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Julie Schweitzer

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Julie Schweitzer. Review of deposition methods of metallic coatings on elastomers for sealing applications. Workshop étanchéité 2016, Oct 2016, Paris, France. cea-02438358

HAL Id: cea-02438358

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Submitted on 14 Jan 2020

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

Julie SCHWEITZER



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- Vincent ROUCOULES



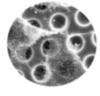


Summary

Introduction

- I. Deposition processes of metallic thin films
- II. Mechanism of metallic thin film growth
- III. Thin film growth: case of polymeric substrate
- IV. Toughness of metallic thin film on elastomeric substrate
- V. Applications of these coatings: sealing

Take home message



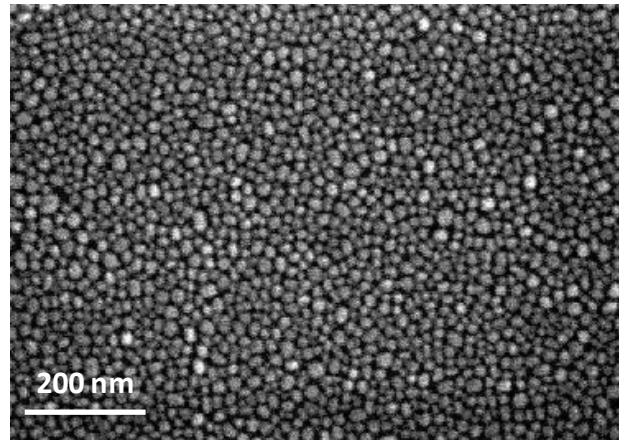
Introduction

Thin film

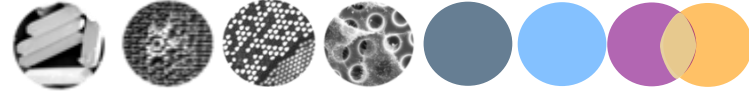
Thickness typically < few μm

Characteristic properties of thin films different from bulk materials:

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

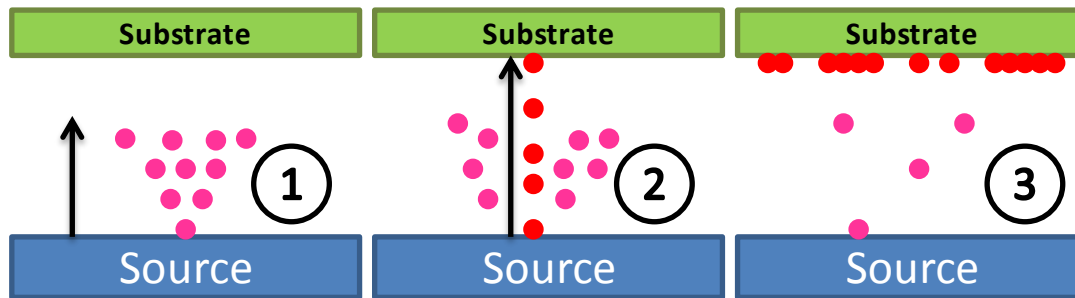


Scanning electron micrography of an Ag thin film^[1]



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

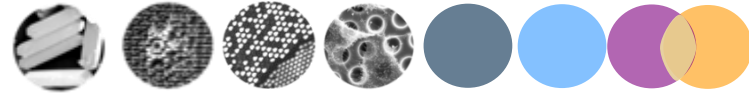
Electrolyte solution

For example : Electroplating
Electroless plating

Physical Vapor Deposition (PVD)

Metal vapor

For example : Evaporation
Sputtering

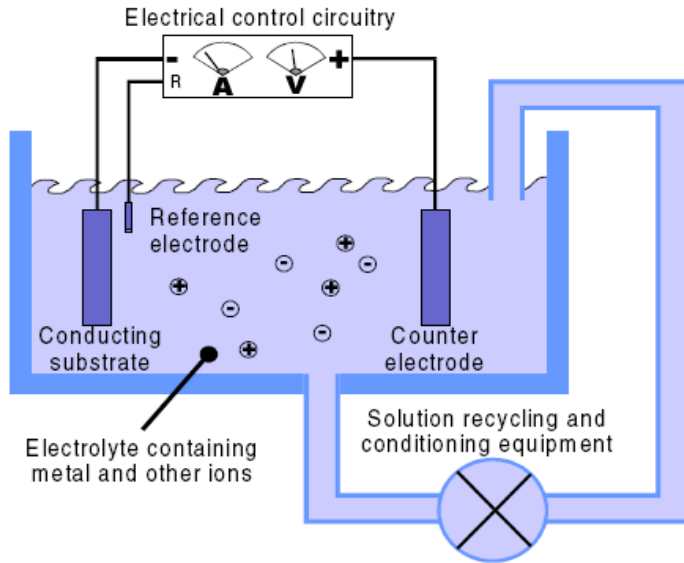


I. Deposition processes of metallic thin films

Liquid-phase chemical deposition

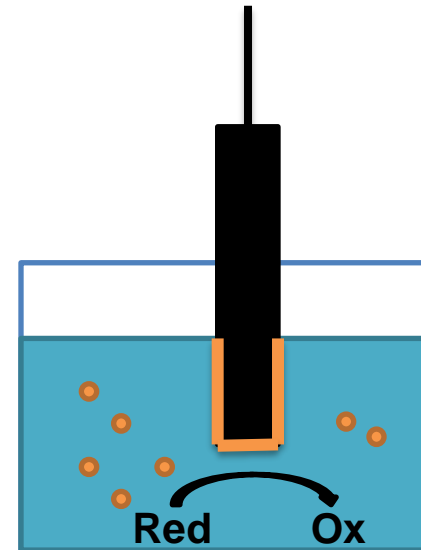
Electroplating [2]

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)

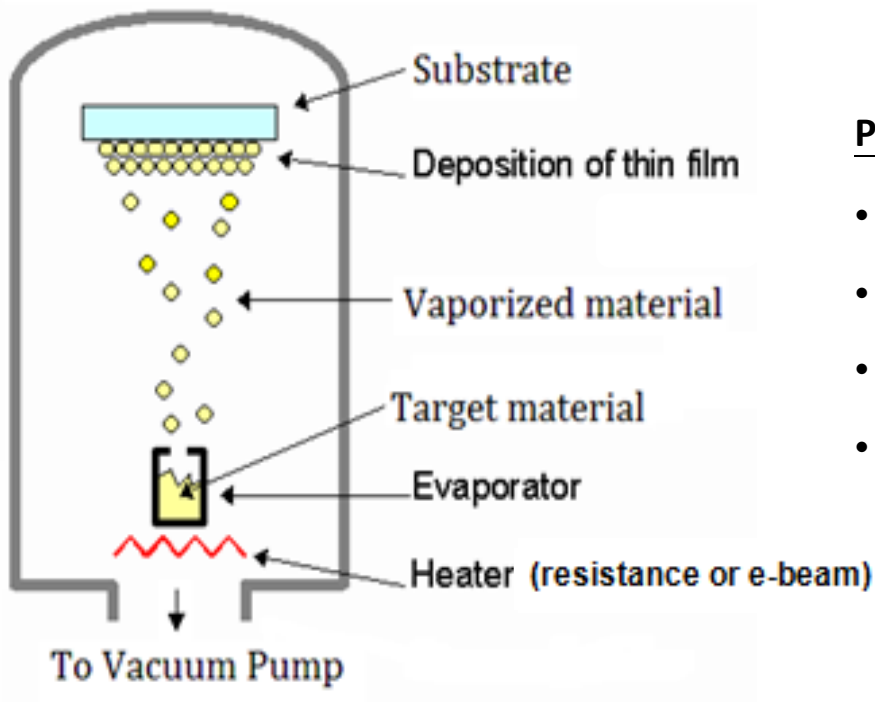
[3] S. Tengsuwan and M. Ohshima, "Electroless nickel plating on polypropylene via hydrophilic modification and supercritical carbon dioxide Pd-complex infusion," J. Supercrit. Fluids, (2012)



