Femtosecond laser 3D micro-structuration in silica-based glasses

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Advanced Materials for Photonics

Femtosecond laser 3D processing in silica

Part 1

Motivations

Fs laser processing in silica-based glasses
Motivations

Why silica glass ?

Owing to both excellent physical and chemical properties such as:

- Optical transparency over a wide range of wavelengths (UV-NIR)
- Stable properties over time and at high temperature
- High damage threshold

Silica-based (SiO_2) glasses prove to be key materials of today's rapidly expanding photonics application areas such as:

- Electronics
- Sensor technologies
- Optical communications (optical fibers)
- Material processing (e.g. Fiber Bragg Gratings, optics)

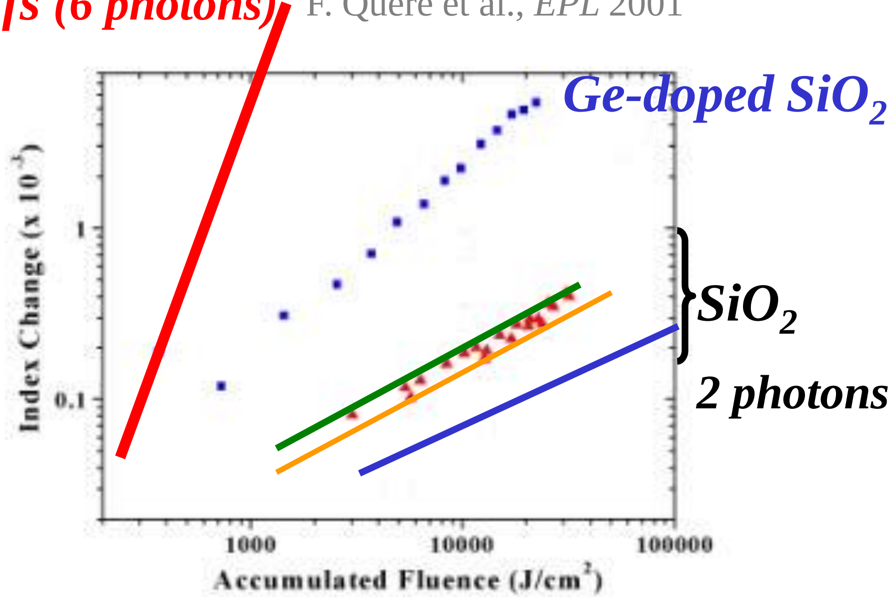
e.g. Over the last 20 years UV-induced Δn profiling in SiO_2 based glasses was widely used for production of in-fibre/waveguide Bragg grating-based (BG) devices…

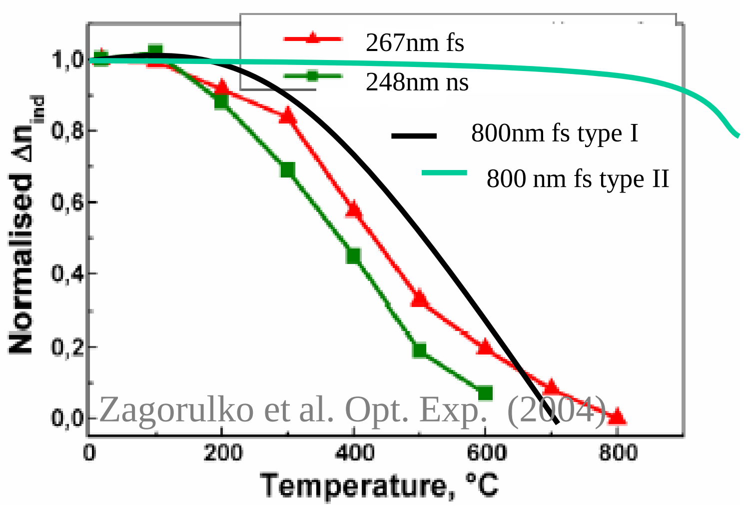
Strong index changes & high thermal stability

Pure silica glasses exhibit poor photosensitivity to UV-laser light !!!

Whereas using IR-fs laser ….. Δn up to 2.2 10^{-2} Eaton et al. JNCS. 2010

IR-fs (6 photons) F. Quéré et al., *EPL* 2001





UV: Similar stability from ns to fs

But IR-fs type II are more stable !

