Review of deposition methods of metallic coatings on elastomers for sealing applications

Julie Schweitzer

Review of deposition methods of metallic coatings on elastomers for sealing applications

Julie SCHWEITZER

Encadrants Maestral :
- François ROUILLARD
- Thierry DAVID
- Jean-François JULIAA
- Alain BEZIAT

Encadrants IS2M :
- Laurent VONNA
- Florence BALLY- LE GALL
- Vincent ROUCOULES

Institut de Science des Matériaux de Mulhouse

October, 14th 2016

Summary

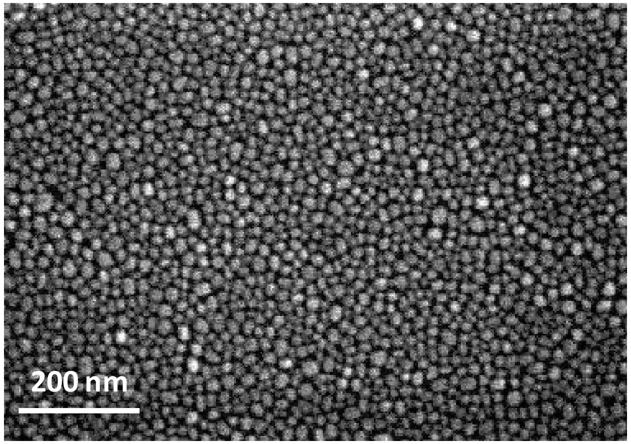
Introduction

Thin film

Thickness typically < few µm

Characteristic properties of thin films different from bulk materials:

- Granular
- Residual stress (intrinsic, thermal, hygroscopic...)
- Defects
- Strongly influenced by substrate properties

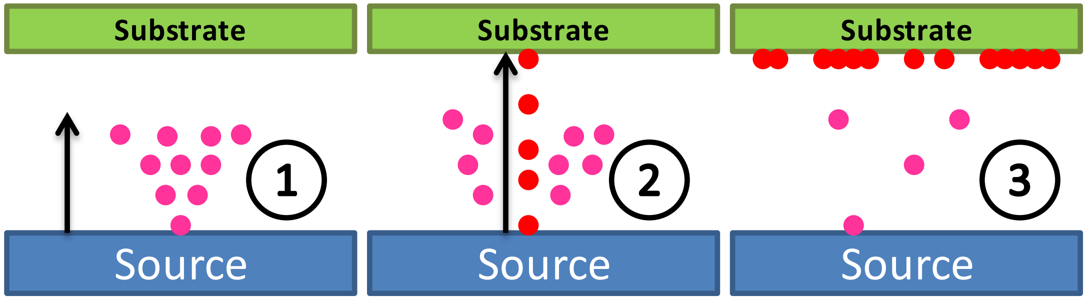


Scanning electron micrography of an Ag thin film[1]

[1] R. Lazzari and I. Simonsen, Thin Solid Films, vol. 419, no. 1–2, pp. 124–136, Nov. 2002.

I. Deposition processes of metallic thin films

Common steps in the fabrication of thin films:



1. Emission of atoms from source
2. Transport of atoms to substrate
3. Deposition of atoms on substrate

Metallic thin film deposition can be achieved *via* two main strategies:

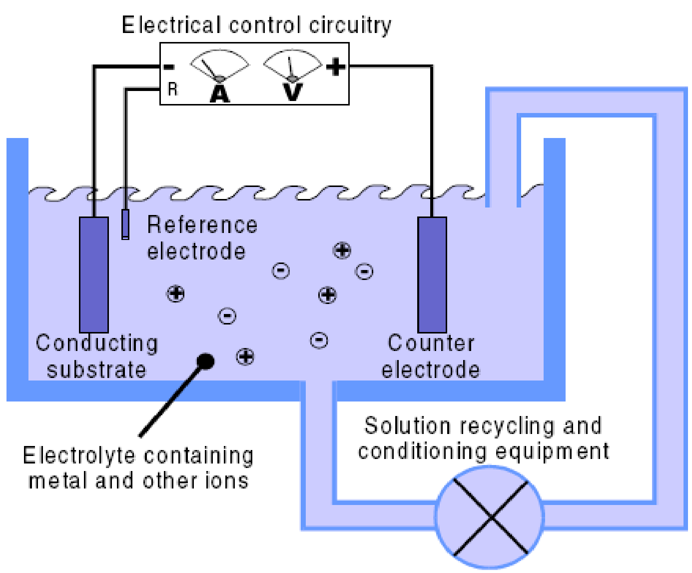
Liquid- Phase Chemical Deposition	***Physical Vapor Deposition (PVD)***
Electrolyte solution	Metal vapor
For example : Electroplating Electroless plating	**For example : Evaporation Sputtering**

I. Deposition processes of metallic thin films

Liquid-phase chemical deposition

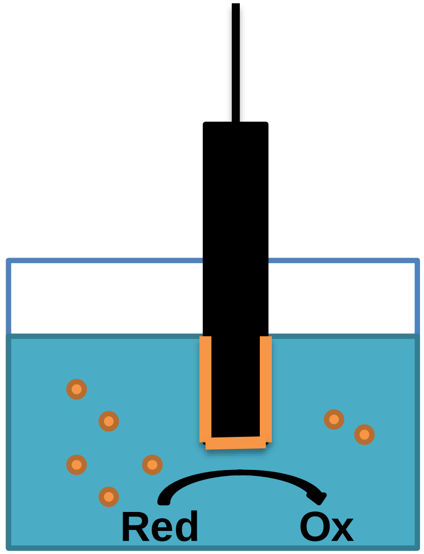
Electroplating [2]

Chemical reduction of ions in solution
Need of electrical power supply



Electroless plating [3]

