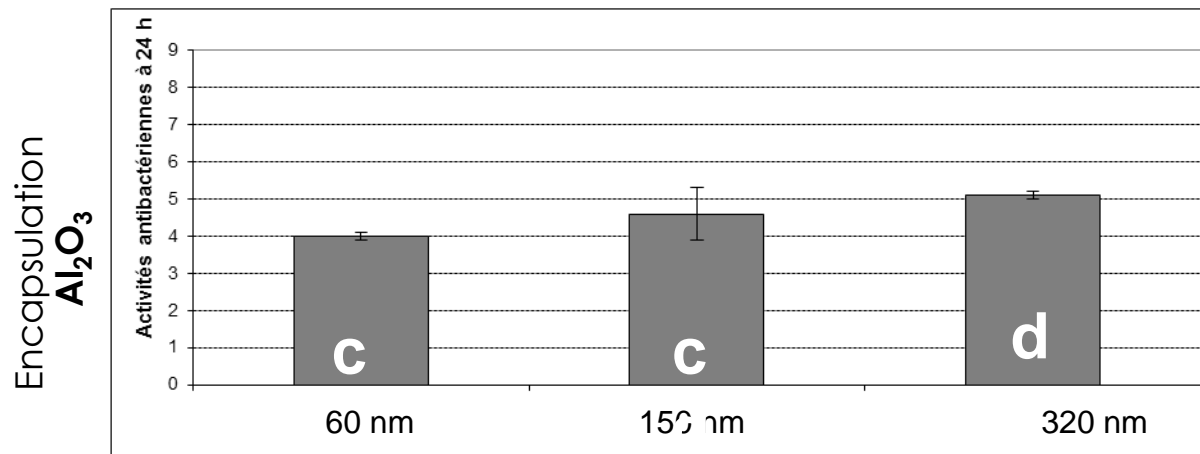
- Gradual and controllable antibacterial activity
- Transparent coating
- Not resistant enough to washing

SiOCH Silver nano composite material with protective layer



Antibac layer
Press0
Power : 300 W

Ref. Activity : 7



Conclusion



- **Np deposition process using magnetron sputtering**
 - **Well mastered silver content**
- **Transparent and antibacterial coating**
- **Other applications**
- **On going development of Ag np in TiO₂ layers**
 - **Target : control size and shape of np**

Actiprotex Partners

D. Leonard ISA – Institut des Sciences Analytiques UCBL
C. Brunon
N. Oulahal – Biodymia UCBL
E. Chadeau
C. Grossiord – Science et Surfaces
F. Rimbault – CTTN
F. Simon – TDV Industries

Fund