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

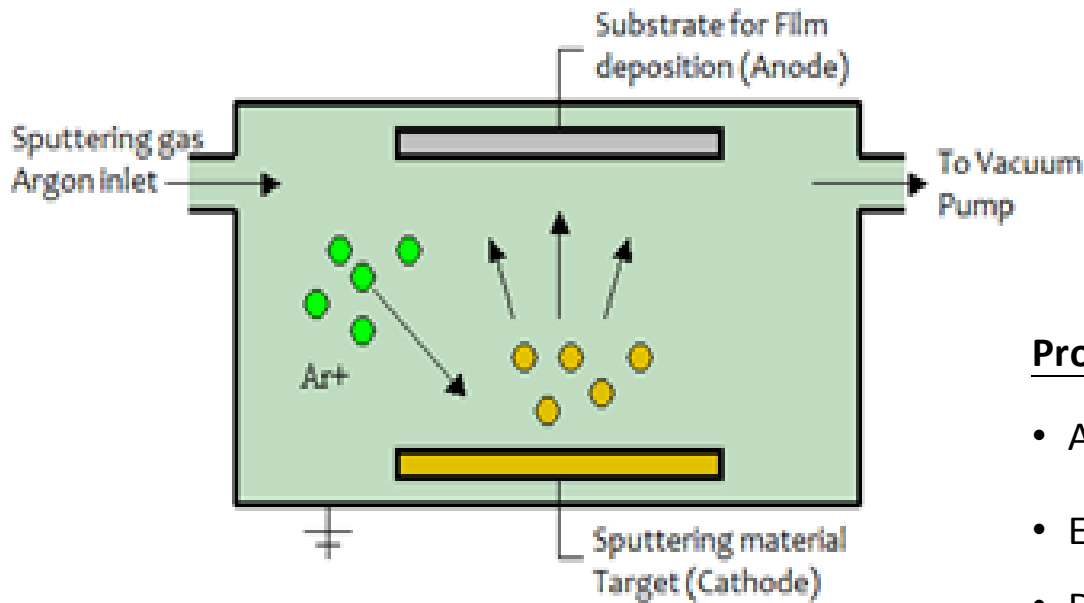
[4] W. Kern and K. K. Schuegraf, "1 - Deposition Technologies and Applications: Introduction and Overview A2 - Seshan, Krisna," in Handbook of Thin Film Deposition Processes and Techniques (Second Edition), Norwich, NY: William Andrew Publishing, 2001, pp. 11–43.



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

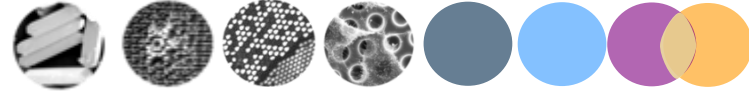


I. Deposition processes of metallic thin films

PVD

Comparison between Evaporation and Sputtering techniques

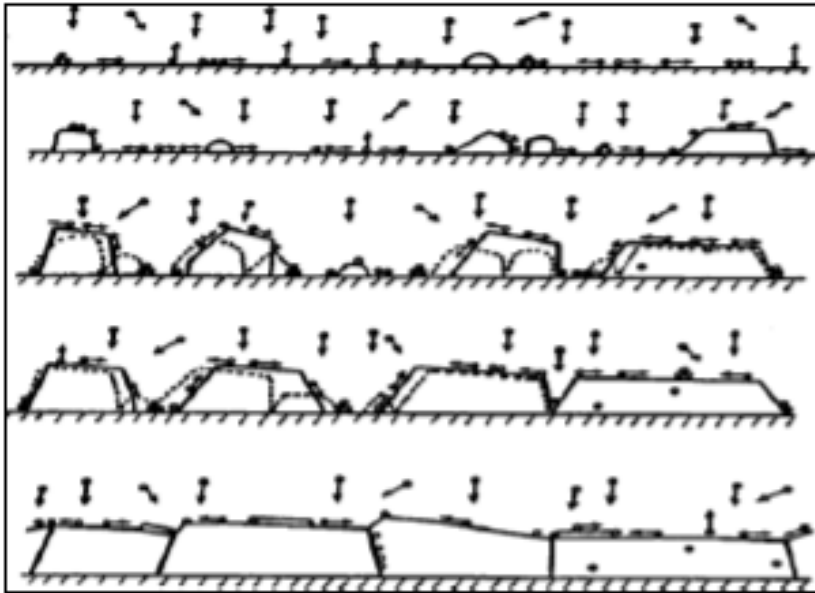
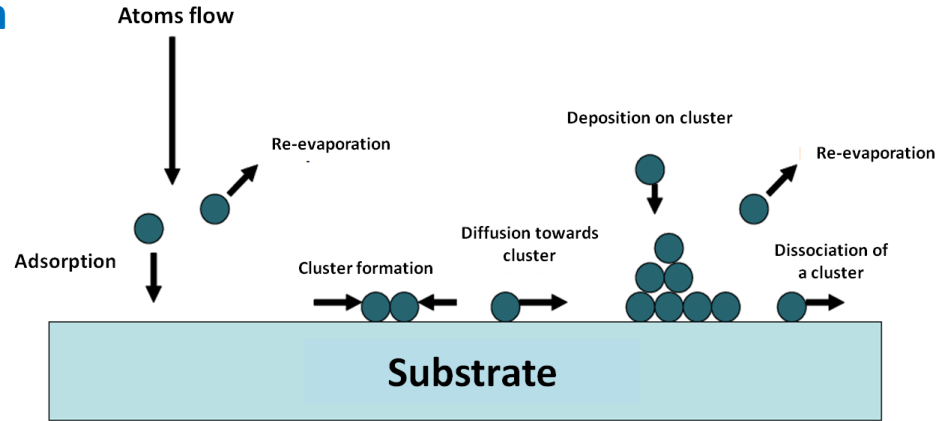
EVAPORATION	SPUTTERING
Low energy atoms	High energy atoms
Large grain size	Small grain size
High vacuum process <ul style="list-style-type: none"> • few collisions • few impurities 	Low vacuum process <ul style="list-style-type: none"> • many collisions (plasma) • presence of impurities
Limited adhesion	Improved adhesion
Choice of material dependent on T_f	Choice of metal almost unlimited



II. Mecanism of metallic thin film growth

Metal atom / Substrate interaction [6]:

Mechanism of thin film growth:

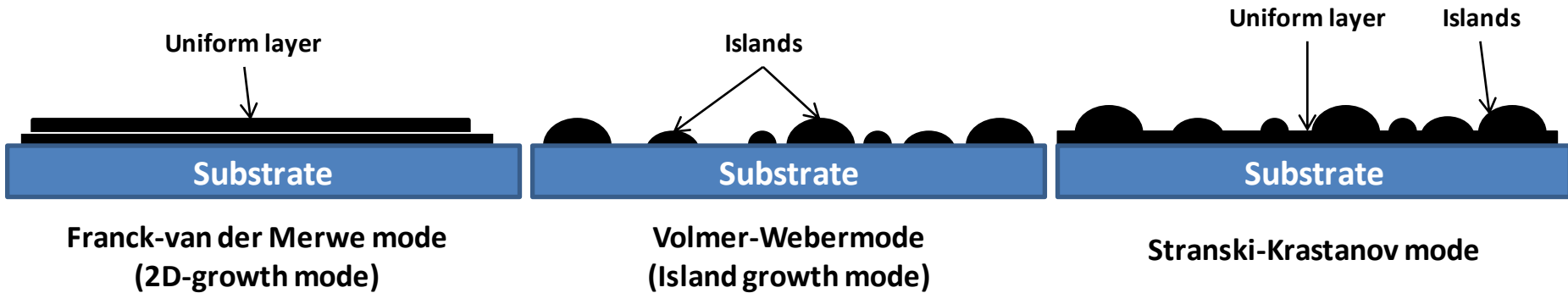


- **Adsorption:** the atoms adsorb on the substrate surface
- **Diffusion:** the atoms diffuse at the surface of the substrate
- **Nucleation:** the formation of islands is initiated by agglomeration of atoms on the substrate
- **Coalescence:** the islands, reaching a critical density, flatten and merge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

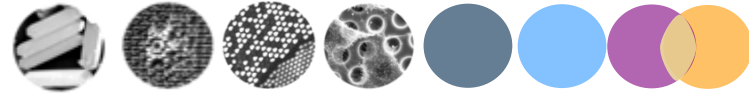


II. Mecanism of metallic thin film growth

Growth modes [7]:



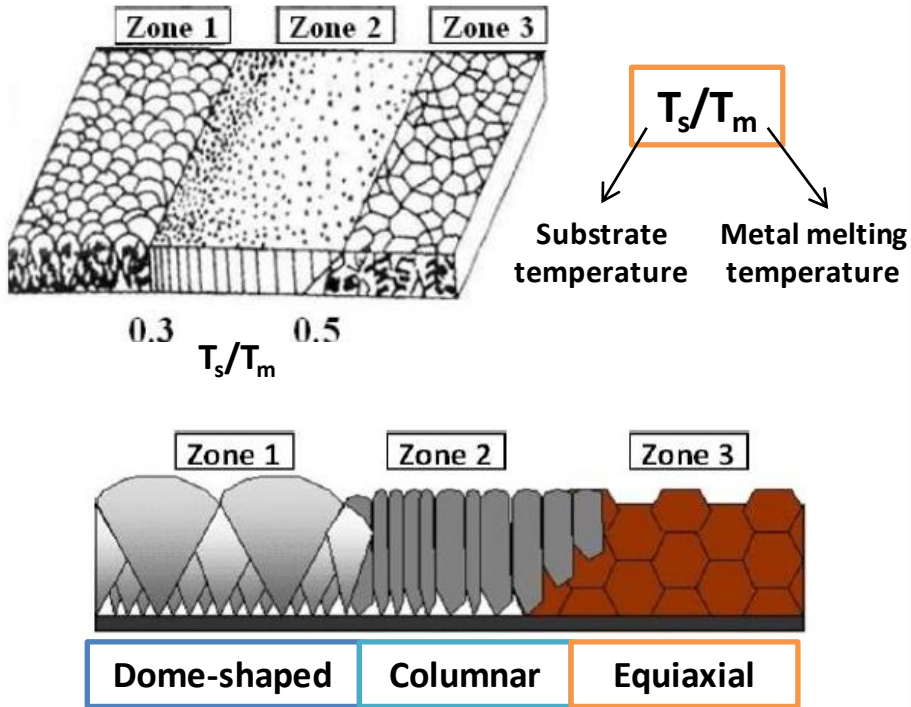
- **Franck-Van der Merwe mode:** atomic layer by atomic layer growth
atom-atom interaction < substrate-atom interaction
- **Volmer-Weber mode:** formation of islands, then coalescence
atom-atom interaction > substrate-atom interaction
- **Stranski-Krastanov mode:** combination of the two former modes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



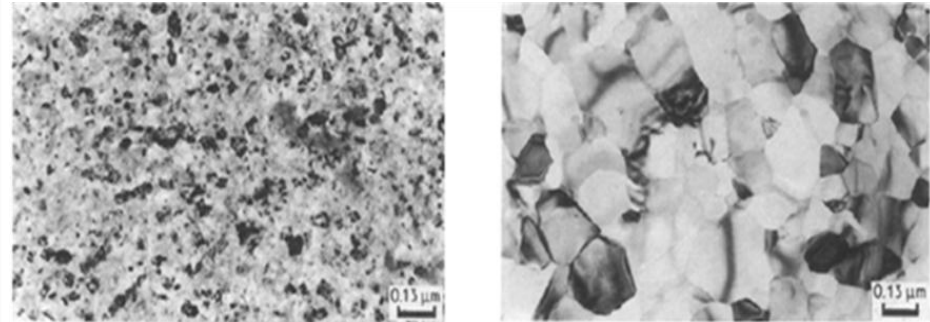
II. Mecanism of metallic thin film growth

Dependence of the film microstructure as a function of deposition conditions

Influence of the substrate temperature [8]



Influence of the deposition rate [9]

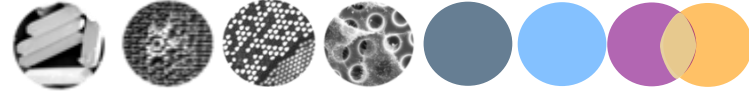


TEM micrographs showing an aluminium film obtained by PVD
Deposition rate: **0,2 nm/s** Deposition rate: **11 nm/s**

→ 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.

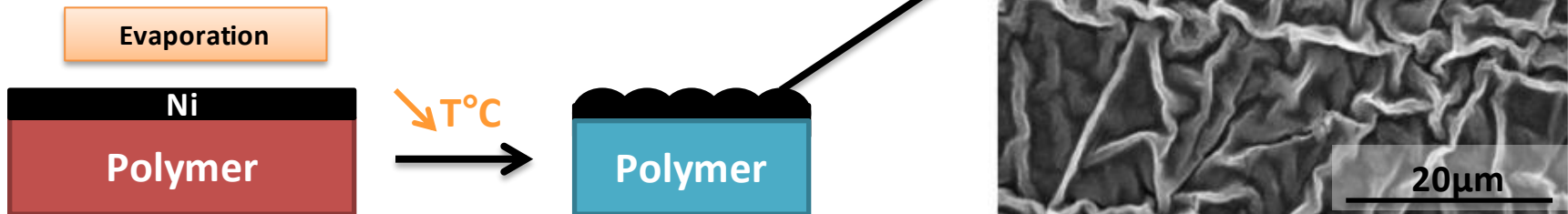


III. Thin film growth: case of polymeric substrate

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

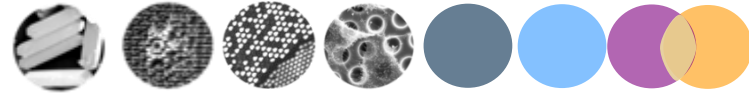
Singular properties of polymers:

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



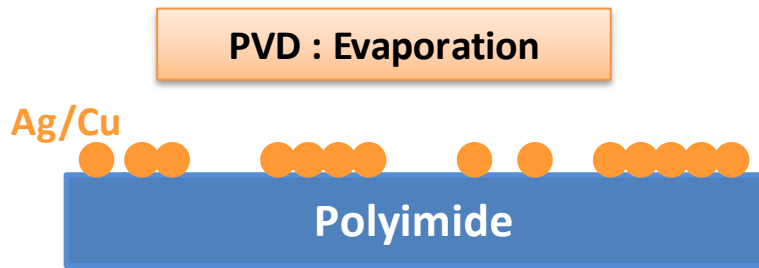
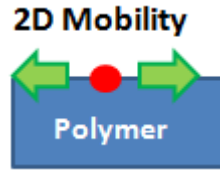
Influence of polymer surface properties on the atoms mobility/diffusion?



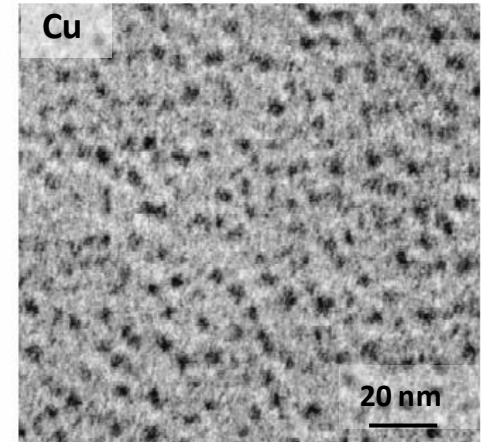
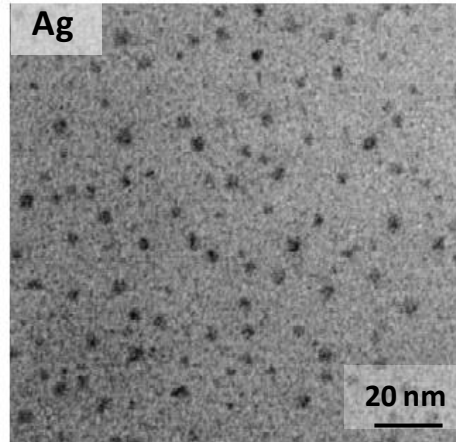


III. Thin film growth: case of polymeric substrate

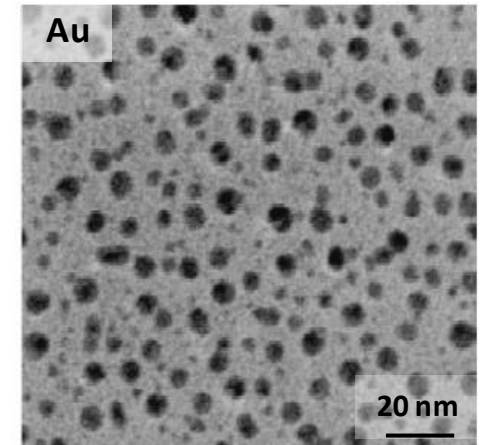
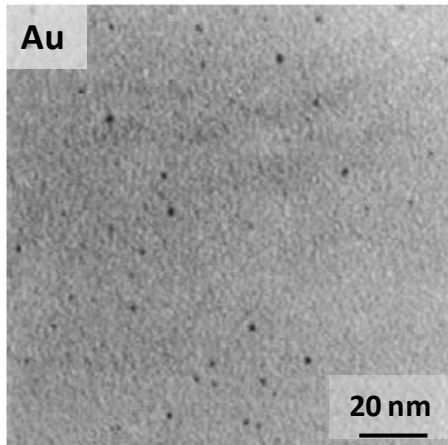
Influence of the metal nature and the surface properties on the atoms mobility



→ Lower clusters density for Ag compared to Cu

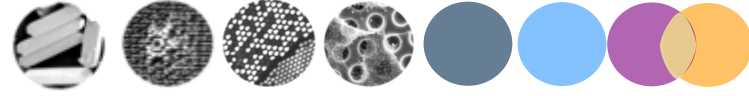


→ Pre-treatment increases the number and the size of clusters

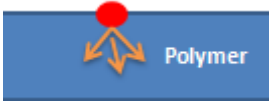


Au film on *untreated* substrate

Au film on *plasma treated* substrate



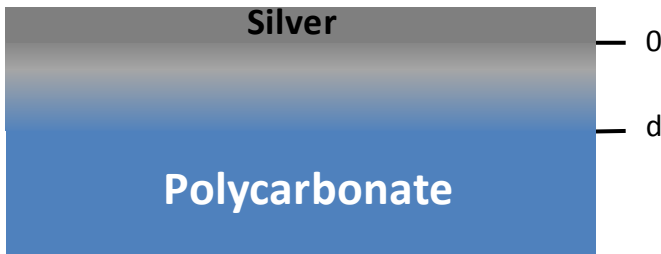
3D Diffusion



III. Thin film growth: case of polymeric substrate

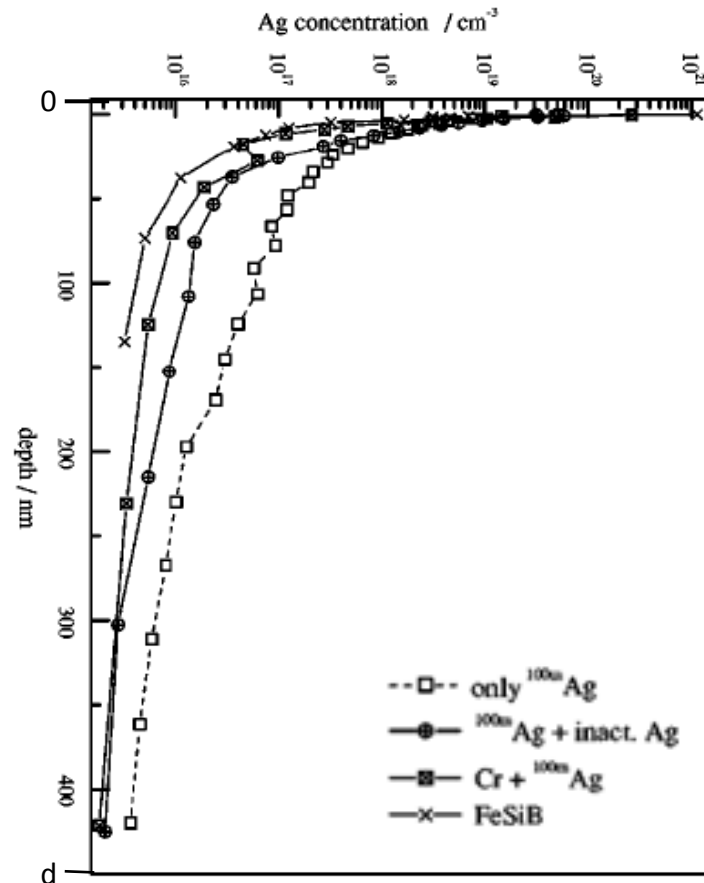
Evidence of metal diffusion in a polymeric substrate (1)

