Matériaux photosensibles et structuration par laser femtoseconde

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I. Introduction Structuration Laser femtoseconde et impression 3D

II. Verres photosensibles : le cas de l'ion argent

III. Impression de motifs luminescents

IV. Processus physico-chimiques : analogie avec une irradiation électronique

V. Effets non linéaires photo-induits

VI. Architecture et co-illumination

VII. Mise en forme : fibres photosensibles

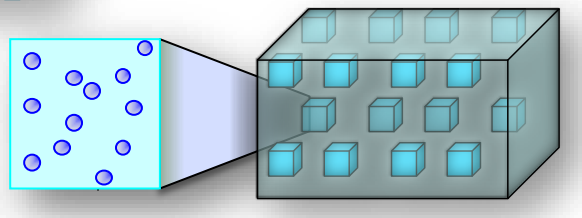
VIII. Verres à l'argent et nanoréseaux

Impression en surface et en volume

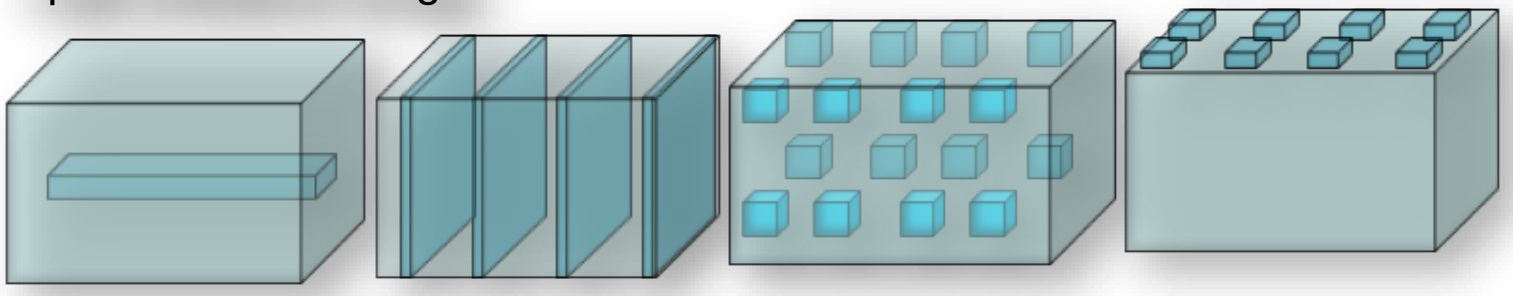
Luminescence

Non linear optical properties

Multi-scale Structuring

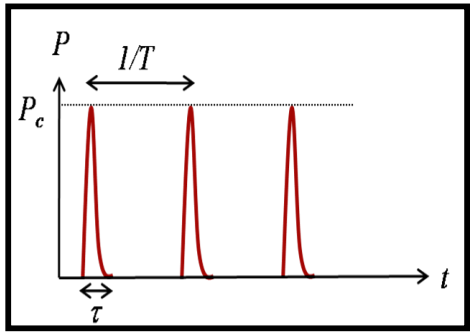


Optical Material design



Absorption linéaire / non linéaire

Lasers impulsionnels

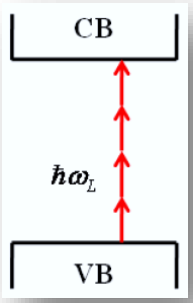


$P_c \approx$ GW - TW

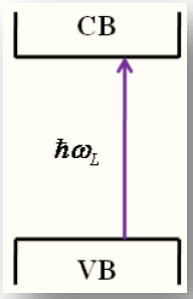
Fluorescence de colorants en solution

Processus non linéaire
= multiphoton

Absorption localisée



Processus linéaire :
Absorption sur tout le trajet du faisceau

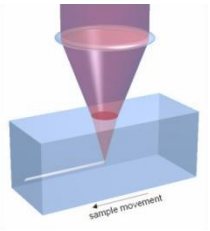


Laser Femtoseconde
Structuration des verres

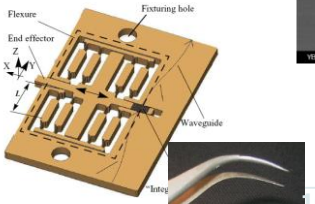
1995

- **Micromètre**

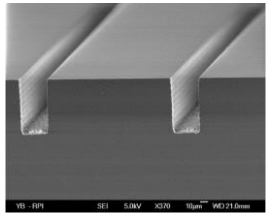
  Inscription de guide d'onde
  Croissance cristalline

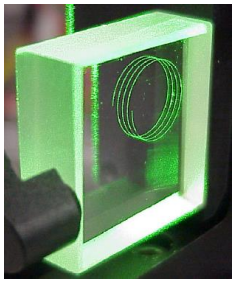


Efimov et al, Optical Materials, Volume 17, Issue 3, August 2001, Pages 379-386



capteur



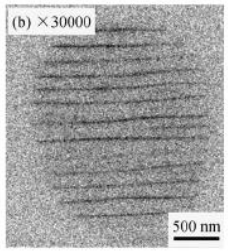


Translume Inc.

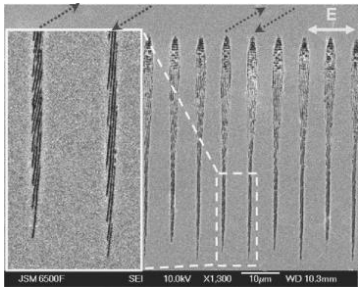
Depuis 2000

- **Nanostructuration**

  Nano Réseaux



Shimotsuma Y., Hirao K. et al.
J. of Non Cryst. Solids, 352, p646, (2006)



P. G. Kazansky et al.
90, (2007), p151120

Processus physico - chimiques

Photo-ionization ***(multiphoton absorption*** and/or ***tunneling ionization)*** (after 1 fs)

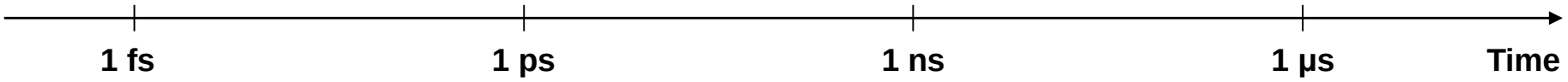
Avalanche ionization (after 50 fs)

Thermalization of the electrons (after 100 fs)

Energy transfer electrons → lattice (after 1 ps)

Thermodynamic processes ***(thermal diffusion***, ***melting*** and/or ***explosion)*** (after 10 ps)

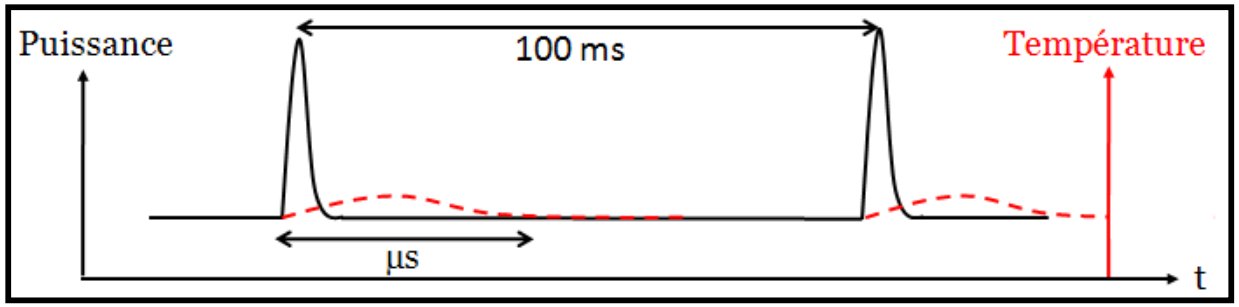
Photochemical processes ***(chemical*** and/or ***structural changes)*** (after 1 ns)



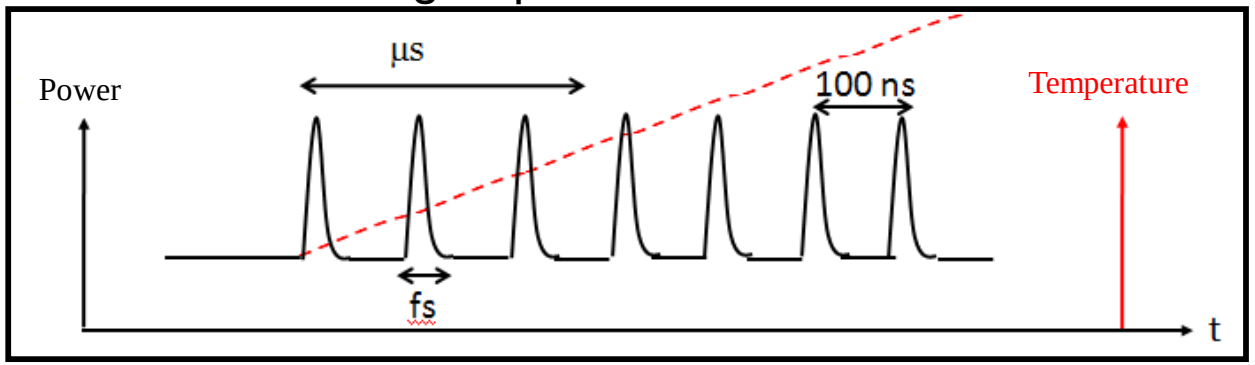
DLW: Repetition rate

Thermal relaxation ≈ µs

Low repetition rate



High repetition rate



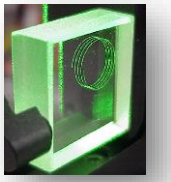
⇒ **Effet thermique**

Régime d'inscription

SiO_2

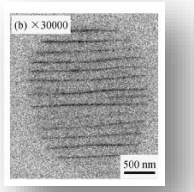
- ***Type I Variation isotrope de l'indice de réfraction***

→ *Δn isotrope – fusion du verre.*
→ *Applications:* **guides d'onde….**



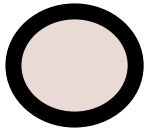
- ***Type 2: Variation anisotrope de l'indice de réfraction***

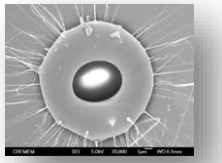
→ *Modification de l'indice de réfraction à des échelles en dessous de la longueur d'onde ("nanograting" structure).*
→ *Applications:* **polarisation….**



- ***Type 3: Formation de cavités***

→ *Coeur de faible densité(Δn < 0) et coque forte densité(Δn > 0).*
→ *Applications:* **mémoires optiques…**

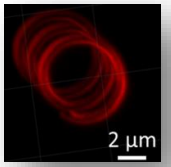




Régime d'inscription

- ***Type 0:* Photochimie**

→ *Changement degré d'oxydation*
→ *Changement de phase…..*



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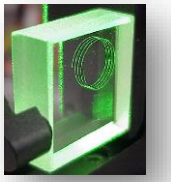

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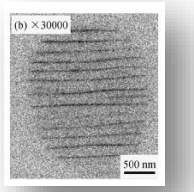

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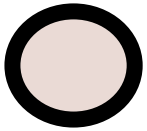

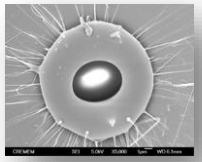

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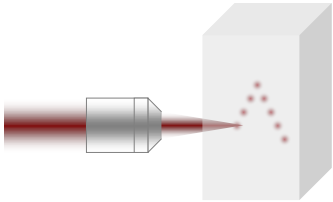
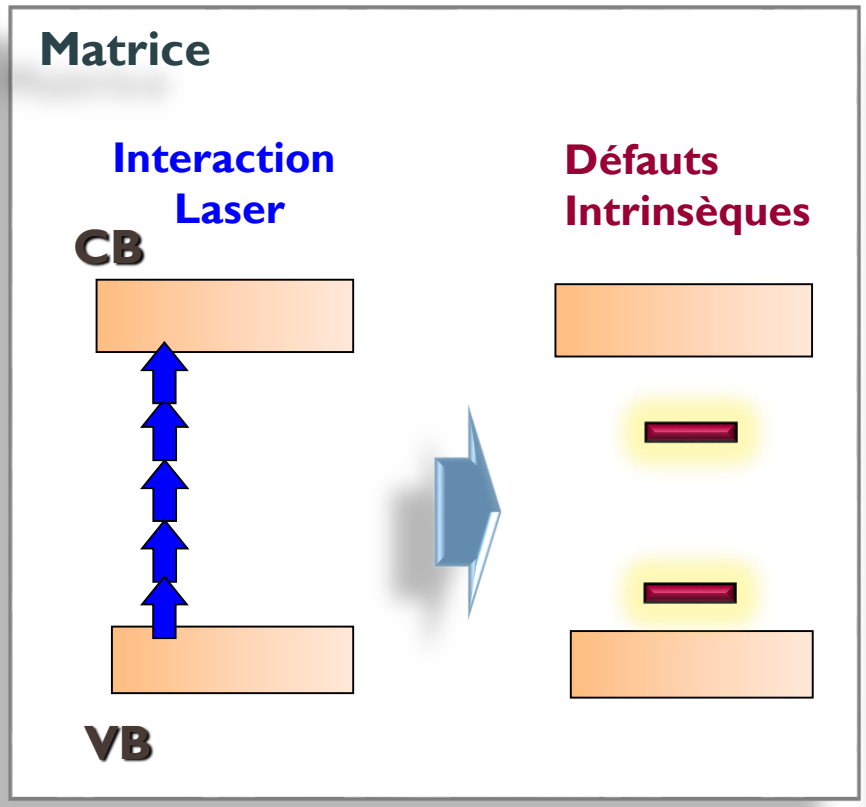
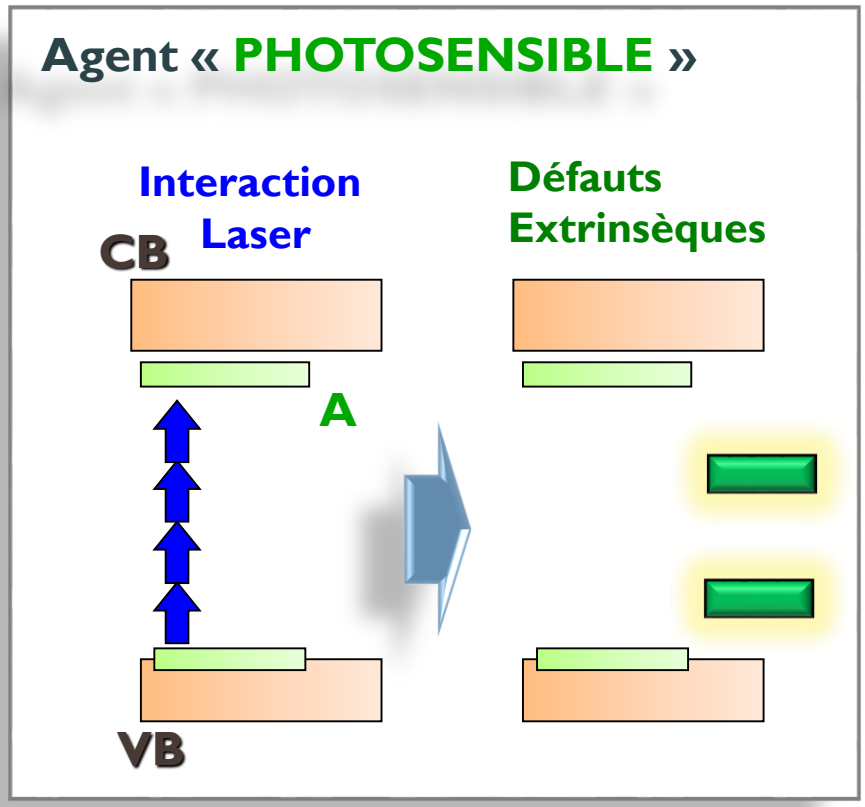
Eléments photosensibles ?





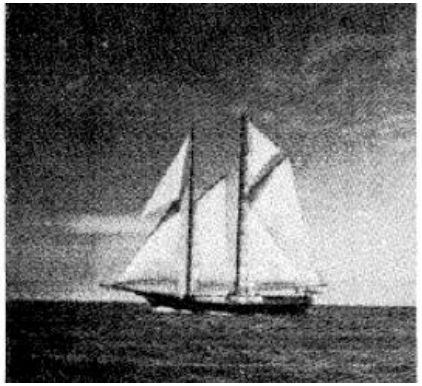


Argent, un élément très utilisé?

