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Synthèse de nanoparticules par plasma (essentiellement dans les liquides)

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16 octobre 2018

0 - Introduction

Nanoparticles for what?

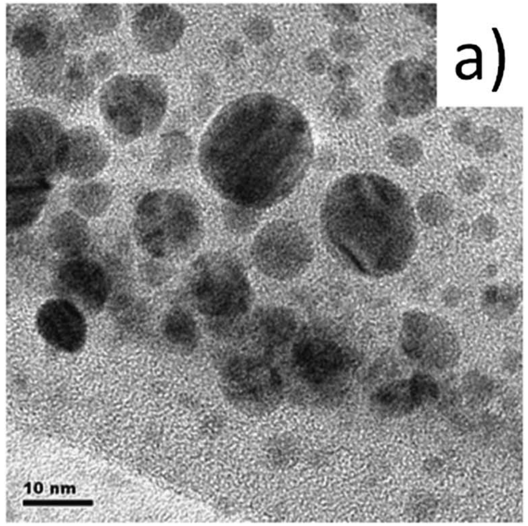
Do what chemists cannot do !

Rules to follow to find the holy grail !

- Rule n°1: benefit from non-equilibrium conditions !
- Rule n°2: benefit from nano-effects, *i.e.* quantum confinement !
- Rule n°3: combine high production yields and narrow size distributions
- Rule n°4: avoid clustering to get isolated nanoparticles.
- Rule n°5: understand to optimize

0 - Introduction

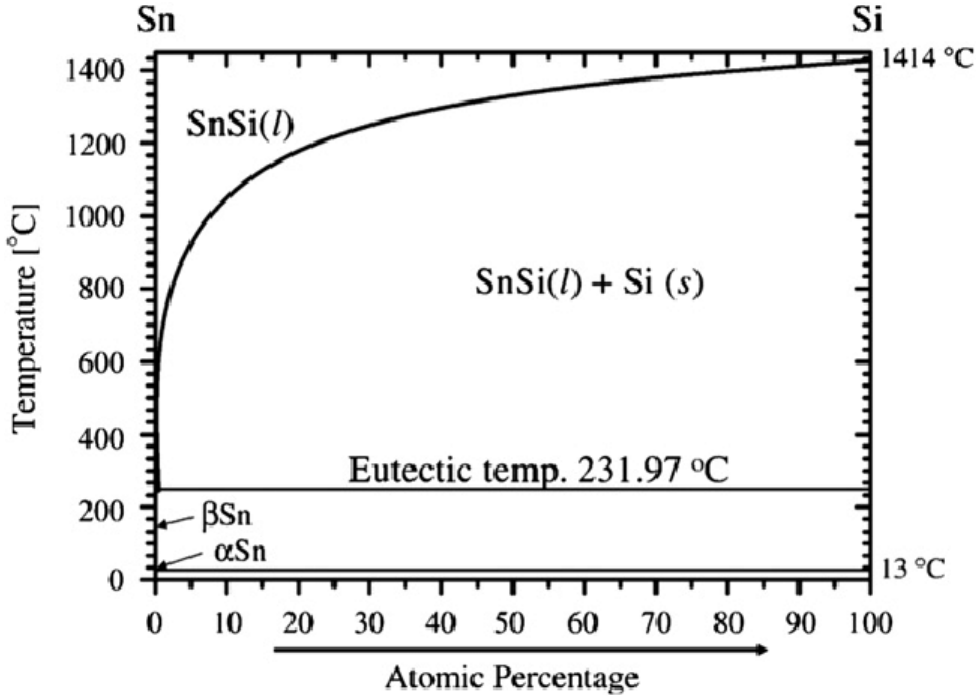
Rule n°1: benefit from non-equilibrium conditions !

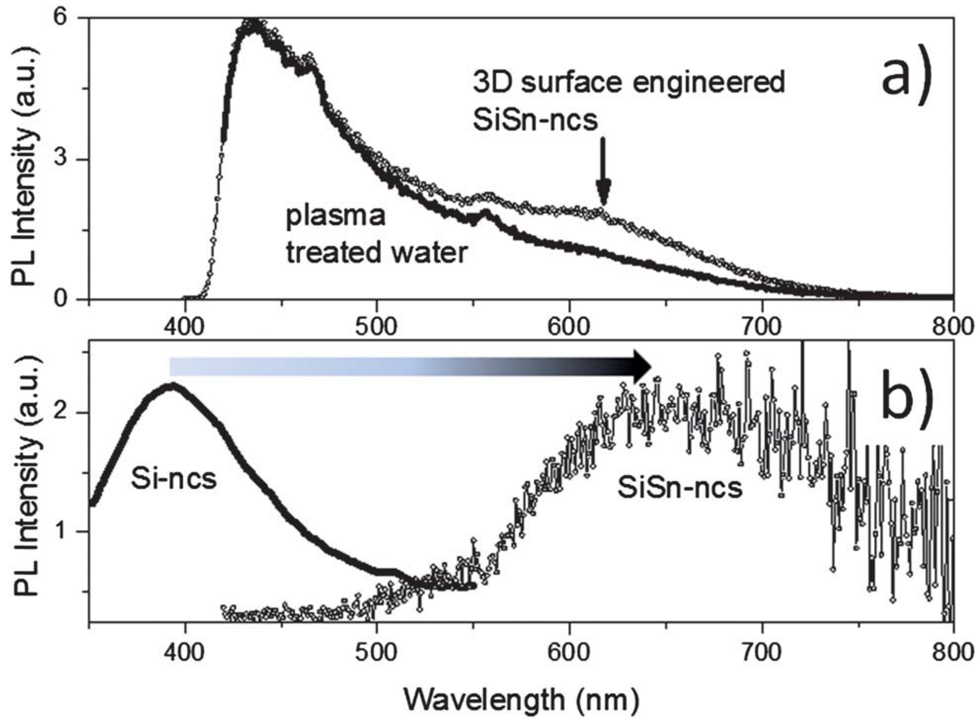


- Example: mix silicon and tin or silicon and germanium

(ns-laser ablation in water)

Švrček et al. Optics express,17 (2009) 520





0 - Introduction

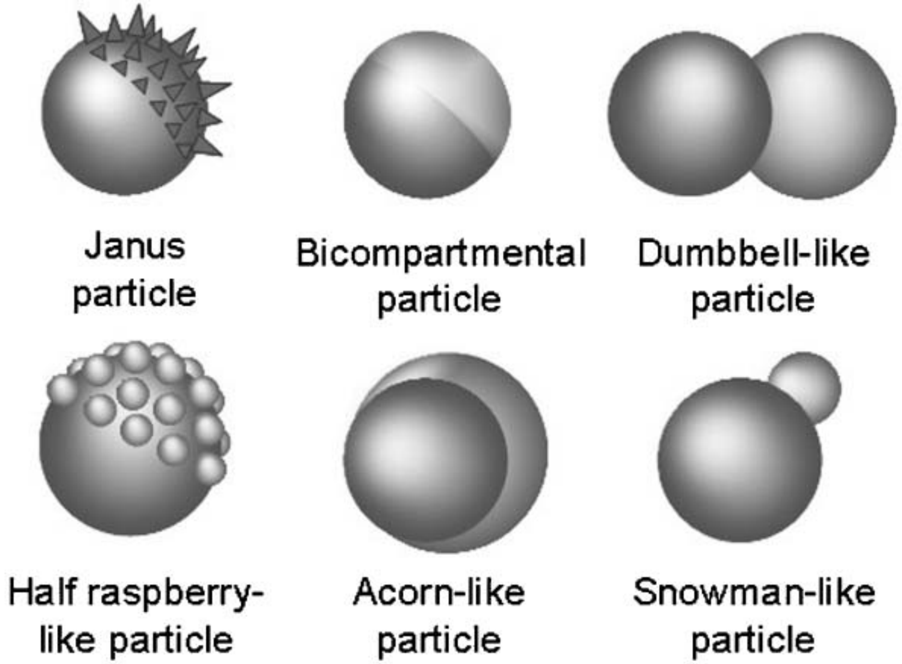
Rule n°1: benefit from non-equilibrium conditions !

- Example: exotic nanoparticles

- Alloy NPs

- Bi-materials

- Core-shell structures

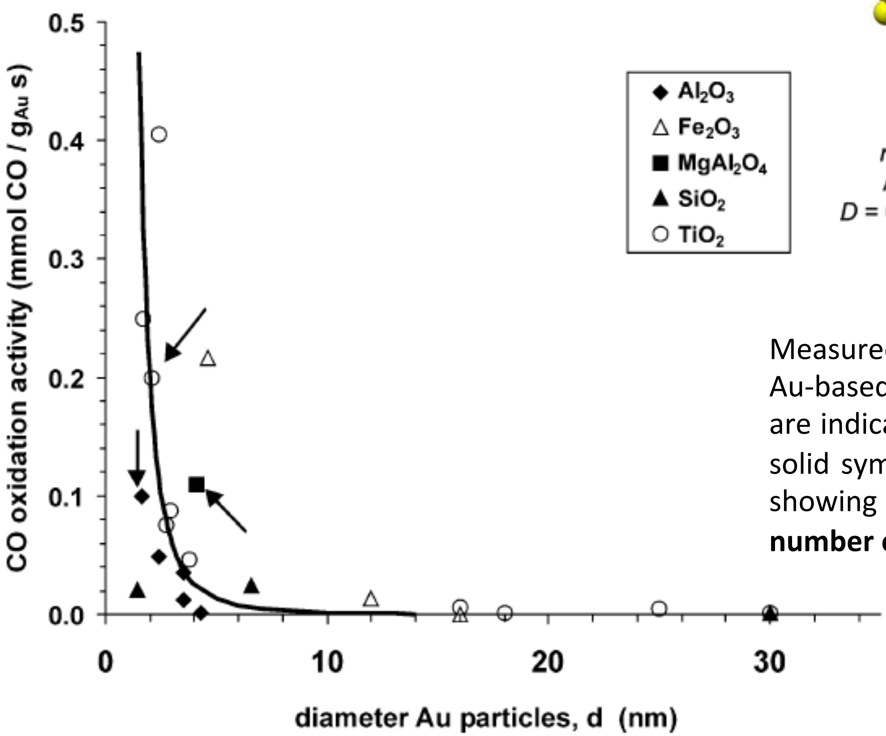


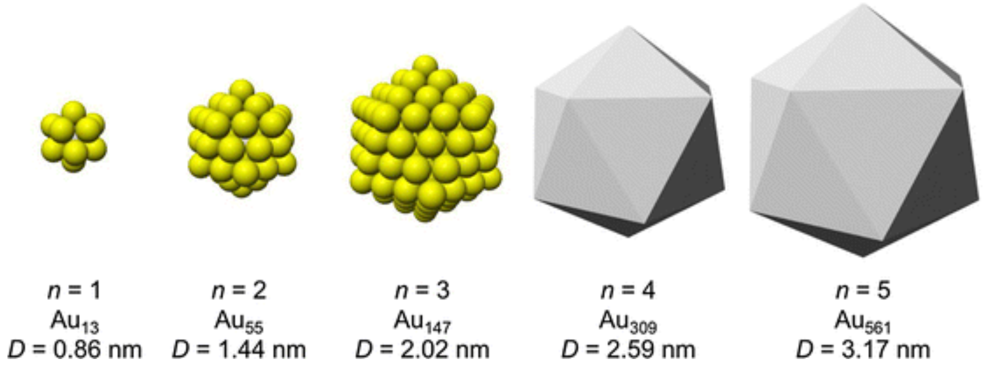
Perro et al. J. Mater. Chem. ***15*** *3745 (2005)*

0 - Introduction

Rule n°2: benefit from nano-effects, *i.e.* quantum confinement

- Example: Gold catalytic activity





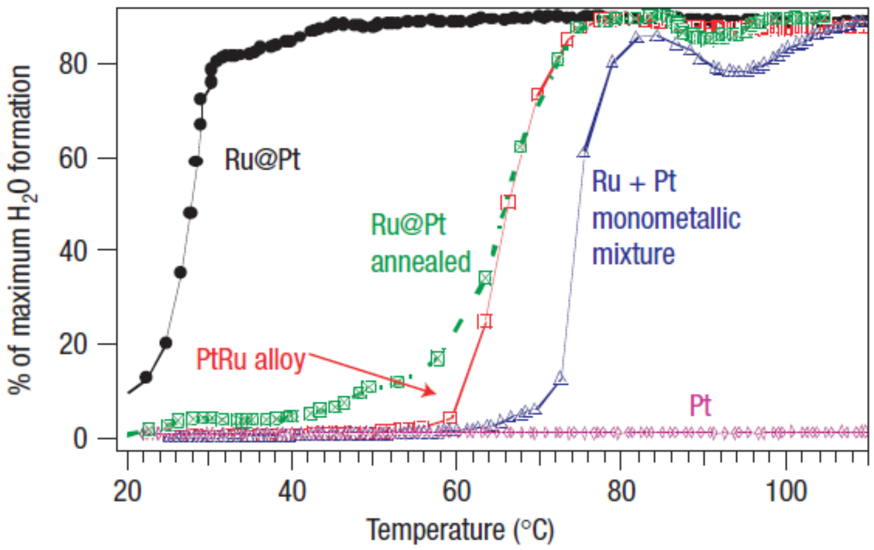
Measured activities (in mmol CO/(gAus)) for CO oxidation at 273 K over different Au-based catalysts as a function of the average particle size (*d*, in nm). Supports are indicated by the symbol shape. Open symbols are used for reducible supports; solid symbols for irreducible supports. The curve shows a 1/*d*3 guide to the eye, showing that the activity of gold catalysts is approximately **proportional with the number of low-coordinated atoms at the corners of the gold particles.**.

N. Lopez et al., J. Catalysis 223 (2004) 232

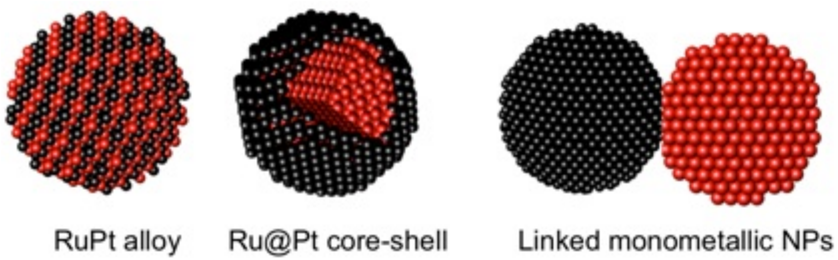
0 - Introduction

Rule n°2: benefit from nano-effects, *i.e.* quantum confinement

0.1 vol.% CO in H_2



Alayoglu et al. Nature Materials 7 333 (2008)



0 - Introduction

Rule n°3: combine high production yields and narrow size distributions

Monodisperse nanoparticles are arbitrarily defined as a predominately homogeneous population with >90% uniformity in size distribution.

It is not only a matter of size, but also of shape !

Common production yields:

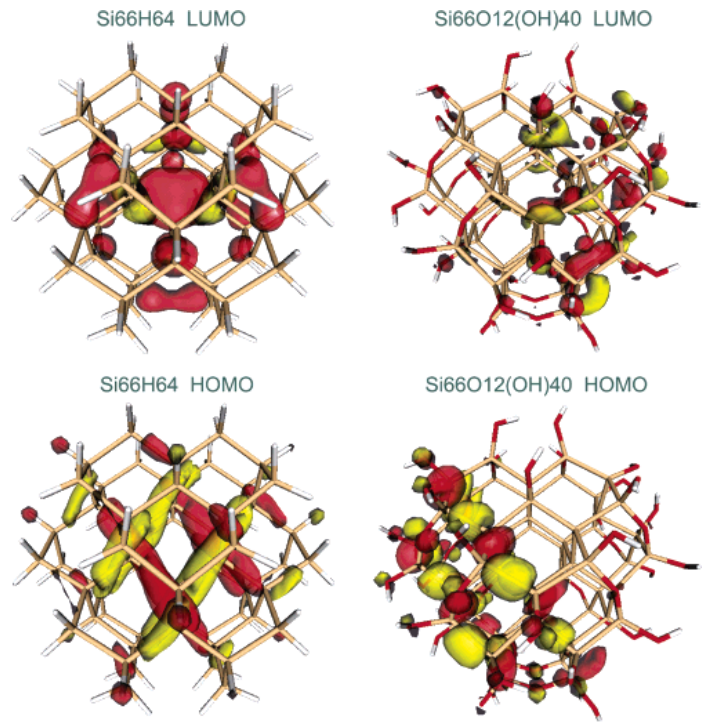
- Laser ablation: 100 mg / h
- Plasma in liquids (liquid conversion): 10 g / h
- Plasma in liquids (electrode erosion): 100 mg / h
- Low pressure CVD : 100 mg / h

0 - Introduction

Rule n°4: avoid clustering to get isolated nanoparticles

- The oxide-passivated nanocrystals have optically forbidden, indirect-gap-type transitions whereas the hydrogen-passivated nanocrystals have optically allowed, direct-gap-type transitions.

- H-passivated Si-nc luminesce in the blue whereas O-passivated Si nanocrystals luminesce in the yellow-red.



DFT calculations for 1.1 to 1.4 nm Si-nc

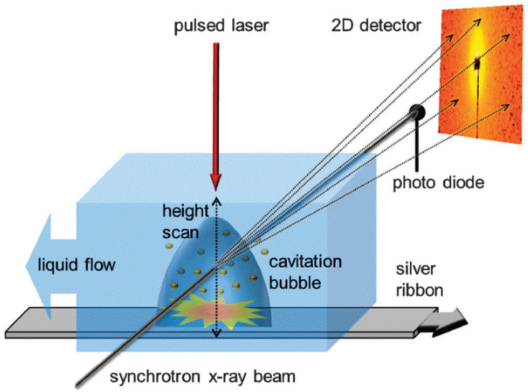
Zhou *et al.* 2003 *Nano Lett.* **3** 163

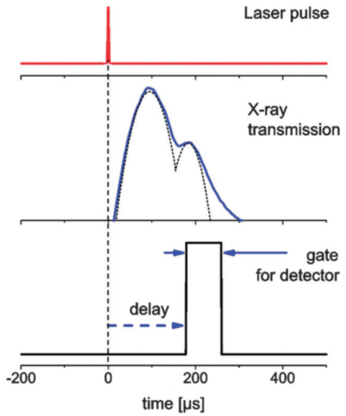
Surface groups strongly affect the final properties of small NPs.