Redox reaction on the substrate
No external voltage source

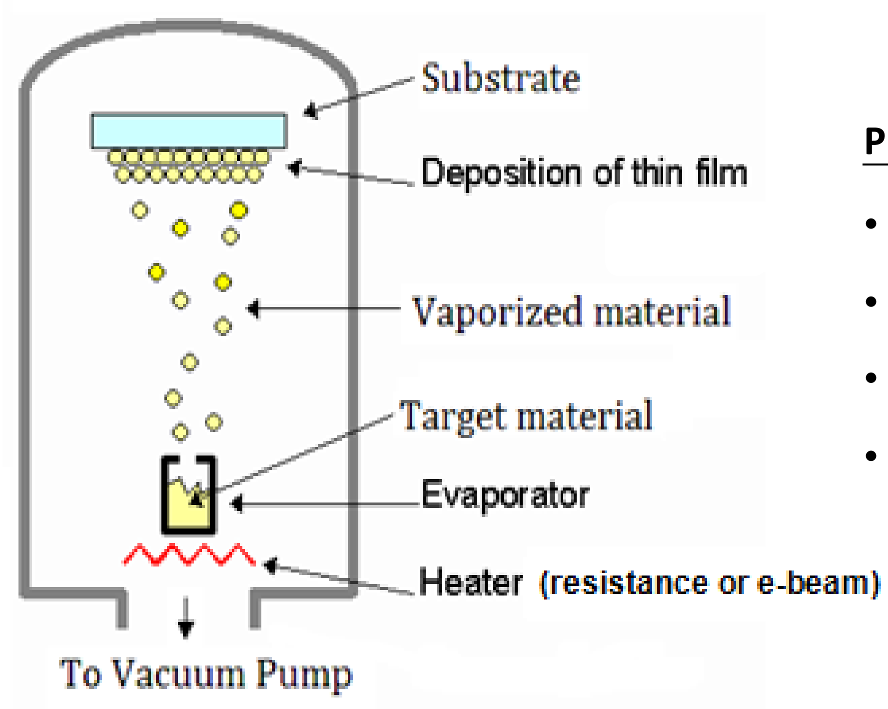


[2] W. Kern and K. K. Schuegraf," Handbook of Thin Film Deposition Processes and Techniques (Second Edition)" (2001)
[3] S. Tengsuwan and M. Ohshima, "Electroless nickel plating on polypropylene via hydrophilic modification and supercritical carbon dioxide Pd-complex infusion," J. Supercrit. Fluids, (2012)

I. Deposition processes of metallic thin films

PVD

Evaporation [4]



Process steps:

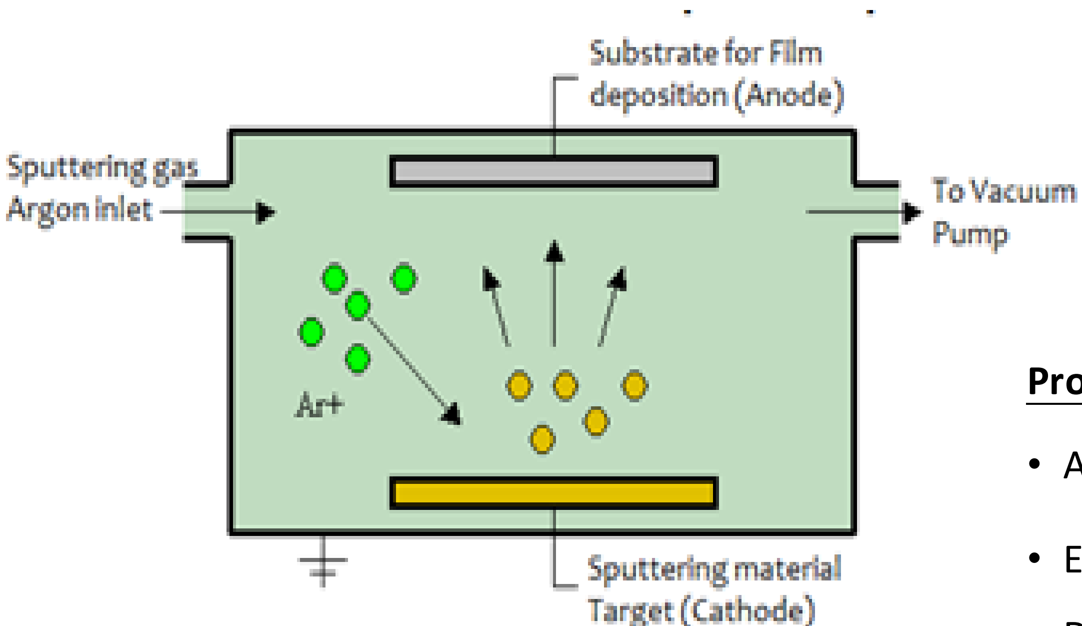
- Target heating (resistance or e-beam)
- Metal evaporation
- Vapor transport to substrate
- Condensation of metal vapor on the substrate

[4] W. Kern and K. K. Schuegraf, "1 - Deposition Technologies and Applications: Introduction and Overview A2 - Seshan, Krisna," in Handbook of Thin Film Deposition Processes and Techniques (Second Edition), Norwich, NY: William Andrew Publishing, 2001, pp. 11–43.

I. Deposition processes of metallic thin films

PVD

Sputtering [5]



Process steps:

- Ar plasma initiation
- Extraction of metal species (from target)
- Deposition of sputtered atoms on the substrate

[5] K. Wasa and S. Hayakawa, Handbook of Sputter Deposition Technology: Principles, Technology, and Applications. 1992.

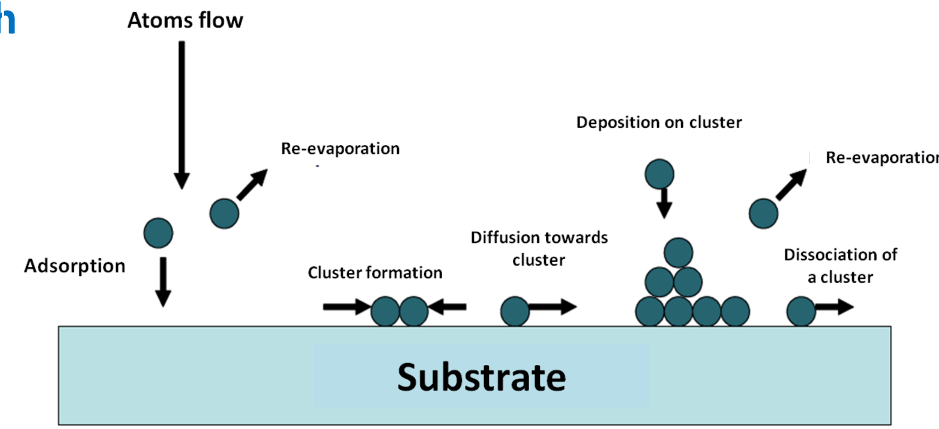
I. Deposition processes of metallic thin films

PVD

Comparison between Evaporation and Sputtering techniques

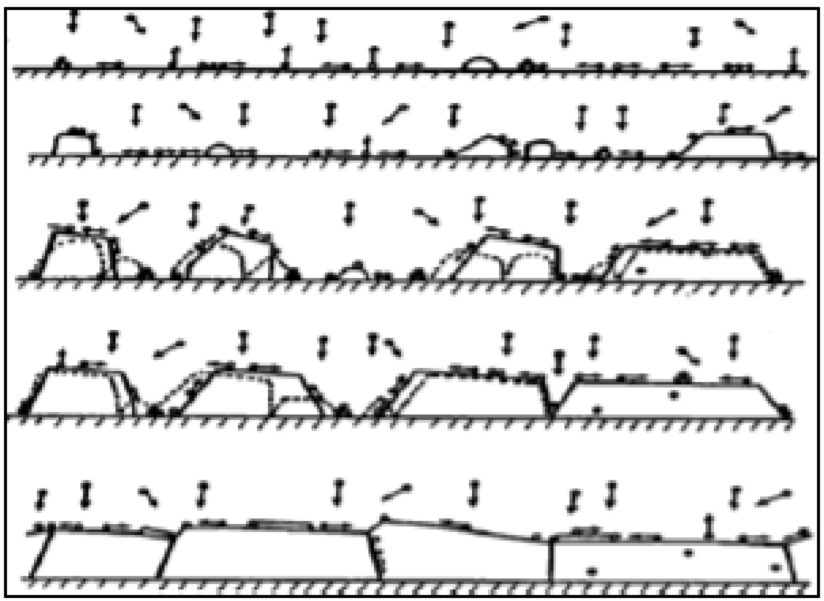
EVAPORATION	SPUTTERING
Low energy atoms	High energy atoms
Large grain size	Small grain size
High vacuum process • few collisions • few impurities	Low vacuum process • many collisions (plasma) • presence of impurities
Limited adhesion	Improved adhesion
Choice of material dependent on T_f	Choice of metal almost unlimited