Film photographique

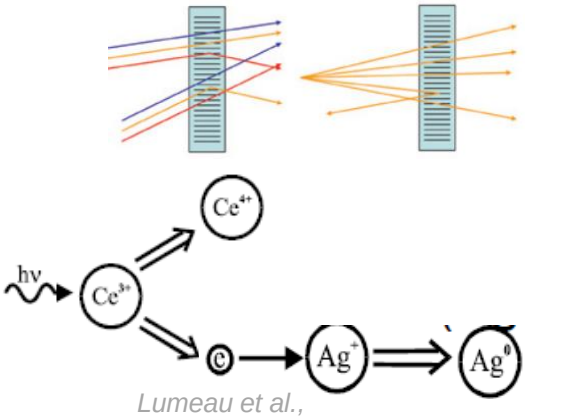
Doisneau, Mathématiques, 1941

Verre photosensible

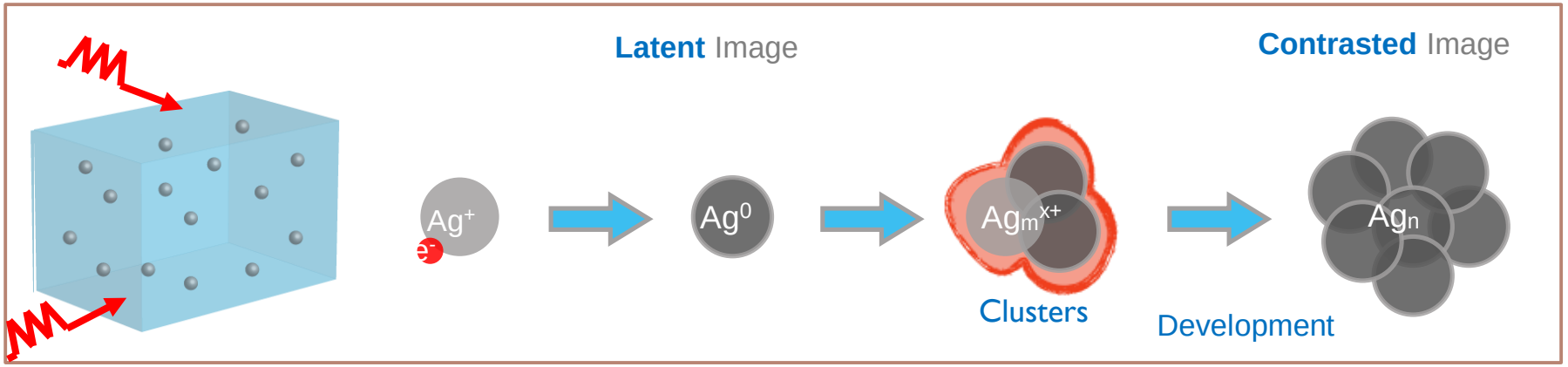


Stookey, Ind. Eng. Chem., 1949

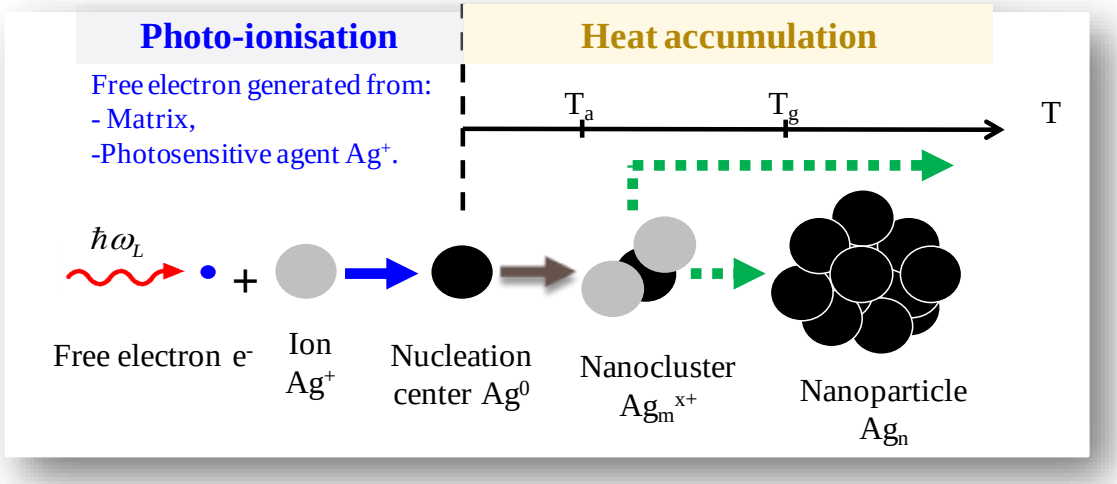
Thermo photo réfractif

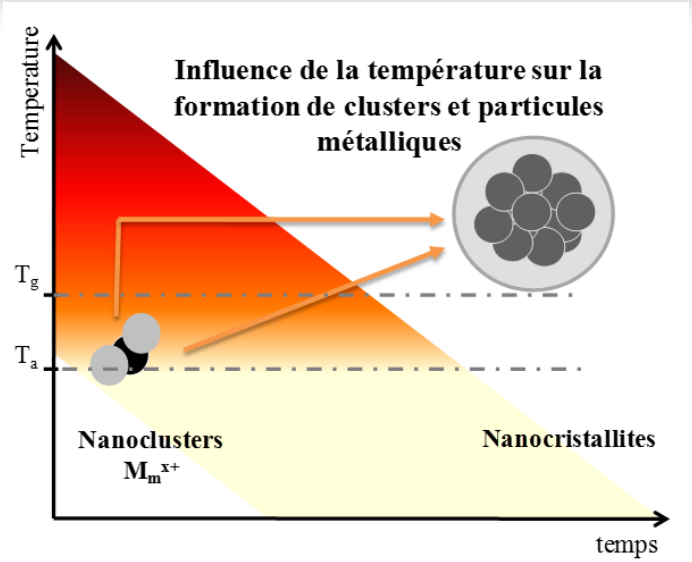


Lumeau et al.,
Optical Materials 32 (2009) 139–146



DLW: Oxydo-Réduction de l'argent





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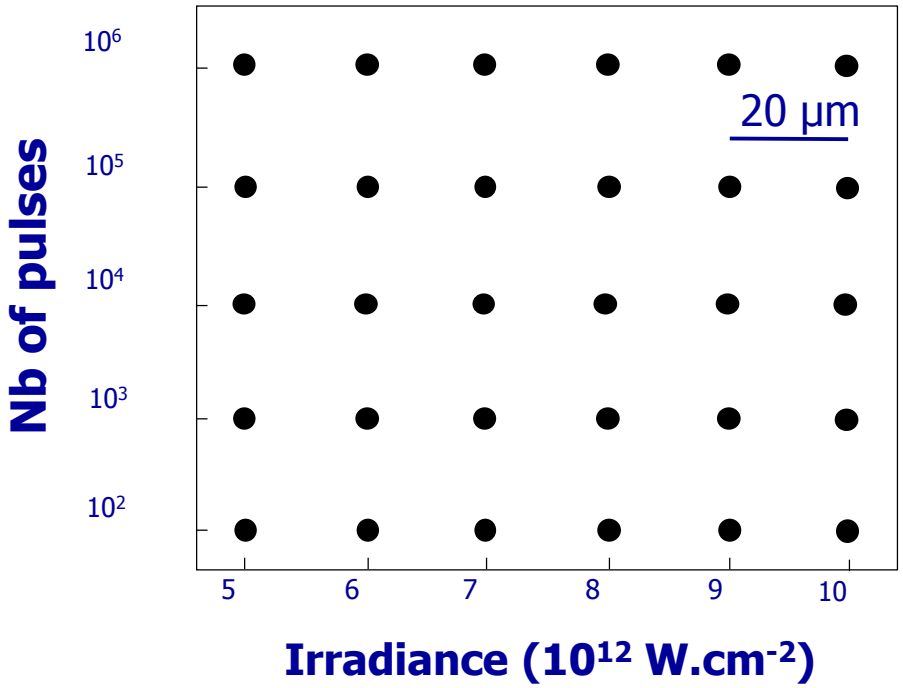
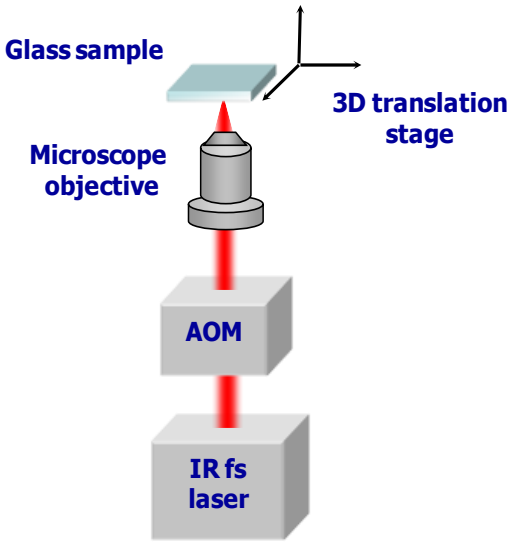
DLW:
Matrice d'interaction Laser Matériaux





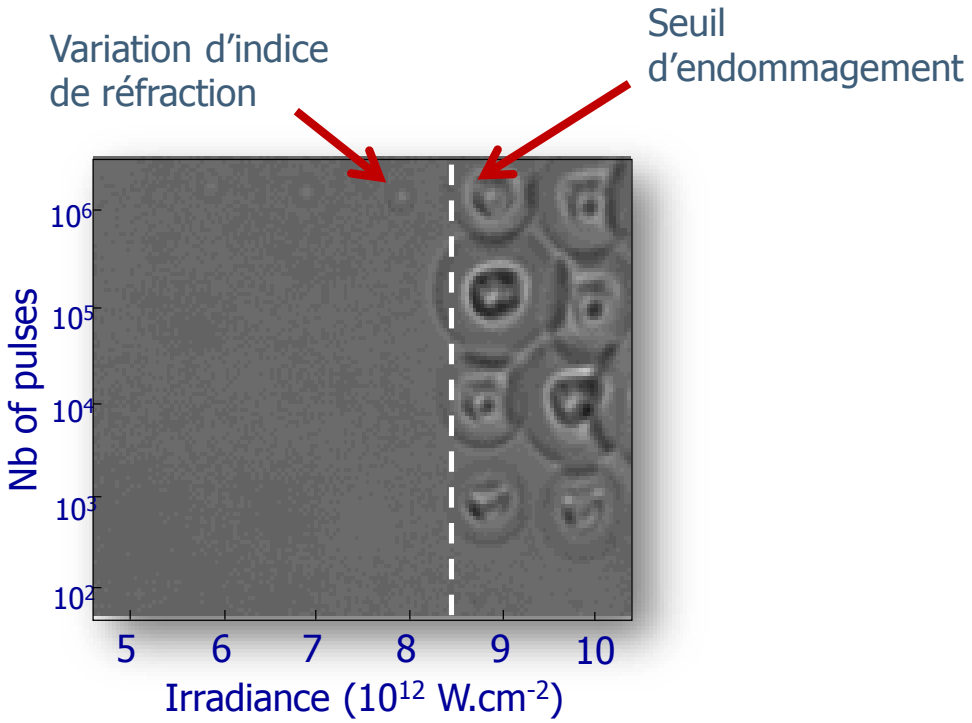
Wavelength:	1.04 µm
Energy :	0→400 nJ
Pulse width :	400 fs
Repetition rate:	10 Mhz

DLW: Spectroscopie corrélative

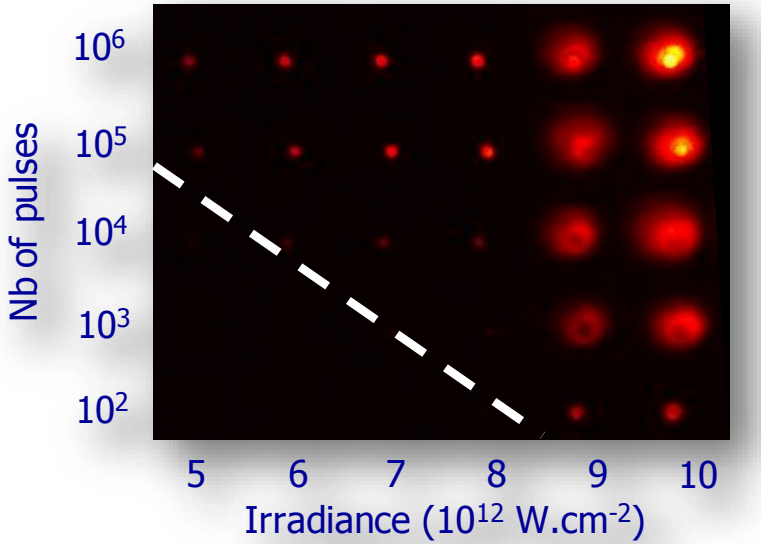
Composition :
55% ZnO – 40% P_2O_5 – x% Ga_2O_3 – (5-x)% Ag_2O

Tg= 380°C

Microscopie en lumière blanche

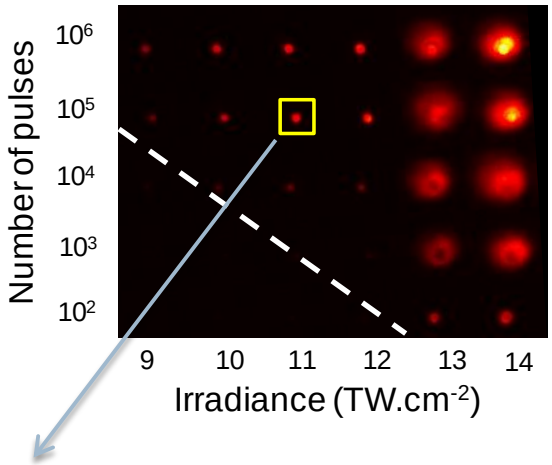


Microscopie de luminescence
Micro Raman
Microspectroscopie SHG
etc…



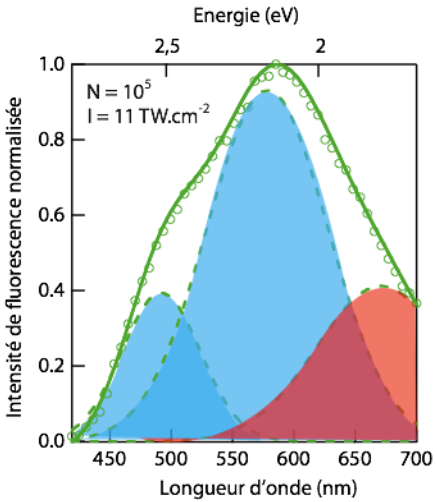
Micro-luminescence
λ_{exc} = 363nm

DLW: Fluorescence

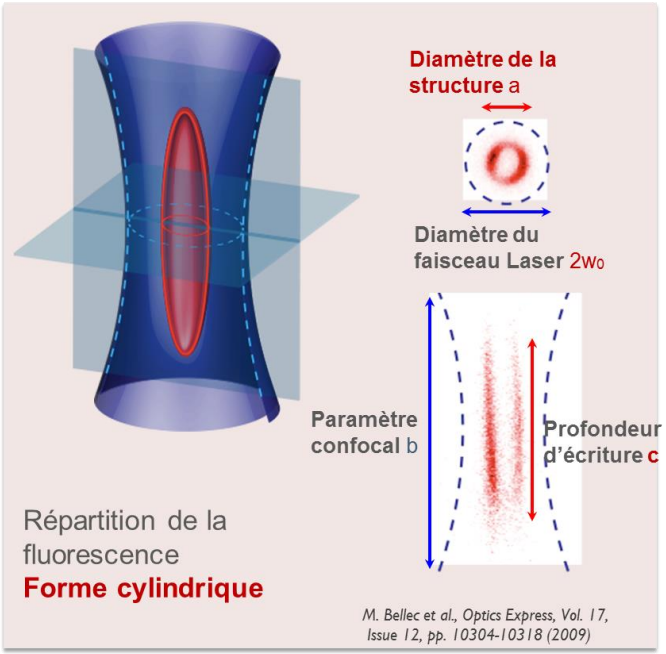


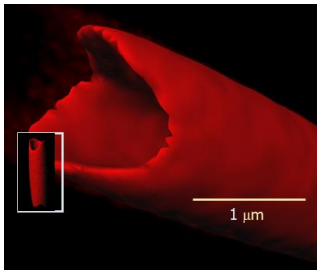
- Fomation de **clusters d'argent fluorescents Ag_m^{x+}.**
- Réactions Photo-chimiques:

$$Matrice + h\nu \rightarrow e^- + h^+$$
$$Ag^+ + h\nu \rightarrow e^- + Ag^{2+}$$
$$Ag^+ + e^- \rightarrow Ag^0$$
$$Ag^+ + Ag^0 \rightarrow Ag_2^+$$
$$Ag_2^+ + Ag^+ \rightarrow Ag_3^{2+} \ldots Ag_m^{x+}$$



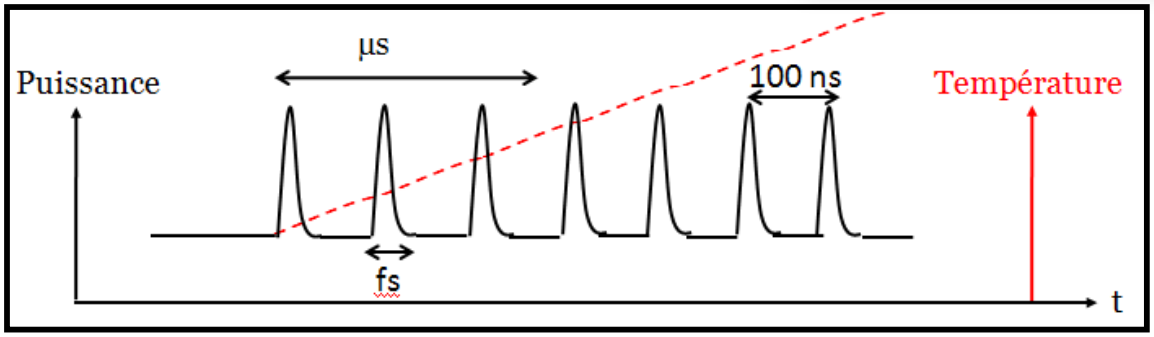
Bellec et al. Journal of Physical Chemistry C 114, (2010), 15584-15588.