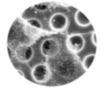
PVD : Evaporation



→ Diffusion of Ag in the polymer

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



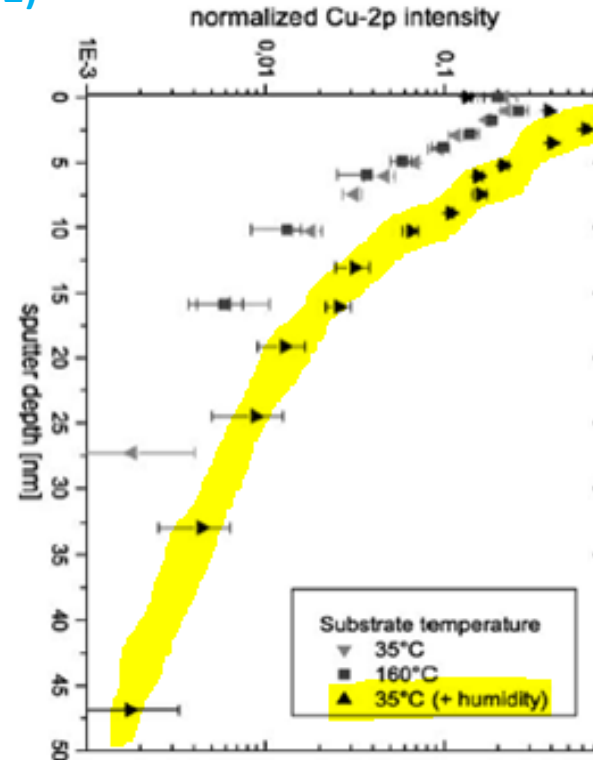
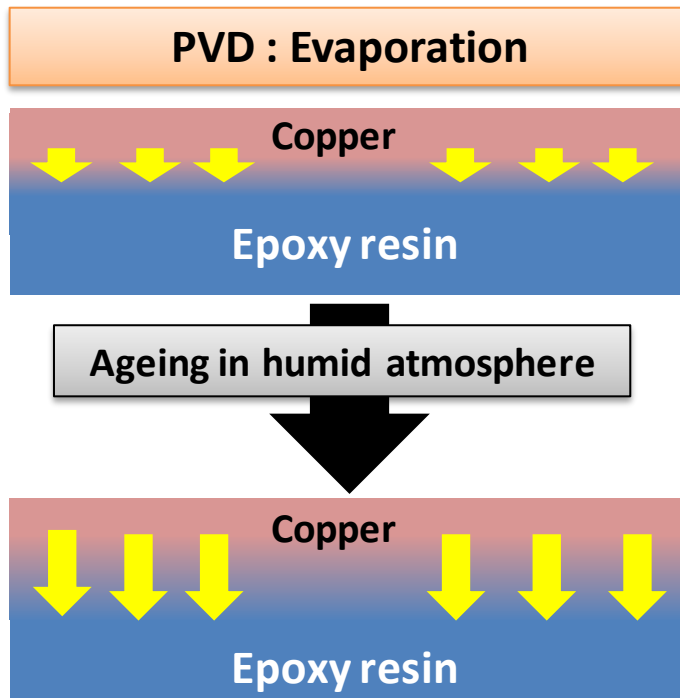


3D Diffusion

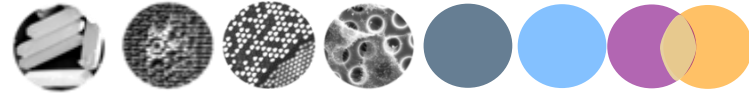


III. Thin film growth: case of polymeric substrate

Evidence of metal diffusion in a polymeric substrate (2)

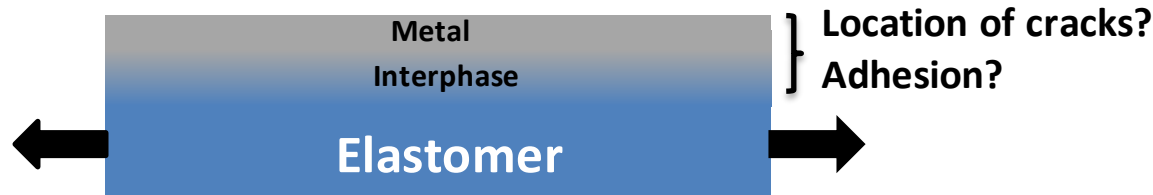


- Negligible diffusion of metal atoms in an epoxy resin (1 nm)
- No influence of epoxy temperature on the metal diffusion
- Humid atmosphere = ageing = increased metal diffusion (5 nm)



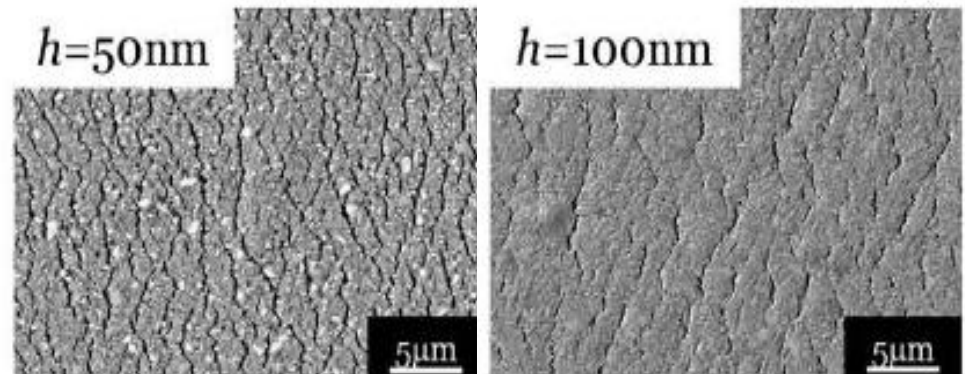
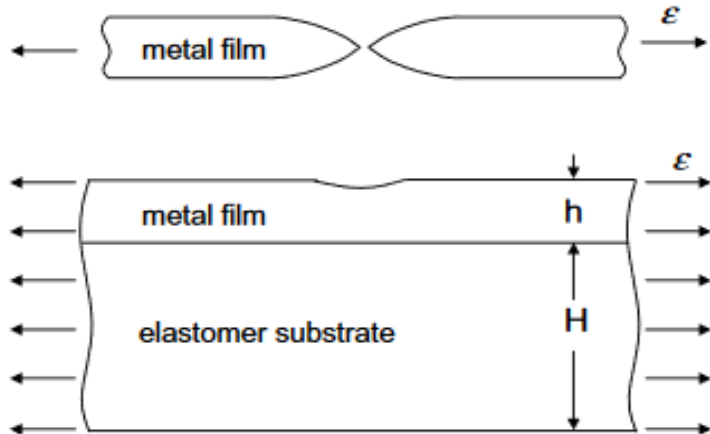
IV. Toughness of metallic thin films on elastomeric substrate

Deformability of elastomeric substrate:



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

Influence of thin film thickness on cracks density

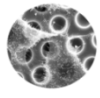


SEM micrographs of Cu thin films on polyimide stretched at 30%^[14]