II. Mecanism of metallic thin film growth



Metal atom / Susbtrate interaction [6]:

Mechanism of thin film growth:

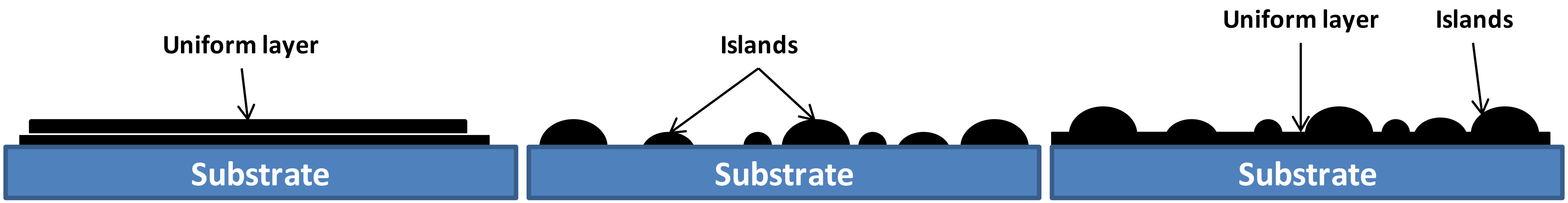


- **Adsorption:** the atoms adsorb on the substrate surface
- **Diffusion:** the atoms diffuse at the surface of the substrate
- **Nucleation:** the formation of islands is initiated by agglomeration of atoms on the substrate
- **Coalescence:** the islands, reaching a critical density, flatten and merge to finally cover the substrate
- **Growth:** the thin film grows perpendicularly to the substrate

[6] L. Pawlowski, "Dépôts physiques", presses polytechniques et universitaires romandes,(2003).

II. Mecanism of metallic thin film growth

Growth modes [7]:



Franck-van der Merwe mode (2D-growth mode)

Volmer-Webermode (Island growth mode)

Stranski-Krastanov mode

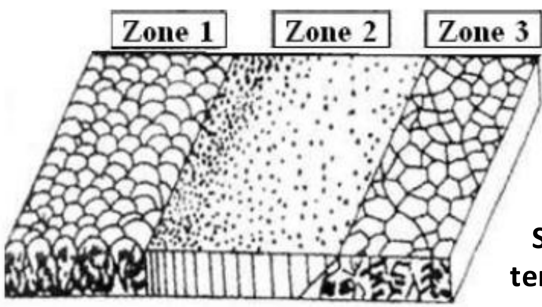
- **Franck-Van der Merwe mode:** atomic layer by atomic layer growth
  atom-atom interaction < substrate-atom interaction
- **Volmer-Weber mode:** formation of islands, then coalescence
  atom-atom interaction > substrate-atom interaction
- **Stranski-Krastanov mode:** combination of the two former modes
  atom-atom interaction ≈ substrate-atom interaction

[7] Y. Pauleau, " Handbook of Thin Films Materials, Volume 1 : Deposition and Processing of Thin Films", 455, Academic Press, 2002

II. Mecanism of metallic thin film growth

Dependence of the film microstructure as a function of deposition conditions

Influence of the substrate temperature [8]

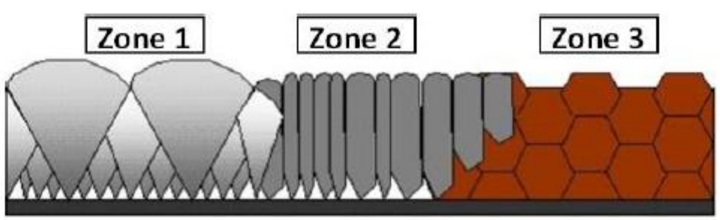


0.3 T_s/T_m 0.5

T_s/T_m

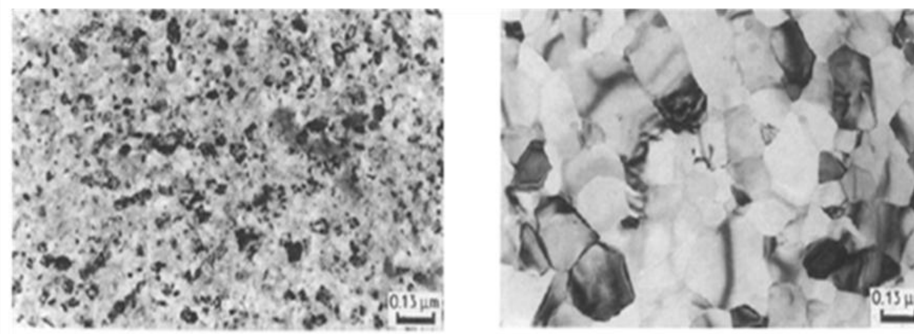
Substrate temperature

Metal melting temperature



Dome-shaped	Columnar	Equiaxial

Influence of the deposition rate [9]



TEM micrographs showing an aluminium film obtained by PVD

Deposition rate: **0,2 nm/s** Deposition rate: **11 nm/s**

→ Higher the deposition rate = larger grains

[8] Movchan BA, Demchishin AV. Phys. of Metals and Metallography (1969) 28:83.

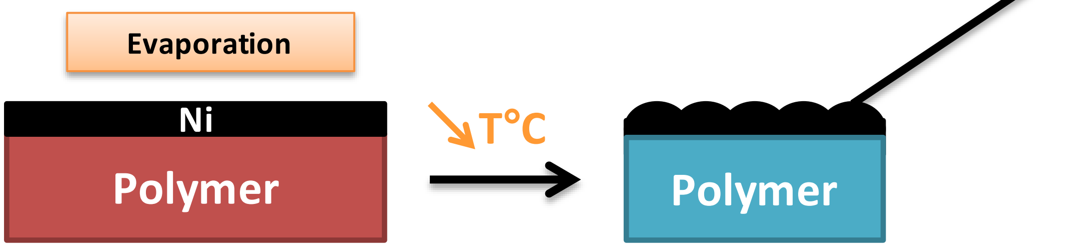
[9] H. Haidara, M. F. Vallat et al. Journal of Materials Science 28 (1993) 3243-3246.