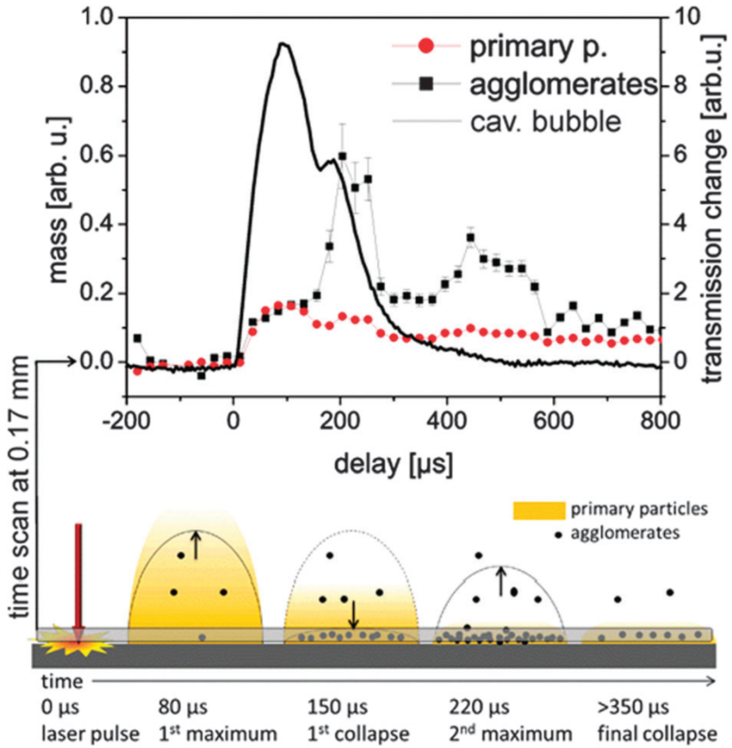
Size distributions

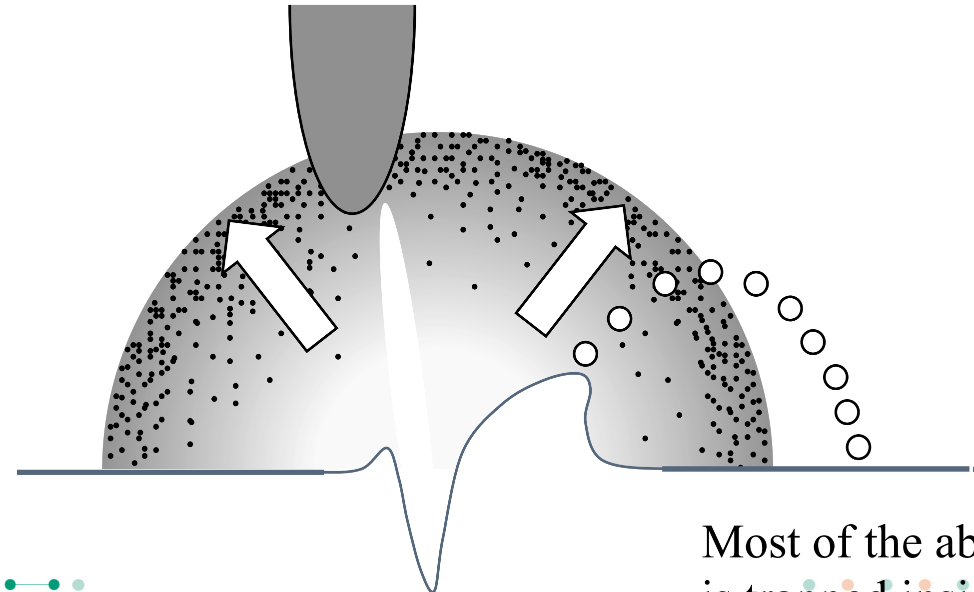
0 - Introduction

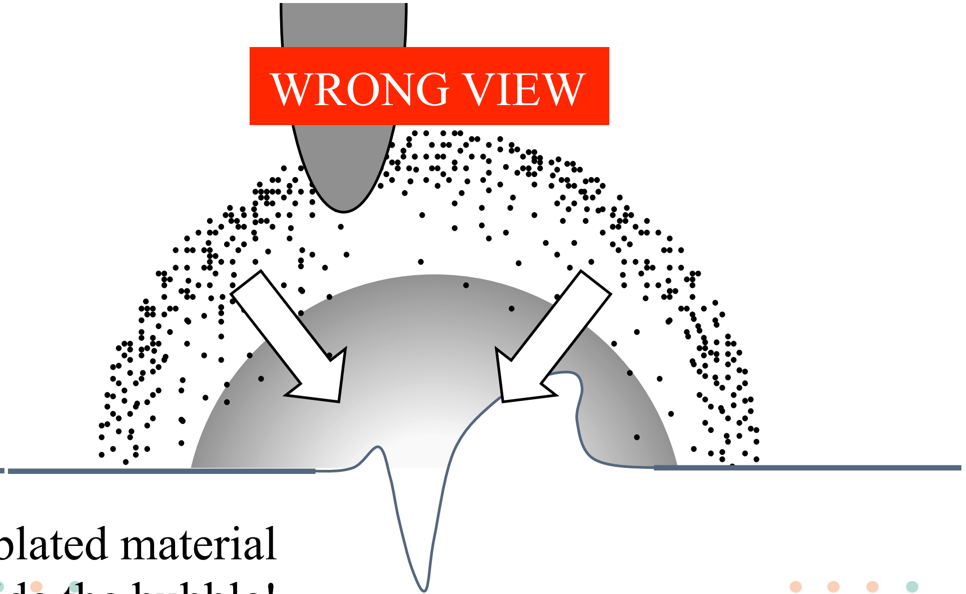
Rule n°5: understand to optimize









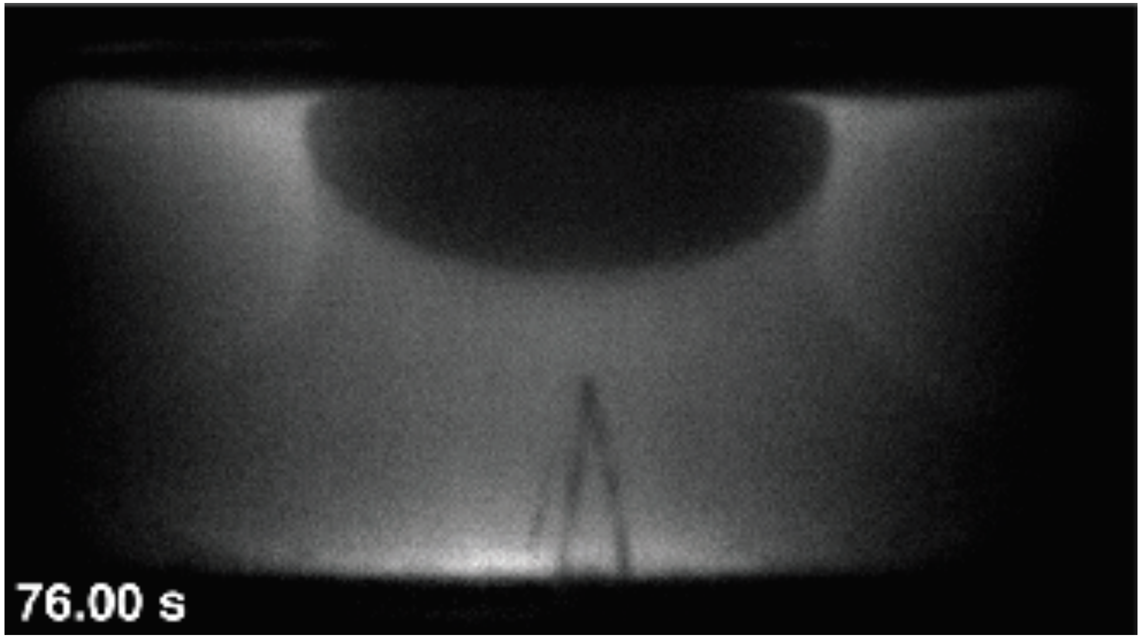


Most of the ablated material is trapped inside the bubble!

Wagener *et al.* 2013 *Phys. Chem. Chem. Phys.* **15** 3068

Chap. I

Nanoparticles and discharges in gases



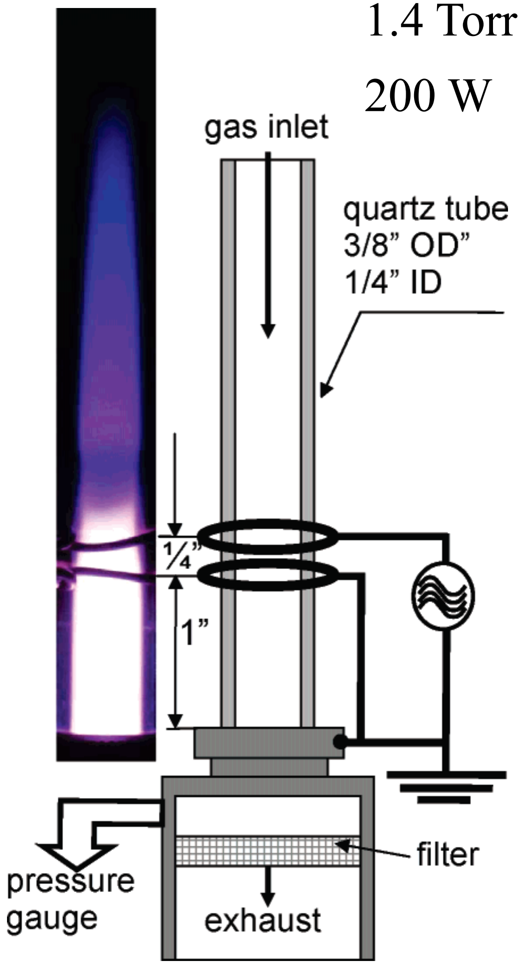
van de Wetering *et al.* 2015 *J. Phys. D: Appl. Phys.* **48** 035204

1 - Nanoparticles and low pressure discharges

High-rate synthesis of Si-nc for PV applications

1.4 Torr

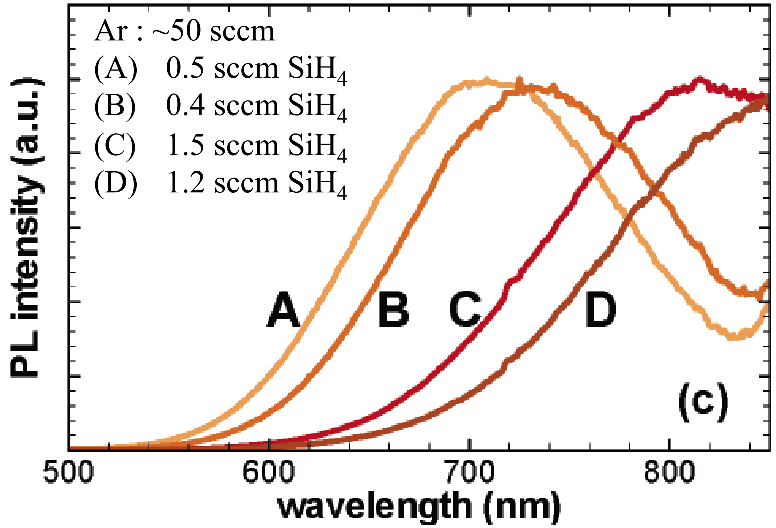
200 W



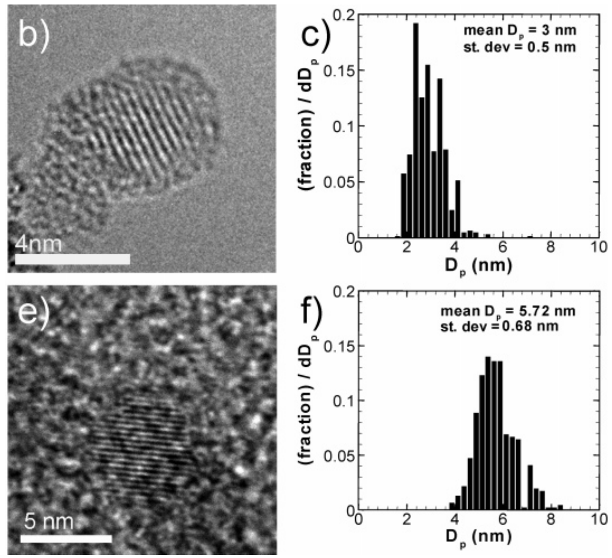
Photoluminescence quantum yields usually < 30% without post-treatment

Fast quenching of the particle temperature
+
High flux of atomic hydrogen to the nanocrystal

Anthony *et al.* 2011 *Adv. Funct. Mater.* **21** 4042



Excellent size distribution

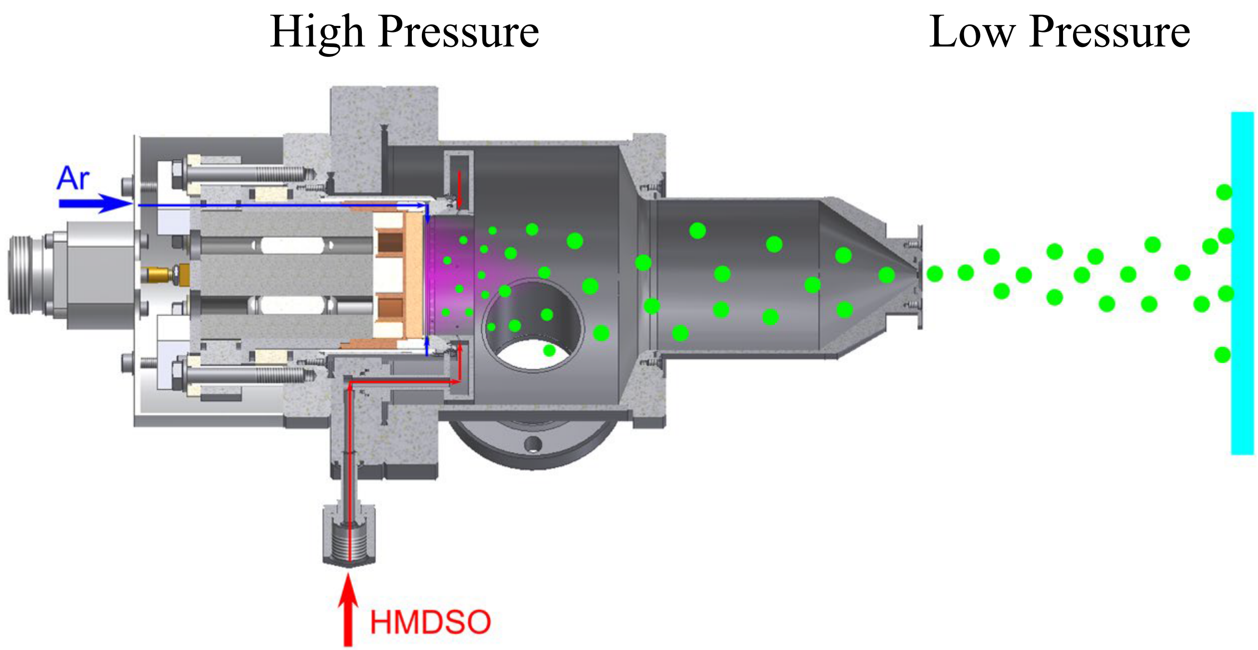


Mangolini *et al.* 2005 *Nano Lett.* **5** 655

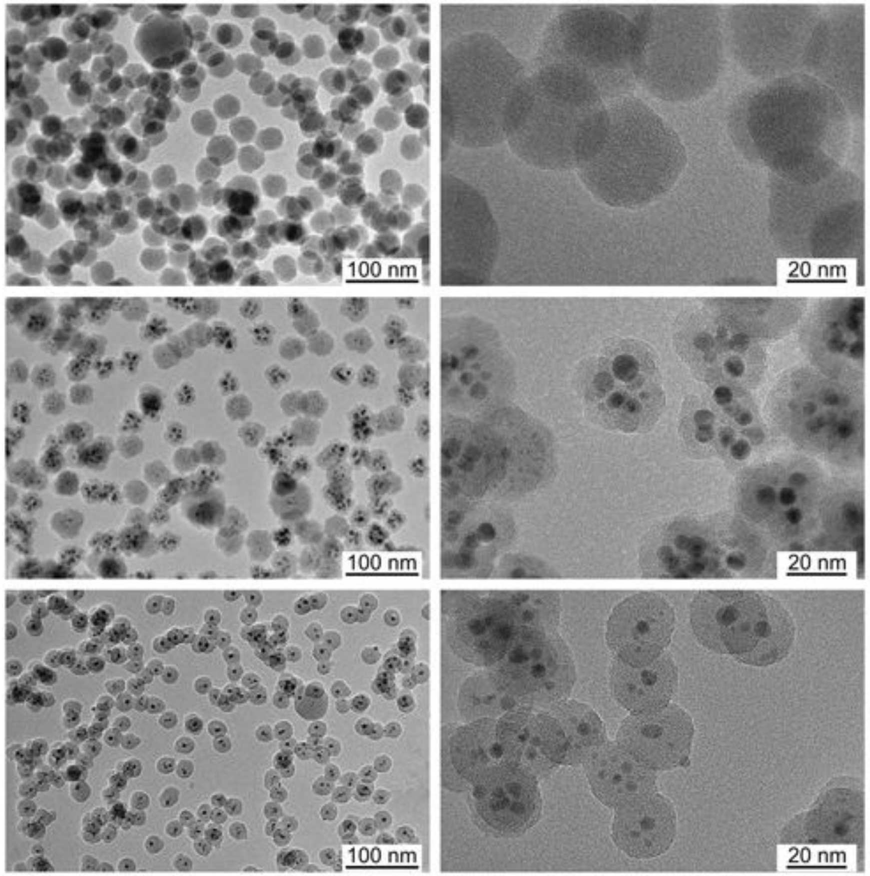
See also: P. Roca, L. Boufendi, H. Kersten, etc.

1 - Nanoparticles and low pressure discharges

Dual chamber Physical Vapor Deposition



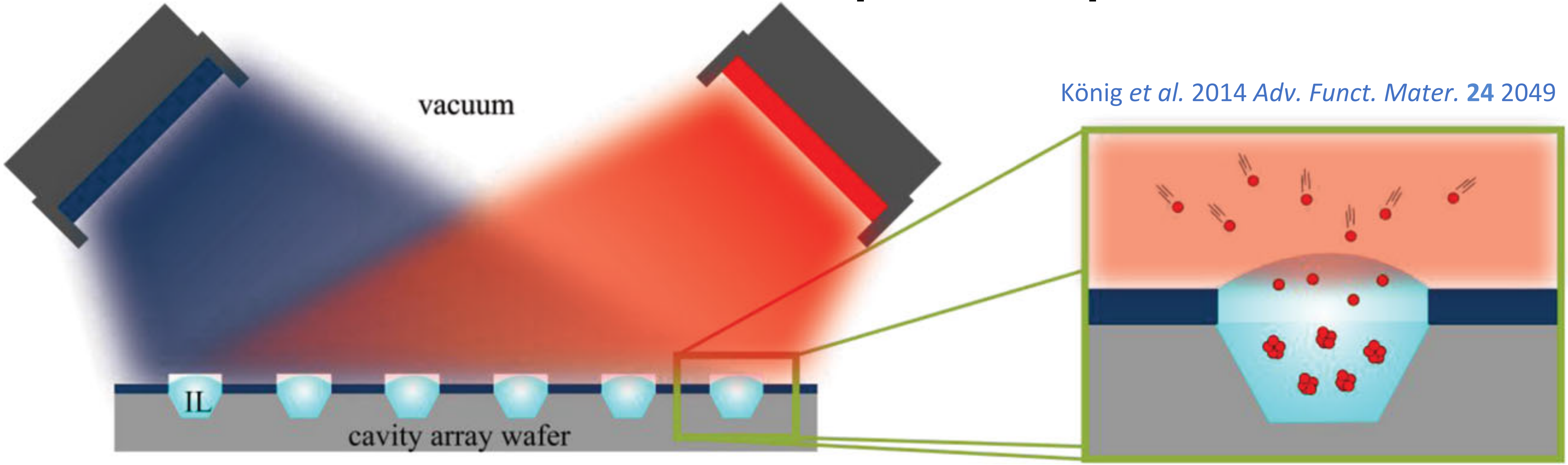
Solař *et al.* 2017 *Scientific Reports* **7** 8514

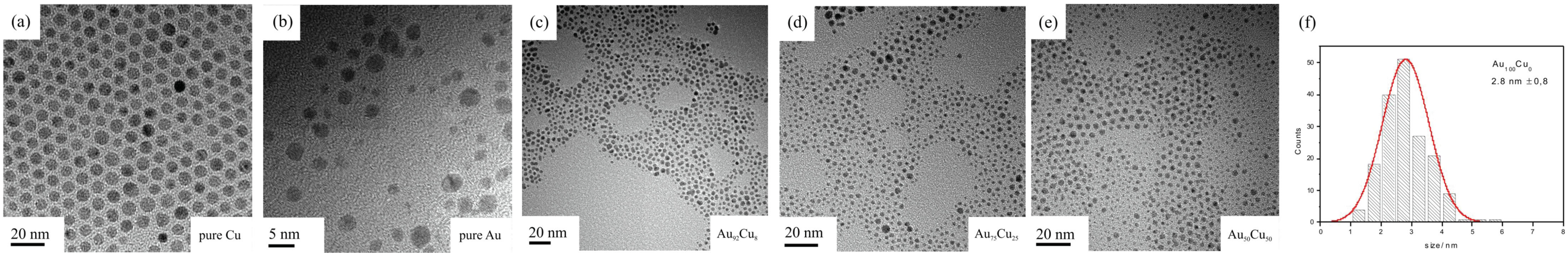


1 - Nanoparticles and low pressure discharges

Pulvérisation combinatoire sur liquide ionique $[C_1C_4im][Tf_2N]$

König *et al.* 2014 *Adv. Funct. Mater.* **24** 2049





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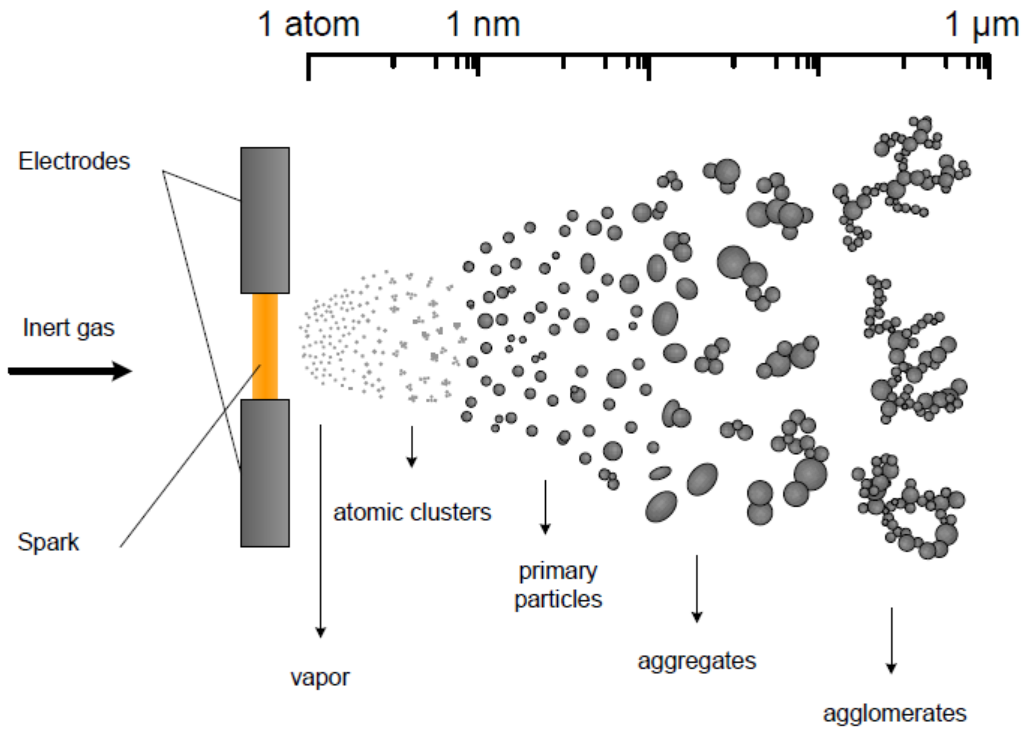
1 - Nanoparticles and high pressure discharges

Spark generator
(thermal plasma - low-powered arc)

Low frequency: yield ~ 1 mg/h

Local melting of electrodes

Why not simply melting electrodes?