Bricchi et al. APL 2006

ns-193nm: Δn ≈ 3 10^{-4} for 140 kJ/cm²

Albert et al. Opt. Lett. 2001

ns-157-nm : Δn ≈ 4 10^{-4} for 30 kJ/cm² Herman et al. Riken Rev. 2001

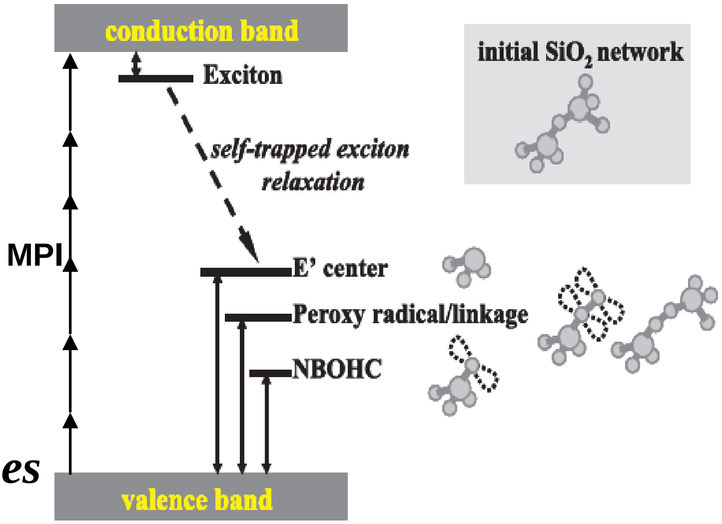
ps-213nm or fs-264nm; Δn = 4 10^{-4} Pissadakis et al. Opt. Exp 2005

Fs laser processing in silica-based glasses
Motivations

Exposing SiO_2 to pulsed (≈50-500 fs) laser → power densities (≈1-100TW/cm²)

Investigation of ***multiphoton reaction-induced*** in glasses that do not linearly absorb efficiently at the laser wavelength

Various permanent changes in macroscopic physical properties such as: ***ablation, 3D photo-structural changes and refractive index changes (i.e. Photosensitivity)***



Mao et al. Appl. Phys. A 79 (2004)

F. Quéré et al., EPL (2001)

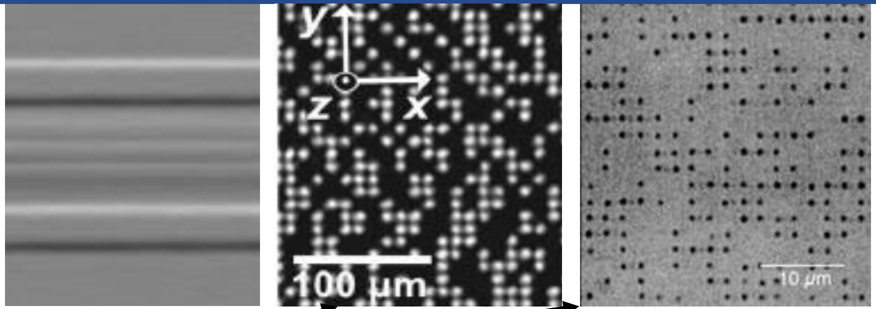
P. Martin et al., PRB 55 (1997)

Today talk about permanent changes !

But we are strongly interested by transient processes e.g. photo-ionization processes, plasma density, STE, thermal effects… since they are at the roots of the permanent structural changes

Fs laser processing in silica-based glasses
Various “properties” can be taylor…

3D localization !!! Due to NL-effects and ultrashort pulse duration



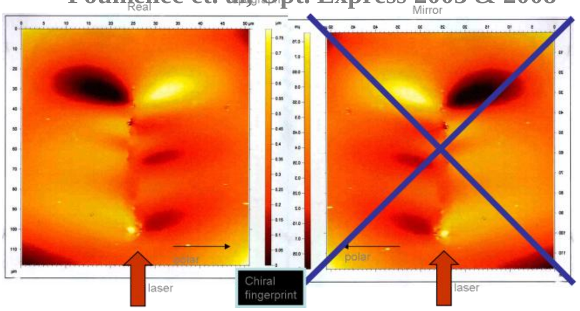
Main optical properties:

- Refractive index (isotropic, anisotropic, voids)
- Absorption (e.g. linear and circular dichroism especially in the VUV-UV)
- Non-linear optical properties (metallic nanoparticules, nano/micro-crystals)

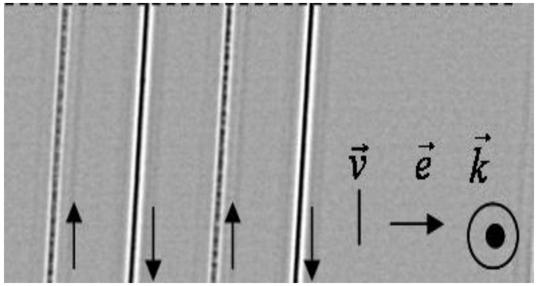
Hence, this renders fs-processing attractive for material laser 3D processing !!!