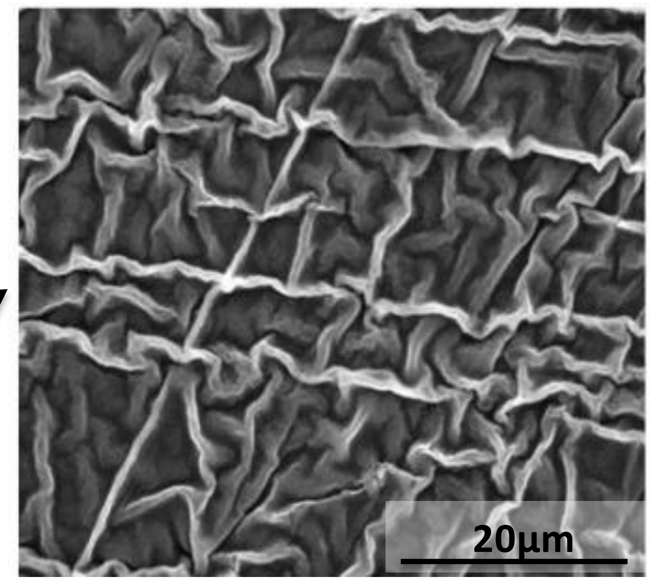
III. Thin film growth: case of polymeric substrate

What about the growth of metallic thin films on a polymeric substrate?

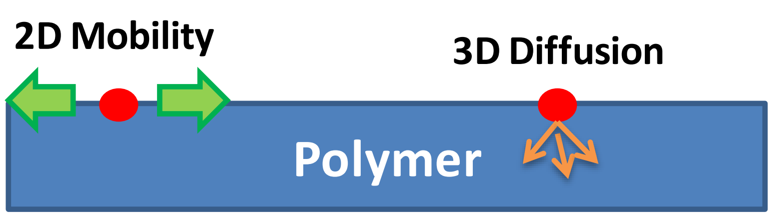
Singular properties of polymers:

- Temperature dependence of properties
- Low Young Modulus
- Low density
- Diversity of chemical interactions

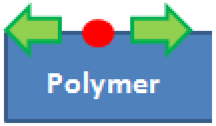




Influence of polymer surface properties on the atoms mobility/diffusion?



2D Mobility

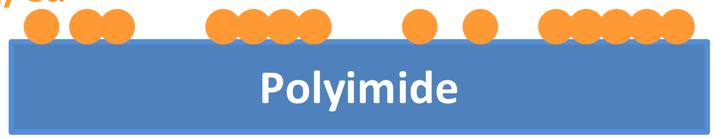


III. Thin film growth: case of polymeric substrate

Influence of the metal nature and the surface properties on the atoms mobility

PVD : Evaporation

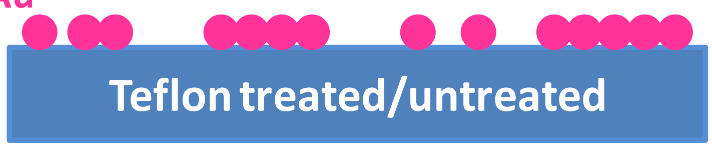
Ag/Cu



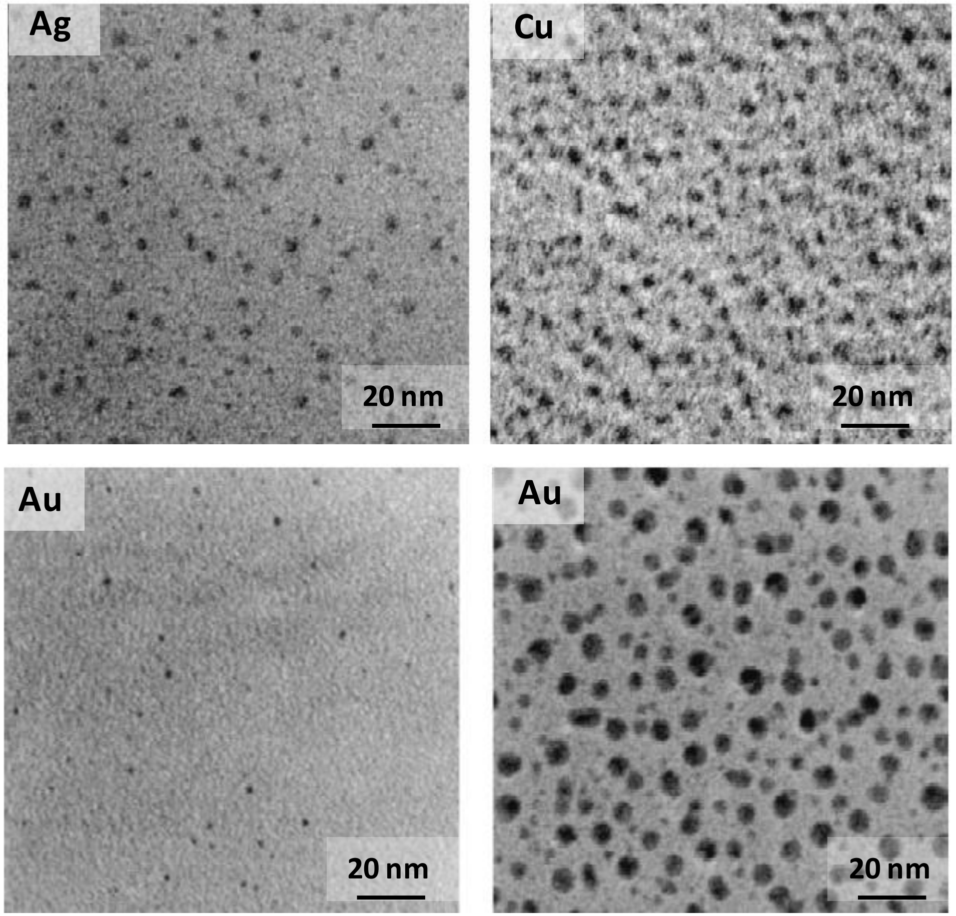
→ **Lower clusters density for Ag compared to Cu**

PVD : Evaporation

Au



→ **Pre-treatment increases the number and the size of clusters**

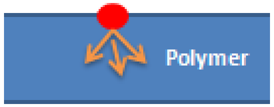


Au film on *untreated substrate*

Au film on *plasma treated substrate*

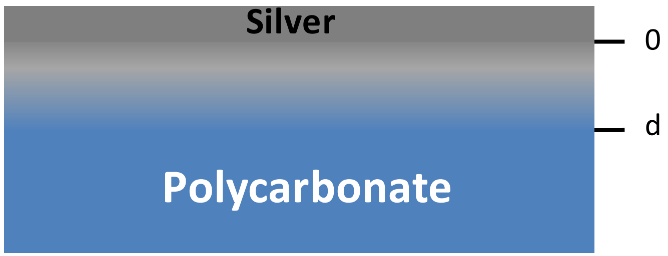
[10] V. Zaporojtchenko, T. Strunskus, K. Behnke. Microelectronic Engineering 50 (2000) 465–471