T: 015-2786751 www.patent.tudelft.nl

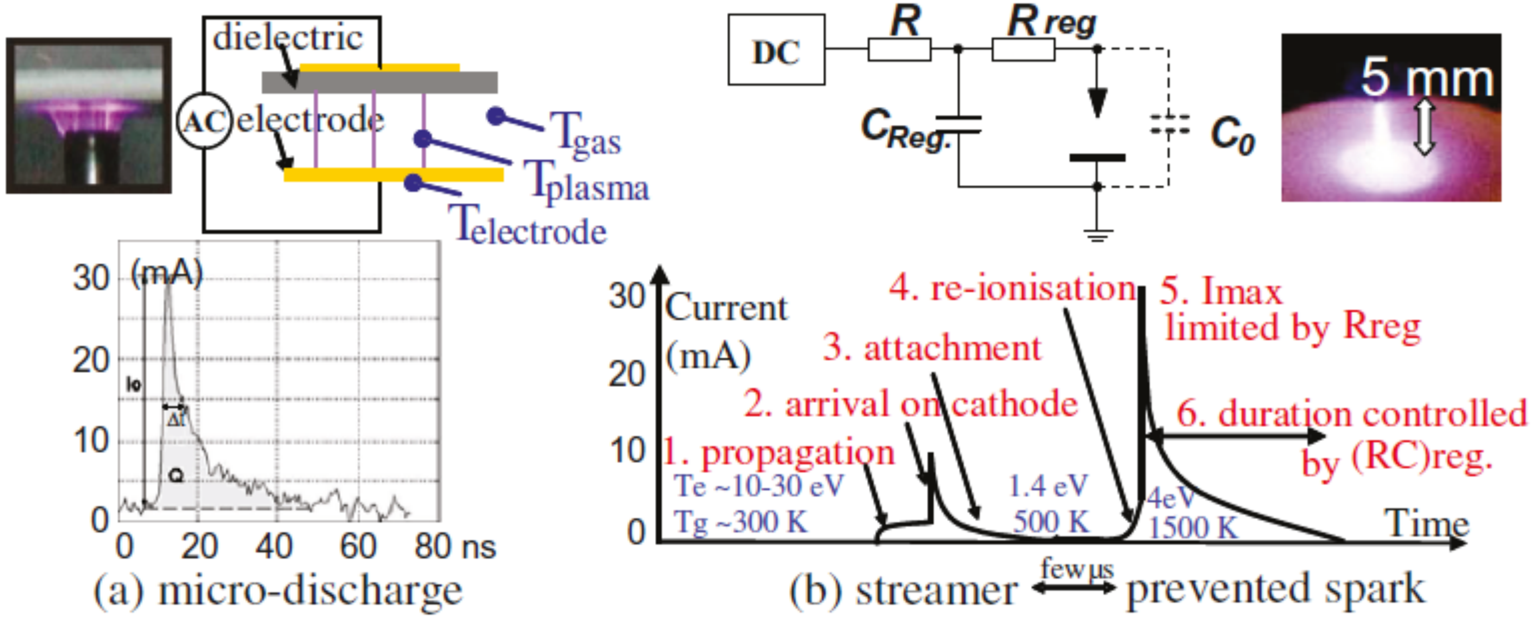
evaporation/condensation method:
PROS - good yield and control over deposition parameters
CONS compared with spark discharge - furnace energy consumption and heating up and cooling down times, clogging of the furnace due to particle deposition on the walls, etc.

1 - Nanoparticles and high pressure discharges

Non-thermal generator

Stop before or prevent arcing

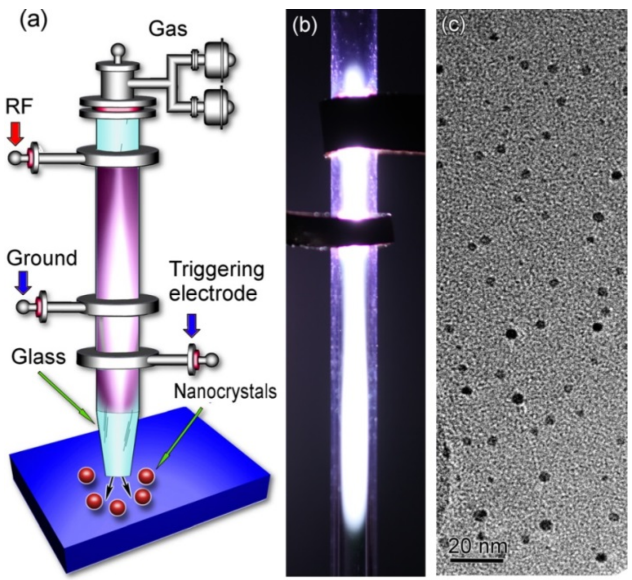
J.P. Borra *et al.* 2006 *J. Phys. D: Appl. Phys.* **39** R19



LOW THROUGHPUT

1 - Nanoparticles and high pressure discharges

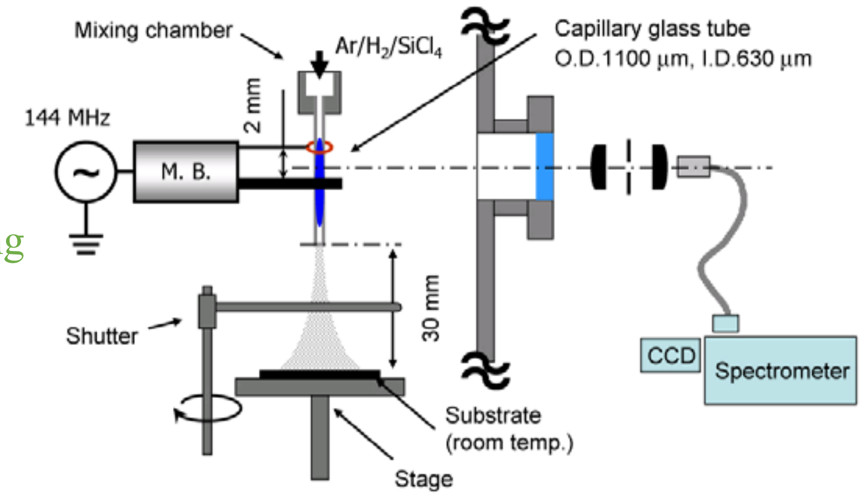
Askari *et al.* 2014 *Appl. Phys. Lett.* **104** 163103



RF power: 100W
250 sccm Ar
SiH_4: 10 ppm
1mm electrode spacing

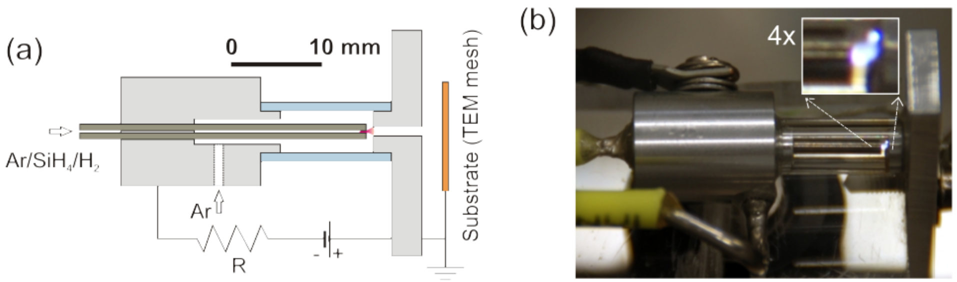
HIGH THROUGHPUT

µwave power: 35W
200 sccm Ar
$H_2 < 5\%$
$SiCl_4$: 100 ppm
2mm electrode spacing



Nozaki *et al.* 2007 *Nanotechnol.* **18** 235603

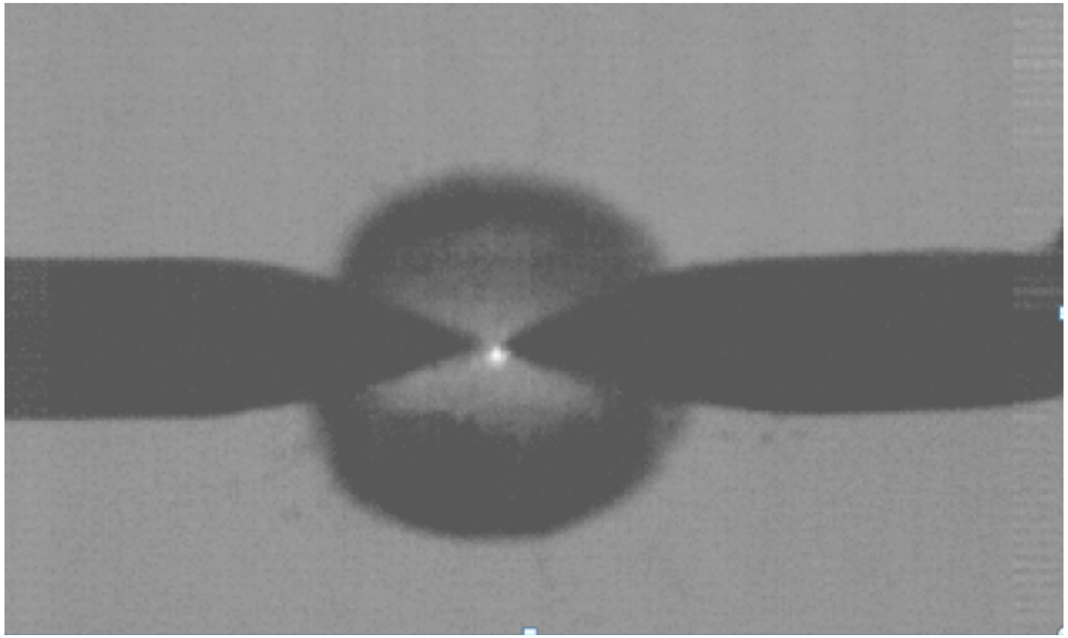
DC power: 2W
100 sccm Ar
$H_2 < 5000$ ppm
$SiCl_4$: 1.5-2.5 ppm
180 µm electrode spacing



Barwe *et al.* 2015 *Plasma Process.Polym,* **12** 132

Chap. II

Discharges in liquids



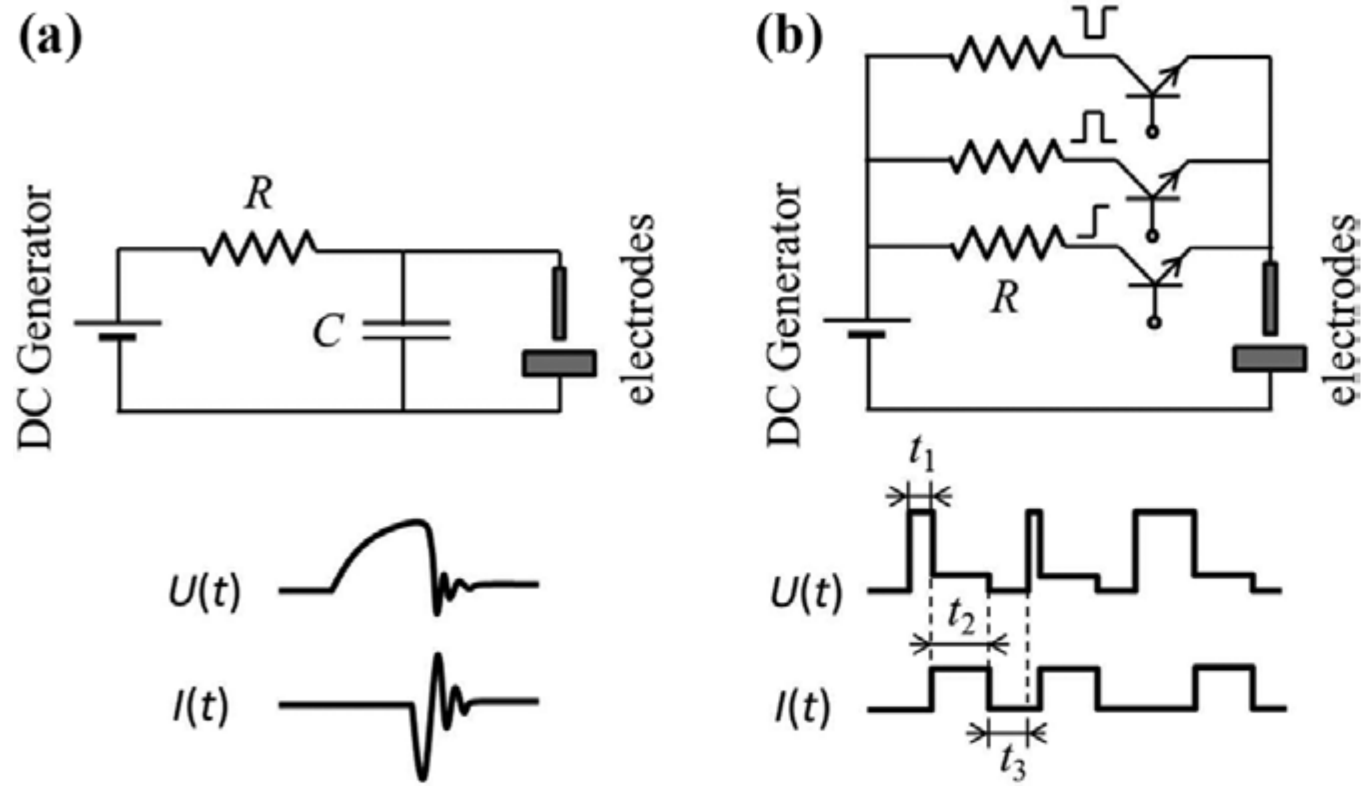
2.1 – Spark discharge in dielectric liquids

Several possibilities:

by electrical characteristics

by liquids

by inter-electrode gap distances



2.1 – Spark discharge in dielectric liquids

- igniting a discharge,
- maintaining the discharge for a given time and, eventually, control the voltage or the current during this step,
- setting an off-time to recharge capacitors and flush the liquid,
- repeating the process as long as necessary

Dielectric or conductive liquid?

The conductance of the liquid is NOT an intrinsic characteristic if the liquid contains non negligible impurity levels.

Pre-treatments of both the liquid and its container to remove dust, particles, dissolved gases, electrolytes, etc.

If the rate constant for the electron–impurity interaction is, say, 10^{-8} cm^3 s^{-1}, an electron lifetime of typically 10^{-4} s, the impurity concentration should not exceed 10^{-9} mol l^{-1}, which is particularly weak (6×10^{11} cm^{-3} *vs* 3.3×10^{22} cm^{-3} for water)

2.1 – Spark discharge in dielectric liquids

Several possibilities:

by electrical characteristics

by liquids

by inter-electrode gap distances

Table 1. Examples of electrical characteristics found for discharges in liquids.

Shape	Liquid	Applied voltage (kV)	Current (A) and pulse width	Gap distance (mm)	Reference
Relaxation	Distilled water	+112	Unknown (∼500 ps)	4	Starikovskiy *et al* (2011)
Relaxation	Distilled water	−35	250 (∼200 ns)	0.4	Schoenbach *et al* (2008)
Relaxation	Oil ITO 100	+4–6	100 (∼1.2 μs)	0.3	Kudelcik *et al* (2010)
Relaxation	Liquid Helium	23	280 (2.5 ms)	5	Hayakawa *et al* (1995)
Relaxation	n-Hexane	15	140 (10 ns)	1	Fuhr *et al* (1986)
Relaxation	n-Decane	0.022	8×10^{-8} (0.6 s)	2×10^{-5}	Virwani *et al* (2007)
Transistor	Oil Daphne Cut HL-25	+0.110	4.2 (∼250 ns)	0.25–1	Kurnia *et al* (2008)
Transistor	Liquid nitrogen	±0.220	10.5 (32 μs)	0.3	Muttamara and Fukuzawa (2012)

2.1 – Spark discharge in dielectric liquids

Several possibilities:

by electrical characteristics

by liquids

by inter-electrode gap distances

Dividing dielectric liquids into three groups:

- Non-polar liquids such as liquefied gases, hexane, benzene and mineral oils.
- Polar liquids with very high permittivity, which have to be distinguished depending on whether they can be self-dissociated (self-ionized) or not.
- Others

  - The former ones, such as water or ethanol, have a high permittivity. A part of their molecules spontaneously dissociates and recombines partially, giving a certain resistivity.

  - The latter ones have either a high permittivity, such as nitrobenzene or propylene, or a low one, such as chlorobenzene.

2.1 – Spark discharge in dielectric liquids

Several possibilities:

by electrical characteristics

by liquids

by inter-electrode gap distances

Table 2. Some physical data of dielectric liquids at 1 atm and 293 K (except for liq.N_2 (75 K), liq.He (5 K) and liq.Ar (85 K)); m.p.: melting point; b.p.: boiling point; B.S.: breakdown strength.

Liquid	ε_r	Ion mobility ($m^2\ V^{-1}\ s^{-1}$)	λ ($W\ m^{-1}\ K^{-1}$)	m.p.–b.p. (K)	μ ($kg\ m^{-1}\ s^{-1}$)	B.S. ($MV\ cm^{-1}$)	Reference
Non-polar liquids							
Liquid N_2	1.44	2.50×10^{-7}	0.137	63.1–77.4	1.66×10^{-4}	1.6–1.9	Henson (1964)
Liquid He	1.05	4.62×10^{-6}	0.0198	b.p.: 4.2	3.32×10^{-6}	0.7	Donnelly and Barenghi (1998)
Liquid Ar	1.6	6.00×10^{-8}	0.132	83.8–87.2	2.78×10^{-4}	1.1–1.42	Henson (1964)
Hexane	2.0	1.90×10^{-8}	0.124	177.9–341.8	3.09×10^{-4}	1.1–1.3	Gray and Lewis (1969)
Benzene	2.3	2.76×10^{-7}	0.167	279.2–353.2	6.50×10^{-4}	1.1	Huang and Freeman (1980)
Vegetal (castor) oil	3.2	1.60×10^{-10}	0.17	260 – >660	0.985	1.0	Yang *et al* (2012)
Mineral (white) oil	2.2	2.60×10^{-9}	0.11	264–648	0.020	1.0	Yang *et al* (2012)
Polar liquids							
Pure water	80	2.00×10^{-7}	0.609	273.2–373.2	1.00×10^{-3}	0.65	Light and Licht (1987)
Ethanol	23	2.10×10^{-7}	0.171	159.2–351.5	1.20×10^{-3}	1.65	Atten and Gosse (1969)
Chlorobenzene	5.69	2.54×10^{-8}	0.132	228.2–404.6	1.06×10^{-3}	0.95	Barret *et al* (1975)
Nitrobenzene	35	2.00×10^{-7}	0.149	278.8–484.1	1.96×10^{-3}	0.5–1	Atten and Gosse (1969)
Propylene carbonate	64.4		0.165	224–515	2.48×10^{-3}	2.2	Atten and Gosse (1969)

2.1 – Spark discharge in dielectric liquids

Several possibilities:

by electrical characteristics

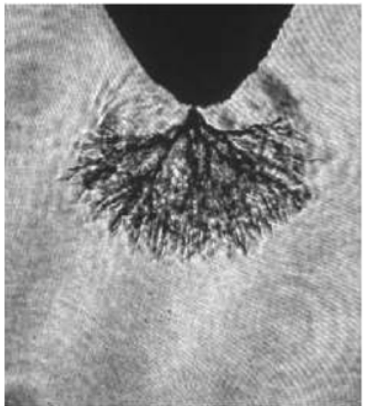
by liquids

by inter-electrode gap distances

mm — µm — nm

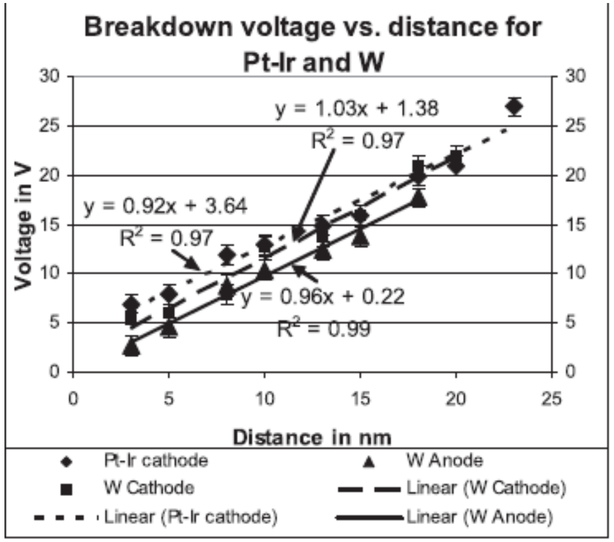
field-emission-assisted avalanche

Bush-like structures



filamentary structures

Unknown structures

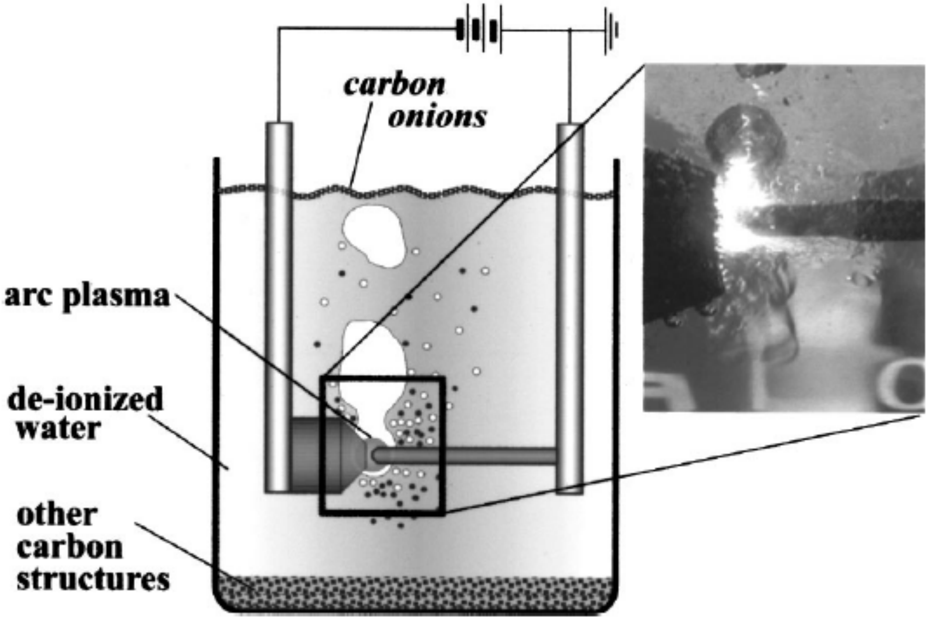


Virwani et al. PRL 99, 017601 (2007)