“Amazing” structures: chiral mechanical structures,orientational dependent writing, “self-organized” nanogratings

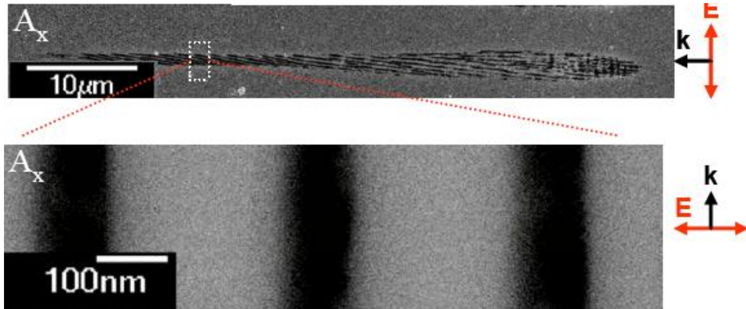
Poumellec et. al, Opt. Express 2003 & 2008



Kazansky et al. APL 2006



Shimotsuma et al. Phys. Rev. L 91 (2003)
Kazansky, et al. Appl. Phys. Lett. 90 (2007) 151120.



Femtosecond laser 3D processing in silica-based glasses

Part 2

Results

Fs laser processing in silica-based glasses
The 3D writing process

Typical irradiation parameters in amorphous SiO_2

λ = 400-1500nm (typ. 800 ou 1030),
Pulse duration typ. 100-300 fs

i.e. the electronic photo-excitation is finished before the transfer to the lattice (temperature increase)

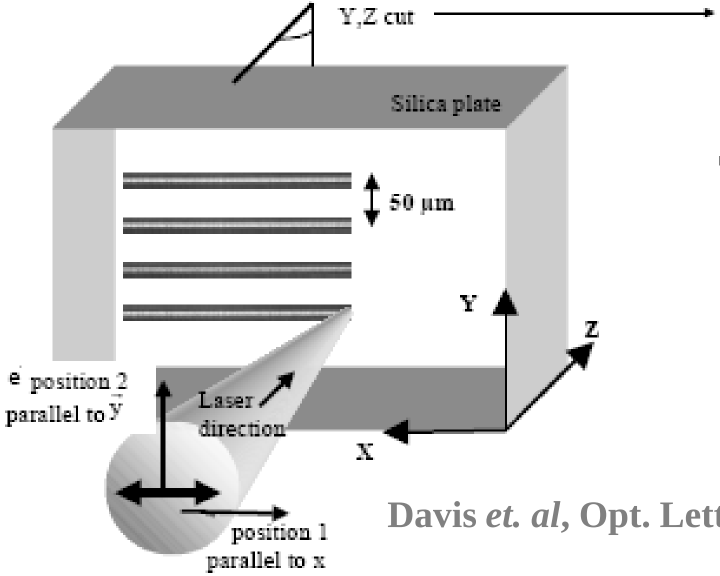
Pulse energy: 0.01-2 µJ
(10^{12-14}W/cm^2)

i.e. energy deposited by 1 pulse in the focal volume ≅ formation energy of the silica oxyde glass

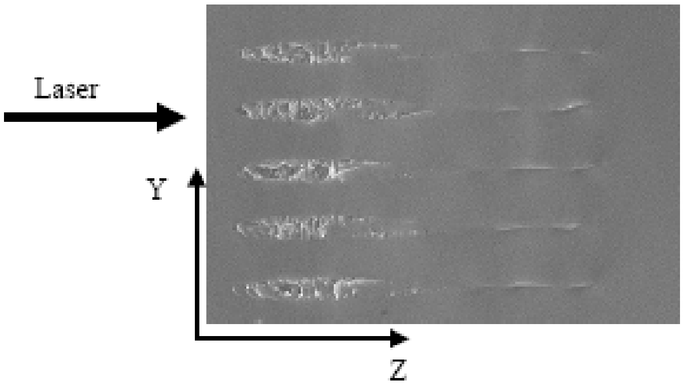
“Tight” focusing in volume NA = 0.1-1.4 (typ. 0.5) i.e. waist ≅ 1.5 µm

Repetition rate: up to 80MHz (typ. 100’s kHz)