→ Relocation of constraints

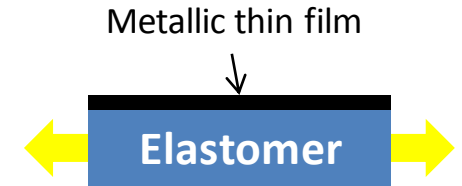
[13] M.J. Cordill et al. Ductile film delamination from compliant substrates using hard overlayers. *Thin Solid Films*. (2014)

[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]

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

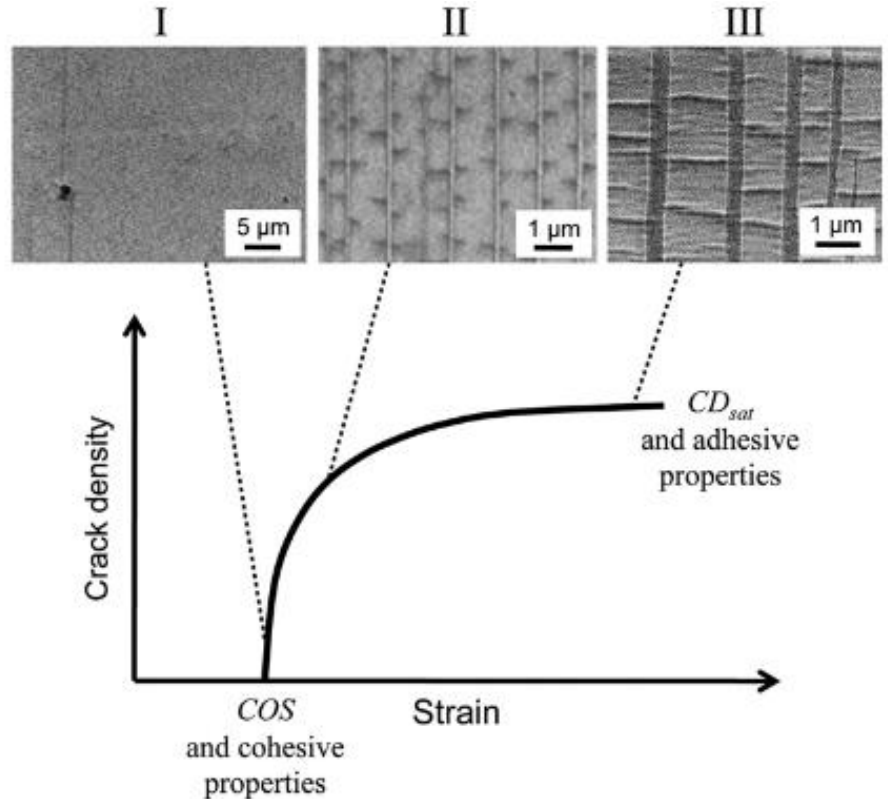
h_c : thickness of the coating

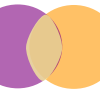
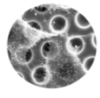
E_c : elastic modulus of the coating

ϵ_{crit} : critical elongation

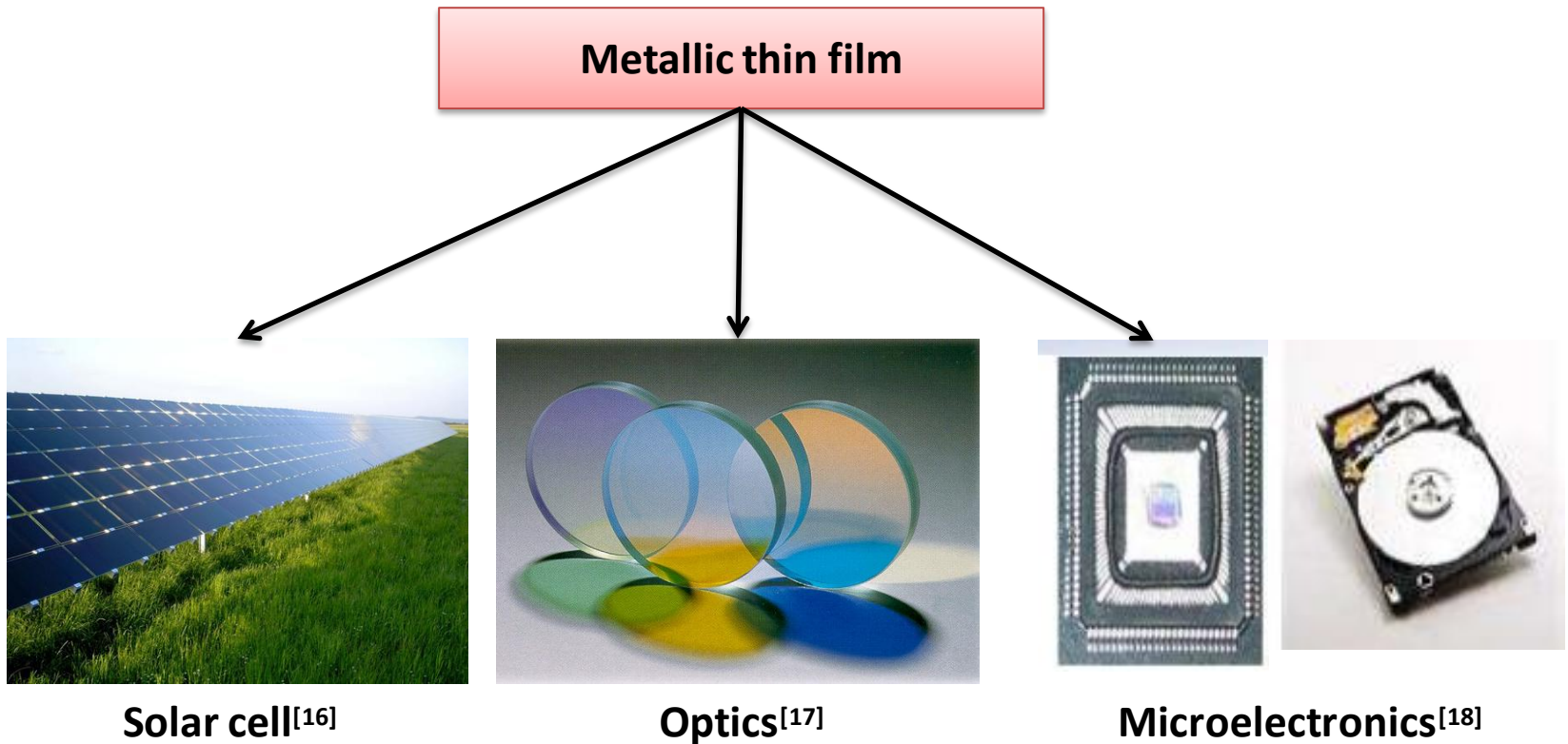
CD_{sat} : fracture density at saturation

→ Number of cracks increases with elongation until saturation





V. Applications of these coatings: sealing

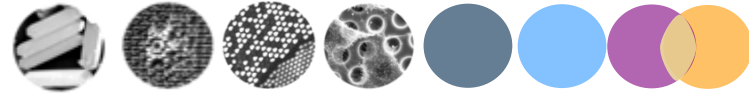


What about the sealing applications ?