2.1 – Spark discharge in dielectric liquids

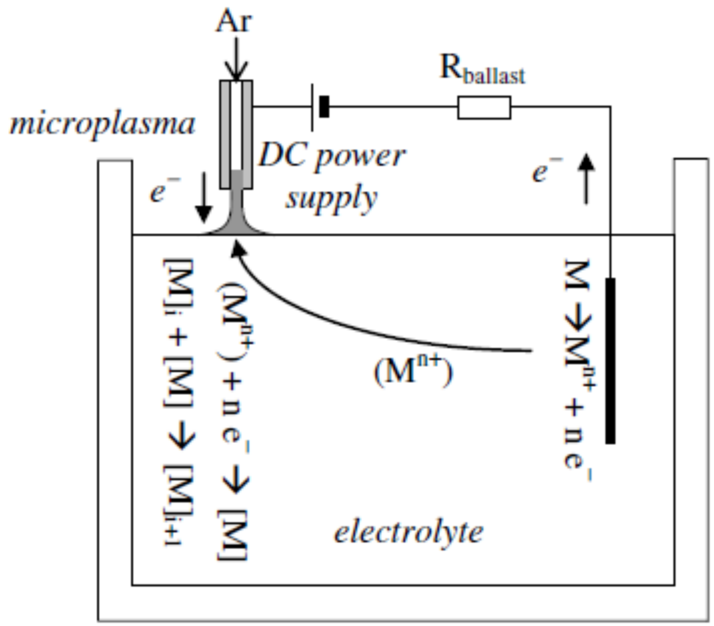
Submerged discharges

Low voltage: breakdown by contact



Sano et al. 2002 *J. Appl. Phys.* **92** 2784

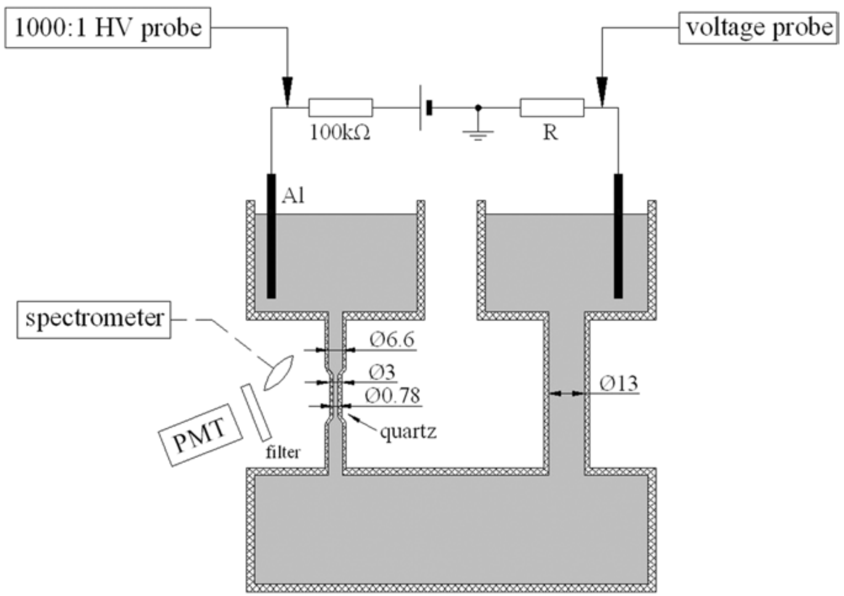
Discharges in contact with liquids



Chiang *et al.* 2010 *Plasma Sources Sci. Technol.* **19** 034011

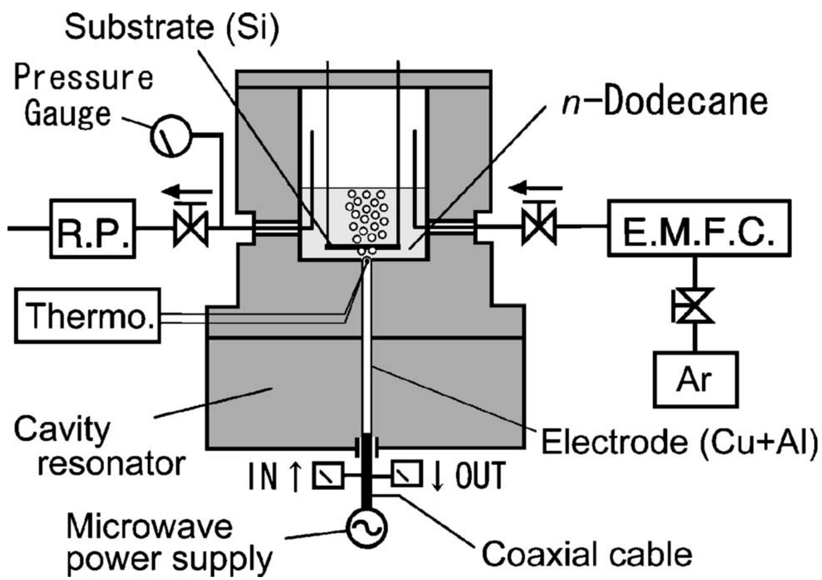
2.1 – Spark discharge in dielectric liquids

Submerged discharges



P. Bruggeman *et al.* 2008 *J. Phys. D: Appl. Phys.* **41** 194007
See also F. Krčma's works

Discharges in bubbles in liquids



Nomura *et al.* 2006 *Appl. Phys. Lett*. **88** 211503
See also A. Hamdan's works

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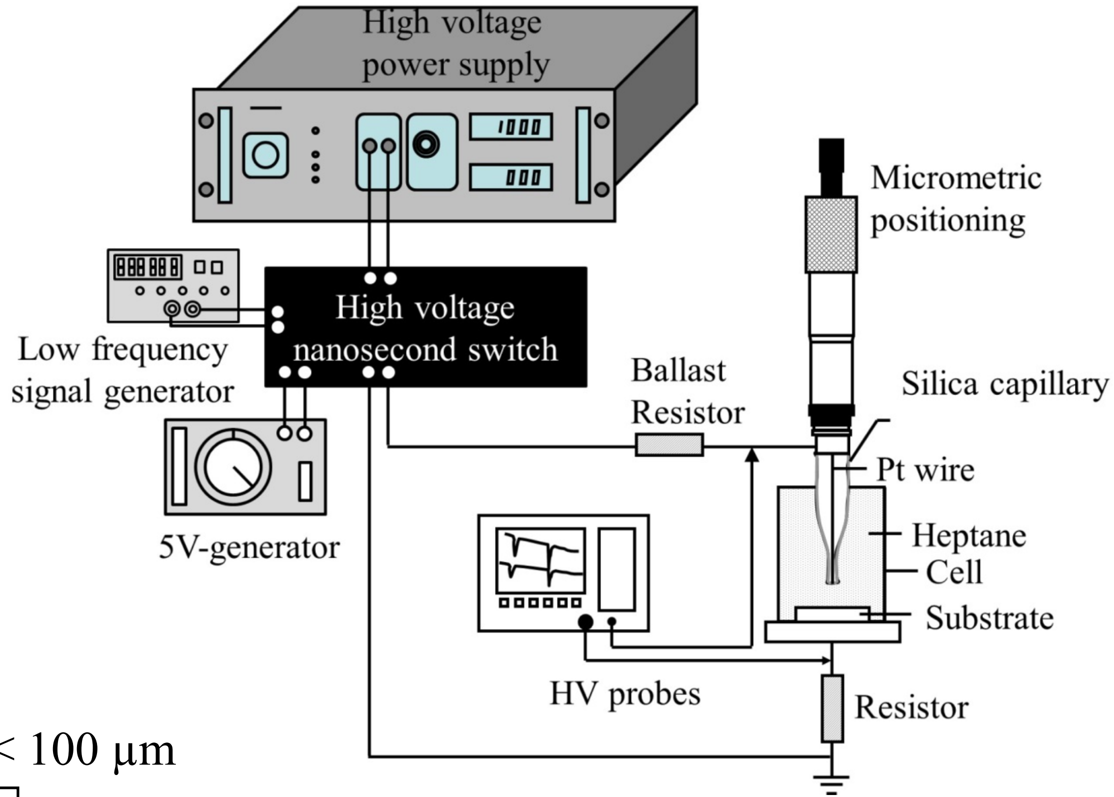
2.1 – Spark discharge in dielectric liquids

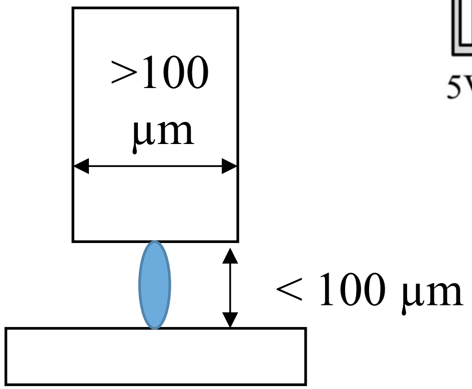
Model : SR15-R-1200
Continous mode : 0 - 15 kV ; 0 – 80 mA
Pulsed by a Low Frequency Generator

Micrometric positioning screw ($\Delta x = 10\mu m$)

Our system in NANCY



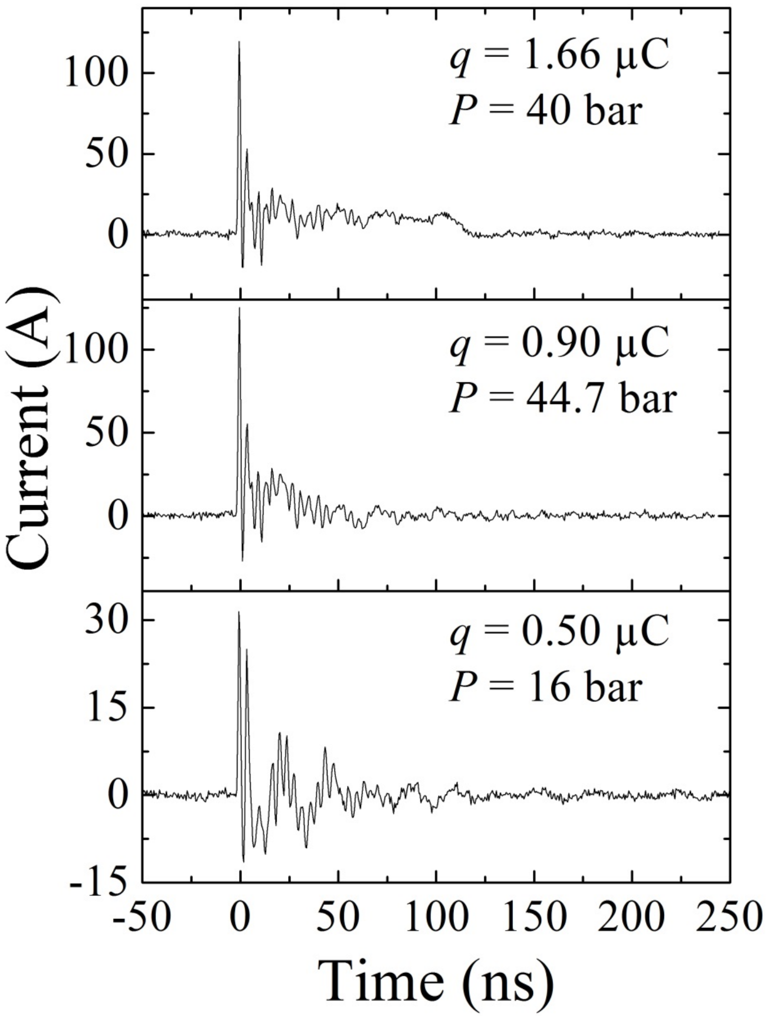
Dielectric liquid
Heptane C_7H_{14}
$\sigma = 10^{-12}$ S/m
$\rho = 684$ kg/m^3

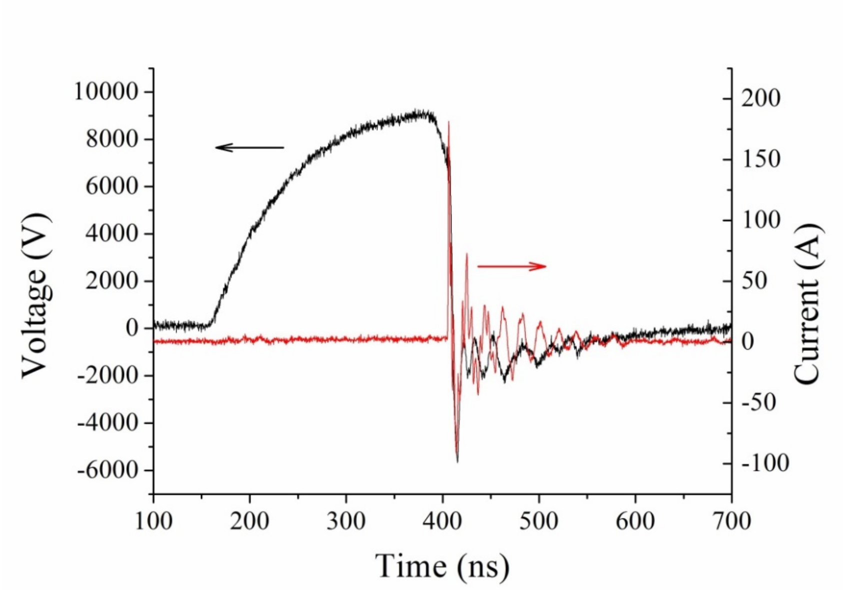


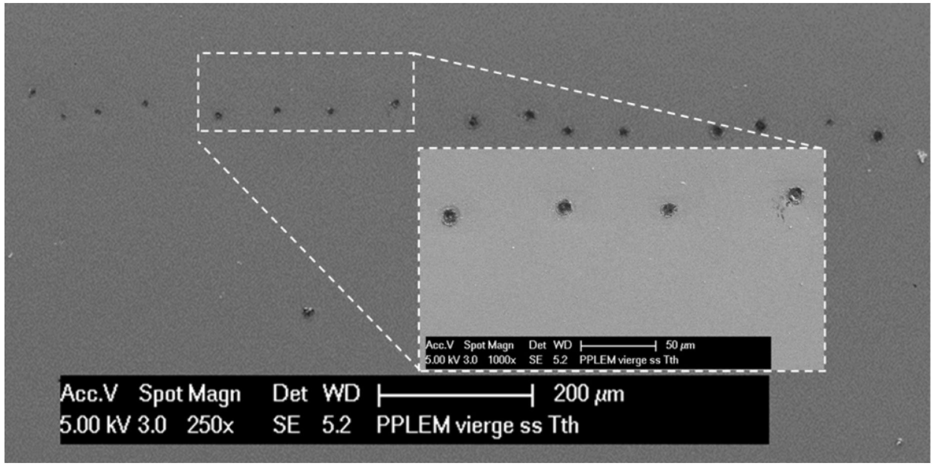
Always plate-to-plate

substrate = counter-electrode

2.1 – Spark discharge in dielectric liquids

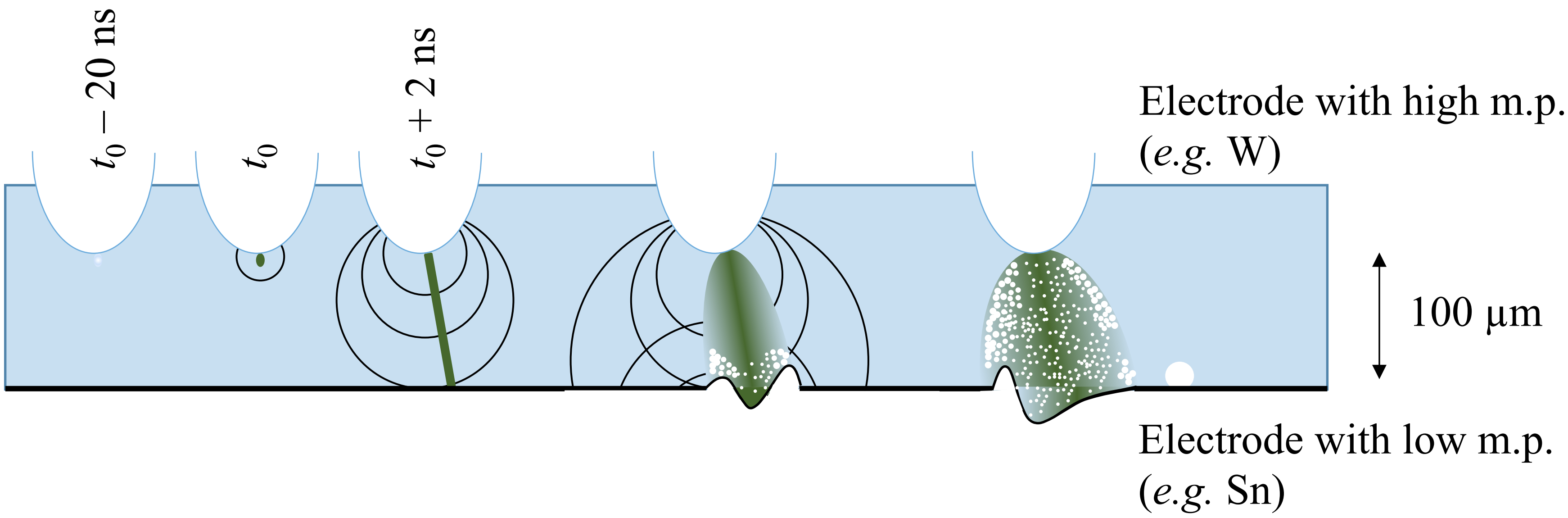






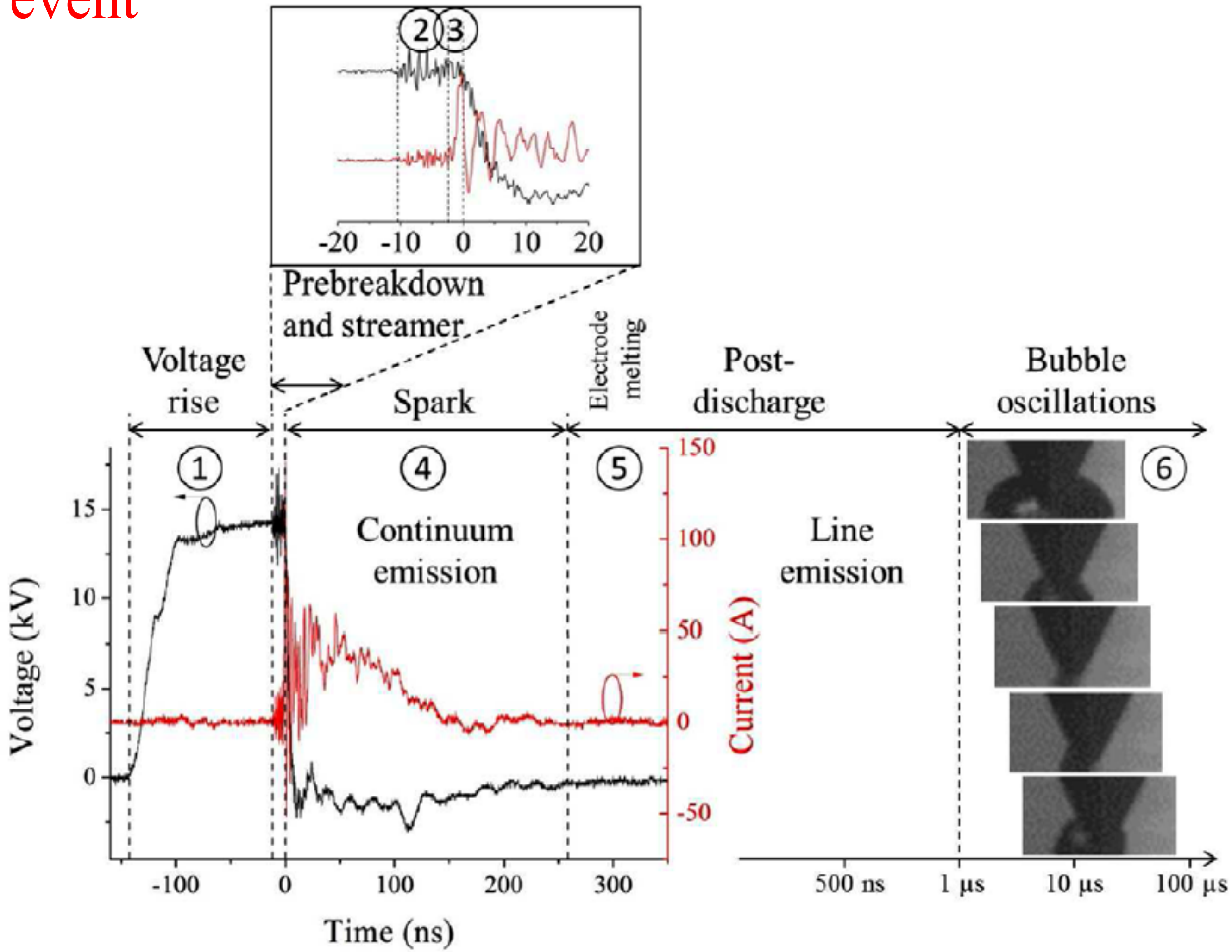
2.2 – Streamers

A simplified sketch of event



2.2 – Streamers

A simplified sketch of event



2.2 – Streamers

Charge injection

• For very weak fields, the regime is purely ohmic.