Heat diffusion in silica = 1µs i.e. no accumulation below 1MHz



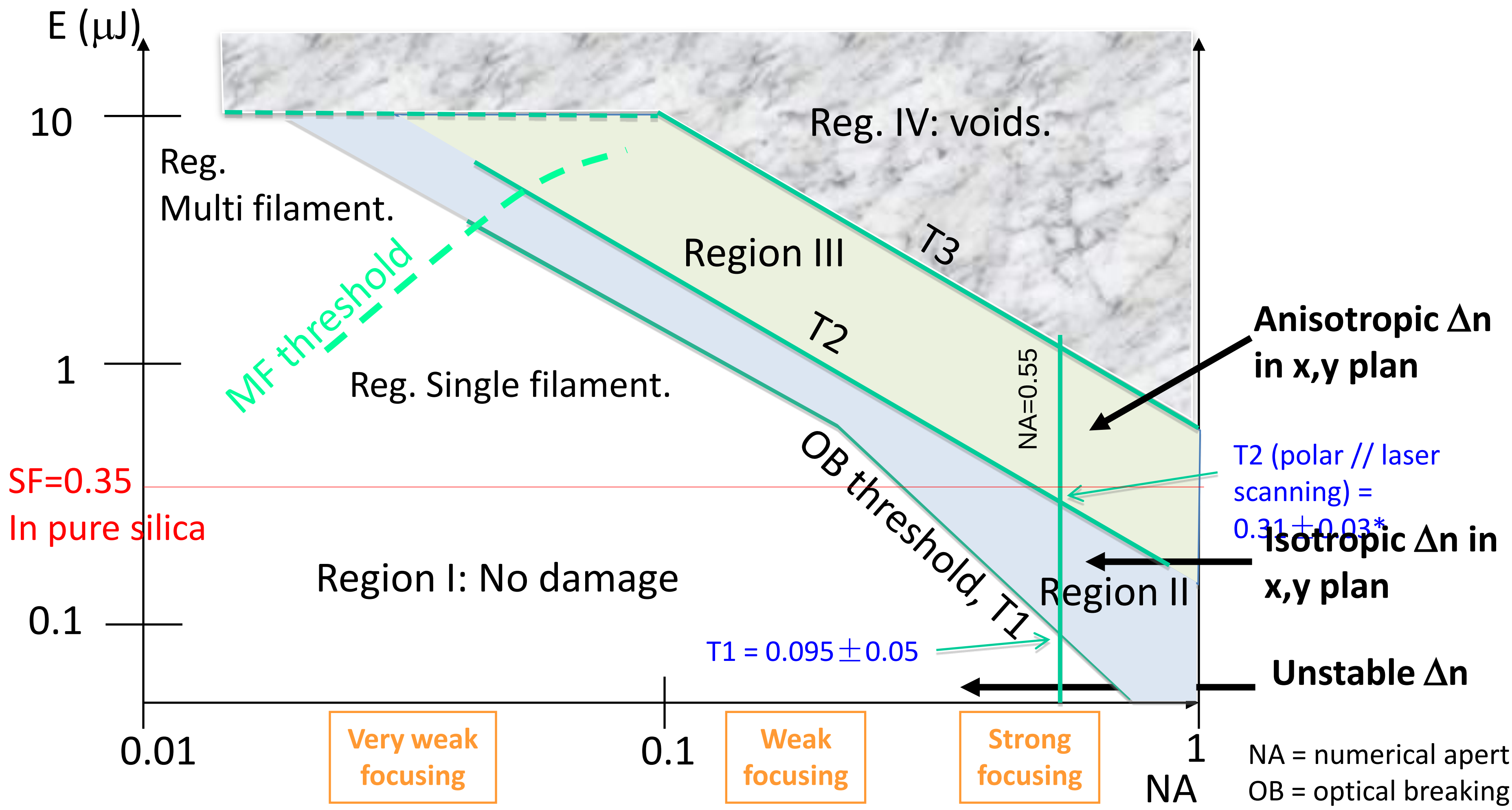
Cross-section



Davis *et. al*, Opt. Lett., 21, 1729 (1996)