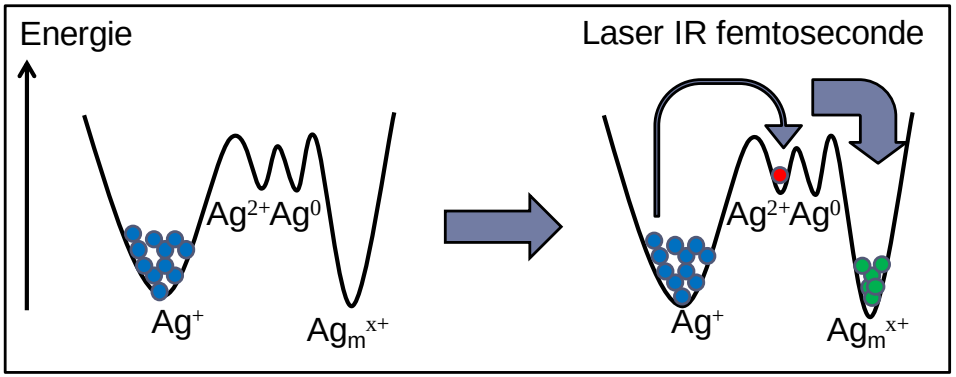


DLW: Fluorescence

L. Binet, D. Caurant, , LCMC, Paris



Taux de répétition élevé

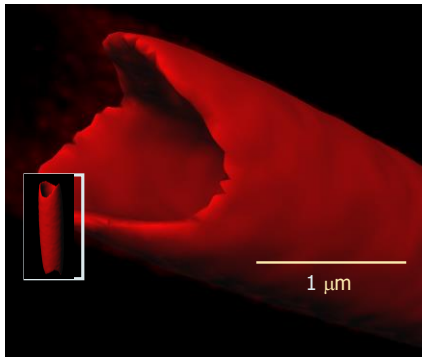


- Formation **localisée** d'agrégats d'argent

Meilleure stabilité des structures

Photo réduction et agrégation

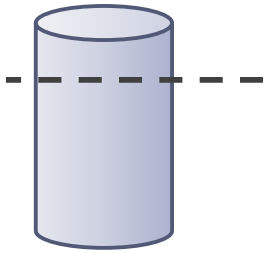
Micro Analyse Chimique



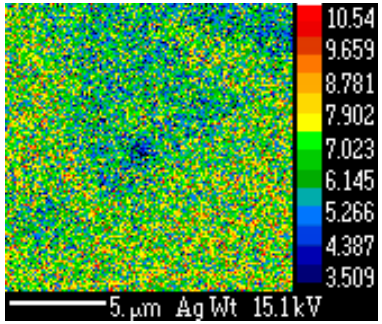
Formation de clusters d'argent luminescents Ag_m^{x+} (formés de Ag^0 et Ag^+)

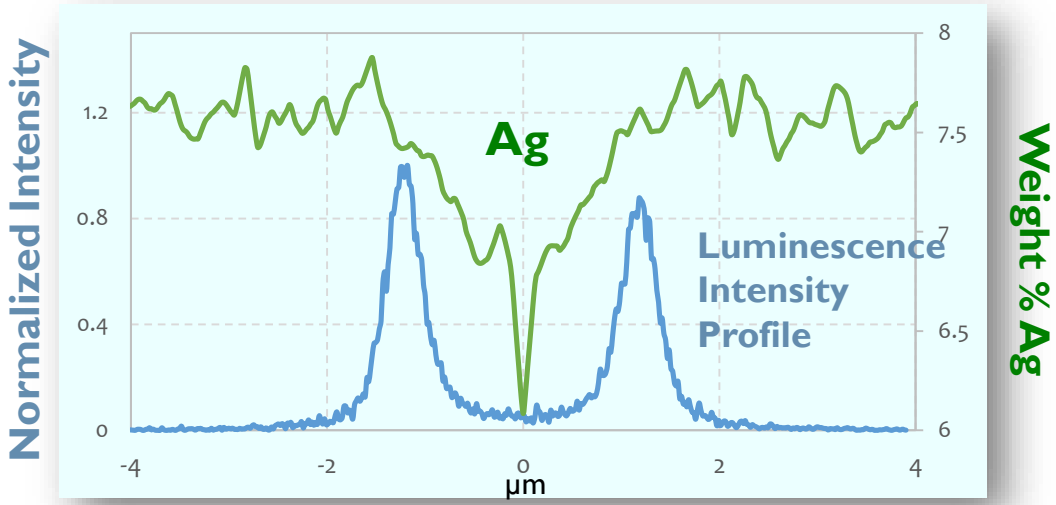
Bellec & al., Opt. Express, 17(12) (2009) 10304-10318

3µm diameter



X Ray microprobe

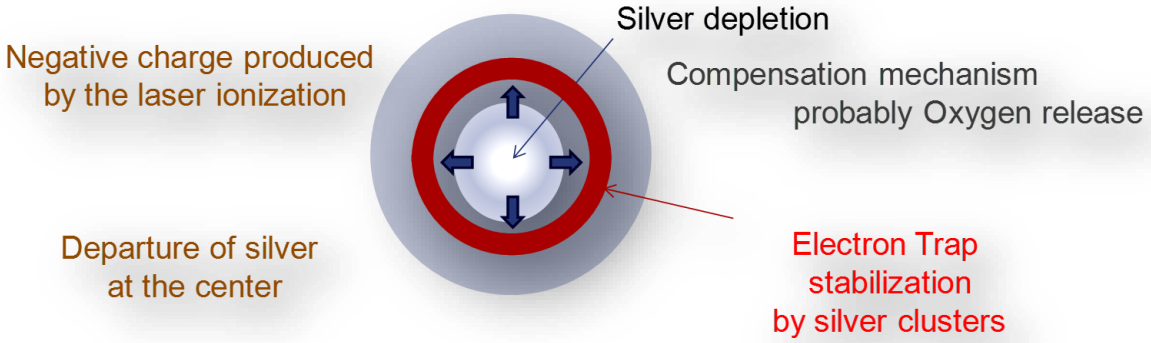




Déplétion de l'argent au centre

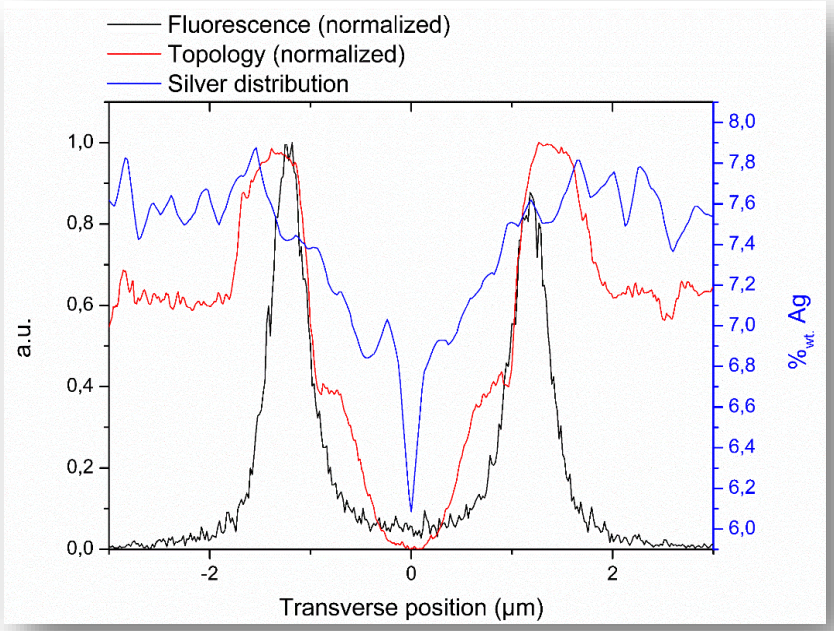
JC Desmoulin et al., J. App Phys. In press

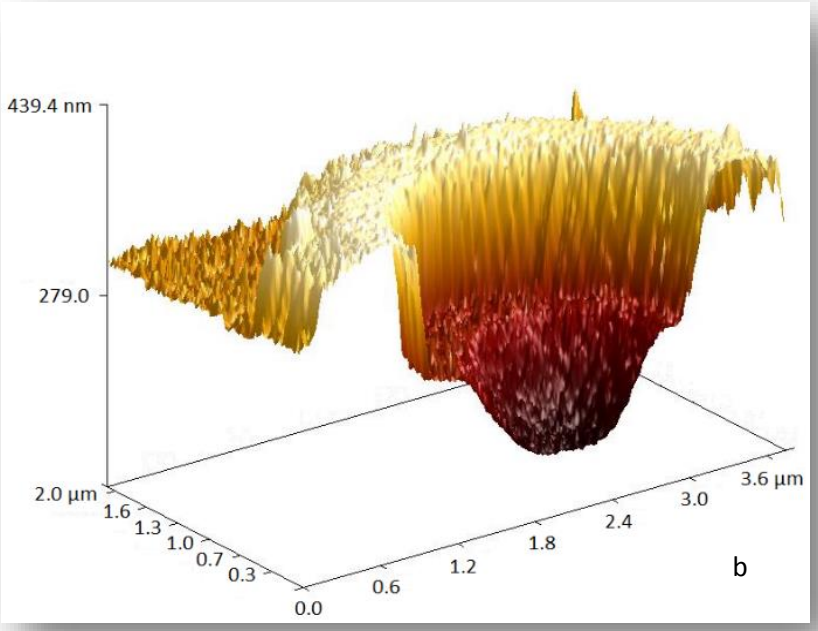
Topologie



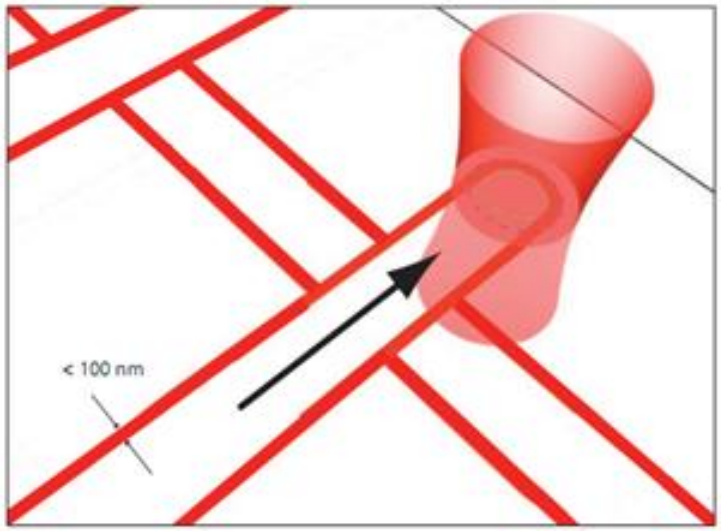
Attaque chimique

JC Desmoulin et al., J. App Phys. In press

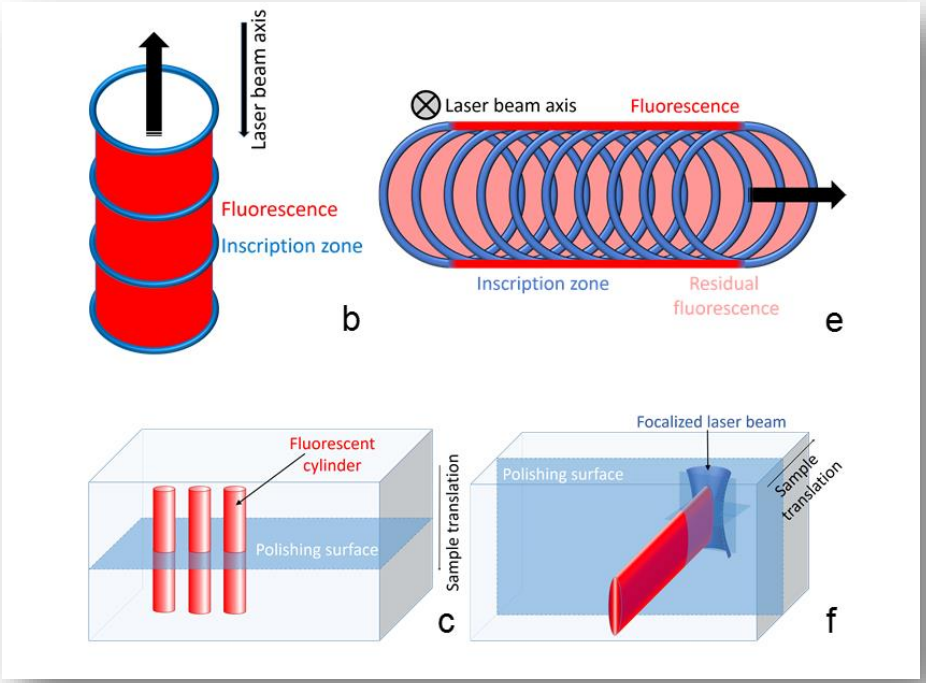




DLW: Laser Writing



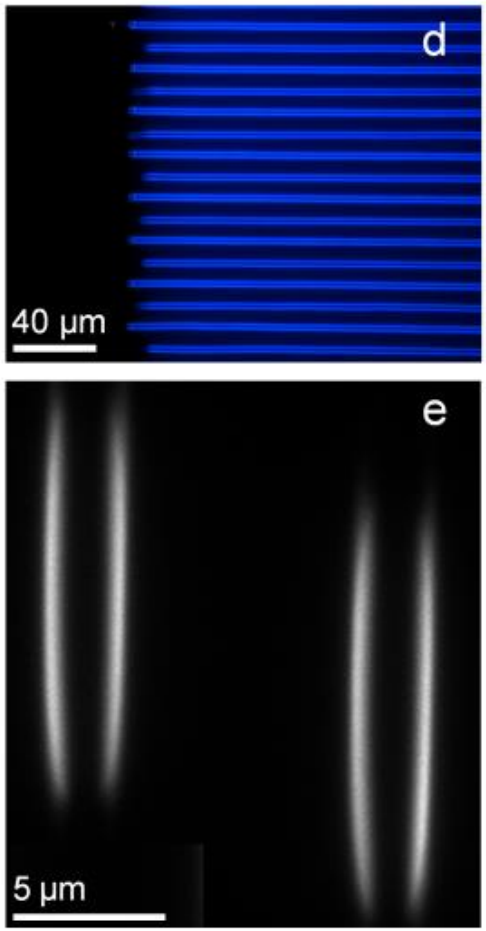
Bord écrit
Centre efface

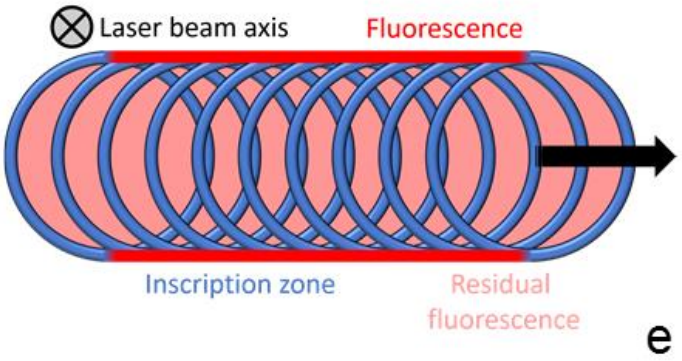


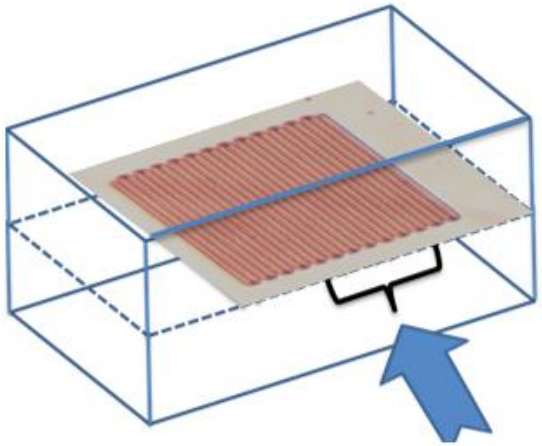
Inscription de doubles lignes fluorescentes