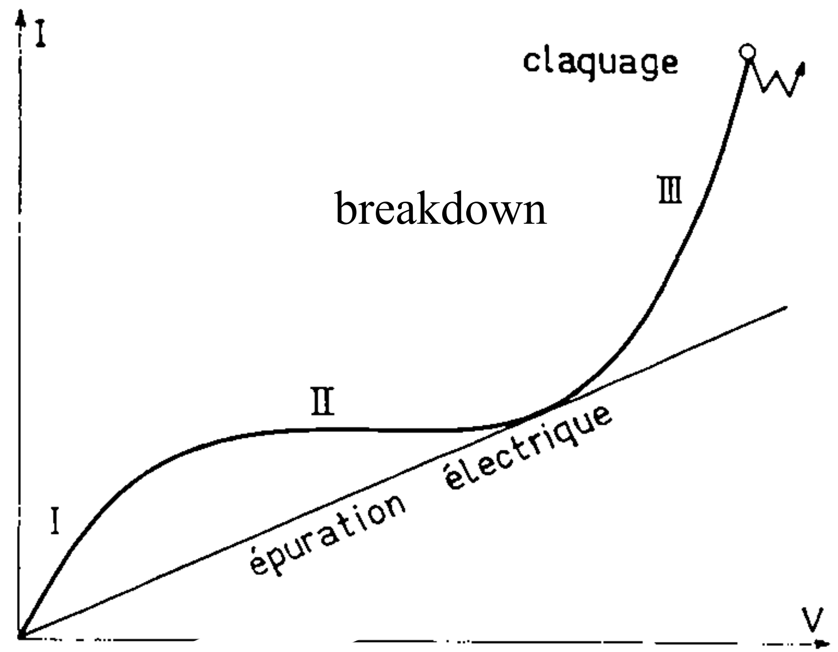
$$I = \sigma \cdot E$$

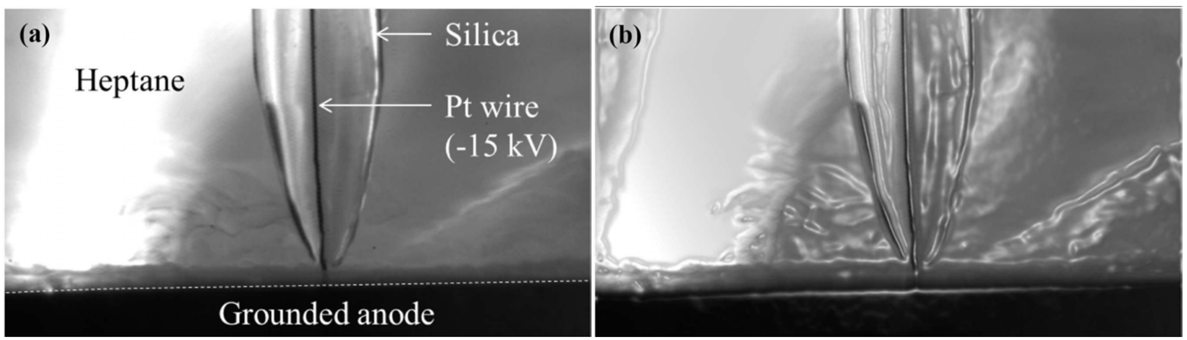
The electric field extracts impurity ions (limited in quantity) from the liquid.

• For intermediate fields, the current saturates. Sometimes, in the *I–V* curve, this saturation regime is reduced to an inflection point or can even be missing.

• When the electric field exceeds a certain threshold, the current rises until breakdown. In this regime, injection of charge carriers occurs via different mechanisms.

Massive injection of charge carriers in the liquid from one electrode induces a space charge gradient which causes turbulence.





2.2 – Streamers

Charge injection

Injection* mechanisms** are many and as much dependent on the electric field (which is typically of the order of several tens to several hundreds of MV·m^{-1}) as they are of the liquid/electrode interfaces. One finds the following:

• Fowler–Nordheim (field emission) tunnelling from bulk metallic electrodes (such as platinum or gold),

• tunnelling through electrodes with semiconductive surfaces (a Schottky barrier such as iron or copper oxides),

• Poole–Frenkel emission by electrodes with insulating surfaces (such as alumina or silica),

• Auger electron emission (due to the relaxation of a hole created by the emission of tunnelling electrons), etc.

--

* injection of electrons, *i.e.* for negative HV at the anode and grounded cathode. For positive HV at the cathode and grounded anode, the story is different (not told here).

** depend on ion distribution in the Helmholtz double layer in electrochemistry. This double layer lowers the liquid–electrode potential barrier, making electronic exchanges easier.

2.2 – Streamers

Breakdown

A matter of time scale!

1°) "long" (microsecond) electric pulse:
As a result of electrostatic repulsion, the formation of low density channels occurs. Consequently, the discharge propagates through the low-density regions.

2°) "Intermediate" (nanosecond) electric pulse:
The electrostatic forces support the expansion of nanoscale voids behind the front of the ionization wave. In the wave front, the extreme electric field provides a strong negative pressure in the dielectric fluid due to the presence of electrostriction forces, forming the initial micro-voids in the continuous medium.

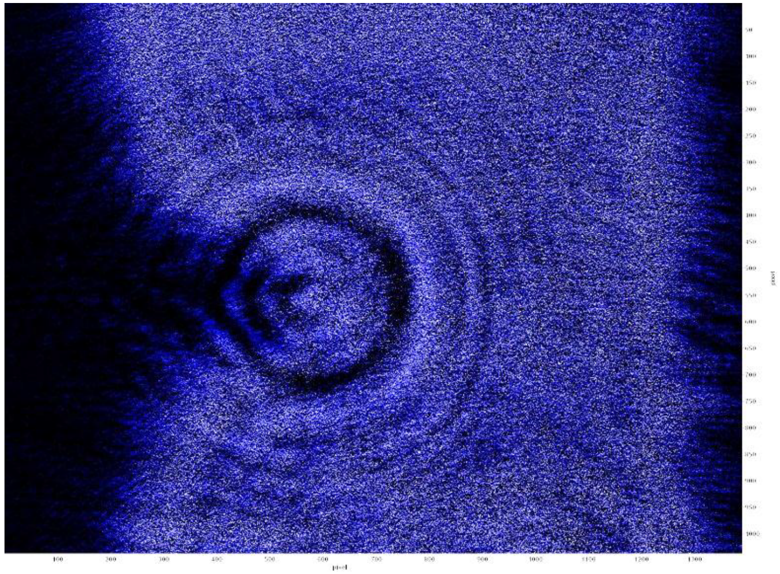
3°) "short" (picosecond) electric pulse:
The regions of reduced density cannot form because of the extremely short duration of the applied electric pulse. Ionization in the liquid phase occurs as a result of direct electron impact without undergoing a phase transition.

2.2 – Streamers

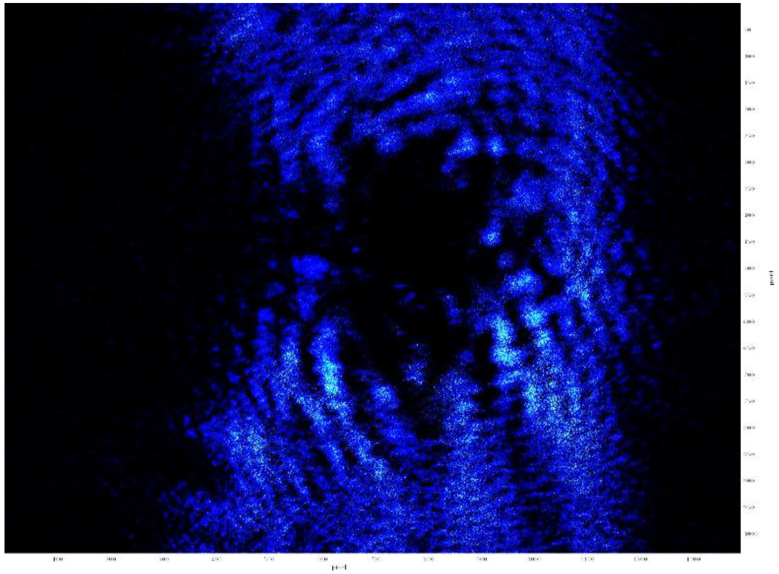
Breakdown

$$\vec{F} = e\,\delta n\,\vec{E} - \frac{\varepsilon_0}{2}E^2\nabla\varepsilon + \frac{\varepsilon_0}{2}\nabla\left(E^2\frac{\partial\varepsilon}{\partial\rho}\rho\right)$$

Free charges *Electrostriction*



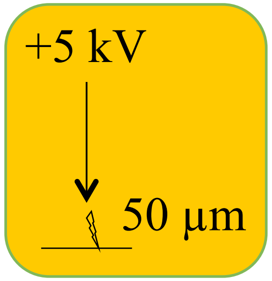
The electrostriction rarefaction wave without breakdown. Water, U = 9 kV, 20 ns. The image was collected 200 ns after the HV pulse.

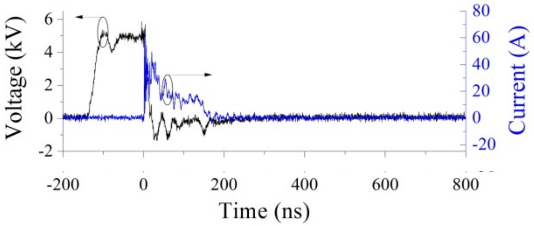


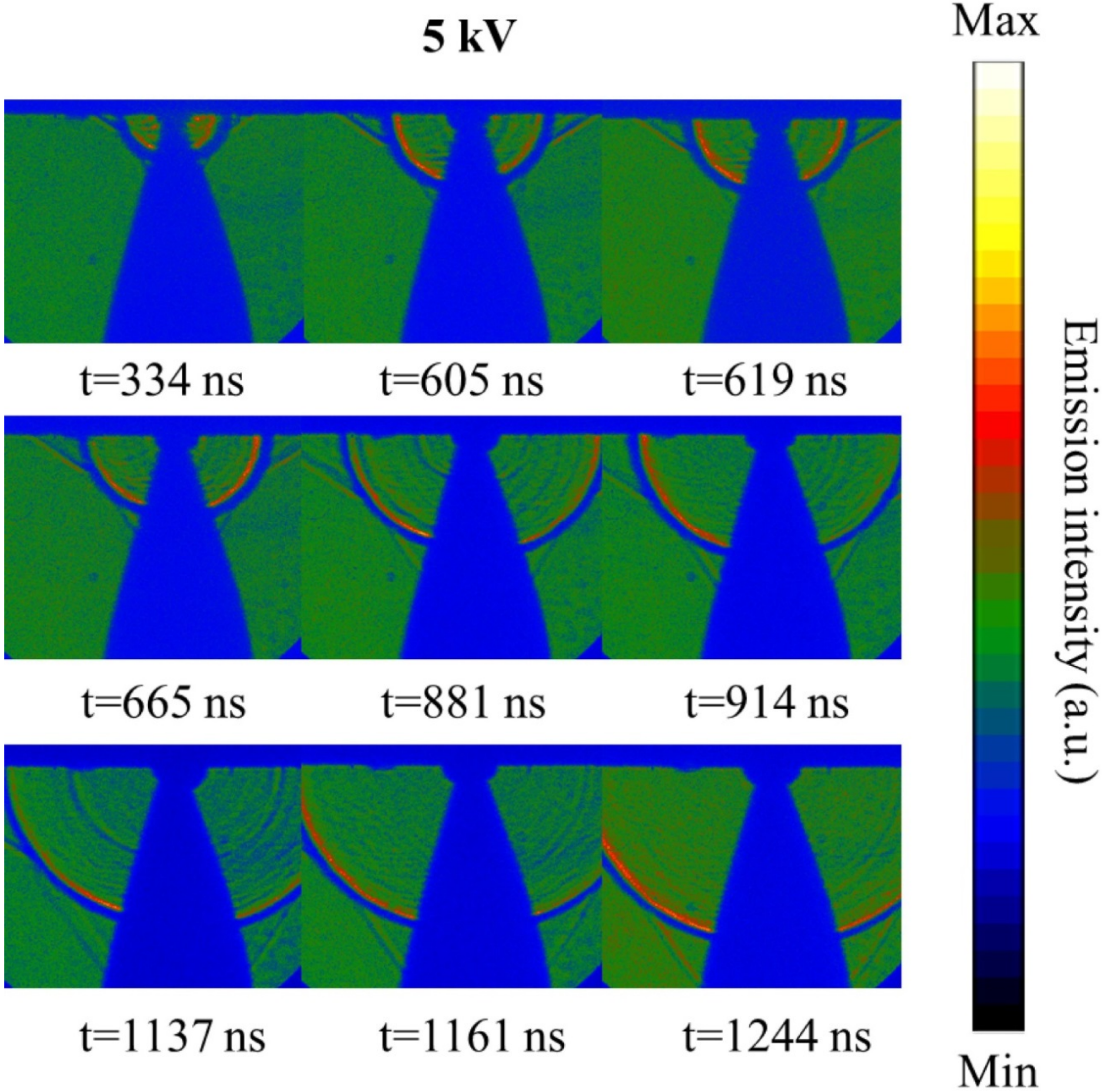
The streamer-leader structure formation. Water, U = 12 kV, 20 ns. The image was collected 200 ns after the HV pulse.

2.2 – Streamers

Emission of shock waves



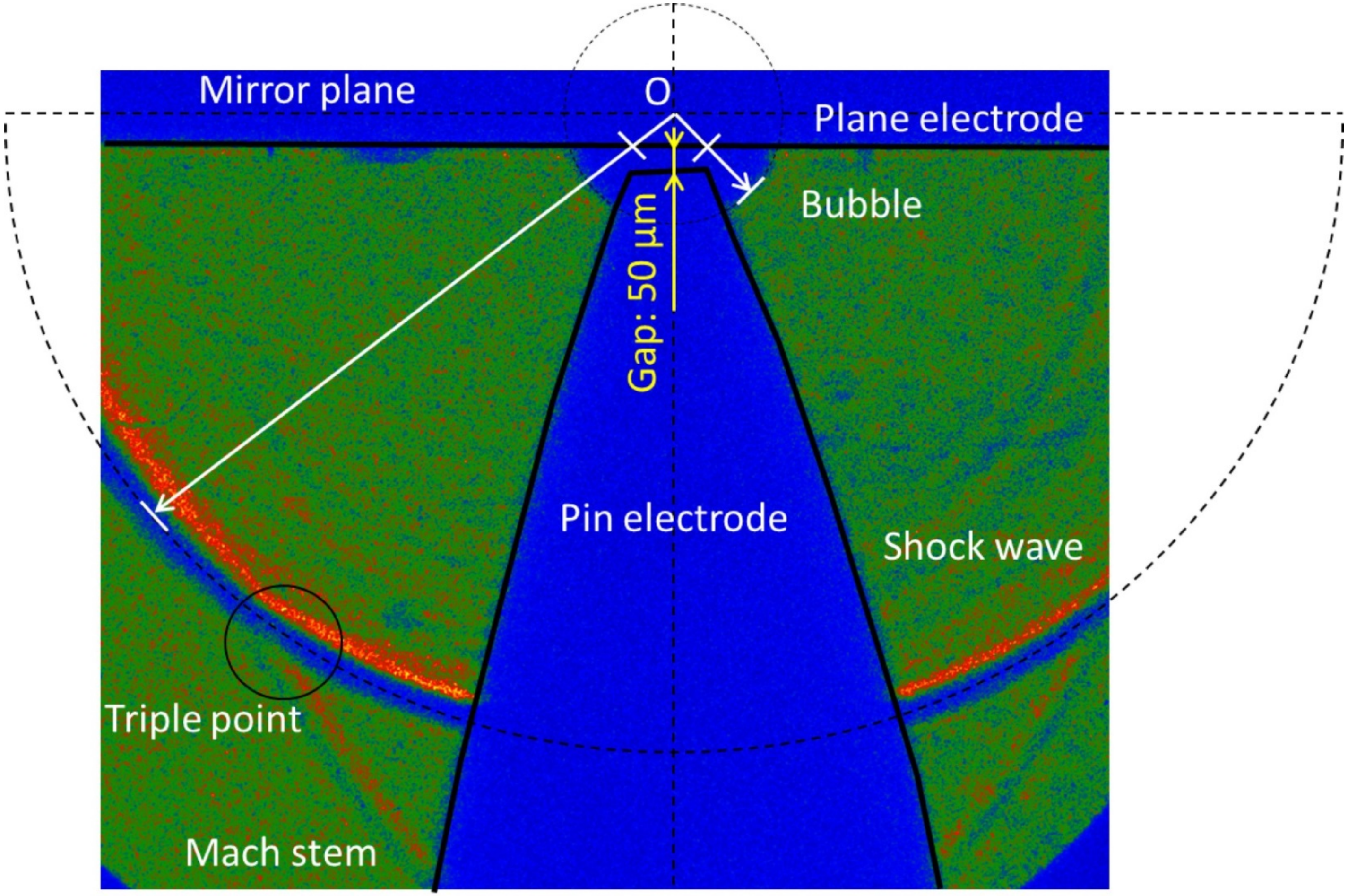




Bubble expansion step

The afterglow lasts about 100 ns

2.2 – Streamers



Hugoniot equations → $P = \rho_0 u_s \frac{u_s - A}{B}$

Acoustic sound velocity

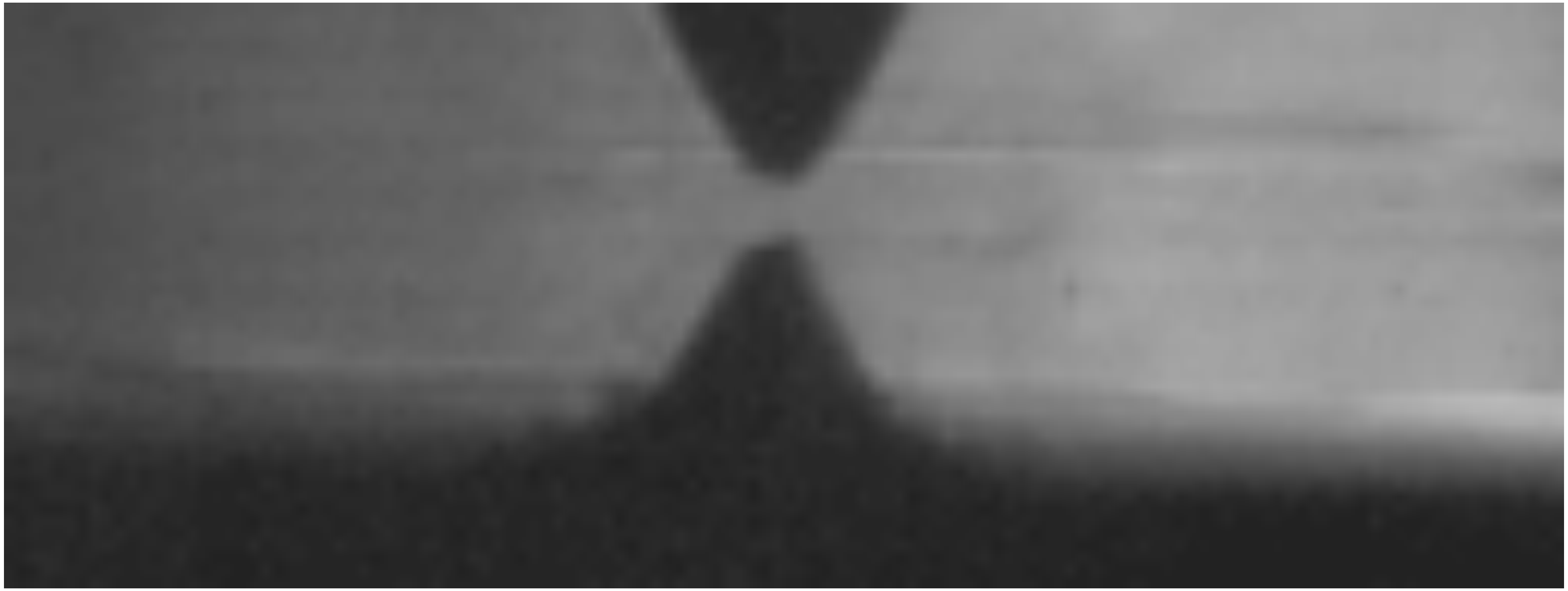
Liquid density

Parameter

Usually a fraction of GPa

2.2 – Streamers

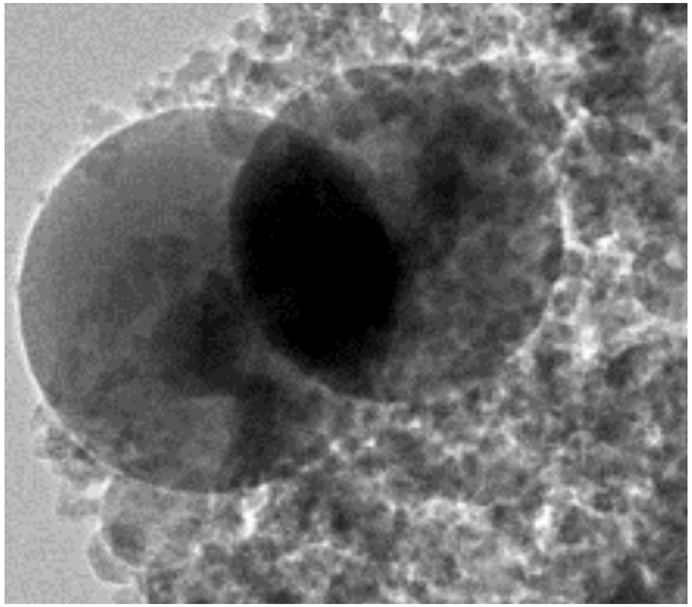
Dynamics of bubbles



1.92 µs / image (movie duration: ~500 µs)