Fs laser processing in silica-based glasses
Various processing windows…

*SiO_2, 800 nm, **160 fs,** 100 kHz, 100 μm/s, conf //*



Anisotropic Δn in x,y plan

T2 (polar // laser scanning) = 0.31±0.03*

Isotropic Δn in x,y plan

T1 = 0.095±0.05

Unstable Δn

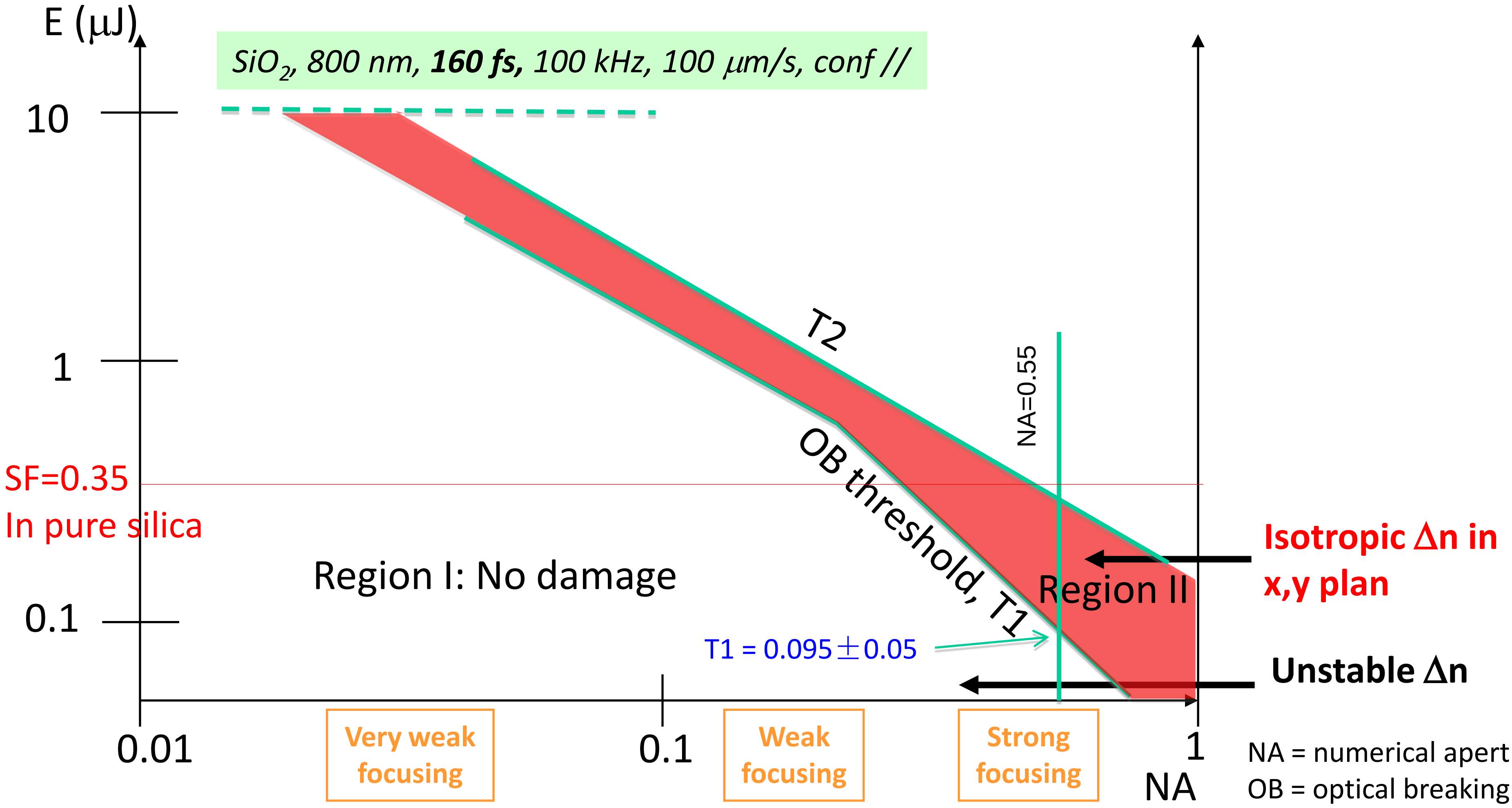
NA = numerical aperture
OB = optical breaking
SF = self focusing
T1,T2,T3 = thresholds

Poumellec et al. BGPP conf (2010)

*T2 (polar perpendicular to laser scanning = 0.17±0.05

Fs laser processing in silica-based glasses
Region II i.e. above T1 and below T2

The first energy threshold (T1) is the minimum energy requested for observing a change in the material (it depends slightly on the number of pulses).


