PE-CVD with organometallic precursors: contribution of aerosol assisted processes.

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INTRODUCTION: PE-CVD

Gas precursors → (+ plasma) → Thin films → Properties → APPLICATIONS

Gas precursors	Thin films	Properties
hydrocarbons	a-C:H DLC	Optiques Mécaniques
organosilicones	SiC:H SiOC:H	Mécaniques

How to generalize:

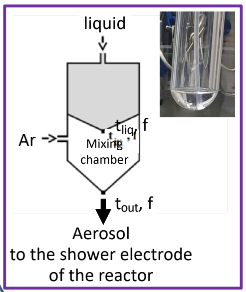
organometallics	DLC:M	

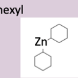
Indeed, problems of
- vaporization
- stability (highly reactive with water vapor and oxygen)

➔ **Dilution in solvents and injection as an aerosol**

MATERIAL AND METHODS

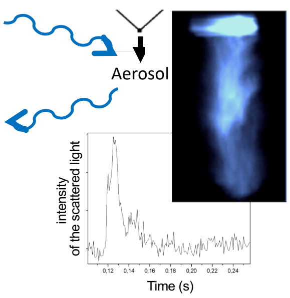
- Low pressure asymmetric radio frequency plasma (13.56MHz)
- Aerosol



Organometallic compound	Critical concentration in pentane ($mol.L^{-1}$)	%Metal / Carbon in the pentane solution
Zinc dicyclohexyl 	1.1	2 / 98
Nickelocene 	0.1	0.25 / 99.75
Ferrocene 	0.1	0.25 / 99.75

AEROSOLS

Light scattering
+ rapid imaging



t_{liq} = 5 ms / t_{out} = 10 ms / f = 1Hz

Fog of small droplets

Average velocity = 0.7 $m.s^{-1}$

for each solution with or without the organometallic compound

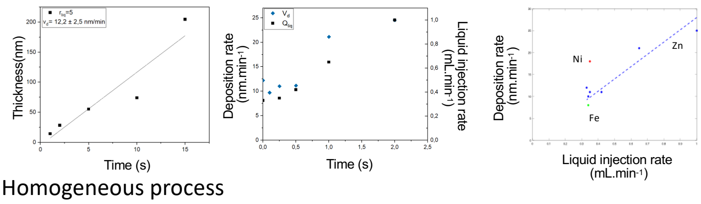
But, role on the liquid injection rate (viscosity?)

Solutions	Concentration ($mol.L^{-1}$)	Q_{liq} ($mL.min^{-1}$)
Pentane	-	0.33
Zinc dicyclohexyl in pentane	0.1 0.2 0.5 1.1	0.35 0.42 0.65 1.00
Nickelocene in pentane	0.1	0.34
Ferrocene in pentane	0.1	0.35

➔ **New method for organometallic thin film deposition**
➔ **Impacts on the plasma physics**

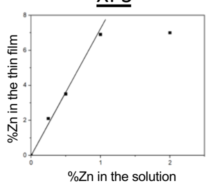
THIN FILMS

Profilometry / Ellipsometry



Homogeneous process
Constant deposition rate
proportionnal to the liquid injection rate, i.e. function of the viscosity
Same behaviour with the different organometallic compounds

XPS



Controlled inclusion of Zn atoms
but contamination with O
(reactivity of the precursor)

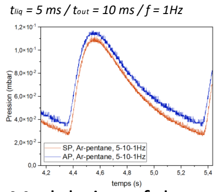
Regression on Ellipsometry

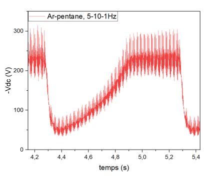
Properties controlled by the %Zn

➔ **Evidences of organometallic based thin films**

PLASMA-AEROSOL INTERACTIONS

t_{liq} = 5 ms / t_{out} = 10 ms / f = 1Hz

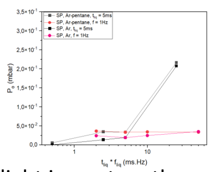


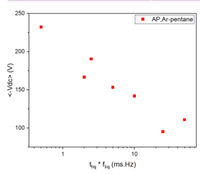


Modulation of the pressure
Modulation of the injected power ➔ self-bias
➔ Same behaviour as a pulsed discharge

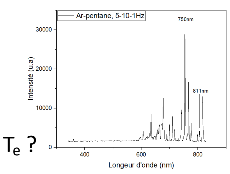
How to modify the aerosol

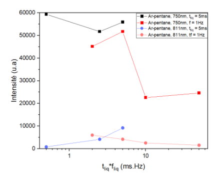
Solvent	Pulse injection $t_{liq\ (ms)}$ / $f_{(Hz)}$ / $Q_{liq\ (mL.min-1)}$	Aerosol
Pentane	5 / 0.1 / 0.03 2 / 1 / 0.13 5 / 0.5 / 0.16 5 / 1 / 0.33 5 / 5 / 1.66 10 / 1 / 1.66 50 / 1 / 3.33	Fog ↓ Isolated large droplets





Slight impact on the pressure range
But, decrease of the self-bias
➔ role of the droplets? ➔ impacts on n_e / T_e ?





➔ **Misty plasma physics**

REFERENCES

- PE-CVD with organometallic compounds, see Suhr et al.
  Journal de Physique Colloques, 1989, 50 (C5), pp.C5-739- C5-746
  Plasma Chemistry and Plasma Processing, Vol 9, No. 2, 1989
  Surface and Coatings Technology, 49(1991) 233—238
- Aerosol assisted PE-CVD and misty plasmas
  Mitronika, et al.. Journal of Physics D: Applied Physics, 54(8), 085206.
  Vangeneugden, et al. Chemical Vapor Deposition, 11(11-12), 491-496.
  Coppins, Physical review letters, 104(6), 065003.

CONCLUSION

New concept for the PE-CVD with organometallic compounds based on aerosols
Initial solution controlling the final process (viscosity, aerosol form)
Introduce new physics (misty plasmas)