Chap. III

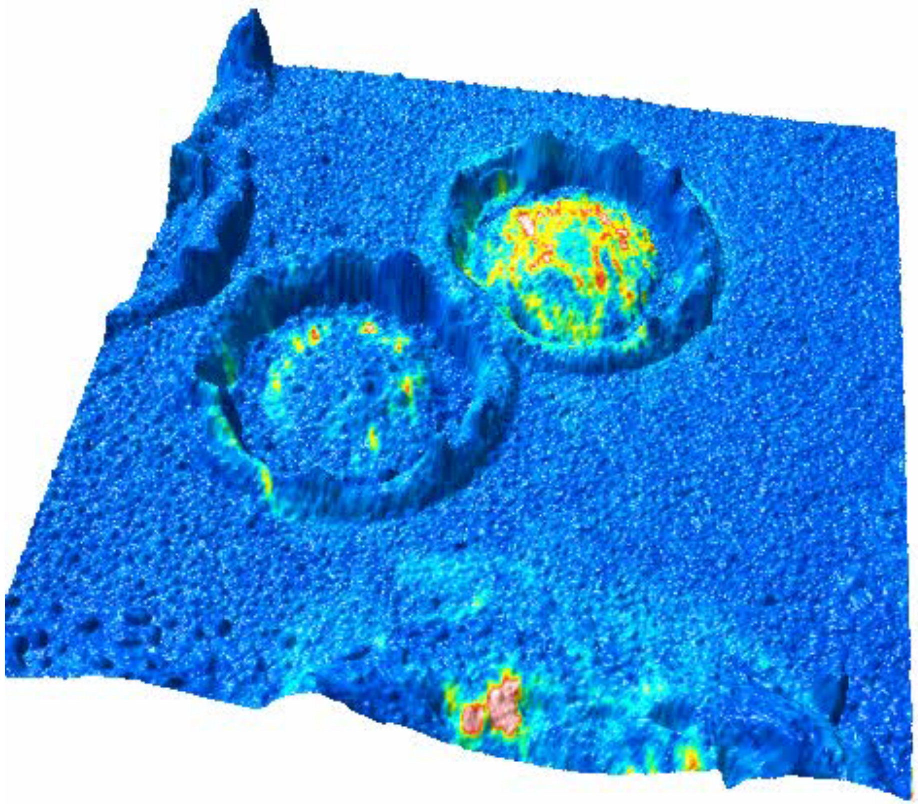
Nanoparticles



3.1 – Electrode erosion

General mechanism: Melting

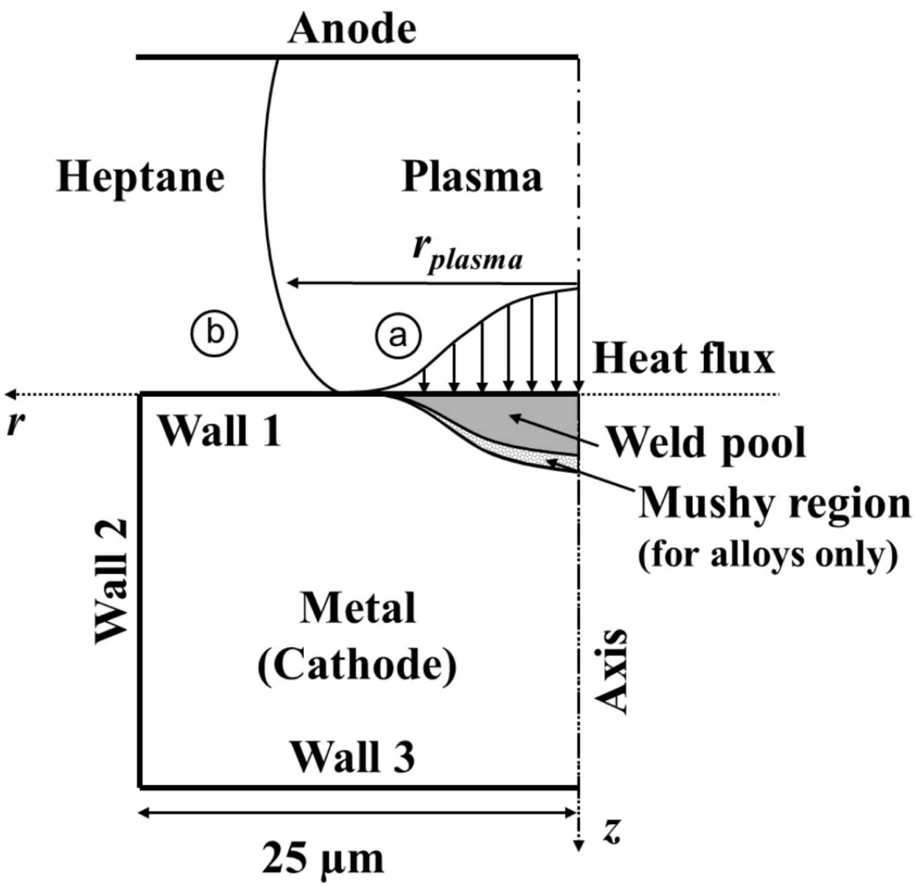
Shape of impacts

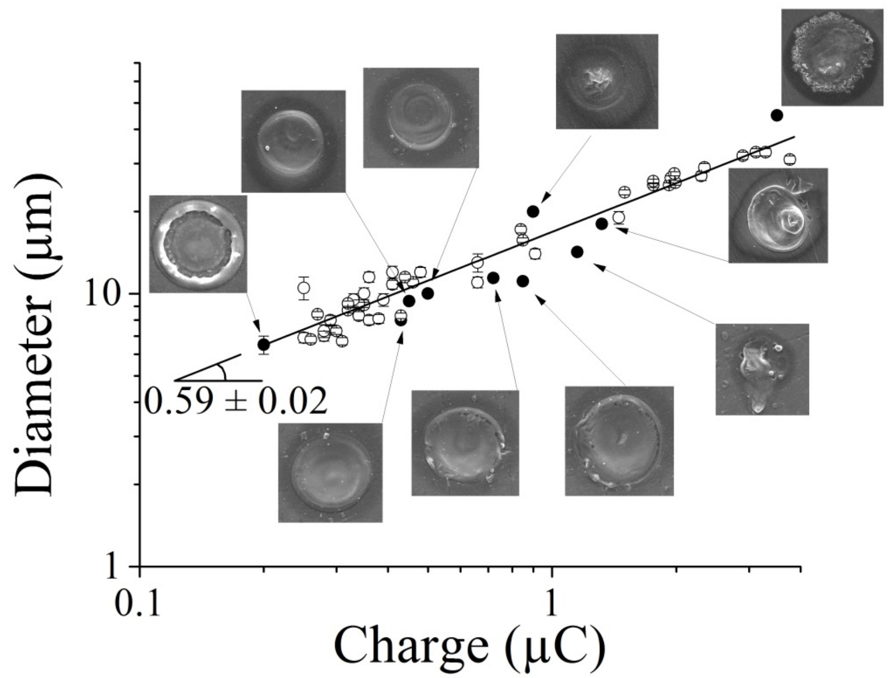


Nano-SIMS analyses of AlO mass peak projected onto the corresponding AFM image

3.1 – Electrode erosion

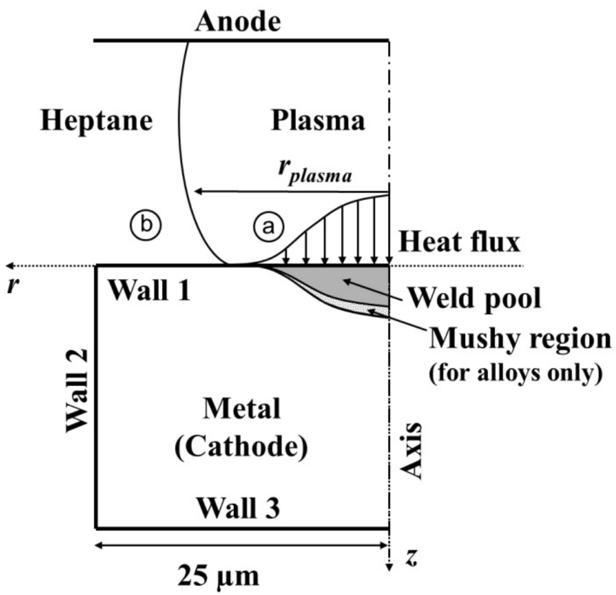
Modelling plasma-surface interaction: example of Al





3.1 – Electrode erosion

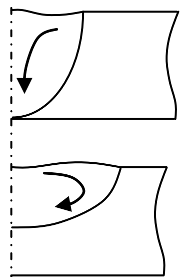
Boundary conditions



Boundary	u	v	T
Wall 1a [$< r_{plasma}$]	$(\tau_{\perp\perp};\tau_{\perp//})_{1a}$	0	$\phi_{1a} = -\alpha \frac{Q_{plasma}}{\pi r_{plasma}^2} \exp\left(-\frac{r^2}{r_{plasma}^2}\right) + h_{1a}(T - T_{plasma}) + \sigma_e \varepsilon_{1a}(T^4 - T_{plasma}^4) + J^{(Al)} L_{SL}^{(Al)}$
Wall 1b [$> r_{plasma}$]	$(\tau_{\perp\perp};\tau_{\perp//})_{1b}$	0	$\phi_{1b} = h_{1b}(T - T_{liquid}) + \sigma_e \varepsilon_{1b}(T^4 - T_{liquid}^4)$
Wall 2	0	0	$\phi_2 = 0$
Wall 3	0	0	$\phi_3 = 0$
Axis	$u=0$	$\left.\frac{\partial v}{\partial r}\right\|_{axis} = 0$	$\left.\frac{\partial T}{\partial r}\right\|_{axis} = 0$

$$\frac{\partial \sigma}{\partial T} = +10^{-4}\, N\, m^{-1}\, K^{-1}$$ **Marangoni positif**

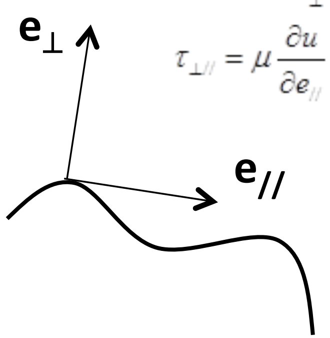
$$\frac{\partial \sigma}{\partial T} = -10^{-4}\, N\, m^{-1}\, K^{-1}$$ **Marangoni négatif**



$$p_{surf} = p_{plasma} - \sigma \nabla . \left(\frac{\vec{n}}{\|\vec{n}\|}\right)$$

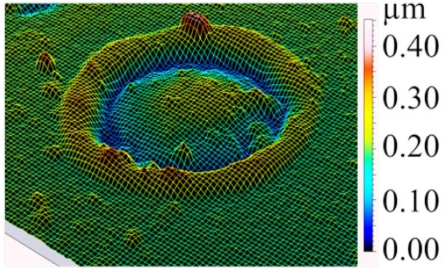
$$\tau_{\perp\perp} = \mu \frac{\partial u}{\partial e_{\perp}} \approx K \gamma e_{\perp}$$

$$\tau_{\perp//} = \mu \frac{\partial u}{\partial e_{//}} = \frac{d\gamma}{dT} \frac{\partial T}{\partial e_{//}}$$

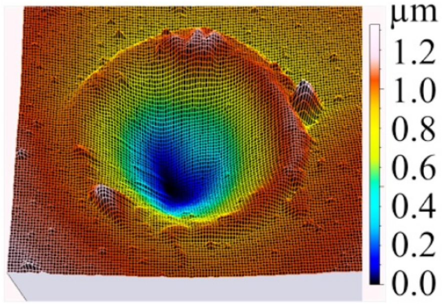


3.1 – Electrode erosion

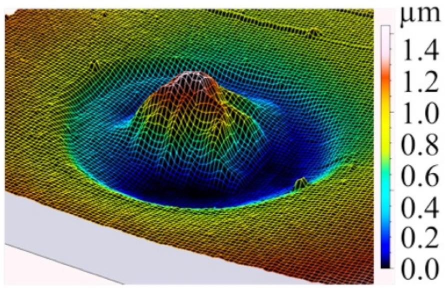
Selection of impacts
Weakly asymmetric



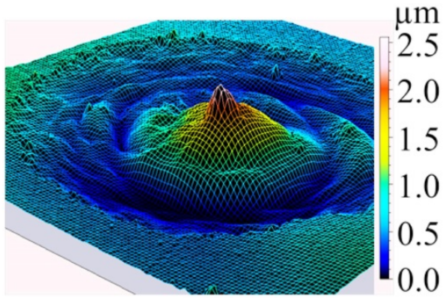
q = 0.20 µC – P = 8.5 bar



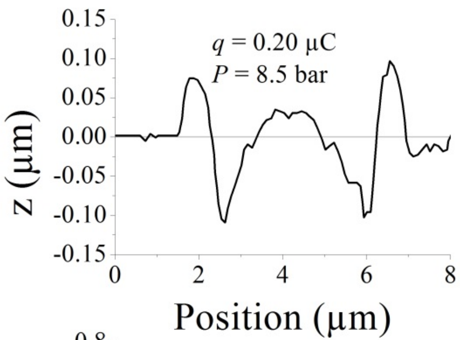
q = 0.50 µC – P = 16 bar

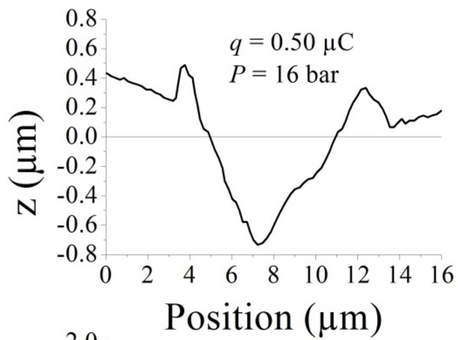


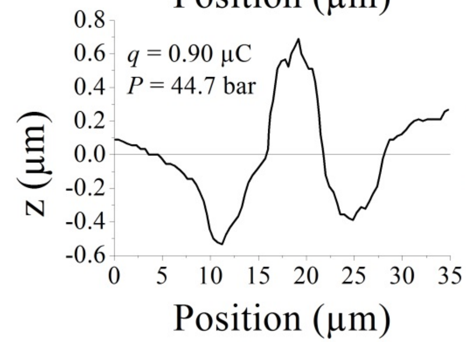
q = 0.90 µC – P = 44.7 bar

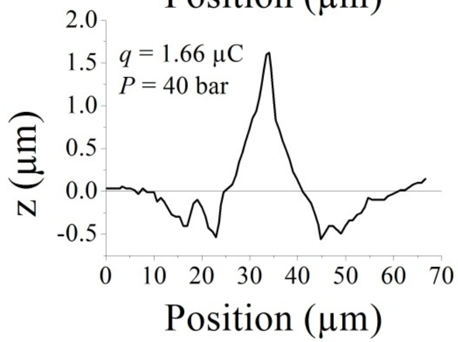


q = 1.66 µC – P = 40 bar



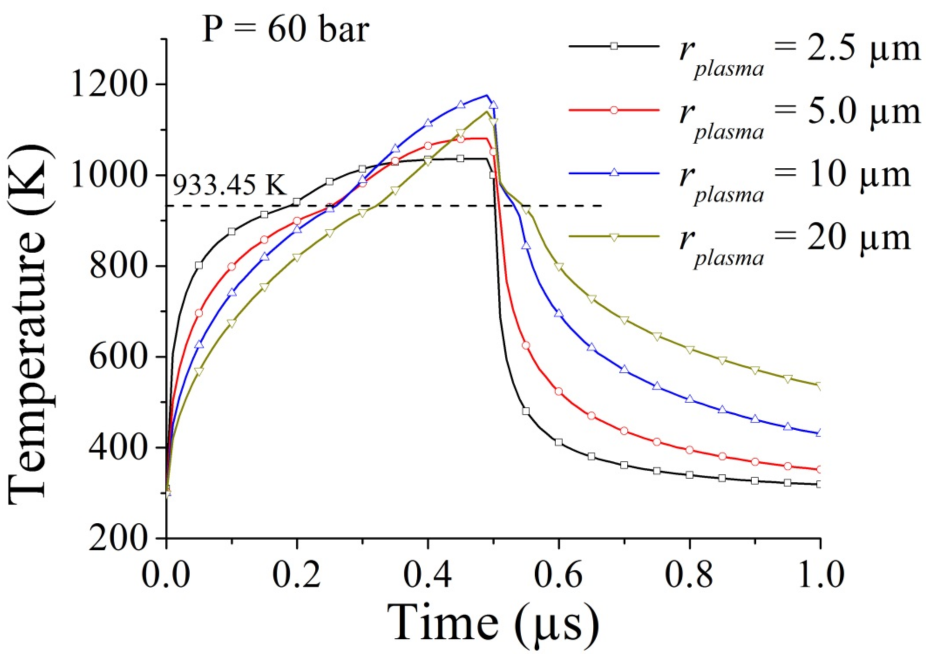






$V_+/V_- = 1$ but practically $V_+/V_- > 0.8$

3.1 – Electrode erosion



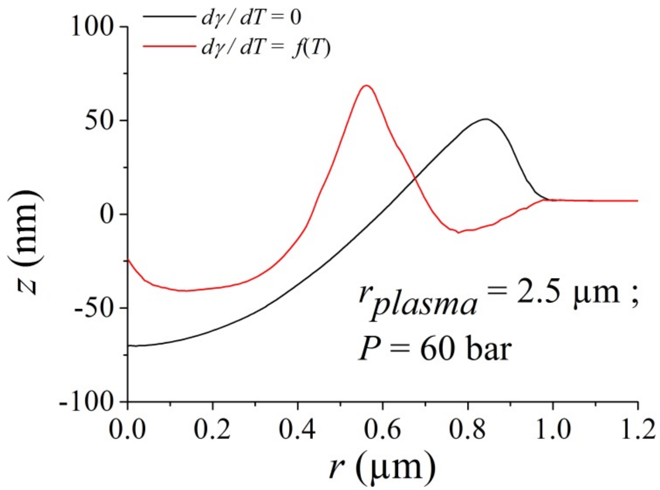
Q=1.6 W/m^2
R_p=2.5 µm
P=60 bar

3.1 – Electrode erosion

Thomson-Marangoni's effect

- Only negligible on large impacts (> 10 µm) where pressure dominates

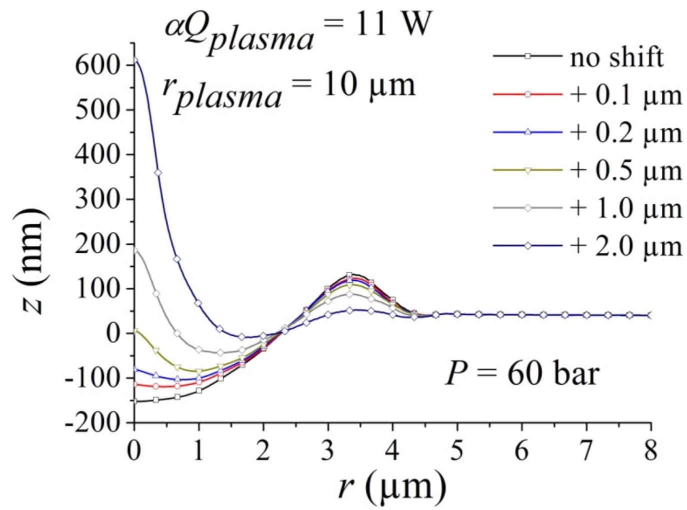
- Strong influence on $d\gamma/dT$



Pressure effect

- Dominant on large impacts (> 10 µm)

- Strong effect of the plasma orientation (tilt)



The plasma cannot be hollow ($\varepsilon = 1.92$)