*SiO_2, 800 nm, **160 fs,** 100 kHz, 100 µm/s, conf //*

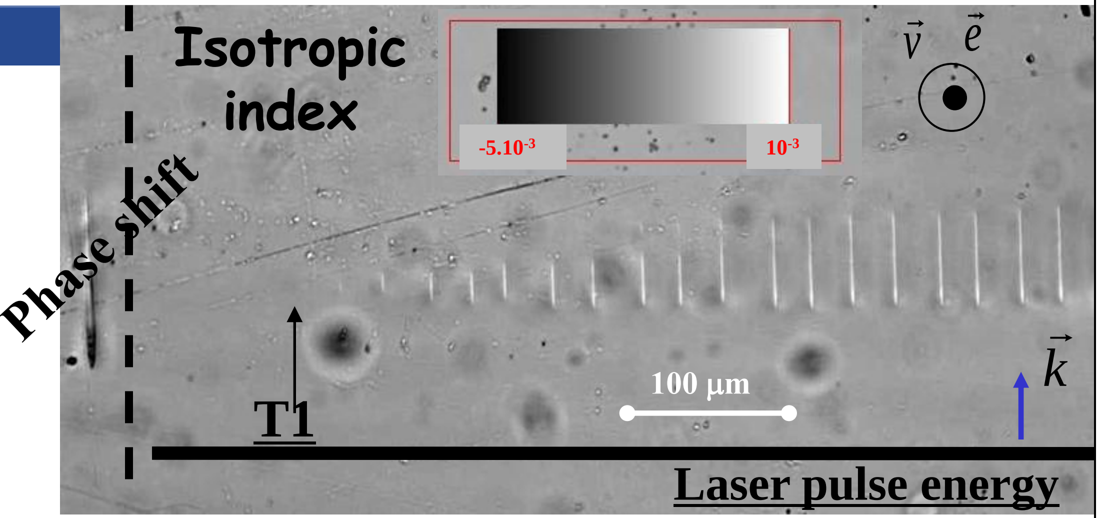
NA = numerical aperture
OB = optical breaking
SF = self focusing
T1,T2,T3 = thresholds

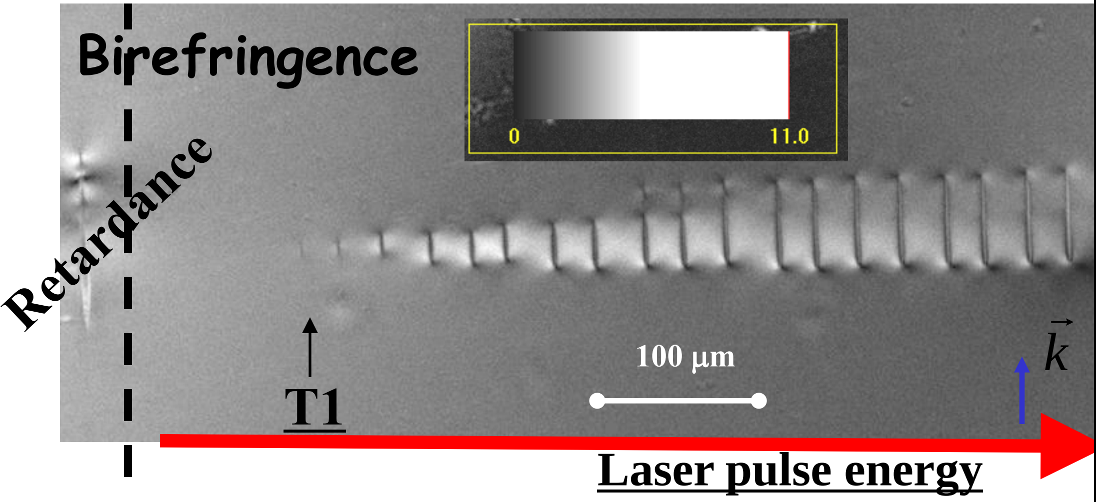
Poumellec et al. OME (2011)

3D localization, “Isotropic” Δn (Type I)