Micro-luminescence

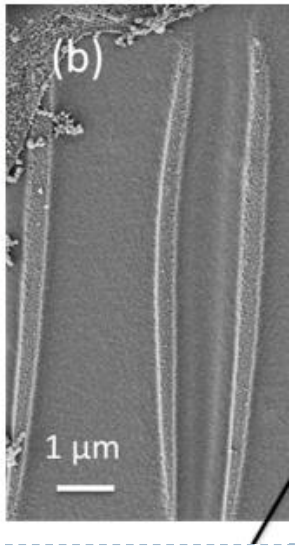
λ_{exc} = 363nm



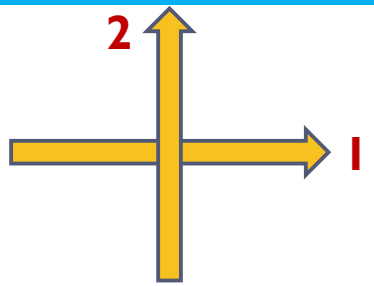




HRSEM imaging



Combinaison de l'oxydo-réduction Et de la migration



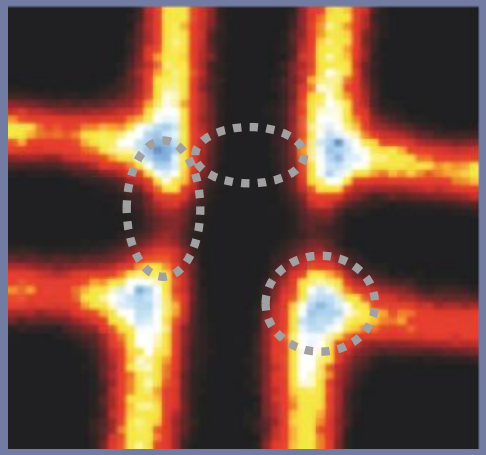


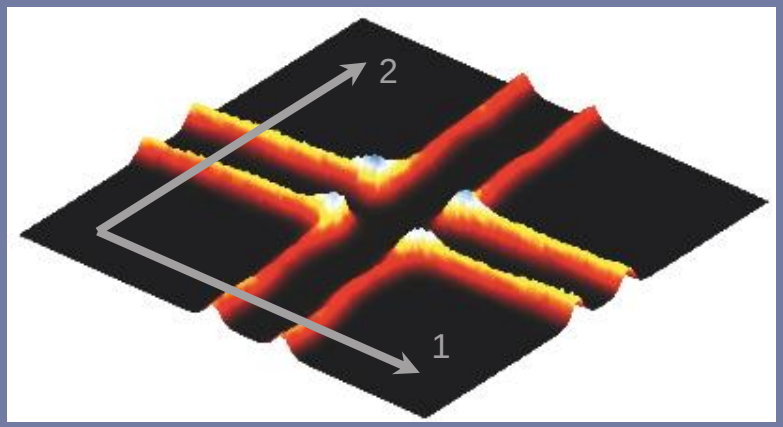
Photo-dissociation in the center

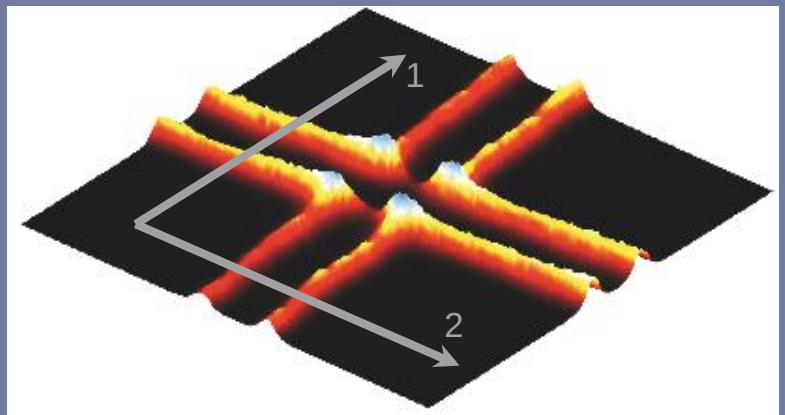
Redistribution on the edge

Accumulation at the corner

Linear displacement

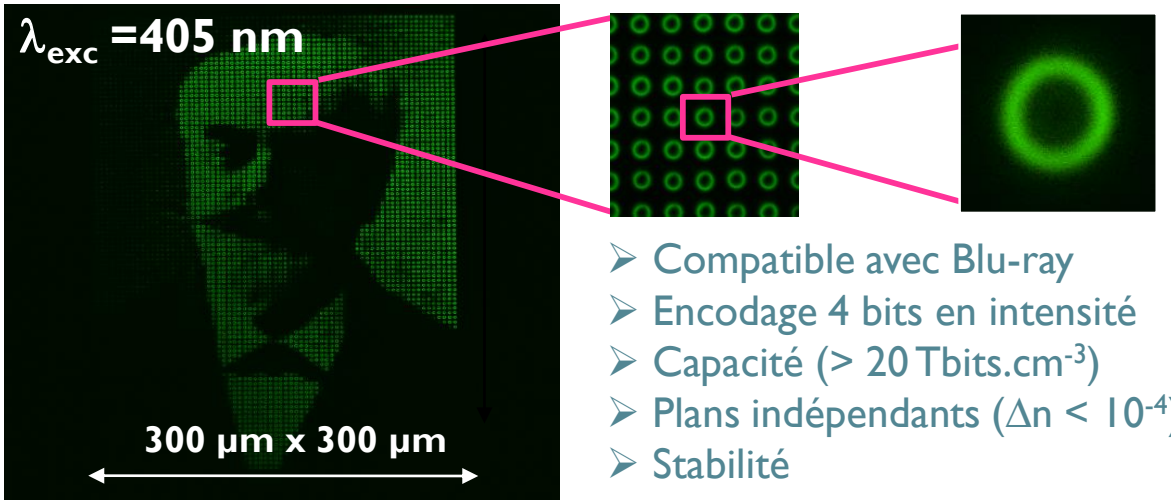
v = 1 mm/s, N = 10^6





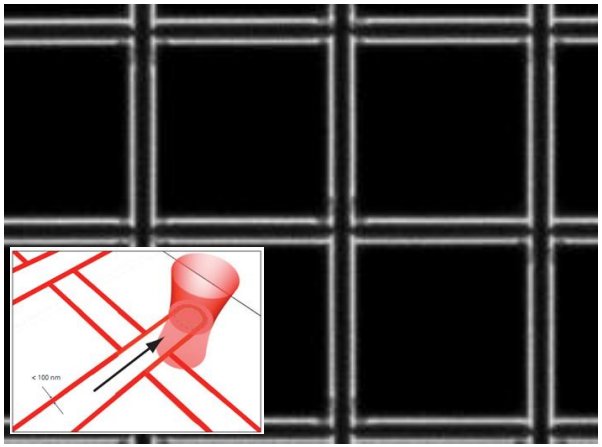
Motifs luminescents

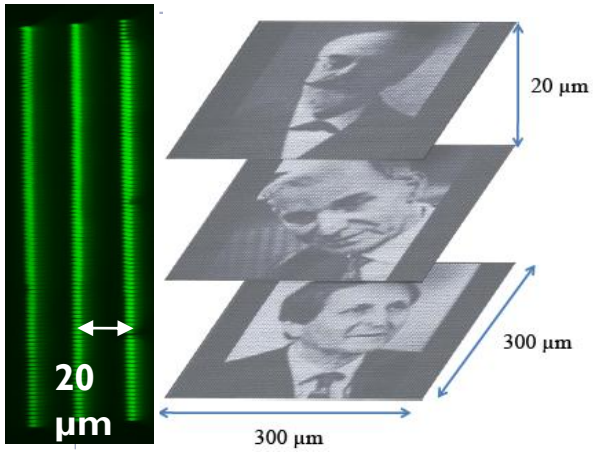
- Stockage pérenne 3D haute densité (lecture confocale)



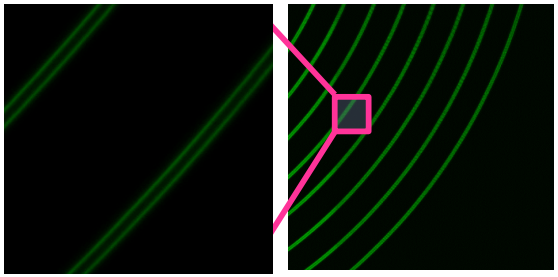
- Compatible avec Blu-ray
- Encodage 4 bits en intensité
- Capacité (> 20 Tbits.cm^{-3})
- Plans indépendants ($\Delta n < 10^{-4}$)
- Stabilité

- Ecriture & ré-inscription





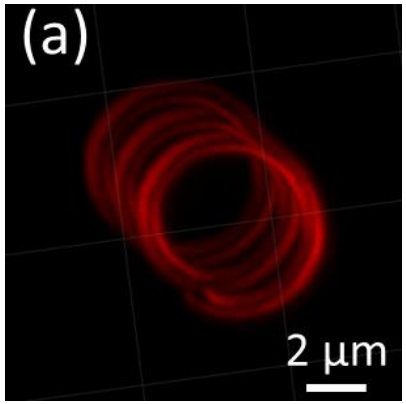
- Encodage 3D de structures pour microscopie de fluo



- Ecriture sur les bords du laser
- Effacement au centre
- Re-écriture selon le réservoir d'ions argent

A. Royon et al., Advanced Materials, 22, 46, 2010, p 5282

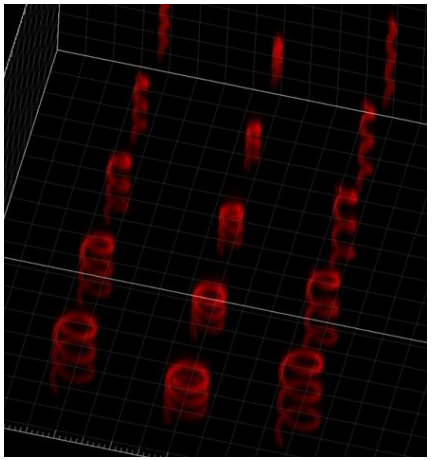
Matériaux orientés



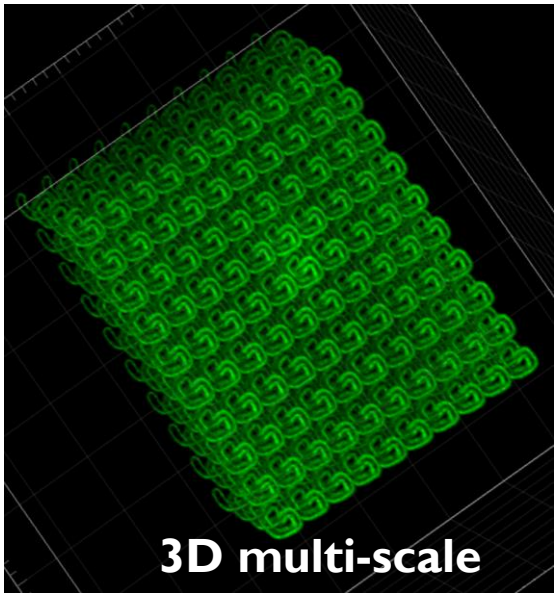
→ Double-line spirals
by confocal imaging

→ Control of both radii
& helicoidal periods

→ Sub-micron dimensions
along the spiral



N. Marquestaut et al., Avd. Funct. Mat. ***24****(37), 5824–5832 (2014).*



Topological chirality

→ Photonics structures
- Linear optics & Refractive index
- Nonlinear optics & SHG / THG

→ Plasmonics structures
- Composite dielectric/metallic materials
- Spirals of disconnected silver NPs

Plan

I. Introduction Structuration Laser femtoseconde et impression 3D

II. Verres photosensibles : le cas de l'ion argent

III. Impression de motifs luminescents

IV. Processus physico-chimiques : analogie avec une irradiation électronique

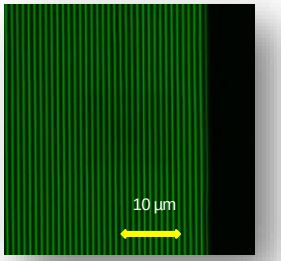
V. Effets non linéaires photo-induits

VI. Architecture et co-illumination

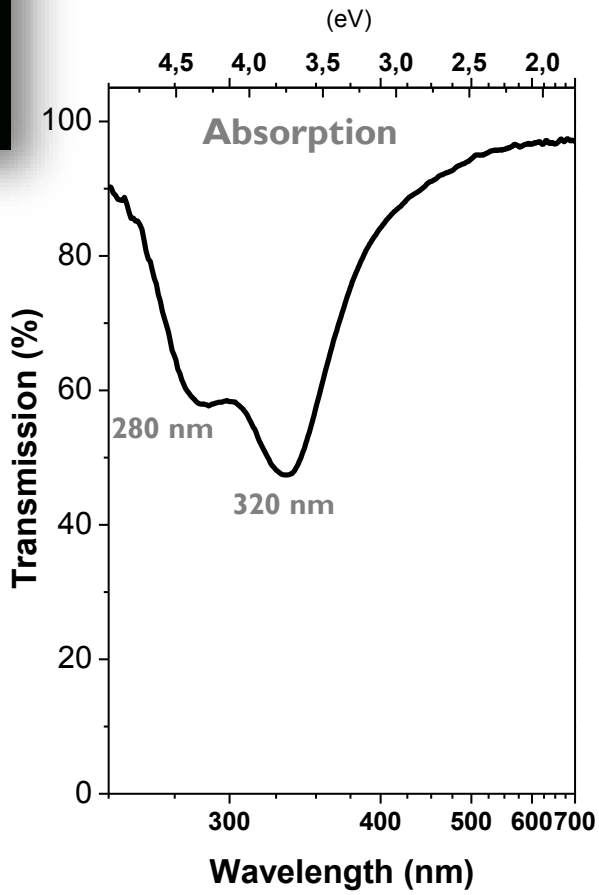
VII. Mise en forme : fibres photosensibles

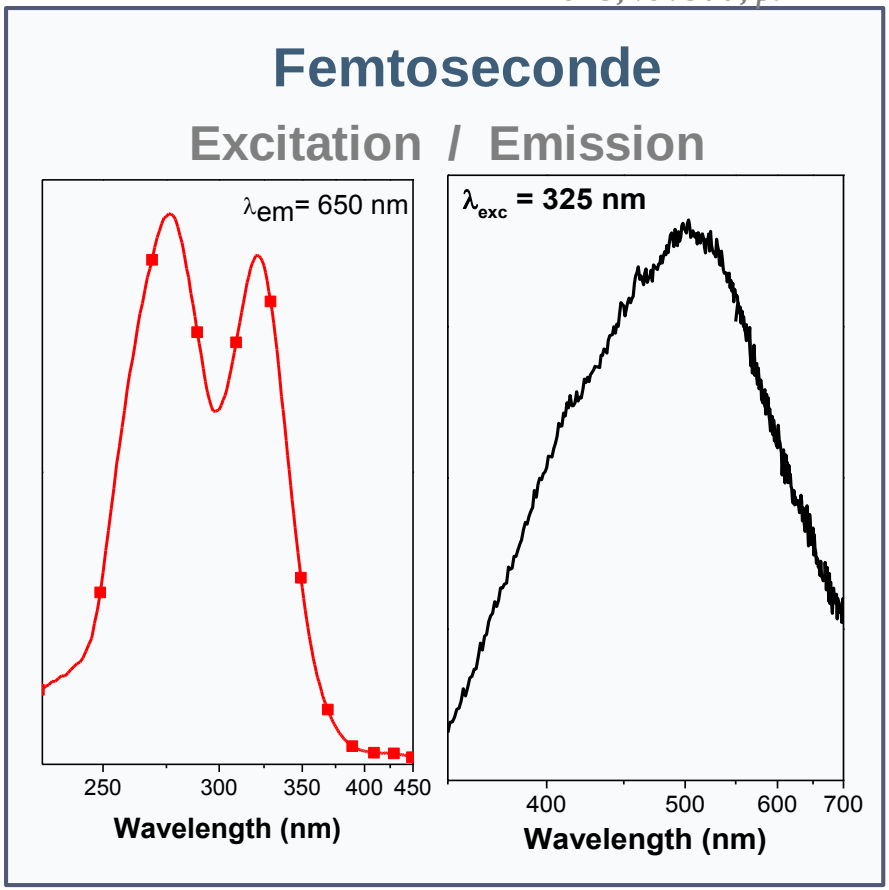
VIII. Verres à l'argent et nanoréseaux

DLW: Luminescence et absorption



Bourhis K., J. Non-Cryst. Solids 2013, vol. 377, p. 142



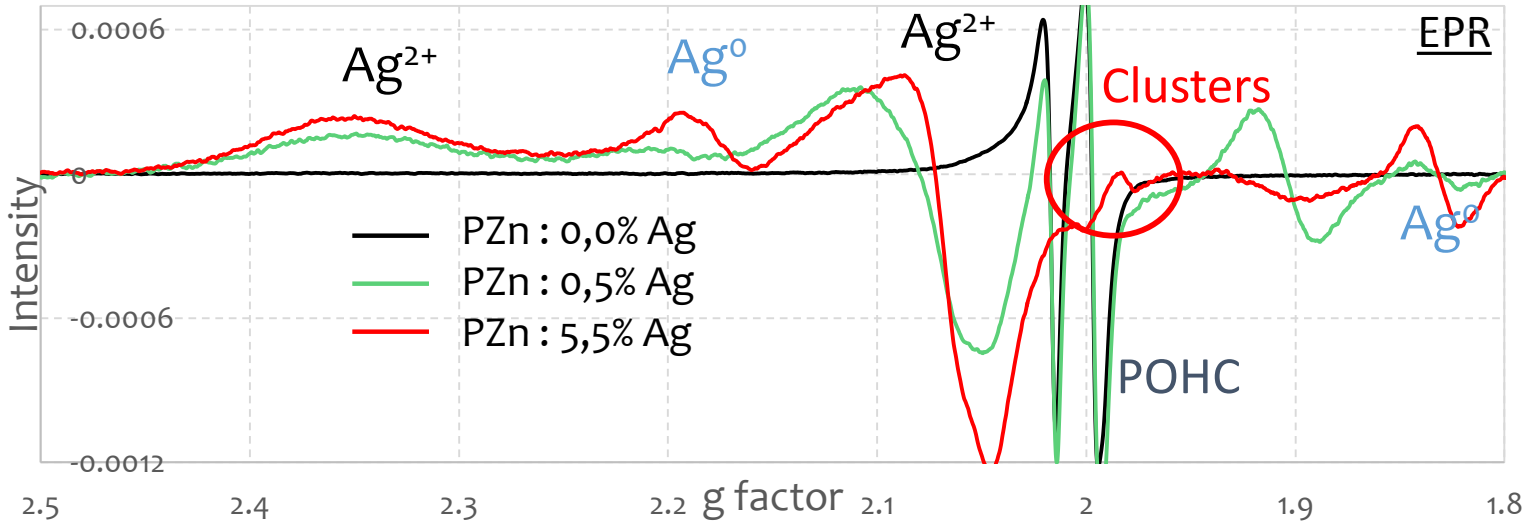


Meilleure sensibilité des verres contenant plus de 4 mol% de Ag_2O

Identification des mécanismes physico-chimiques

N. Ollier, LSI, Paris

Irradiation électronique (1MGy) de verres phosphate d'argent pour différentes concentrations en argent



Verre sans Argent :

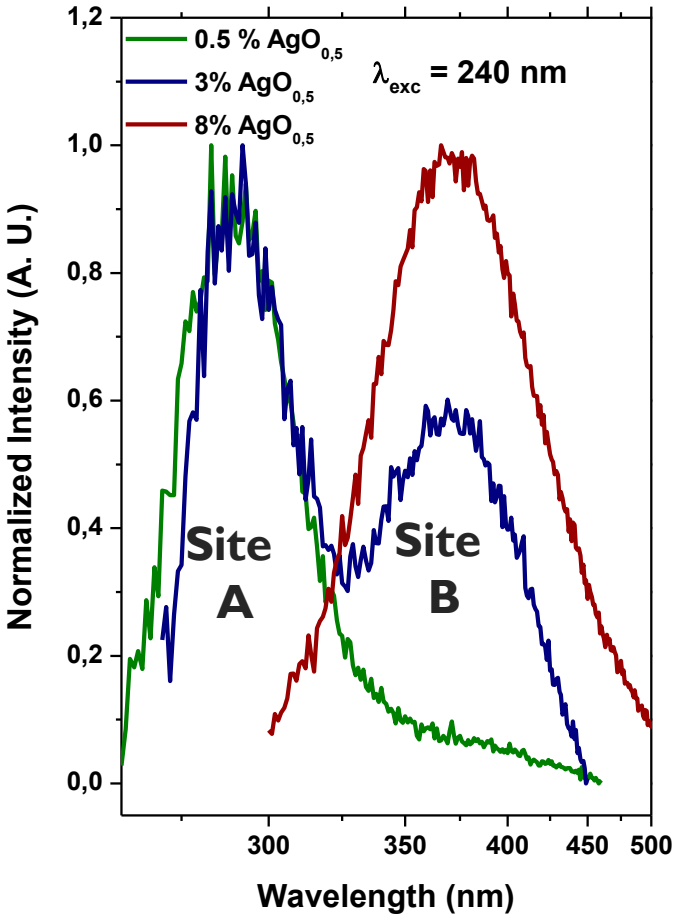
- *Formation de POHC*

Verre avec Argent :