Babaeva et al., J. Phys. D: Appl. Phys. (2009) 42, 132003

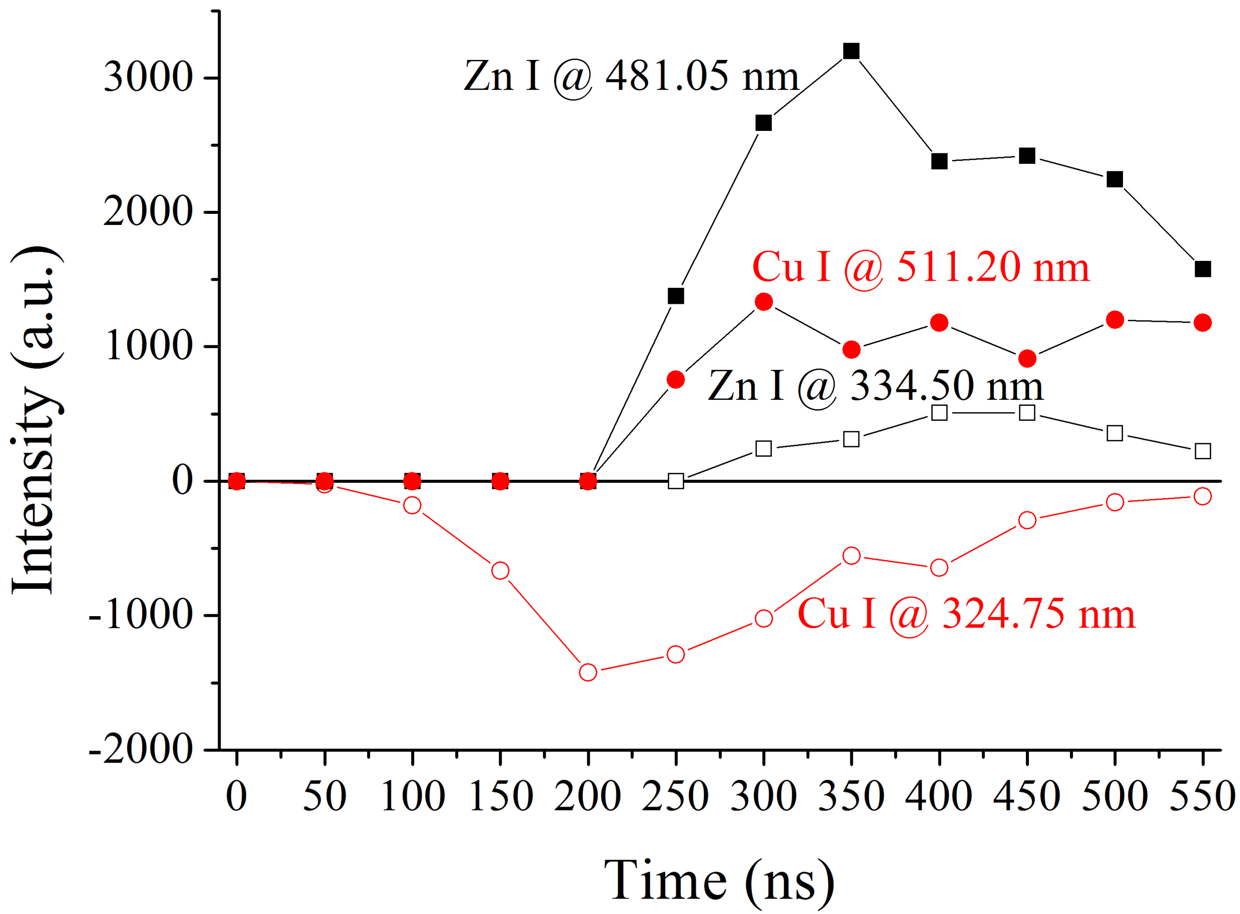
3.1 – Electrode erosion

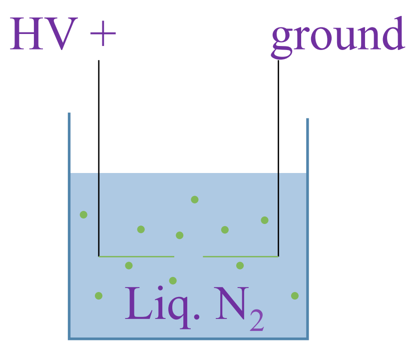
Plasma radius r_{plasma} [µm]	Heat flux αQ_{plasma} [W]	Maximal temperature [K]	Impact radius [µm]	Energy to create impact [µJ]	Total energy (exp. data) [mJ]
2.5	1.6	1036	0.96	0.80	**0.02**
5.0	3.8	1080	2.05	1.90	**0.50**
10	11	1176	4.67	5.50	**0.90**
20	35	1140	8.69	17.5	**1.66**

From 0.4 to 4% of the total energy is used in electrode erosion

3.1 – Electrode erosion

Appearance of Cu I lines much before melting

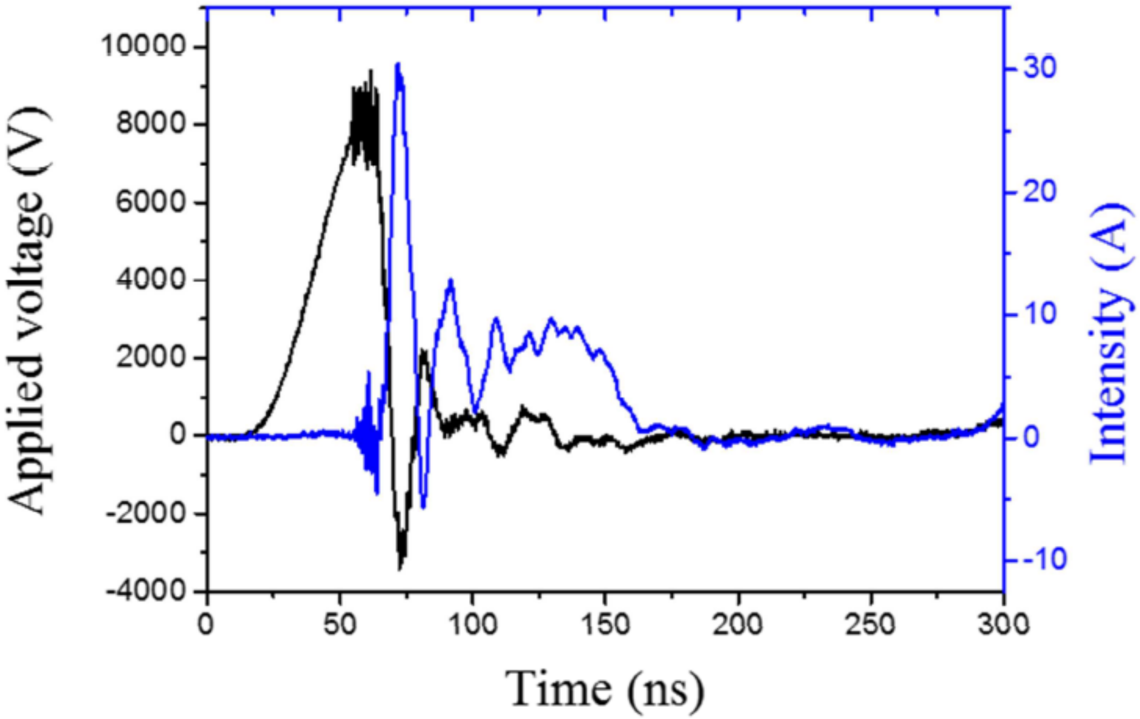


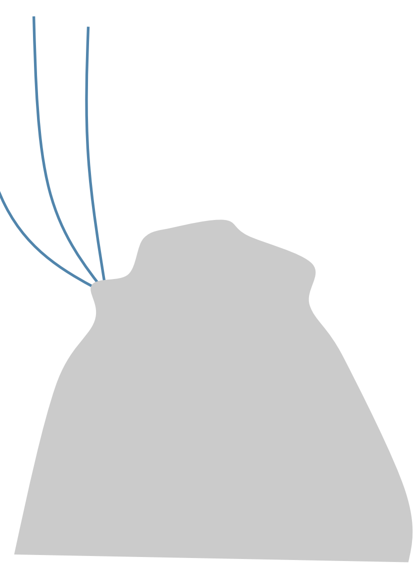


$Cu_{63}Zn_{37}$ electrodes
1000 discharges

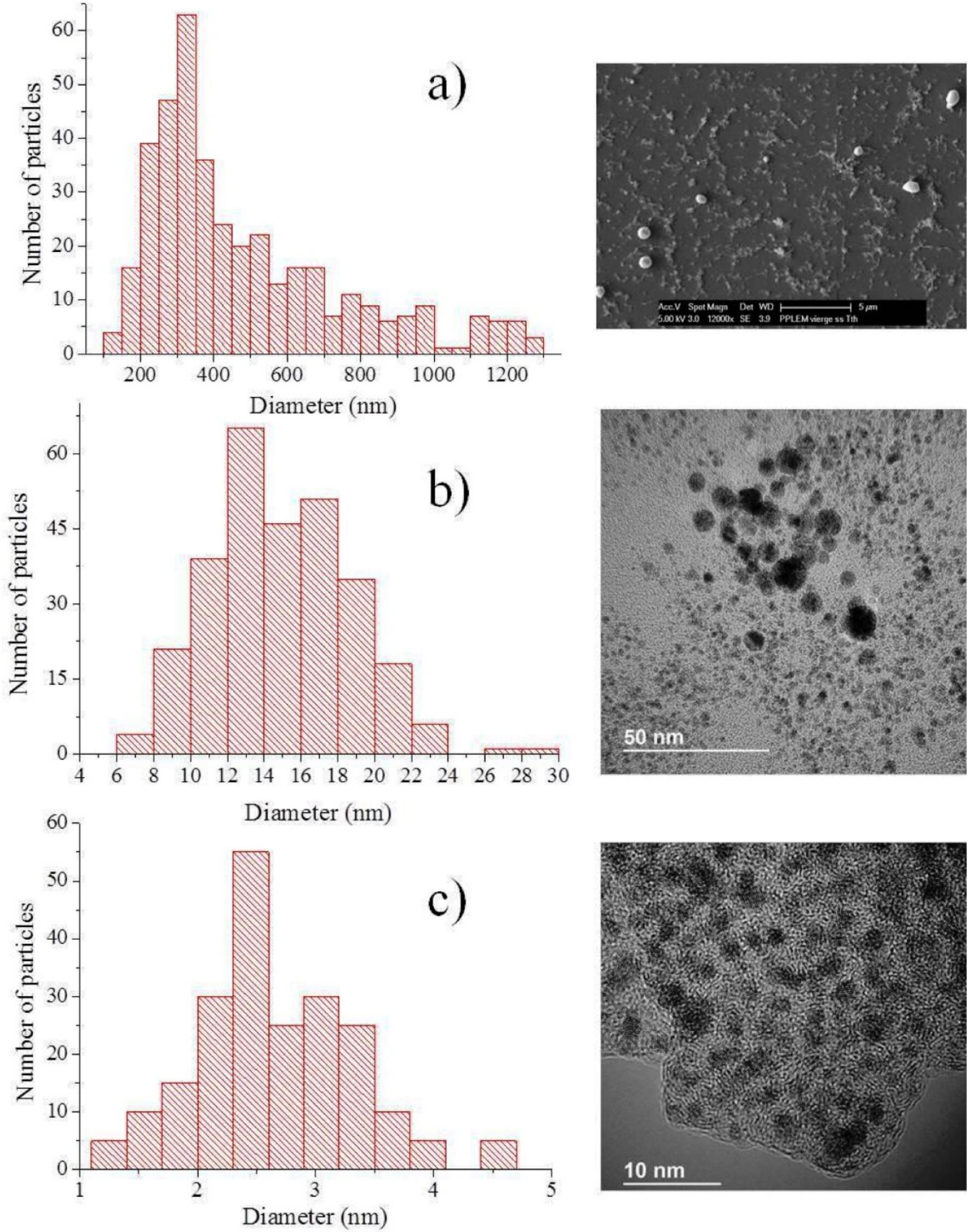
3.1 – Electrode erosion

Ohmic overheating when a high-current density is conducting via a protrusion





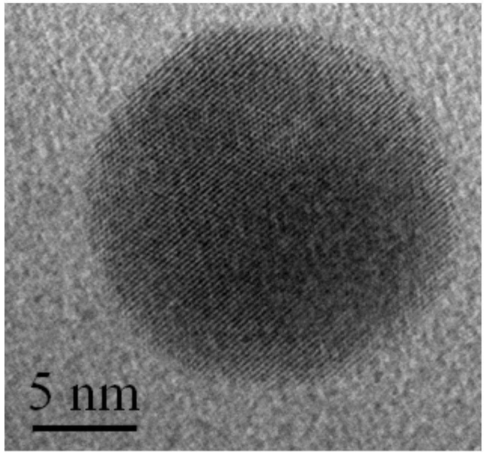
3.2 – Size distribution

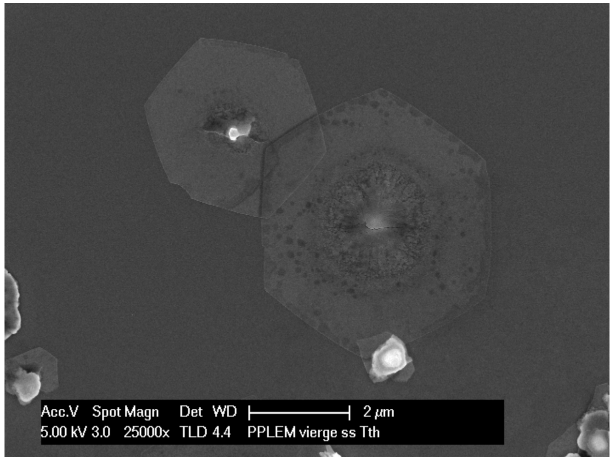


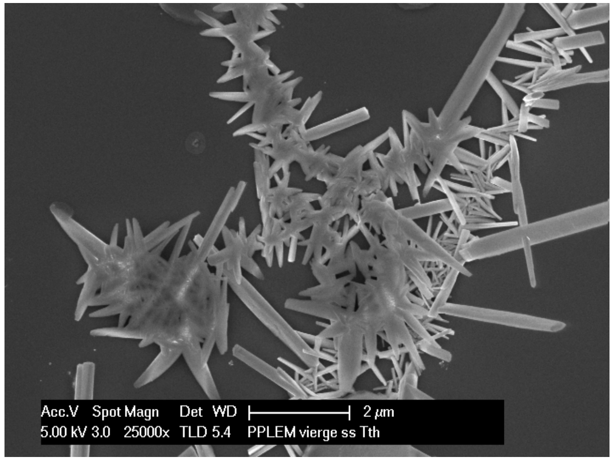
3.3 – Nanoparticles

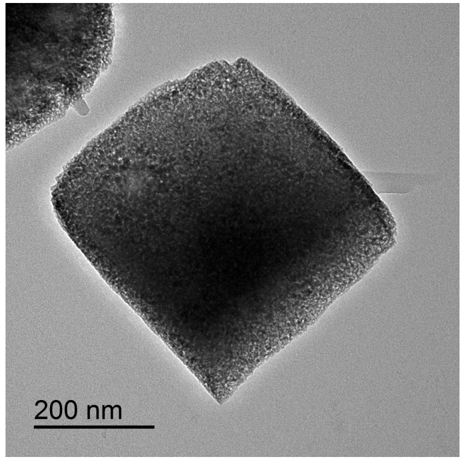
Shape

Spheres	Sheets	Wires	Cubes
Al, Cu, Ag, Pt, Au, Fe, W, Sn	Ag, Bi, **P**b, Zn	Ag, Pb	Cd, Ge



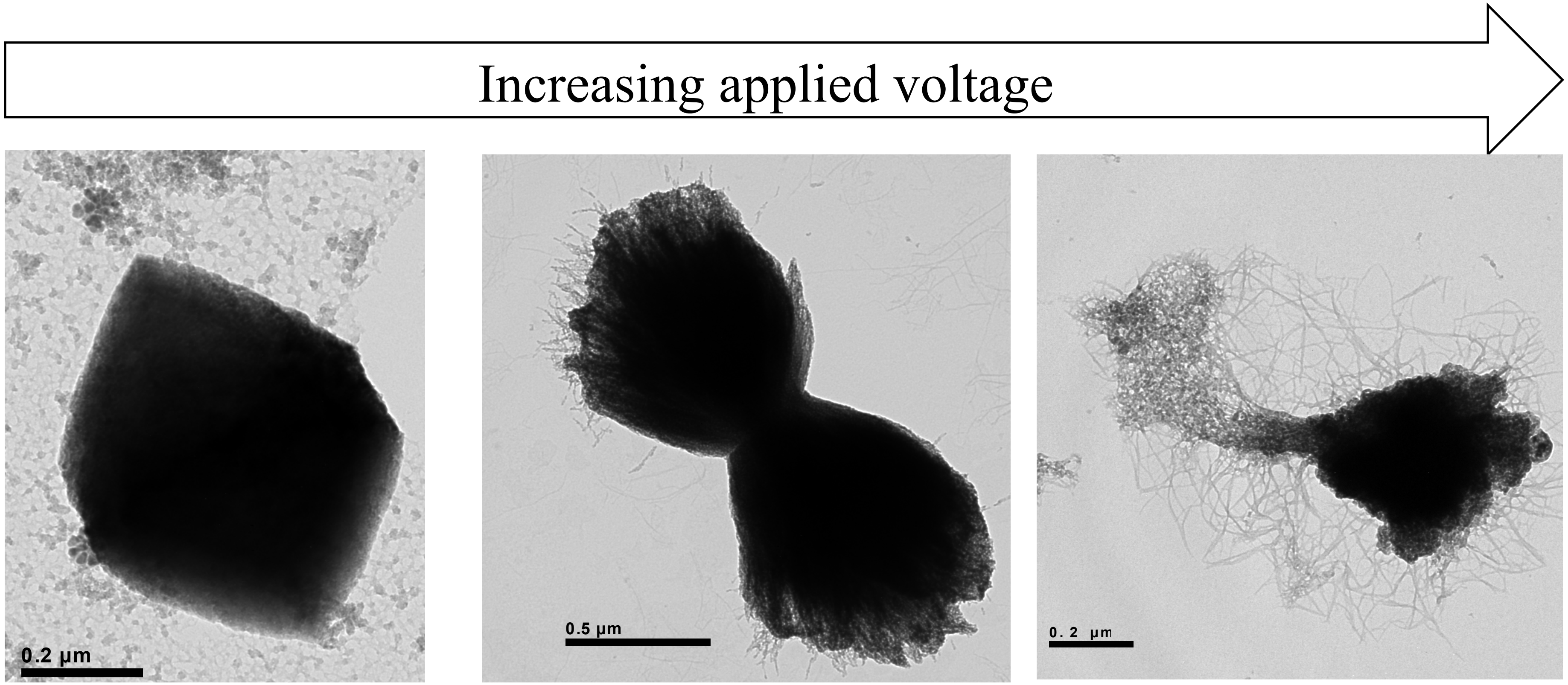






3.3 – Nanoparticles

Role of the electric field



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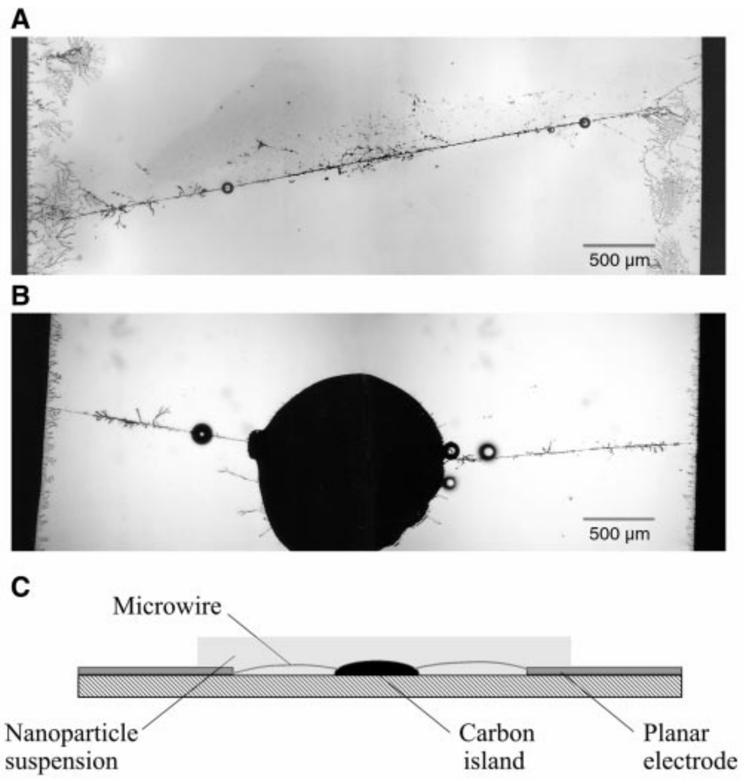
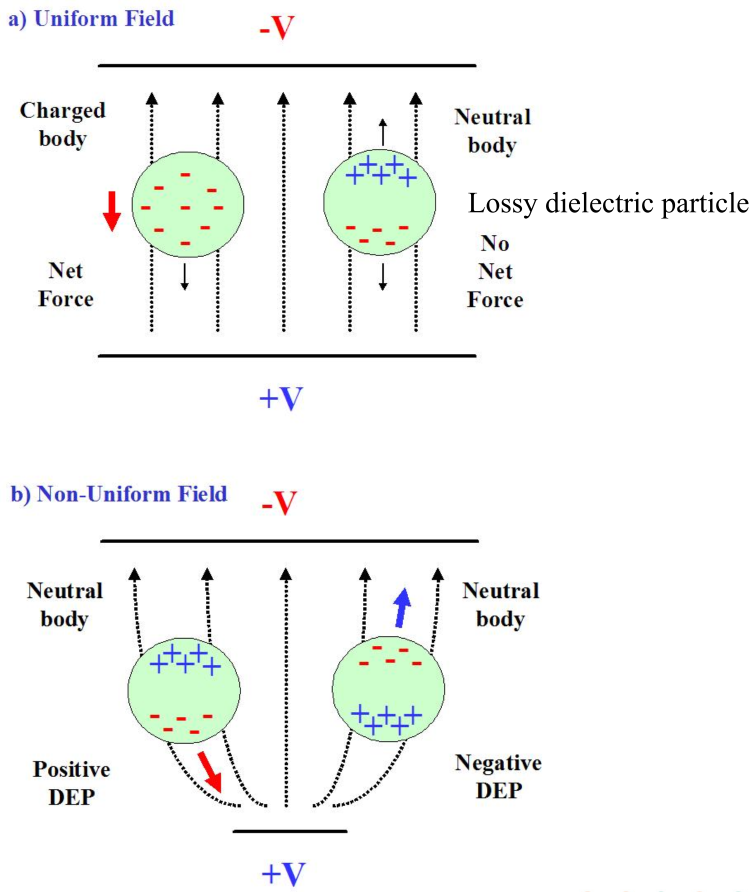
3.3 – Nanoparticles