Laser track cross section

SiO_2





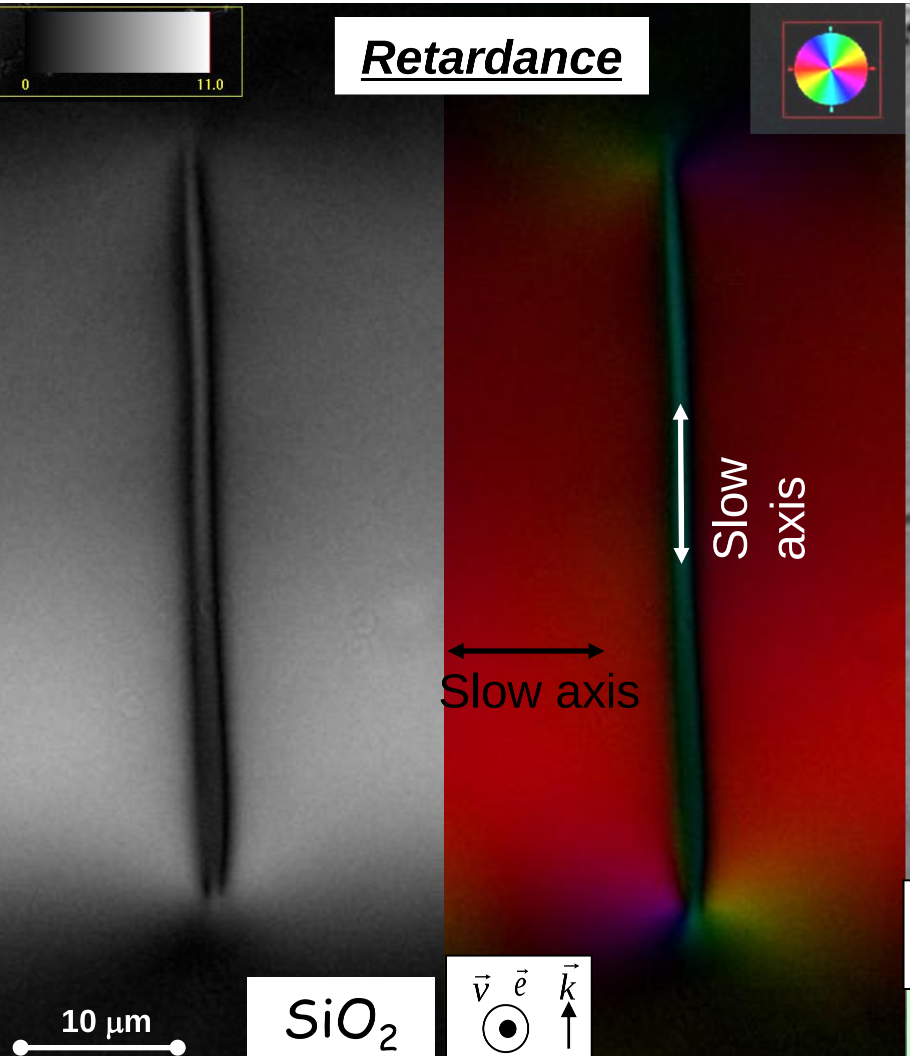
*SiO_2, 800 nm, **160 fs,** 100 kHz, 100 µm/s, 0.05-0.4µJ, conf //*

3D localization, “Isotropic” Δn (Type I)

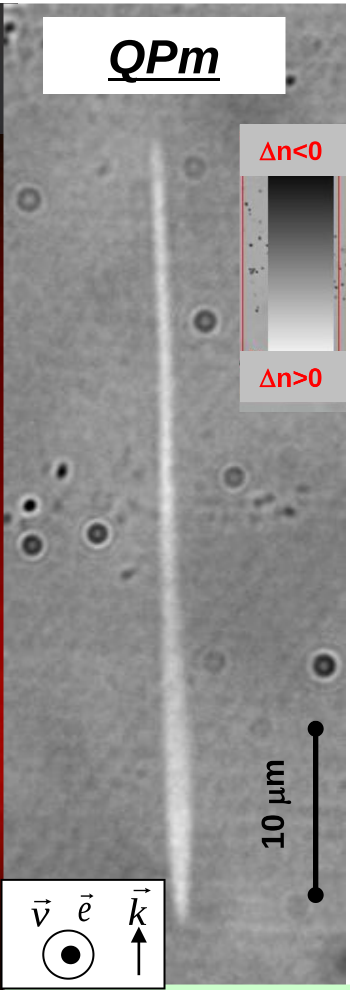
Laser track cross section

Uniform Δn along the laser track i.e. Δn > 0 in the laser tracks (≈ typ. 10^{-3})

Lancry et al. BGPP conf (2010)



SiO_2



Δn origins are similar to UV laser irradiation i.e.