- *Disparition des POHC*
- *Capture des trous et des électrons par l'argent*

Identification des mécanismes physico-chimiques

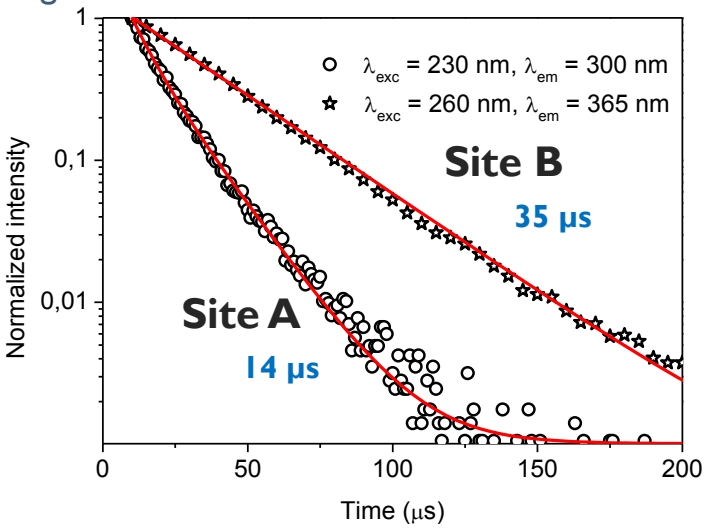
Deux sites pour l'argent



Composition

55% ZnO – 40% P_2O_5 – x% Ga_2O_3 – (5-x)% Ag_2O

Tg= 380°C



Durée de vie

Faible concentration en argent

Ag^+ isolé

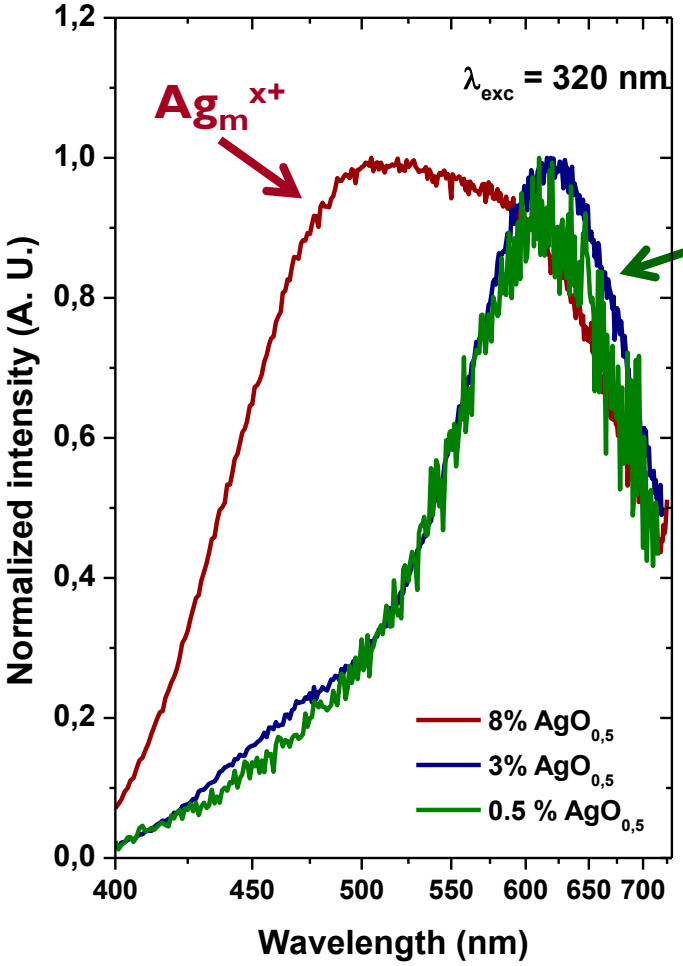
Forte concentration en argent

d

Ag^+----Ag^+

Dimères ? **Segregation ?**

Identification des mécanismes physico-chimiques



Ag^{2+} or Ag_3^{2+}

Electron beam Irradiation 5 KGy
(10 MeV, 13.7µs)

For low silver concentration

$Ag^+ + h^+ \longrightarrow Ag^{2+}$

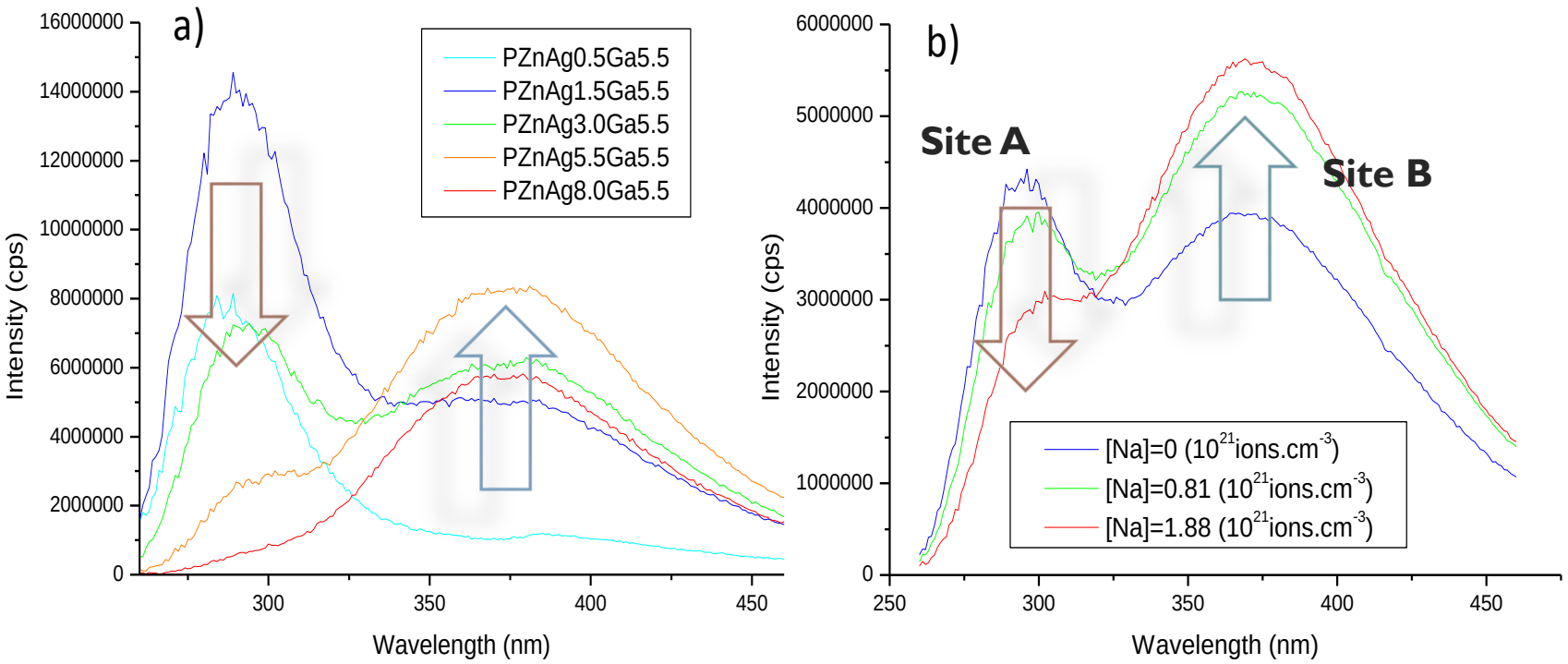
$Ag^+ + e^- \longrightarrow Ag^0$

For High silver concentration

$Ag^+ \overset{d}{\text{- - - -}} Ag^+ \longrightarrow (Ag^+ Ag^0)$

Ag_m^{x+}

Sodium / Argent



Incorporation du sodium → **Dimères ?** **Segregation des ions Ag^+ ?**

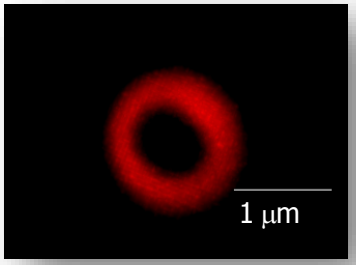
Augmentation notable de la sensibilité du verre

Plan

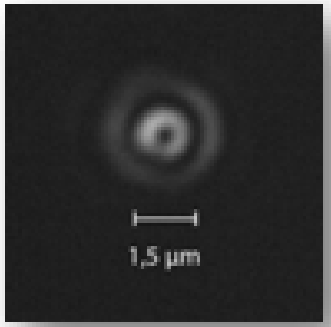
DLW: Second Harmonic Generation

Fixed position

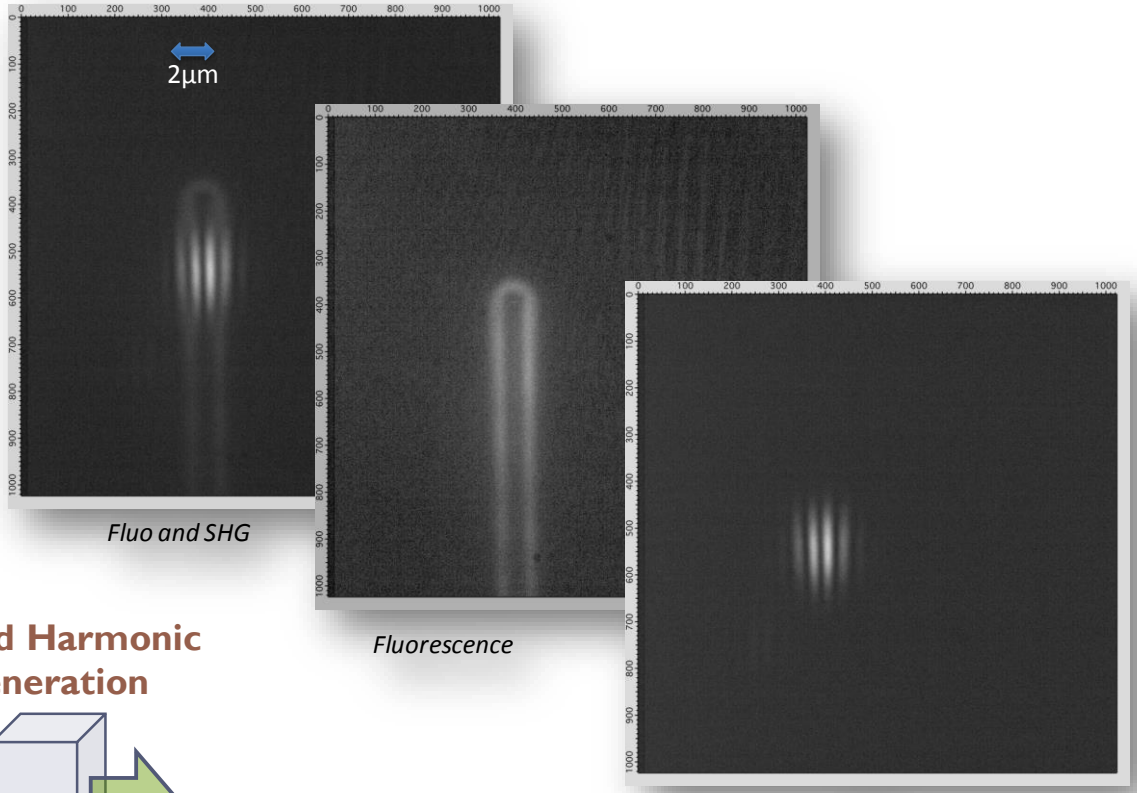
Fluorescence



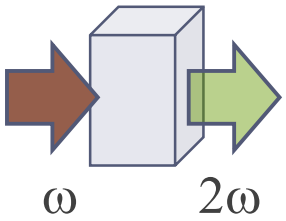
SHG



Linear motion



Second Harmonic Generation



Laser:

Wavelength:	1.04 µm
Pulse duratiion:	400 fs
Repetition rate:	10 Mhz

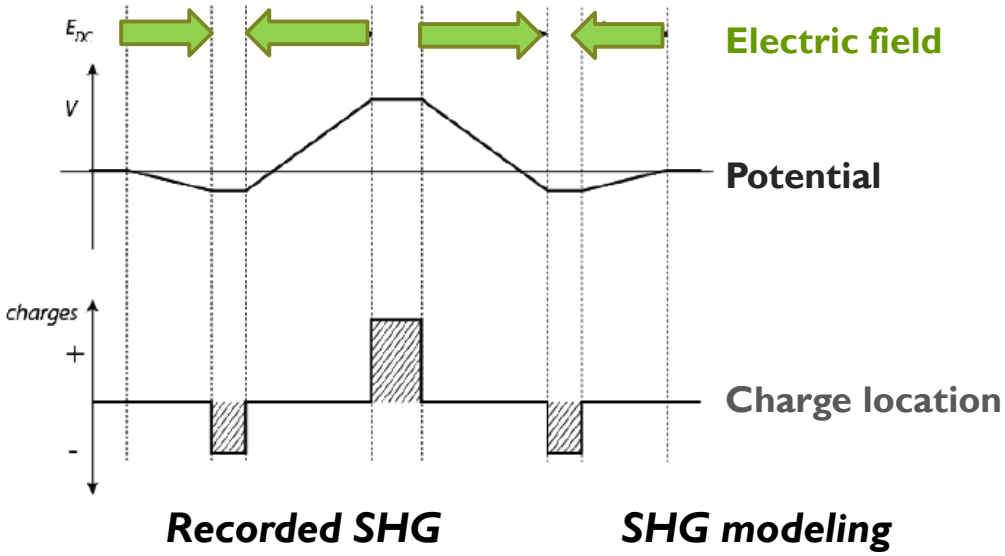
Papon G., Journal of Applied Physics 115, (2014), 113103

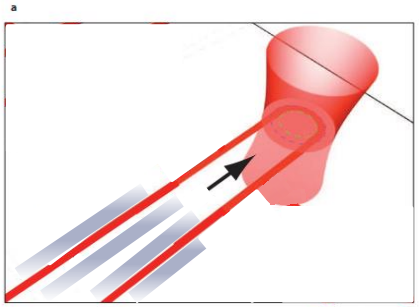
DLW: Electric field

In Glass

$$\mathbf{P} = \varepsilon_0 \left(\chi^{(1)}\mathbf{E}(\omega) + \chi^{(2)}\mathbf{E}(\omega)\mathbf{E}(\omega) + \chi^{(3)}\mathbf{E}(\omega)\mathbf{E}(\omega)\mathbf{E}(\omega) + \ldots \right)$$

P : *Polarisation*
E : *Electric Field*
$\chi^{(n)}$: *Linear and Nonlinear susceptibilities*





SHG
Fluorescence

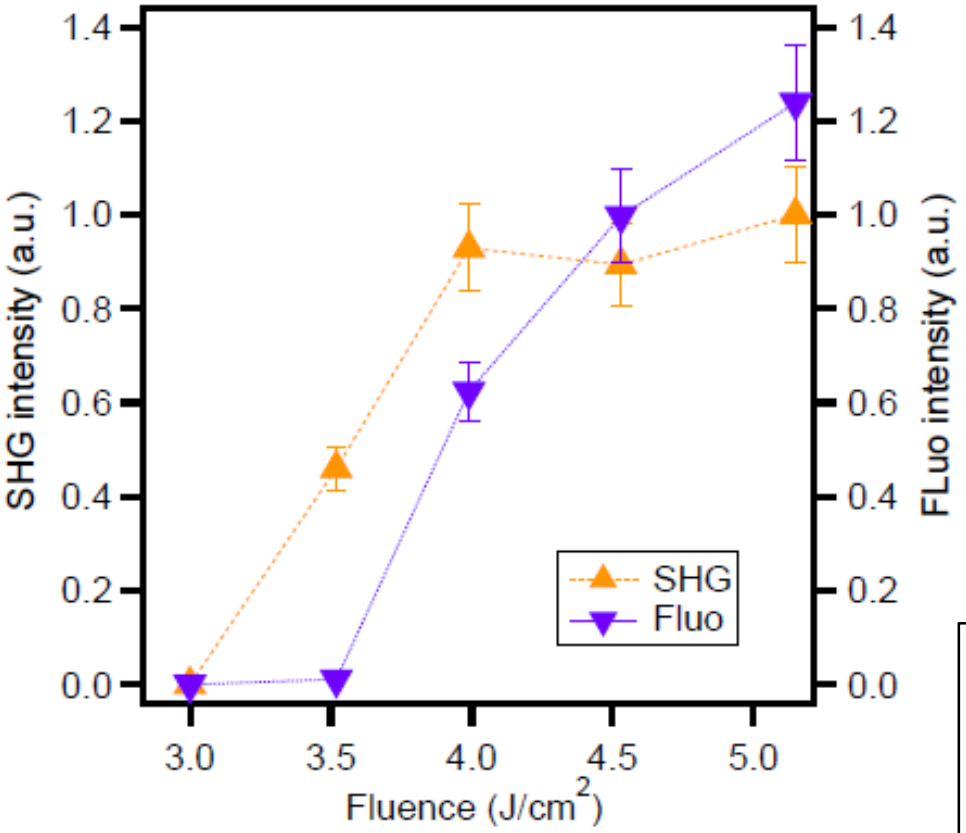
Papon G., Optical Materials Express, (2013), 855

Charge separation and stabilization

$$P^{NL}(2\omega) = \boxed{\chi^{(3)}\,E_{dc}}\,\mathbf{E}(\omega)\mathbf{E}(\omega)$$

$$\approx \chi^{(2)}$$

DLW: Steps

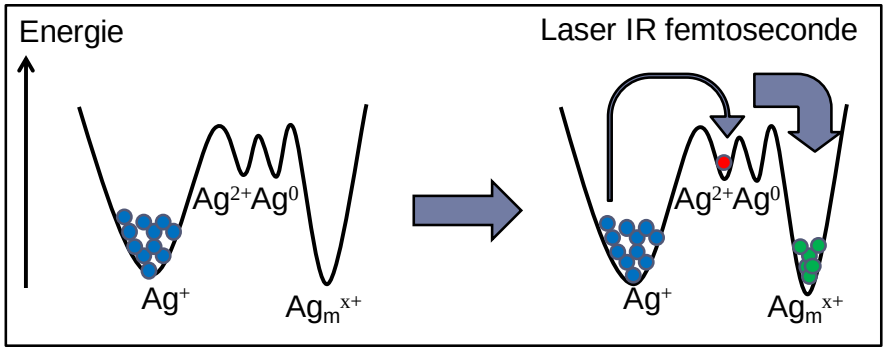


1 - charge dissociation

2 - Silver cations and atoms migration

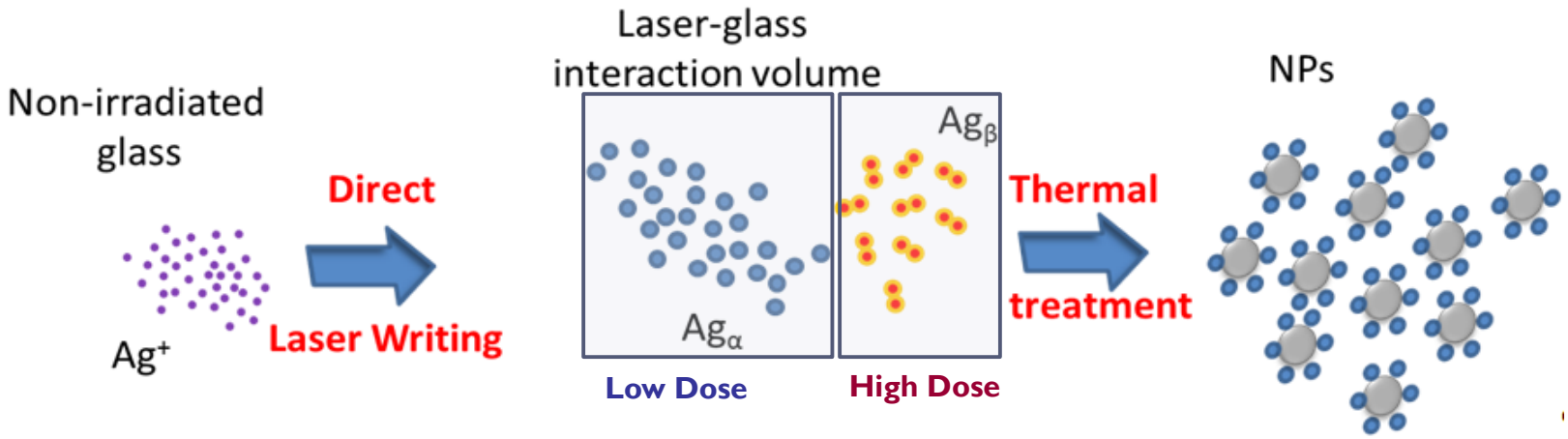
3 - Silver cluster formation

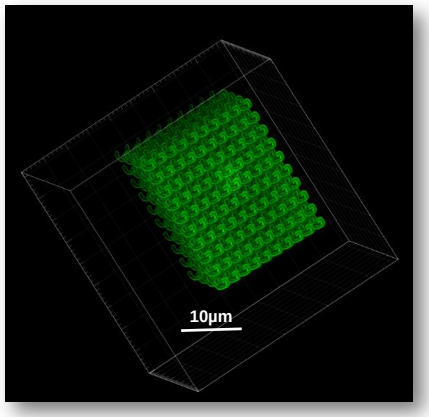
4 - Silver and oxygen mobility in the center?