III. Thin film growth: case of polymeric substrate



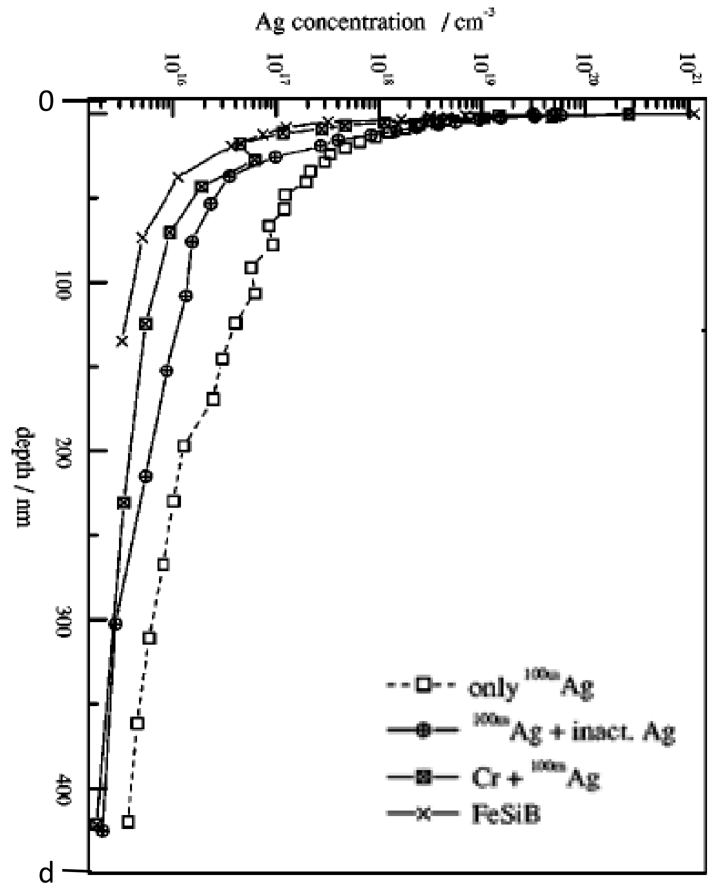
Evidence of metal diffusion in a polymeric substrate (1)

PVD : Evaporation



→ **Diffusion of Ag in the polymer**

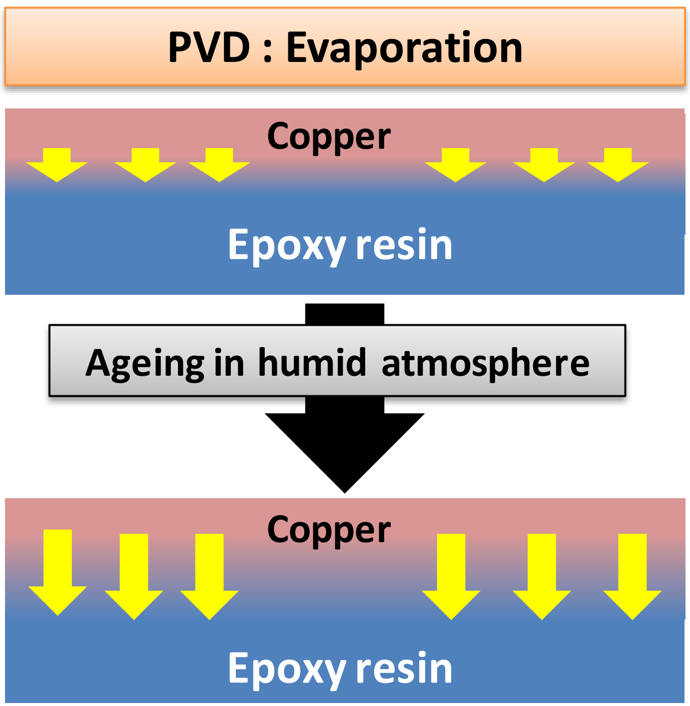
→ **Traces of Ag up to hundreds of nanometers (decreased with Cr barrier layer)**

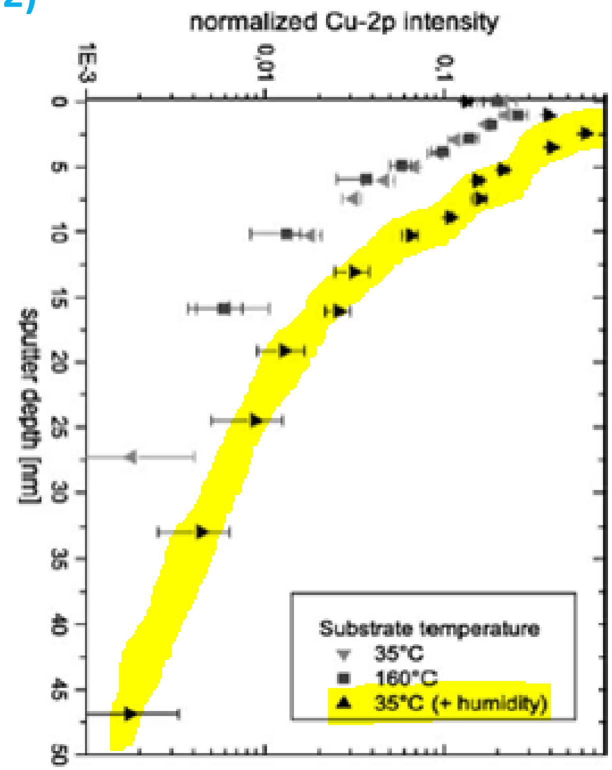


[11] A. Thran, T. Strunskus, V. Zaporojtchenko, and F. Faupel, « Evidence of noble metal diffusion in polymers at room temperature and its retardation by a chromium barrier », Applied Physics Letters 81, 244 (2002)

III. Thin film growth: case of polymeric substrate

Evidence of metal diffusion in a polymeric substrate (2)





→ **Negligible diffusion of metal atoms in an epoxy resin (1 nm)**

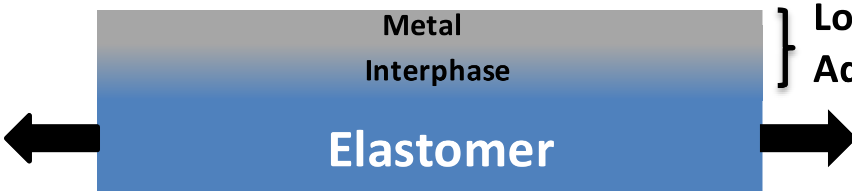
→ **No influence of epoxy temperature on the metal diffusion**

→ **Humid atmosphere = ageing = increased metal diffusion (5 nm)**

[12] J. Kanzow, P. S. Horn, M. Kirschmann, V. Zaporojtchenko, K. Dolgner, F. Faupel, and W. Possart, "Formation of a metal/epoxy resin interface," Applied Surface Science, vol. 239, no. 2, pp. 227–236, Jan. 2005.