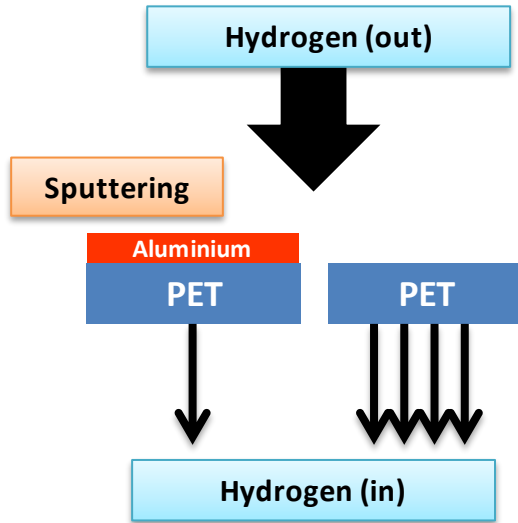
[16] A. G. Aberle, "Thin-film solar cells," *Thin Solid Films*, vol. 517, no. 17, pp. 4706–4710, juillet 2009.

[17] W. Kern, « *Thin Film Processes II* ». Academic Press, 2012.

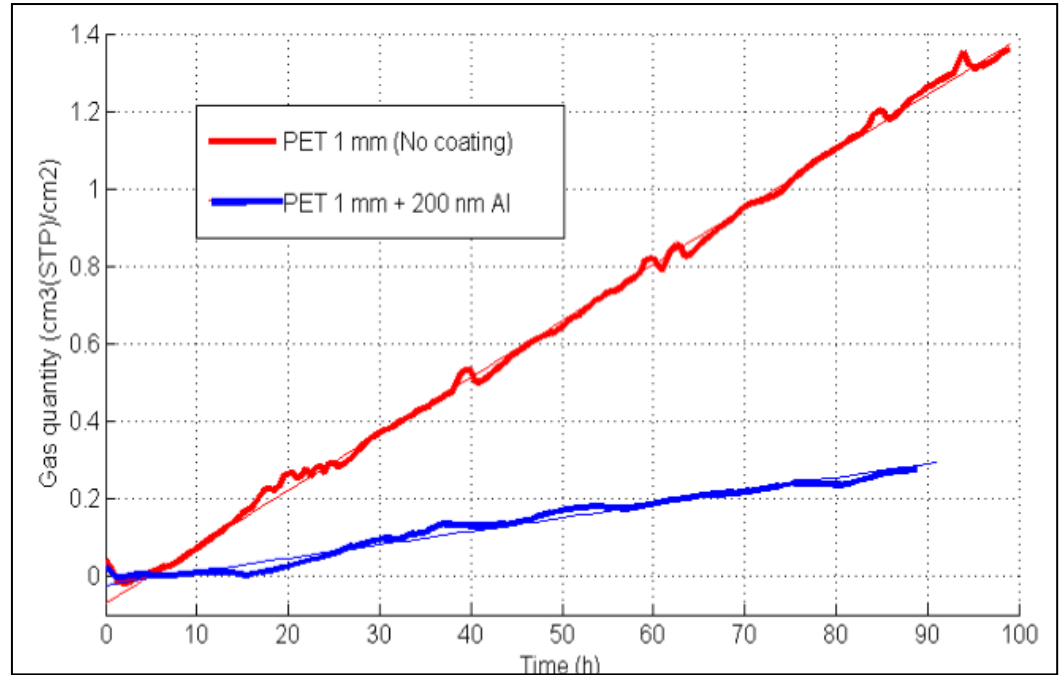
[18] D. M. Mattox, "Thin film metallization of oxides in microelectronics," *Thin Solid Films*, vol. 18, no. 2, pp. 173–186, Nov. 1973.



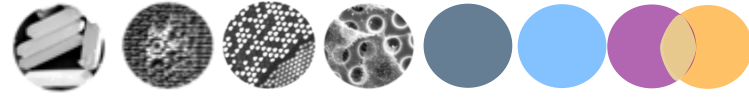
V. Applications of these coatings: sealing



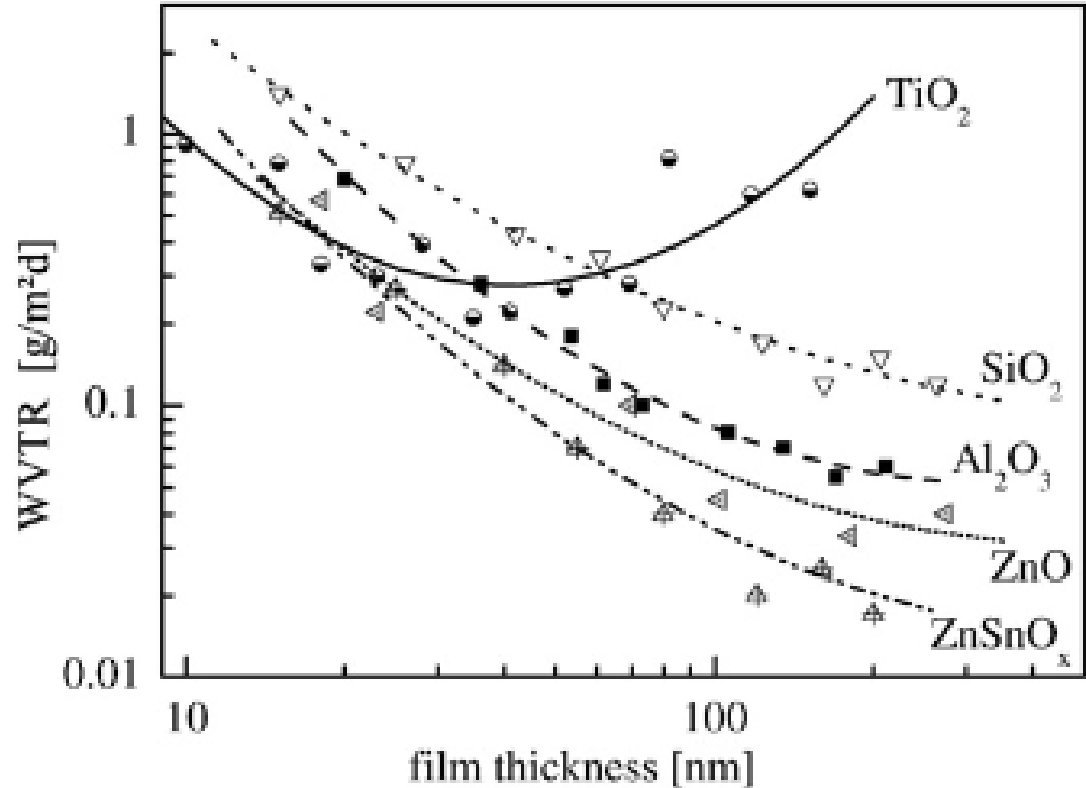
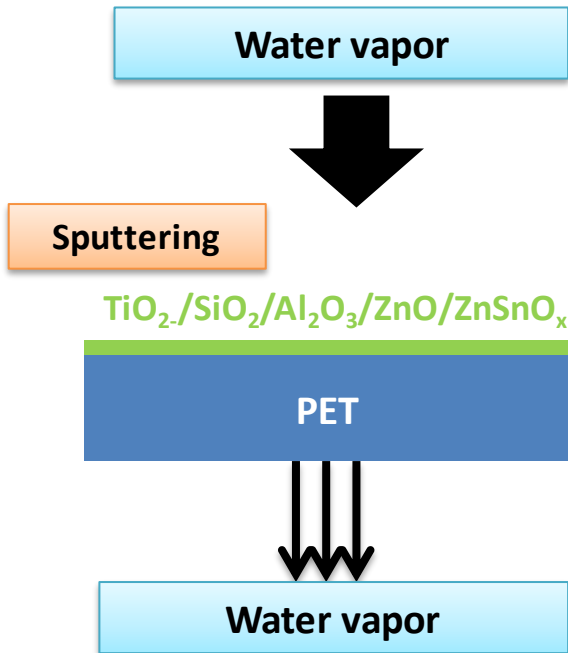
Permeation cell and test bench