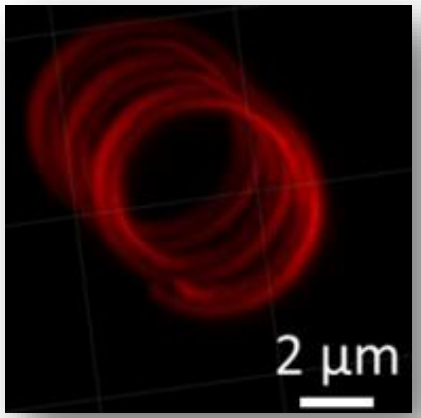


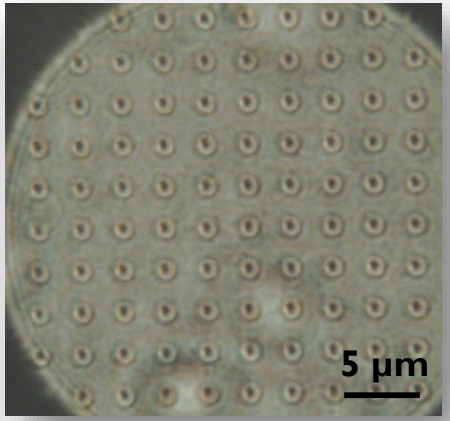
Plan

DLW: Thermal treatment above Tg after DLW in zinc phosphate matrix







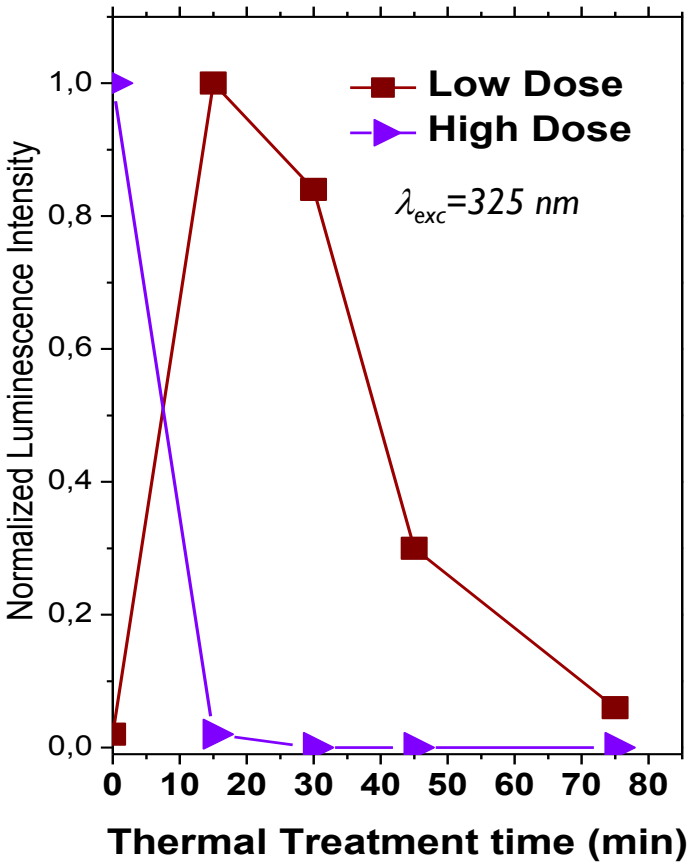


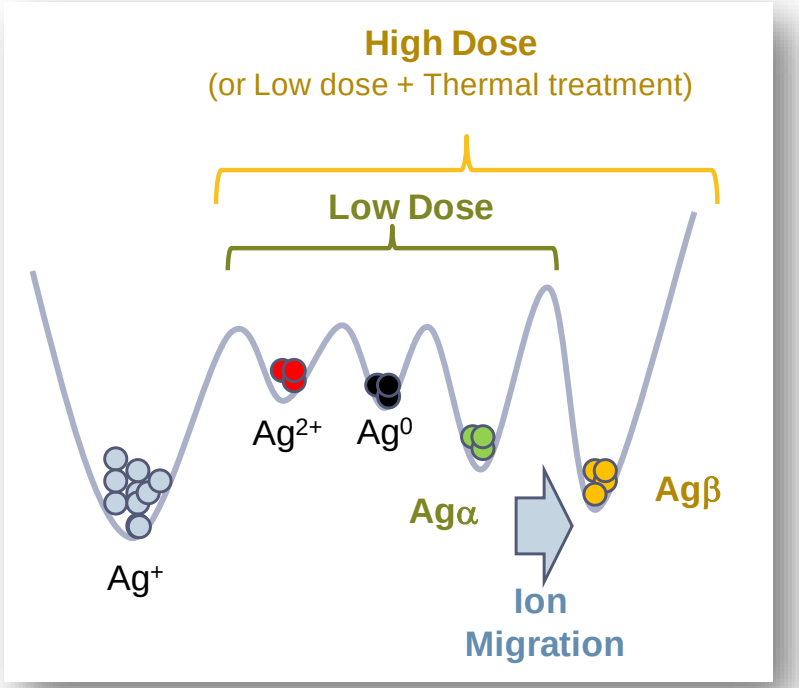
Complex plasmonic structure can be engineered in bulk glass

N. Marquestaut, Adv. Funct. Mater., 24, 37, 2014, Pages: 5824–5832

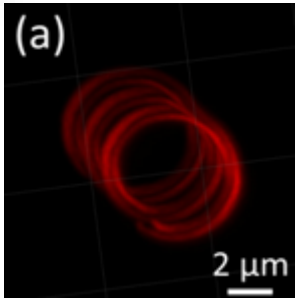
Des clusters spécifiques pour la formation de nanoparticules métalliques

T = 425°C

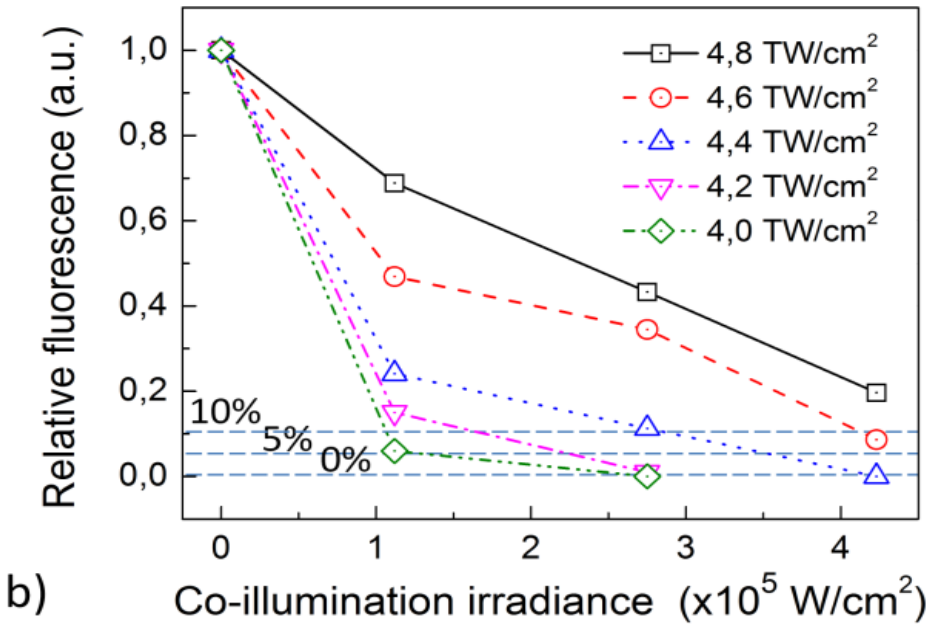




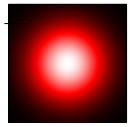
Agβ → **Particules métalliques**



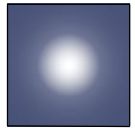
Co-illumination & inhibition

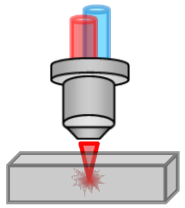


800 nm, 100 fs
250 kHz



396 nm, cw,
100 mW





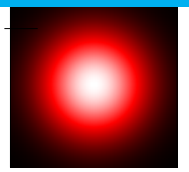
$N_{pulses} = 10^4$

up to **100% inhibition** of the DLW fluorescence
by cw blue **co-illumination**

Active feedback **control on**
silver cluster creation efficiency

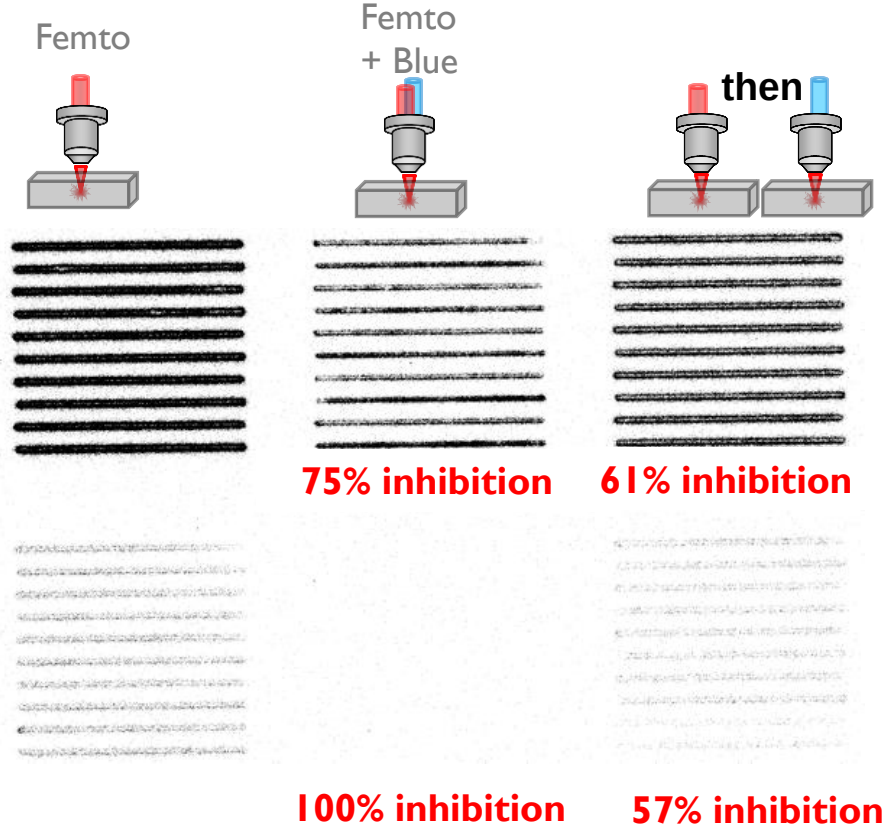
Y. Petit et al., Opt. Lett., 40, 17, p 4134, 2015.

Co-illumination versus post-illumination



800 nm, 100 fs
250 kHz

396 nm, cw,
100 mW

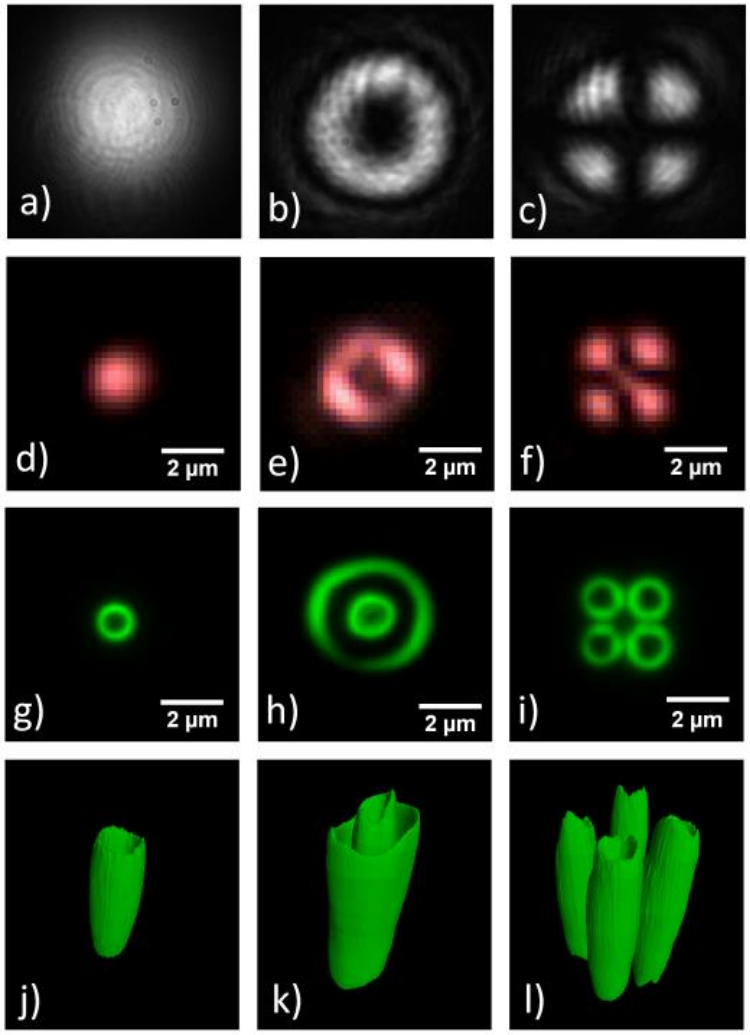


$E_{pulse\ @800nm}$ 41.7 nJ

$E_{pulse\ @800nm}$ 37.8 nJ

DLW: Vortex-induced linear patterns

LOMA, Univ. Bordeaux

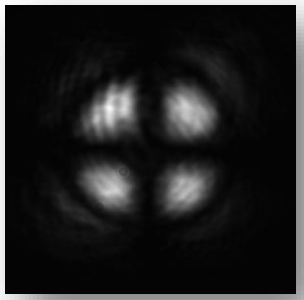


- Light structuring
- Photo-induced generation of original fluorescents patterns
- Realization of patterns *a priori* non accessible by successive irradiations with a Gaussian beam
- Conditions of laser writing with different laser parameters

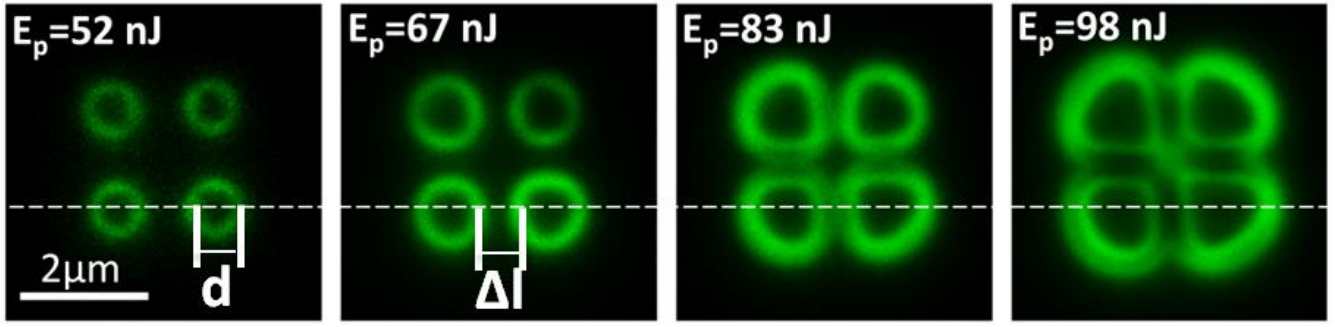
K. Mishchik et al., Optics Letters, 40, 2, p201, 2015.