Role of the electric field

Dielectrophoresis might be used
if insulating materials are synthesized

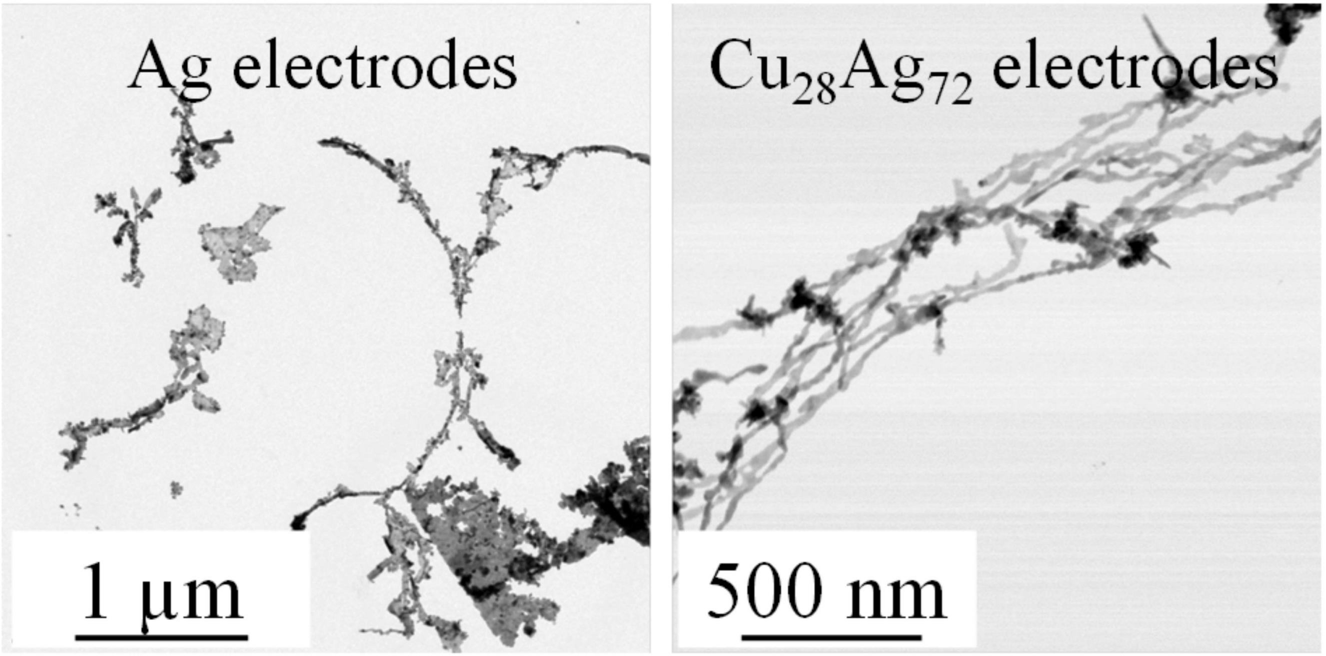


Hermanson *et al.* 2001 *Science* **294** 1082



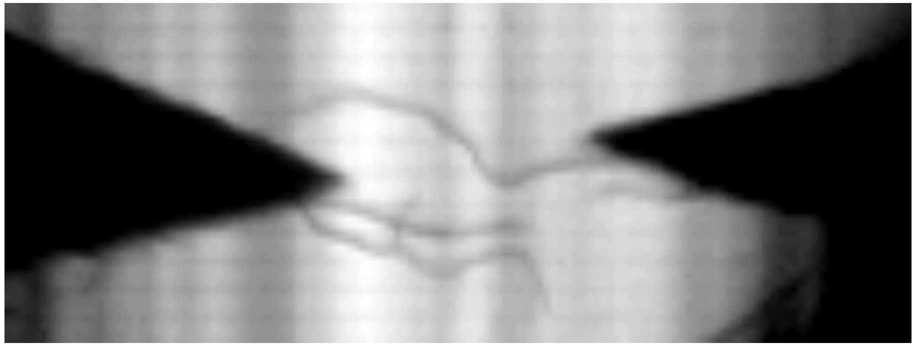
3.3 – Nanoparticles

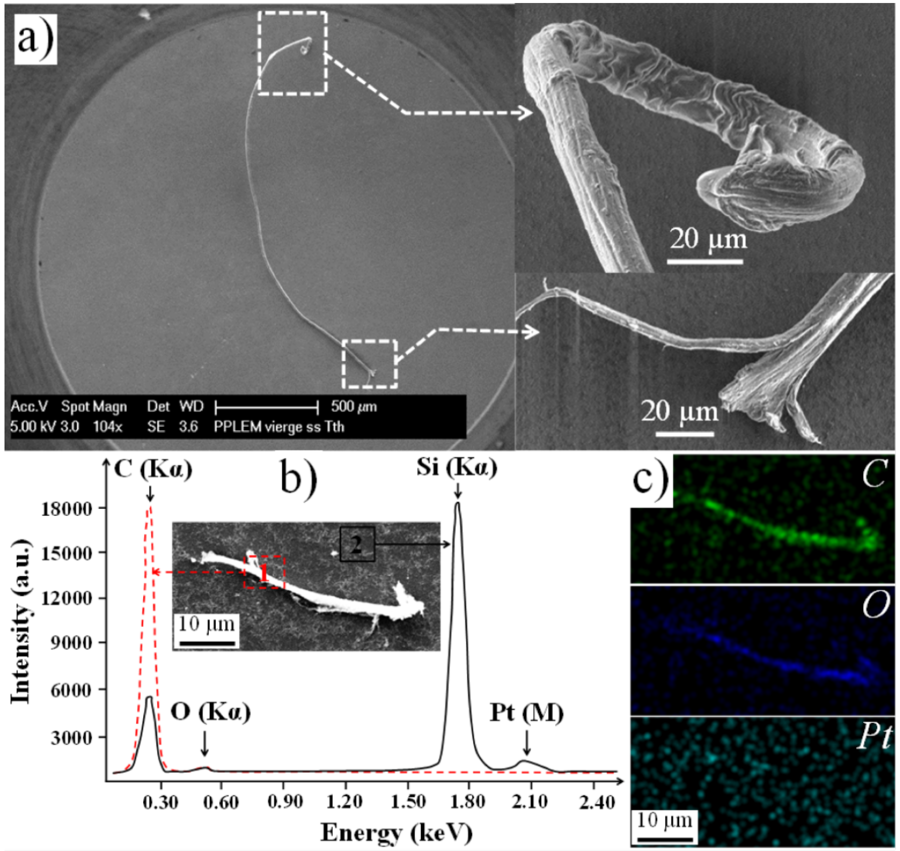
Role of the electric field



3.3 – Nanoparticles

Role of the electric field

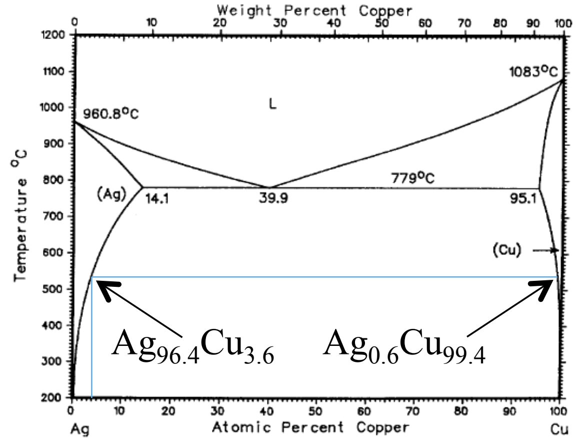




Hamdan *et al.* 2014 *Mater. Lett.* **135** 115

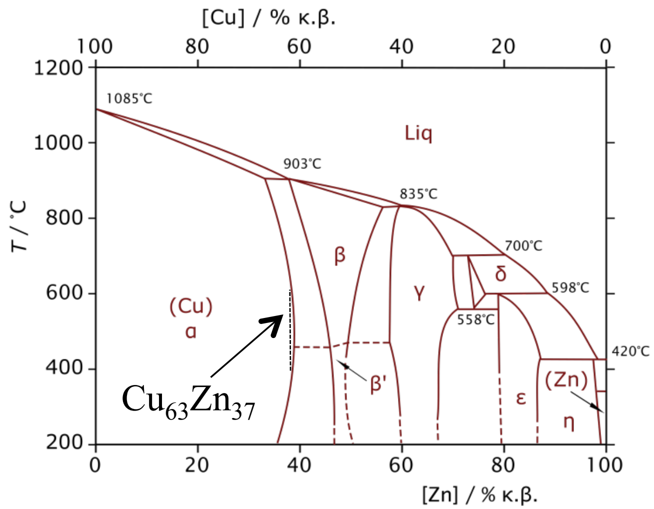
3.3 – Nanoparticles

m.p. (Cu) = 1356 K
m.p. (Ag) = 1234 K



Alloy nanoparticles

$Cu_{63}Zn_{37}$-$Cu_{63}Zn_{37}$
Cu-Zn
$Cu_{28}Ag_{72}$-$Cu_{28}Ag_{72}$
Cu-Ag



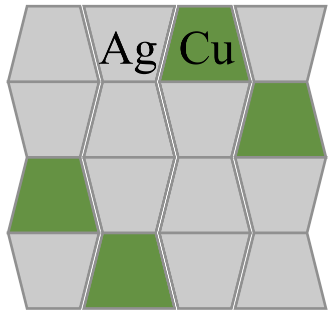
m.p. (Cu) = 1356 K
m.p. (Zn) = 907 K

$Cu_{28}Ag_{72}$ (at.%) =

73wt.%$Ag_{96.4}Cu_{3.6}$ + 27wt.

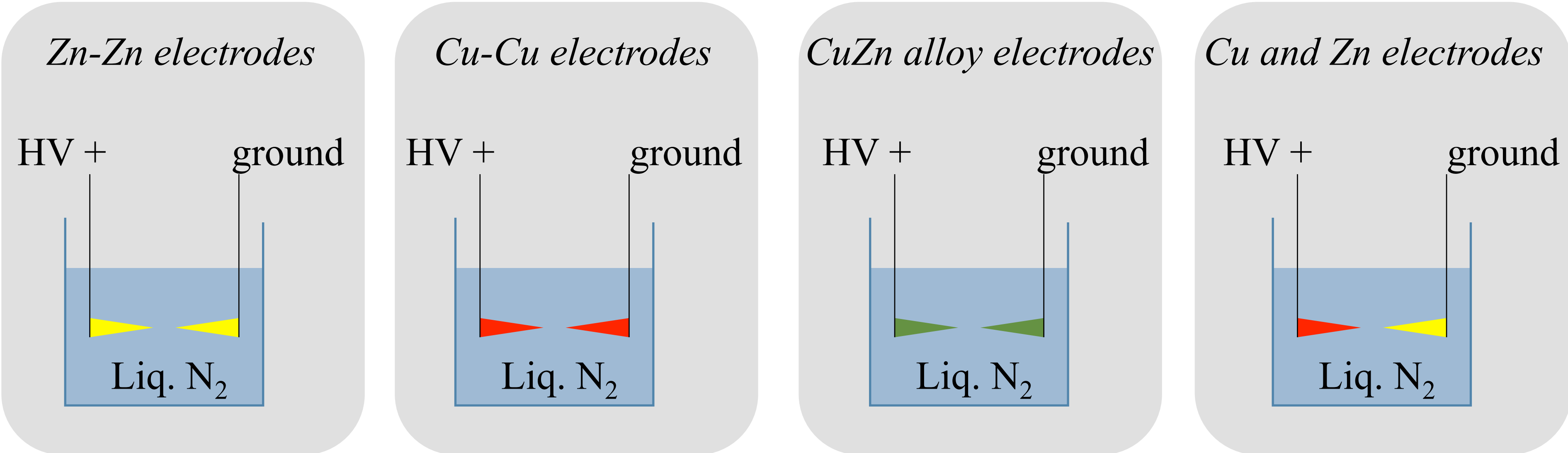
%$Ag_{0.6}Cu_{99.4}$

as determined by XRD



3.3 – Nanoparticles

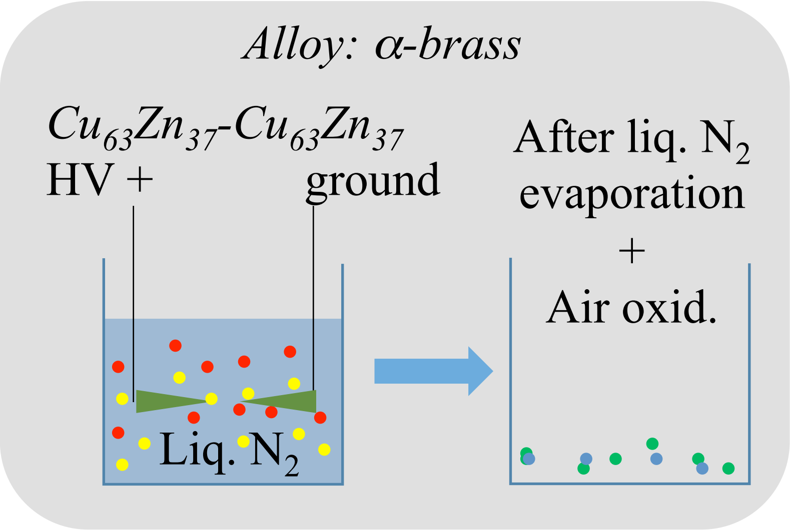
Alloy nanoparticles



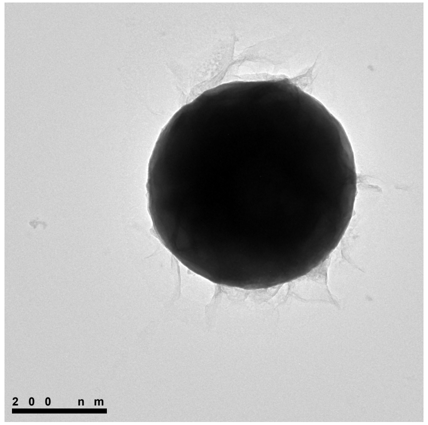
3.3 – Nanoparticles

Alloy nanoparticles

Shift in the phase diagramme



$Cu_{63}Zn_{37}$ wires
∅ 1 mm



Particles are enriched in copper (dezincification)

Cu (73 wt.%), Zn(25 wt.%) & O(2 wt.%)

3.3 – Nanoparticles

Alloy nanoparticles

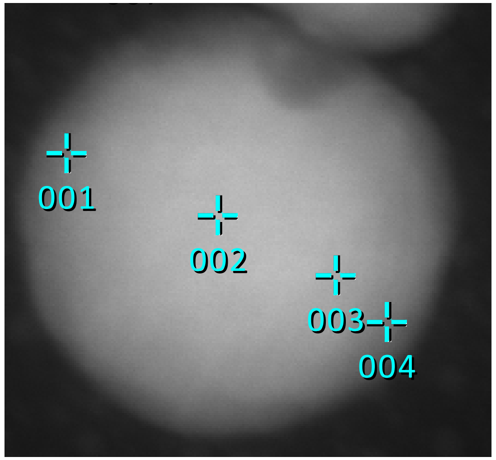
$$Cu_{28}Ag_{72} =$$

$$73\%Cu_{3.6}Ag_{96.4} + 27\%Cu_{99.4}Ag_{0.6}$$

vs.

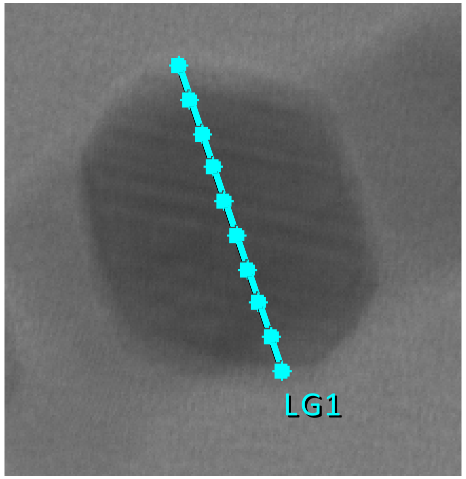
$$Cu_{91.7}Ag_{4.9}O_{3.4} + Cu_{5.0}Ag_{95.0}$$

Memo	O	Cu	Ag
1	2.39	19.91	77.7
2	0	8.38	91.62
3	0	6.91	93.09
4	0	5.73	94.27
5	0	4.95	95.05
6	0	5.73	94.27
7	0	4.18	95.82
8	0	5	95
9	0	8.58	91.42
10	0	17.81	82.19



No significant shift in the phase diagramme

Only single-phase nanoparticles are obtained



Memo	O	Cu	Ag	Total(Atom %)
1	11.43	84.27	4.3	100
2	3.38	91.73	4.89	100
3	6.55	90.04	3.41	100
4	14.7	80.65	4.66	100

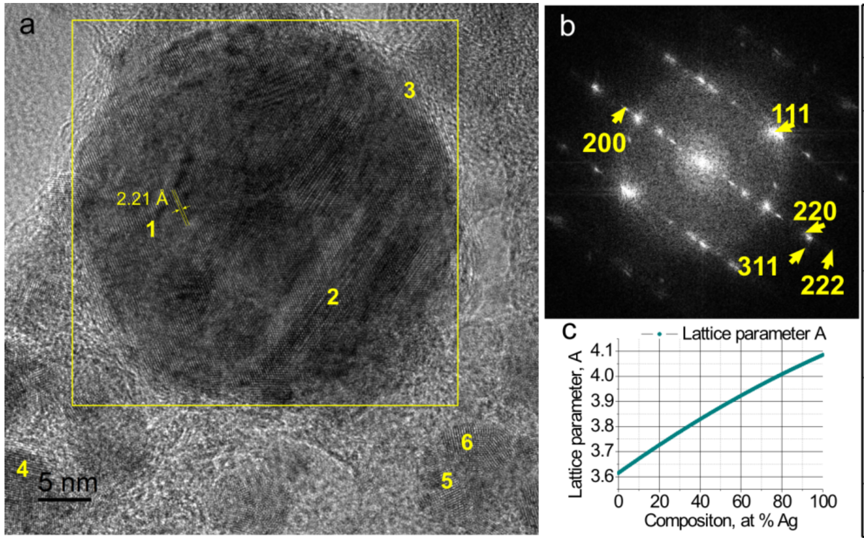
3.3 – Nanoparticles

Alloy nanoparticles

No alloying from metallic vapours (no mixing?)

Shift in the phase diagramme for elements with different melting points

The HRTEM image of as-prepared alloyed nanoparticle (a) and results of FFT processing of the corresponding area (b). The interplanar spacings found correspond to the (111) plane of the cubic AgCu alloy of the composition $Ag_{0.4}Cu_{0.6}$ as determined from the lattice parameter – composition dependence (c).



point	dhkl	hkl	a, Å	composition Ag	composition Cu
1	2.21	111	3.83	0.4	0.6
	1.13	222			
2	2.26	111	3.91	0.58	0.42
	1.94	200			
	1.39	220			
3	2.34	111	4.04	0.9	0.1
	1.43	220			
	1.16	222			
4	2.34	111	4.03	0.91	0.09
	2.02	200			
	1.42	220			
	1.16	222			
5	2.24	111	3.90	0.51	0.49
	1.85	200			
	1.44	220			
	1.15	222			
6	2.32	111	4.03	0.91	0.09
	2.02	200			

A $Ag_{0.4}Cu_{0.6}$ NP cannot be predicted by the phase diagram

4 – Conclusion

Safe process for the user

Specifity due to pressure gradients

Several erosions processes at stake, early processes having to be clarified

Producing alloy nanoparticles is possible directly from alloy electrodes with pre-determined composition to account for element removals at high temperature but the final composition usually depends on the size of the produced NP.

The control of compositions is still to be studied, but likely possible. Anyway, getting very small NPs is a real challenge.

Phase stability seems to be surprisingly high. New tests are in progress for confirmation…

5 – Acknowledgements

Cédric Noël

Cédric Vandenabeele

Thomas Gries

Ahmad Hamdan

Gérard Henrion

Ilya Marinov

Hiba Kabbara

Malek Tabbal

Alexandre Nominé

Antoine Rousseau

Mahmoud Trad

Rachel Pflieger

Nelly Bonifaci

PLATHINIUM
PLASMA THIN FILM INTERNATIONAL UNION MEETING

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Antibes, French Riviera

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Société française du Vide

http://www.plathinium.com/


Дякую
Merci
Ευχαριστώ
Gracias
धन्यवाद
shukrān
Grazie
Danke schön
THANK YOU
Dzięki
Dankie
Terima kasih
Tack så mycket
Спасибо!
唔該
ありがとう
תודה
감사합니다