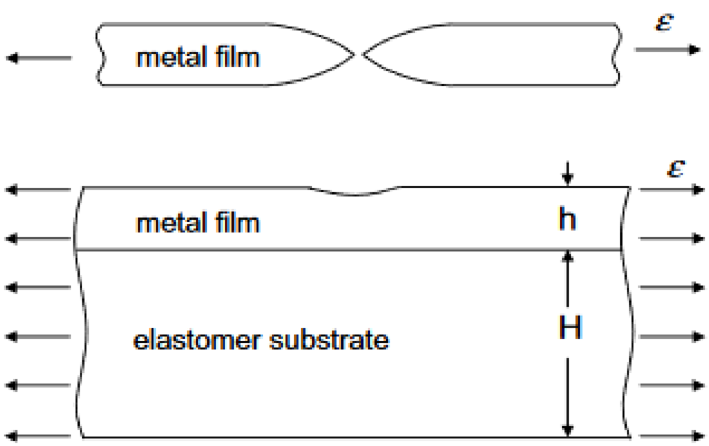
IV. Toughness of metallic thin films on elastomeric substrate

Deformability of elastomeric substrate:

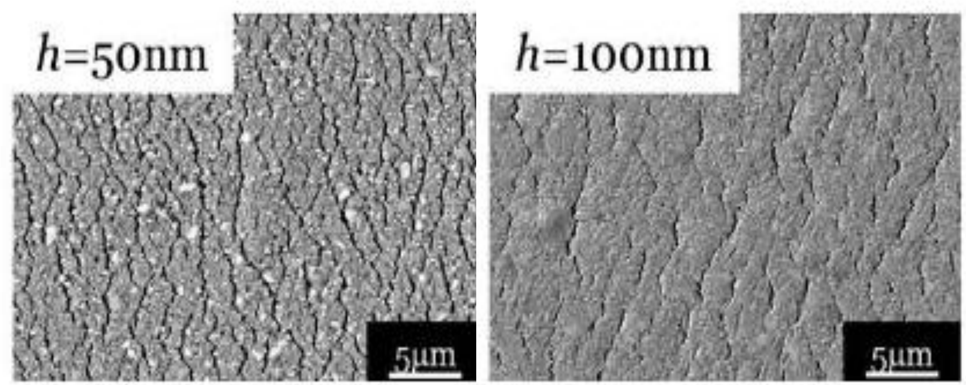


} Location of cracks?
Adhesion?

What about the toughness/adhesion of the metallic thin film on a deformable substrate?



Influence of thin film thickness on cracks density



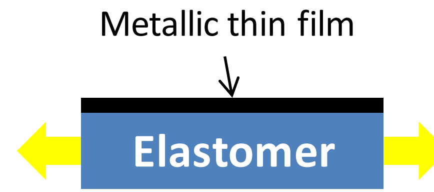
SEM micrographs of Cu thin films on polyimide stretched at 30% [14]

→ **Relocation of constraints**

[13] M.J. Cordill et al. Ductile film delamination from compliant substrates using hard overlayers. Thin Solid Films. (2014)

[14]Nanshu Lu et al. The effect of film thickness on the failure strain of polymer-supported metal films. Acta Materialia. (2010)

IV. Toughness of metallic thin films on elastomeric substrate



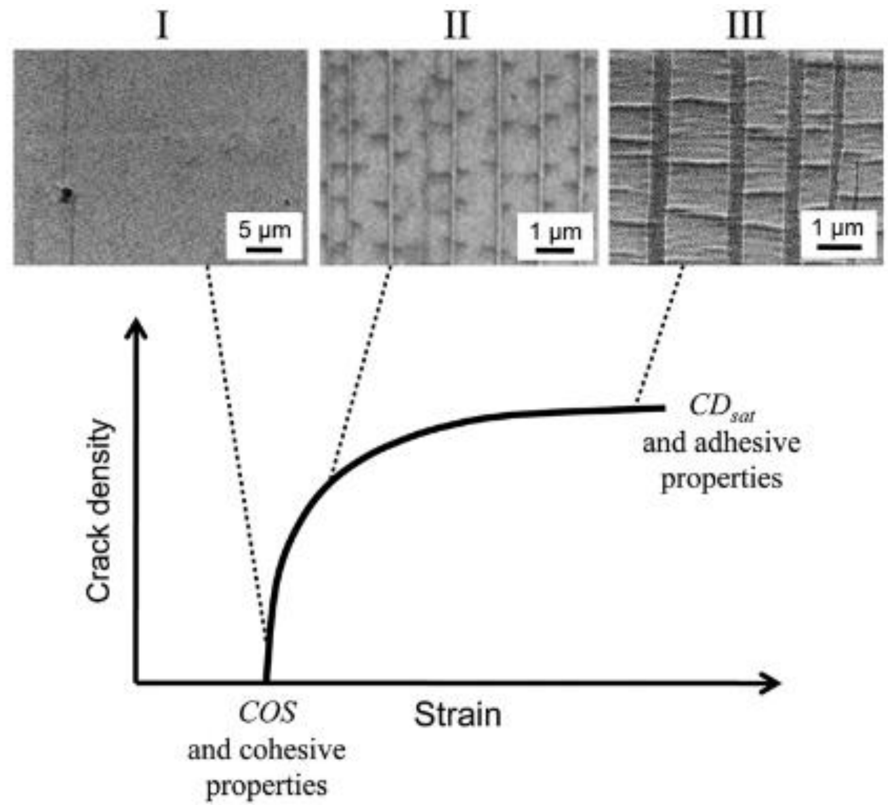
Fragmentation test: evaluation of the toughness of metallic thin film

Determination of interfacial shear strength (IFSS) = adhesive strength of the coating layer on the substrate [15]

$$IFSS = 1{,}337 * h_c * E_c * \varepsilon_{crit} * CD_{sat}$$

h_c : thickness of the coating
E_c : elastic modulus of the coating
ε_{crit} : critical elongation
CD_{sat} : fracture density at saturation

→ **Number of cracks increases with elongation until saturation**

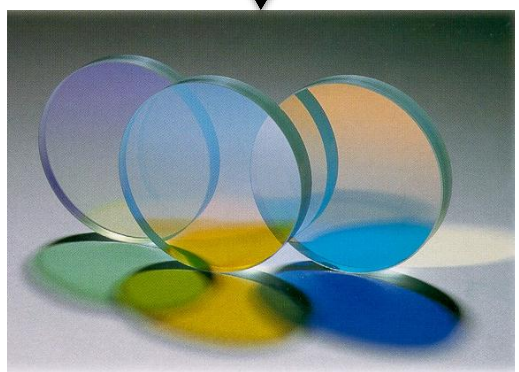


[15] Y. Leterrier. Fragmentation Test method for Adhesion Analysis of Coatings In Situ a Microscope. EPFL. 2009.