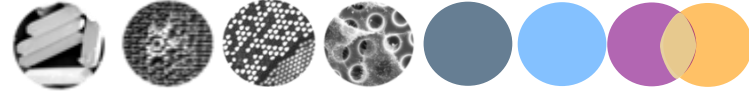
→ 200 nm of aluminum leads to a reduction of hydrogen permeation by a factor of 4



V. Applications of these coatings: sealing

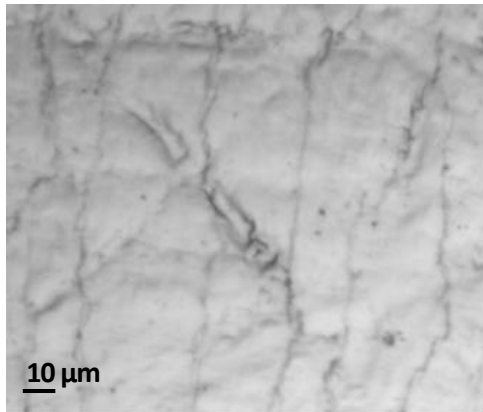
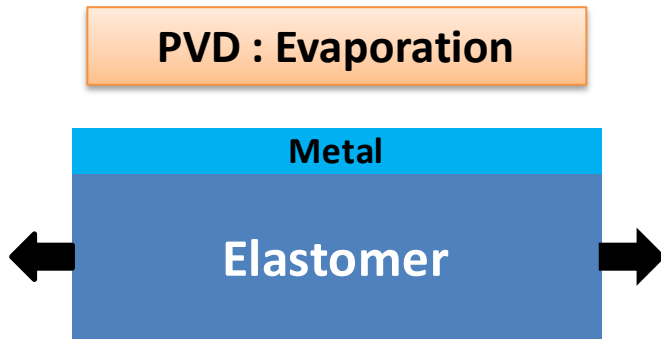


→ Zinc-tin-oxide (ZnSnO_x) layers show a very good barrier performance on PET substrate

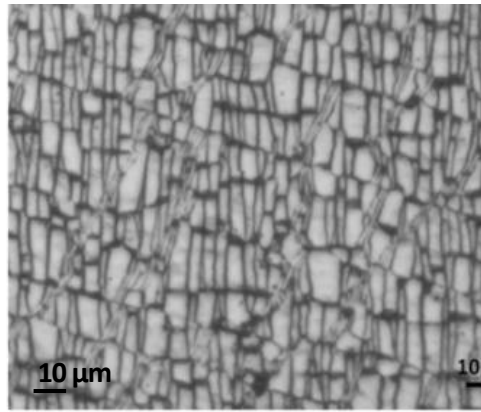


V. Applications of these coatings: sealing

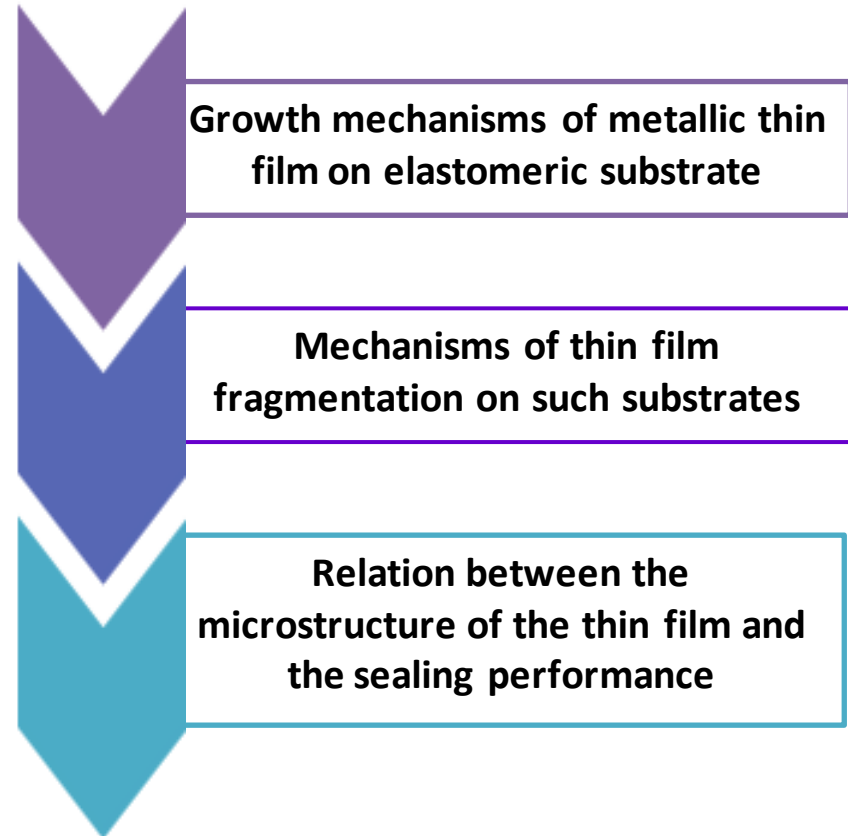
My thesis work aims at developing a metallic thin film on an elastomeric joint

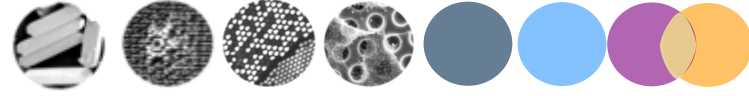


Elongation : 3%



Elongation : 30%

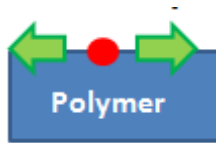




Take home message

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 ($T^{\circ}\text{C}$, chemical nature, Young Modulus...)

3D Diffusion of atoms:

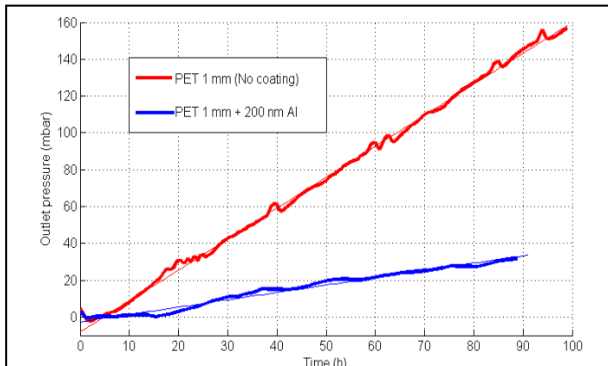


- Occurs even at room temperature
- May be enhanced by ageing (humid atmosphere)

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 !