DLW: Lumière structurée

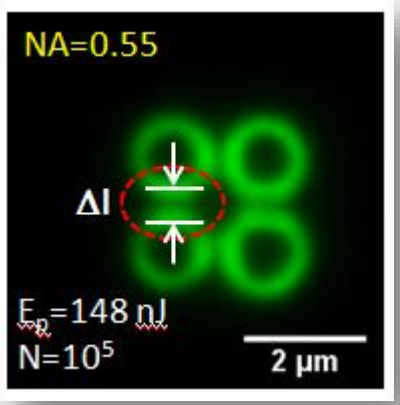
LOMA, Univ. Bordeaux

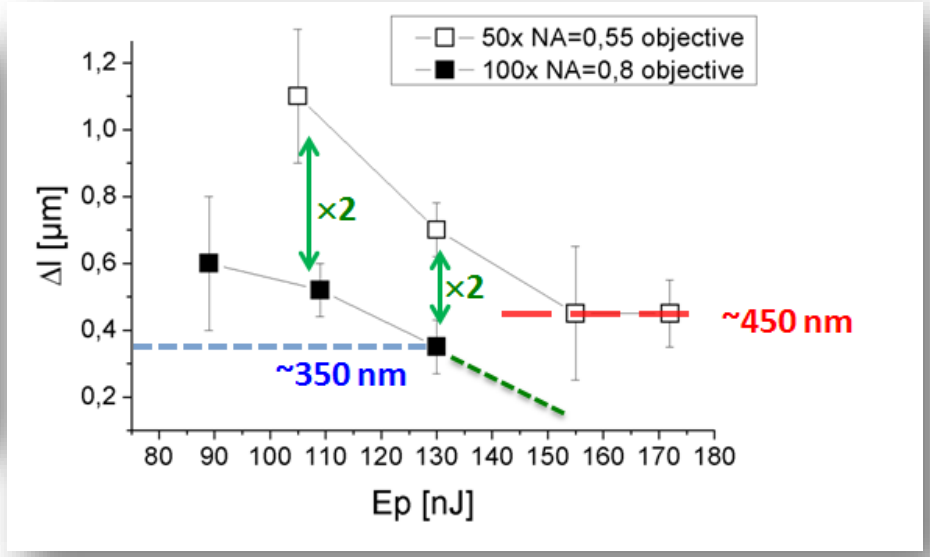


Beam intensity profile



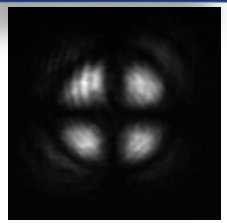
Increase of energy



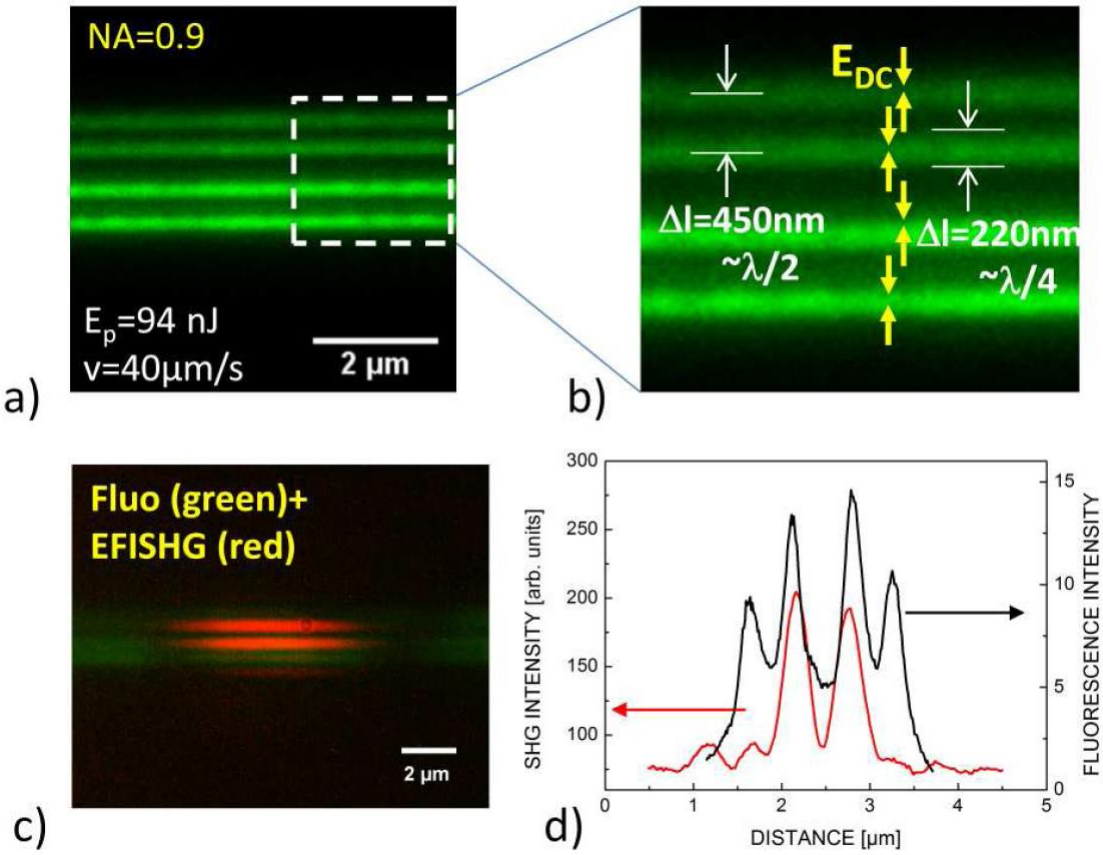


- **Non inter-penetration of the fluorescent rings**
- **Confirmation of the diffusion of charged species**
- **Mechanism/modeling: still *open question***

LOMA, Univ. Bordeaux



Nonlinear patterns under translation



- Correlative microscopy fluo/SHG
  → **multi-functionalized materials**

- Sub-wavelength micro-processing
- Buried electric field engineering

- Parallelizing of single-beam multi-line DLW

- **Towards new electro-optics photonic devices**

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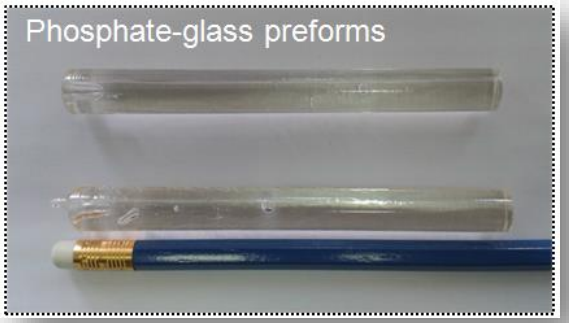
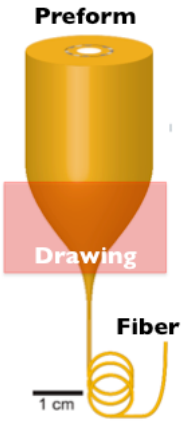
DLW: Photosensitive glass and fiber technology

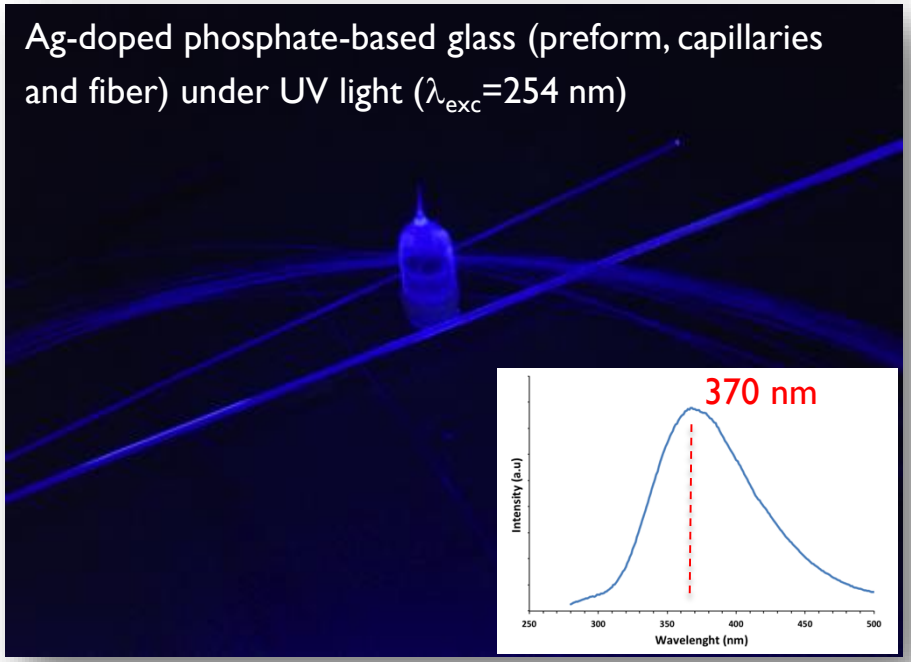
Frédéric Smektala, ICB, Dijon





- P_2O_5-ZnO-Ga_2O_3- 2%Na_2O-2%Ag_2O
- Draw at T_d ~700 °C under oxidizing condition (O_2)
- α~1.60 dB.m^{-1} @ 1064 nm

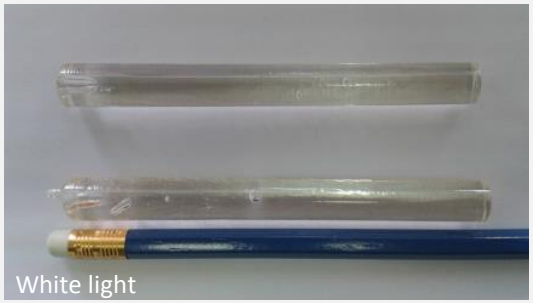
Fluorescence emission properties of the glass bulk is **Preserved into fiber form**

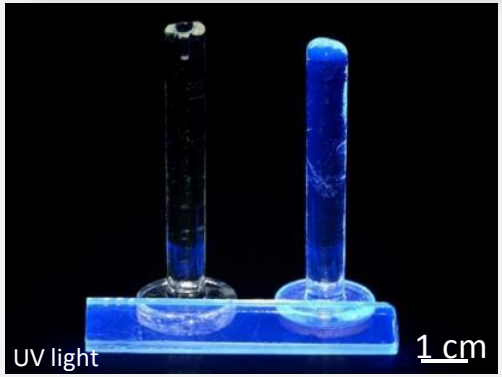


DLW: Photosensitive glass and fiber technology

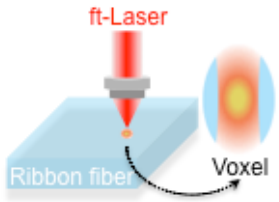
Frédéric Smektala, ICB, Dijon

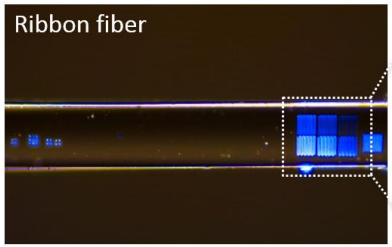
Phosphate-based glass preforms

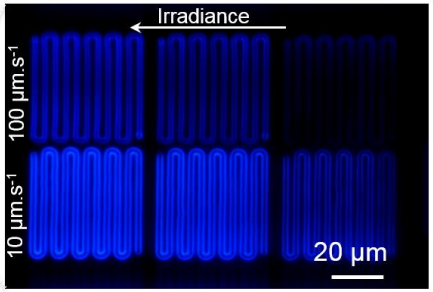


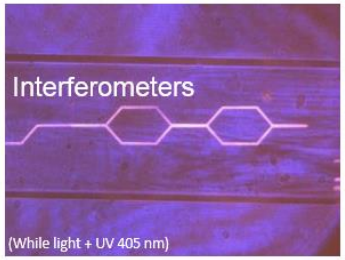


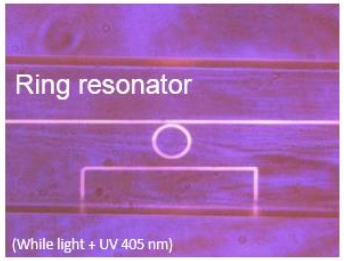
Direct Laser Writing











Local inscription of nano-features (Ag_m^{x+} clusters) with luminescence and/or non-linear optical properties

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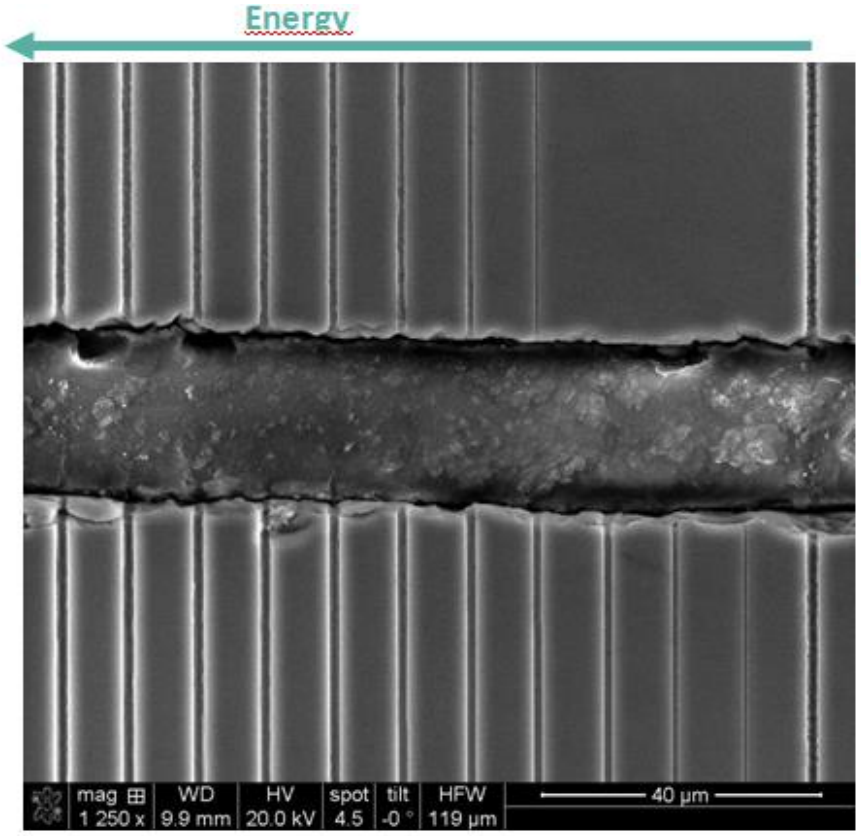
DLW:
Gallium Phosphate glass
20% Ga_2O_3 – 80% $NaPO_3$

COPL, Univ. Laval

GPN

Laser (Spitfire)
λ=800 nm;
τ=40 fs;
f=1kHz.

GPN
+ 3% $AgO_{1/2}$



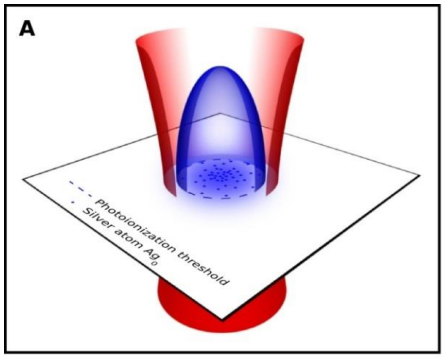
Scanning
Speed
= 10 µm/s

Laser propagation

Laser displacement

Laser polarization

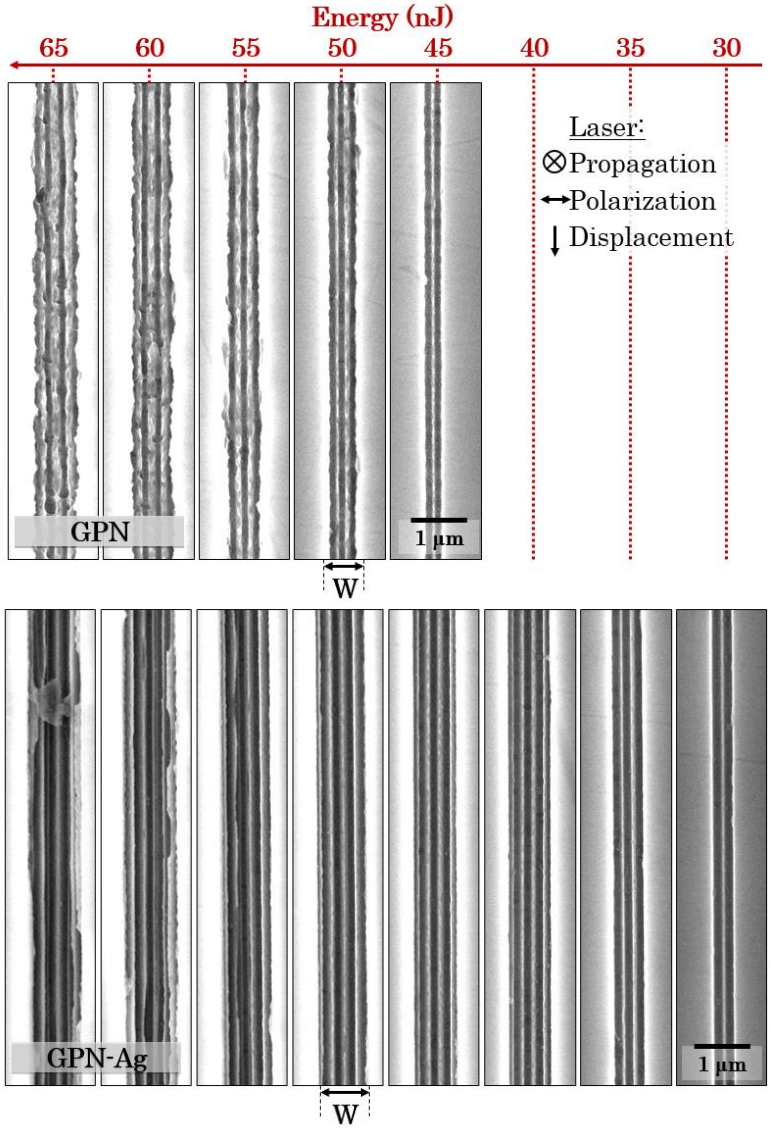
Silver lowers the threshold



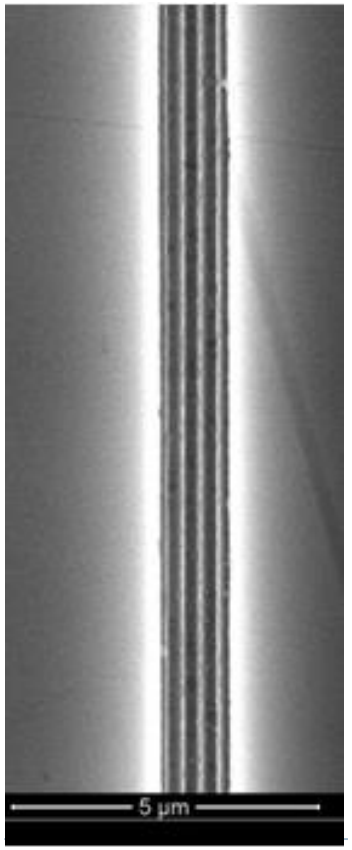
P. Hee, Journal of Materials Chemistry, 2, 37, p7906, 2014
M. Vangheluwe, Optics Letters, 19, p 5491-5494, 2014