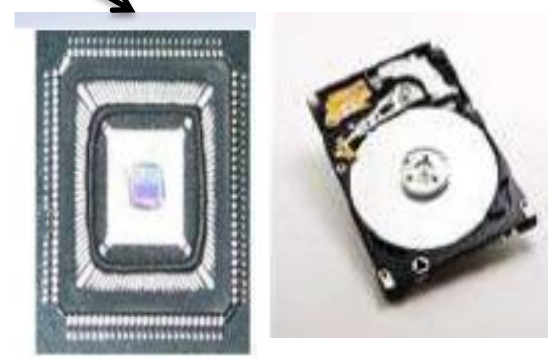
V. Applications of these coatings: sealing

Metallic thin film

Solar cell[16]



Optics[17]

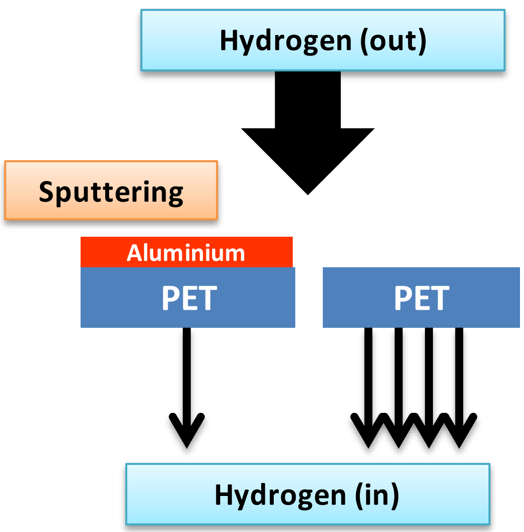


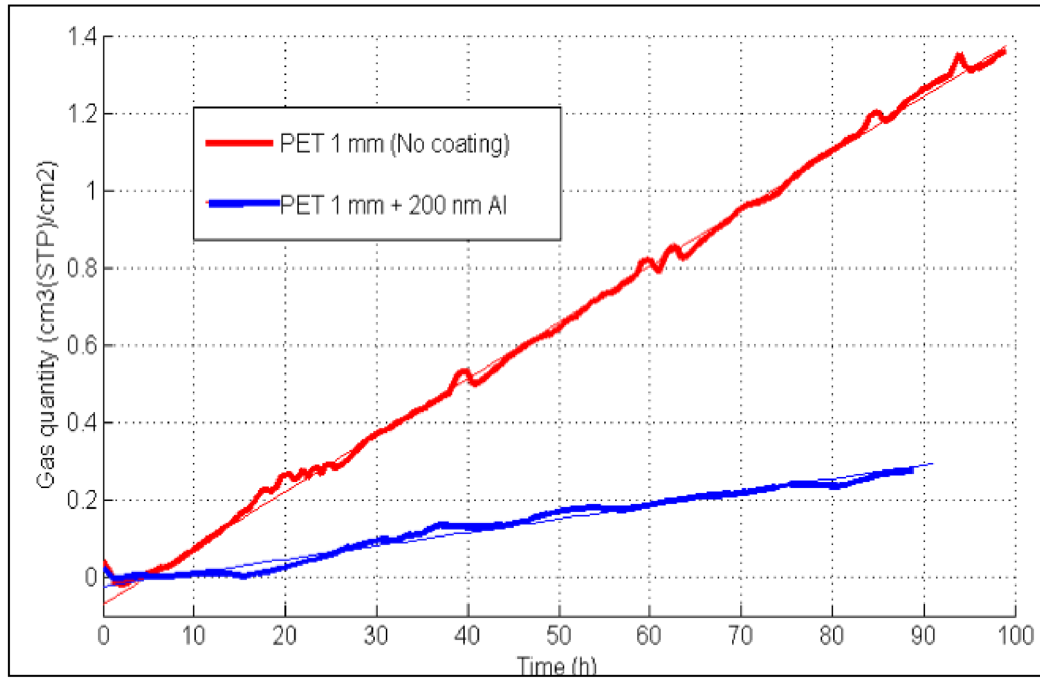
Microelectronics[18]

What about the sealing applications ?

[16] A. G. Aberle, "Thin-film solar cells," Thin Solid Films, vol. 517, no. 17, pp. 4706–4710, juillet 2009.
[17] W. Kern, « Thin Film Processes II ». Academic Press, 2012.
[18] D. M. Mattox, "Thin film metallization of oxides in microelectronics," Thin Solid Films, vol. 18, no. 2, pp. 173–186, Nov. 1973.

V. Applications of these coatings: sealing



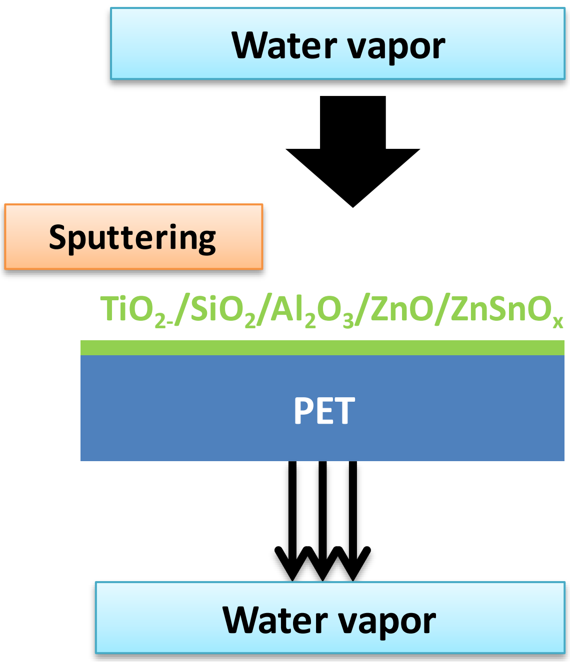


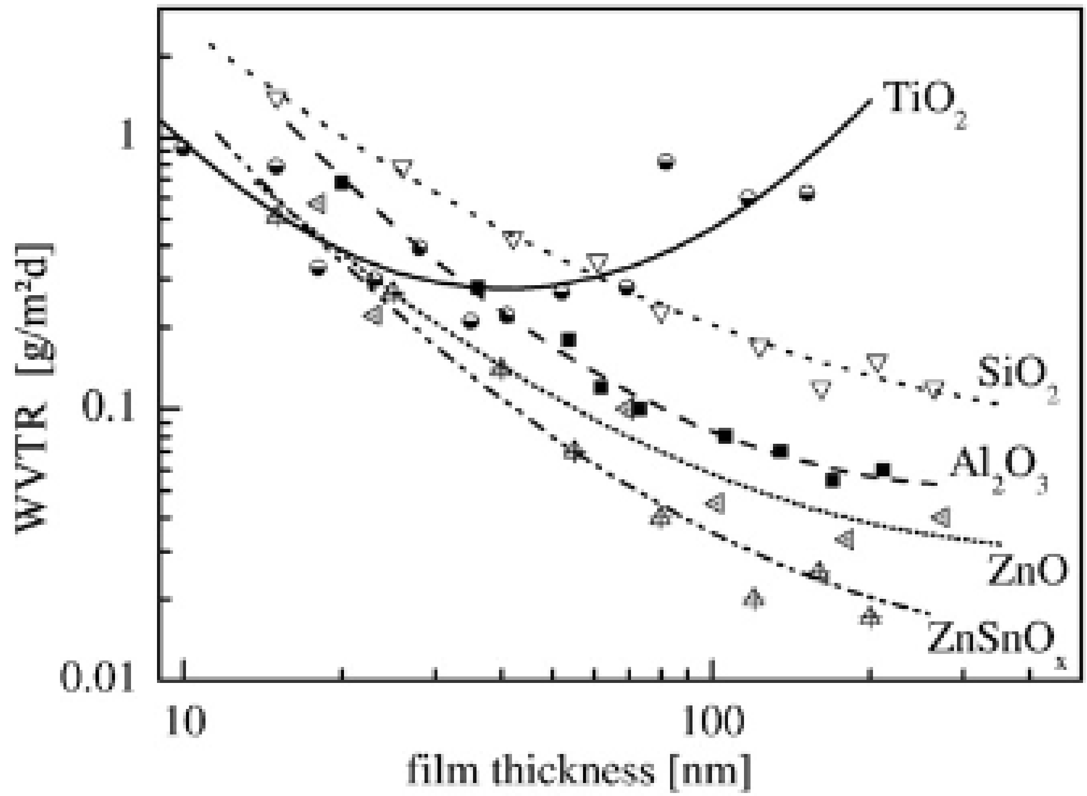
→ 200 nm of aluminum leads to a reduction of hydrogen permeation by a factor of 4

Permeation cell and test bench

[16] D. Chapelle., L. Feng., J-Y. Rauch., P. Nardin., Dépôt de couches minces comme barrière au transport gazeux, 20ème Congrès Français de Mécanique (2011)

V. Applications of these coatings: sealing



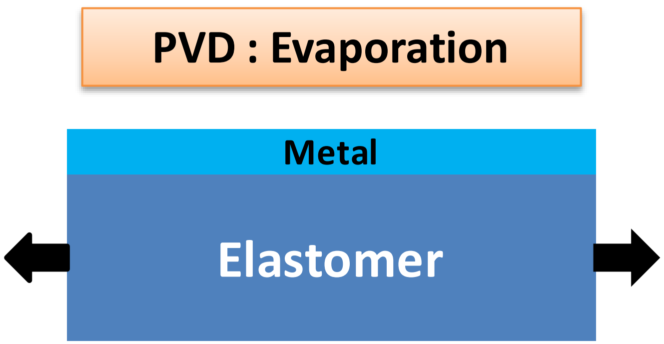


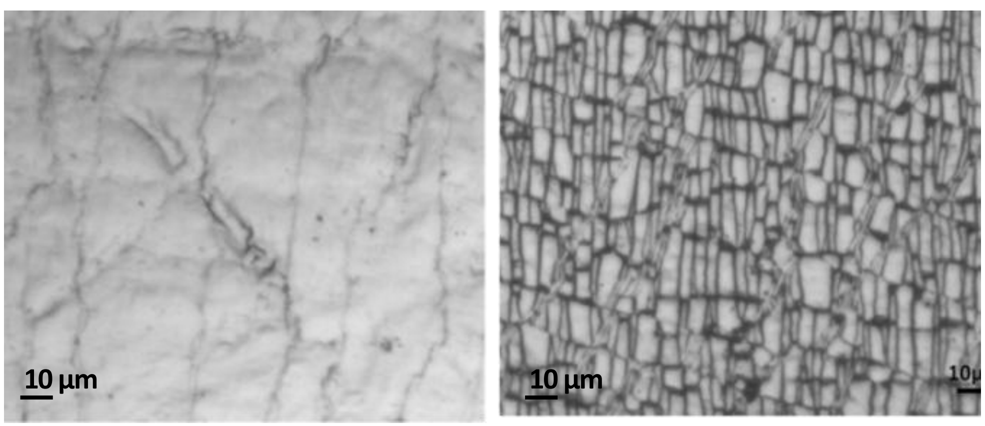
→ **Zinc-tin-oxide ($ZnSnO_x$) layers show a very good barrier performance on PET substrate**

[17] J. Fahlteich, M. Fahland, W. Schönberger, and N. Schiller, "Permeation barrier properties of thin oxide films on flexible polymer substrates," Thin Solid Films, vol. 517, no. 10, pp. 3075–3080, Mar. 2009.

V. Applications of these coatings: sealing

My thesis work aims at developping a metallic thin film on an elastomeric joint





Elongation : 3%   Elongation : 30%

Growth mechanisms of metallic thin film on elastomeric substrate

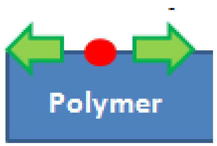
Mechanisms of thin film fragmentation on such substrates

Relation between the microstructure of the thin film and the sealing performance

Take home message

Singular behavior of metallic thin films on an elastomeric substrate:

2D Mobility of atoms:



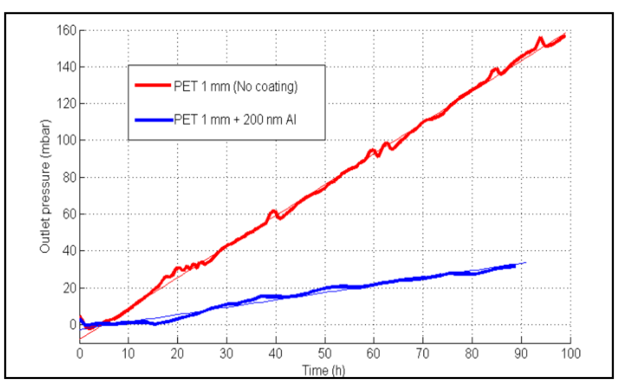
Depends on:
- Nature of metal
- Properties of the surface of the substrate (T°C, chemical nature, Young Modulus…)

3D Diffusion of atoms:

- Occurs even at room temperature
- May be enhanced by ageing (humid atmosphere)

Relative deformability of the coating:

- Relocation of constraints
- Critical elongation before appearance of cracks



Permeability performance improved with the presence of metallic thin films on polymeric substrate:

What about sealing performance when metallic thin films are deposited on elastomers?

Thank you for your attention !