DLW:
Gallium Phosphate glass
20% Ga_2O_3 – 80% $NaPO_3$

COPL, Univ. Laval



Silver



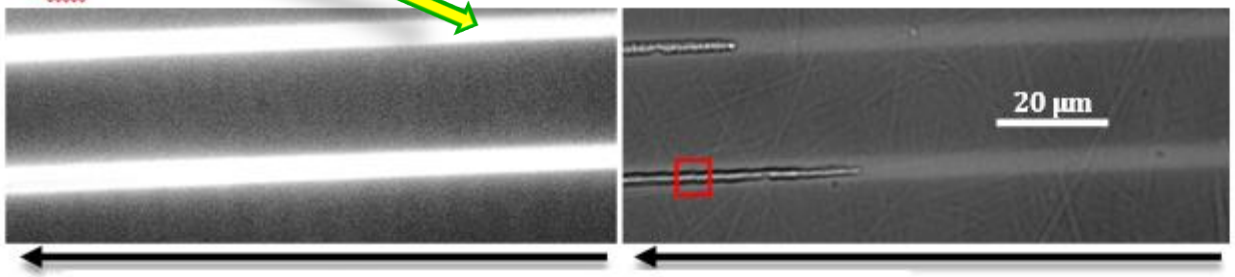
DLW:
Gallium Phosphate glass
20% Ga_2O_3 – 80% $NaPO_3$

GPN-Ag

COPL, Univ. Laval

Luminescence
λ_{exc} = 483 nm

Luminescence
+ white light microscopy



Laser:

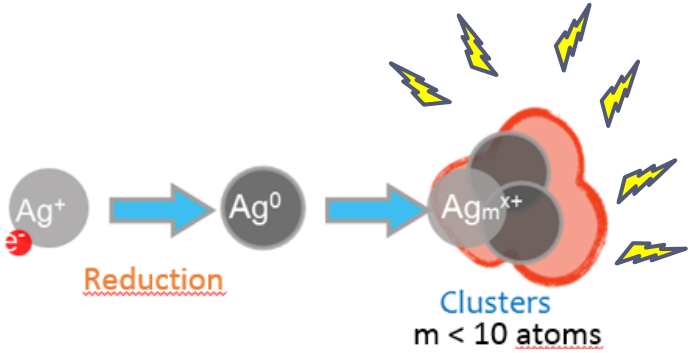
⊗ Propagation

↕ Polarization

↓ Displacement

Sample motion speed = 10µm/s

Pulse energy = 113 nJ



E_{th} > Threshold energy for formation of silver cluster

The silver play a role in the electron and hole generation and trapping processes

Nano-gratings quality improvement with silver

COPL, Univ. Laval

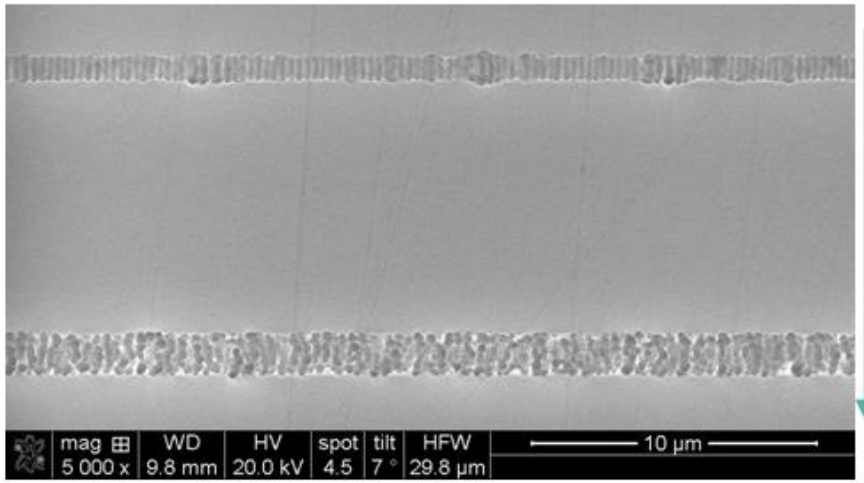
GPN

Laser propagation

Laser displacement

Laser polarization

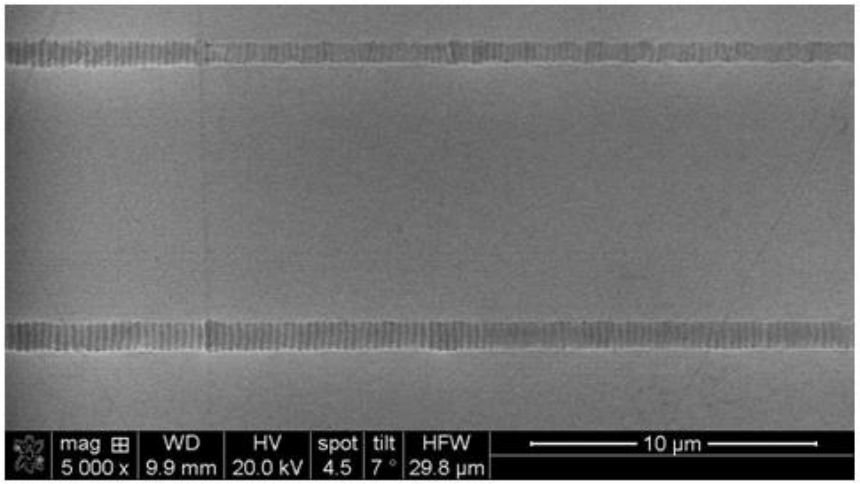
GPN
+ 3% $AgO_{1/2}$



80 nJ

Scanning speed= 80 µm/s

90 nJ



65 nJ

70 nJ

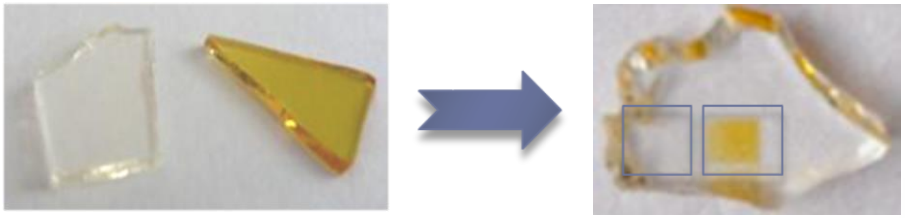
Finest structure in silver containing glass

The presence of silver lowers the threshold for free electron generation

Better nano gratings quality

COPL, Univ. Laval

Verres d'oxydes lourds



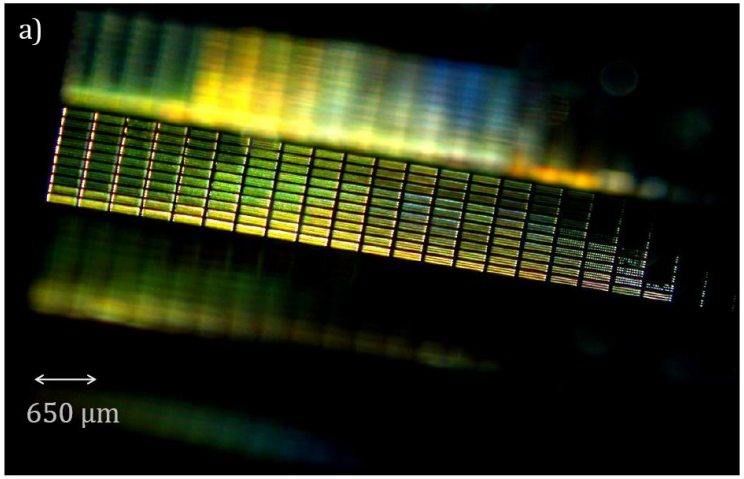
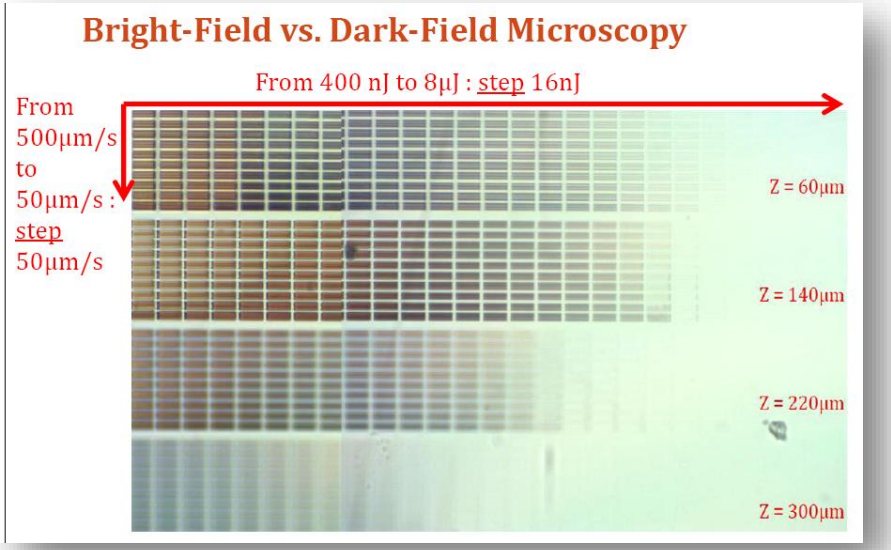


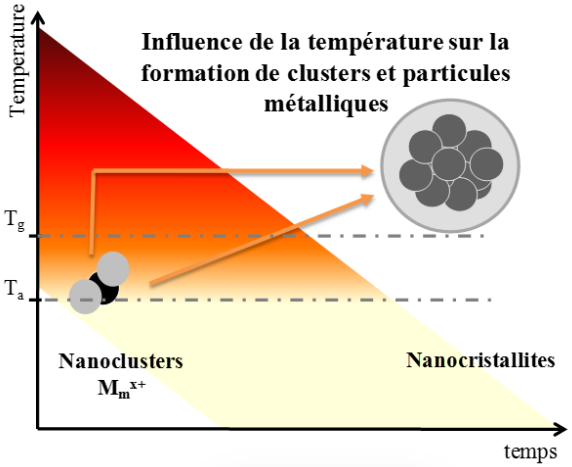
Fig 3. Darkfield images of irradiated zones
a) 10x b) 40x - imaging of lines irradiated @ z=220 µm

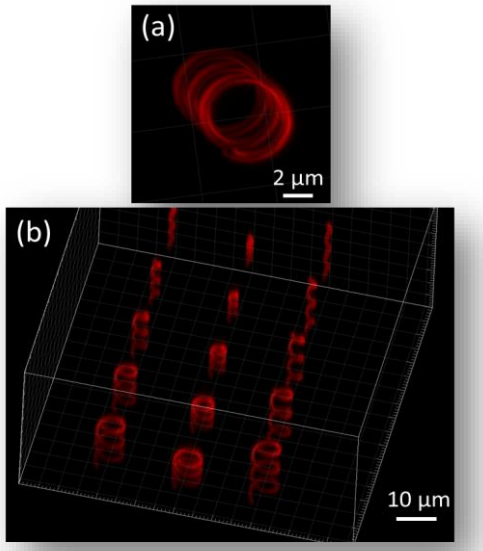


Conclusion

Verres photosensibles

- Photochimie et oxydo-réduction
- Processus de diffusion, effet des alcalins
- Structuration et impression Laser
  - ✓ Formation de clusters Ag_m^{x+}
  - ✓ Luminescence
  - ✓ Propriétés optiques Non Linéaires
  - ✓ Formation localisée de particules métalliques





Remerciements

F. Désévédavy, F. Smektala
ICB, Université de Bourgogne, Dijon, France

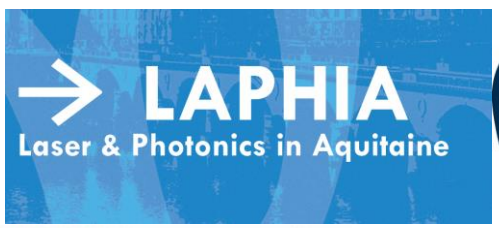
E. Brasselet
LOMA, Université Bordeaux, France

K. Richardson, M. Richardson
CREOL, University of Central Florida, USA.

V. Rodriguez, D. Talaga
I.S.M., Université Bordeaux.

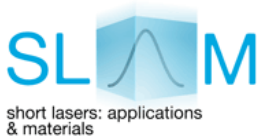
A. Piarristeguy, A. Pradel
ICGM, Université Montpellier, Montpellier, France

Merci pour votre attention



Thierry Cardinal Group; E. Fargin, J.-C. Desmoulin, P. Hée, S. Thomas, A. Corcoran,

A. Fargues, S. Danto, B. Glorieux, A. Garcia, V. Jubera



Lionel Canioni group: **K. Mishchik**, N. Marquestaut, M. Vangheluwe, E.-J. Lee, S. Gouin,
A. Abou Khalil, N. Varkentina, J. Lopez, I. Manek-Hönninger, B. Bousquet & P. Mounaix

LAPHIA Collaborative project « PROMACH »

Vincent Rodriguez group: M. Dussauze, F. Adamietz, F. Talaga & F. Bondu

LAPHIA Risky project « MOBILE »

Etienne Brasselet & H. Magallanes

Guillaume Duchateau, B. Chimier & Y. Smetanina

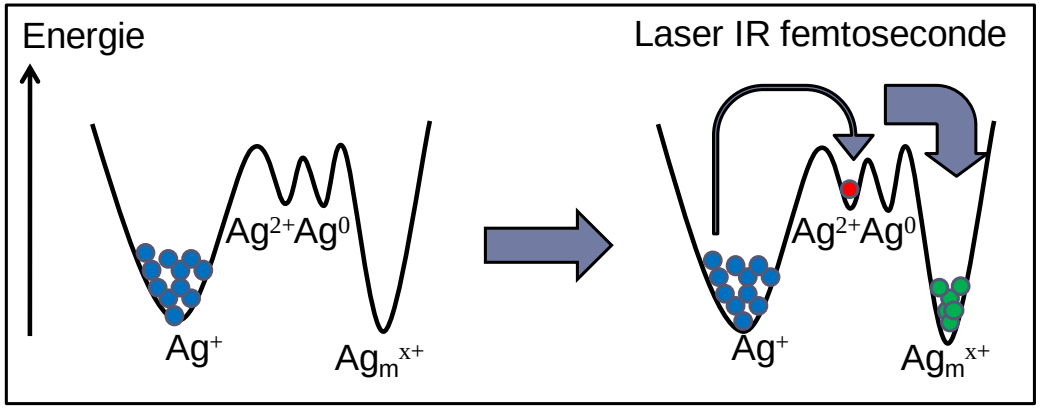
d Royon, K. Bourhis & G. Papon

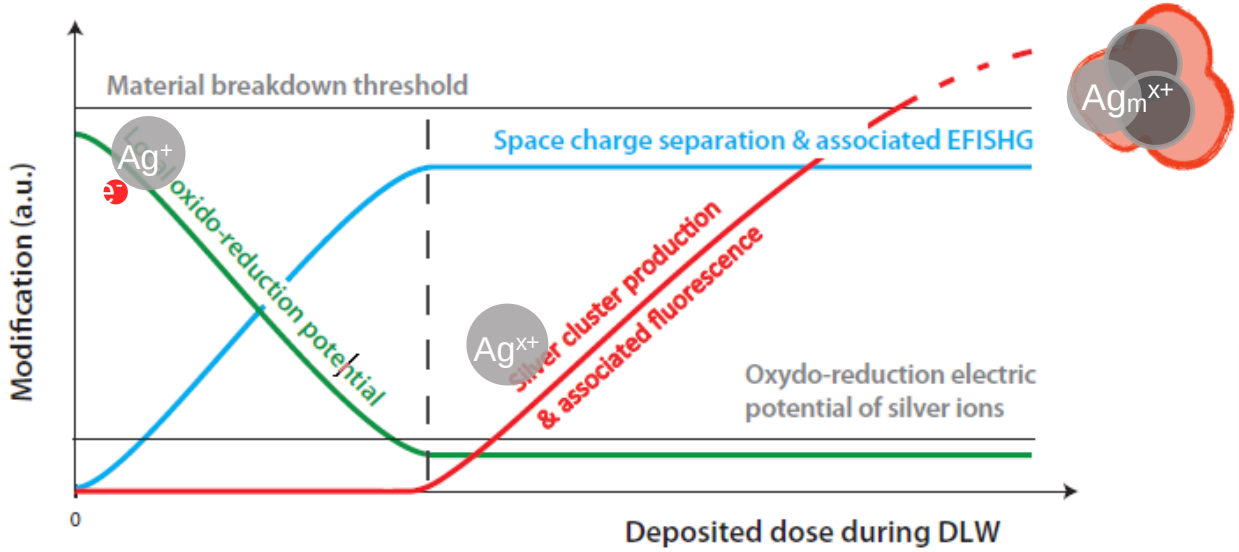
→ *LAPHIA Risky project « STEDn'STRUCT » (2013)*

Prof. Réal Vallée & L. Fen,
Prof. Y. Messaddeq & Y. Ledemi

Many thanks to colleagues, agencies & for your attention

SHG and Luminescence





Photoreduction & aggregation