- **Permanent densification**

  Chan et al. Appl. Phys. A 76 (2003) 367

  Hosono et al. NIM PRB 191 (2002) 89

- **Related stress field**

  Erraji-Chahid et al. BGPP conf (2010)

  Poumellec et al. Opt. Express (2008)

- **Defects centers**

  Hosono et al. NIM PRB 191 (2002) 89

  Sun et al. J. Phys. Chem. B 104 (2000) 3450

  Lancry et al. OME (2012, In proof)

*SiO_2, 800 nm, **160 fs,** 100 kHz, 100 µm/s, 0.2 µJ, conf //*

3D localization, “Isotropic” Δn (Type I)

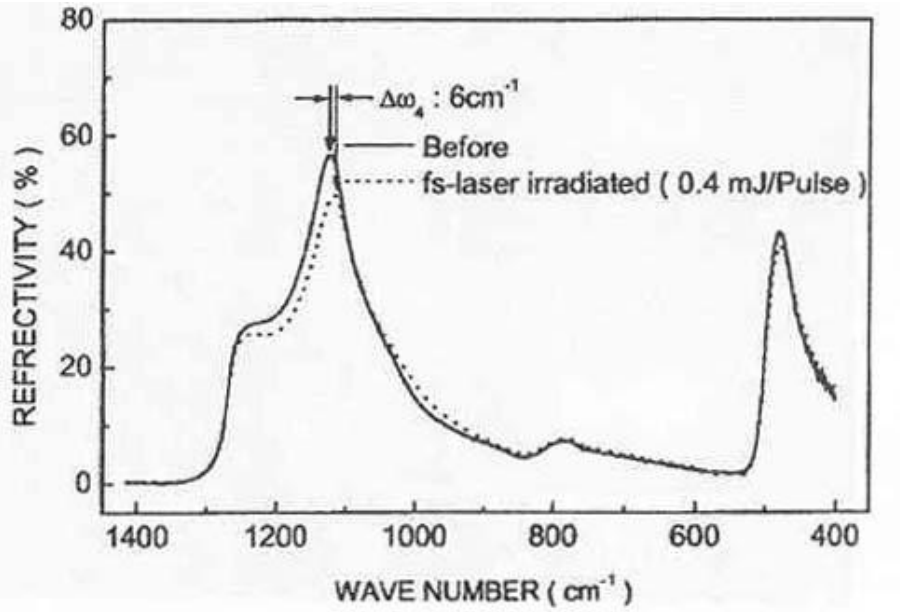
Δn origin: T_f local increases and related specific volume change

Energy « deposition », large increase in local temperature (after a few 10’s ps), thermal diffusion and temperature decreases in a time δt that depends on W and on material properties

If δt is larger than the time required for the glass structure to change (the relaxation time η/G, η(T) the glass viscosity, G(T) the glass shear modulus), the modification is permanent i.e. the average disorder of the glass or the fictive temperature is changed.

$$\boxed{h(T_c)/G(T_c)=dt(T_c)}$$

*SiO_2, 800 nm, **160 fs,** 100 kHz, 100 μm/s, 0.2 μJ, conf //*



Chan et al. Appl. Phys. A 76 (2003) 367

Hosono et al. NIM PRB 191 (2002) 89

T_c is the new fictive temperature

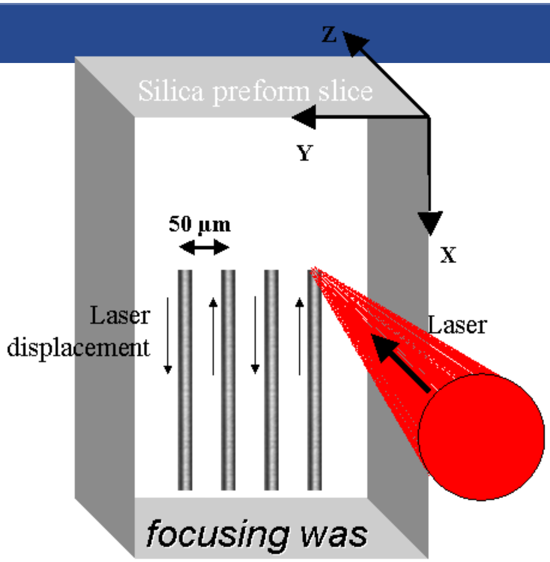
In most glasses, the increase of fictive temperature corresponds to the decrease of density and thus to a decrease of average index. But in silica, it is the reverse (anomalous behaviour)

Waveguide / gratings fabrication

e.g. T_f increases of 500° C leads to $\Delta n=+10^{-3}$ [Bru70, She04]

3D localization, "Isotropic" Δn (Type I)

Δn origin : permanent densification and related stress field



focusing was beneath the surface

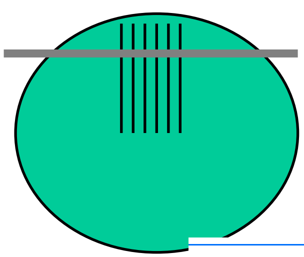
Ti :Sa laser at 800 nm, 160 fs, 0.35-1.5 µJ, 100 kHz, 0.5 NA, Pure silica

- **Related stress field relaxation**

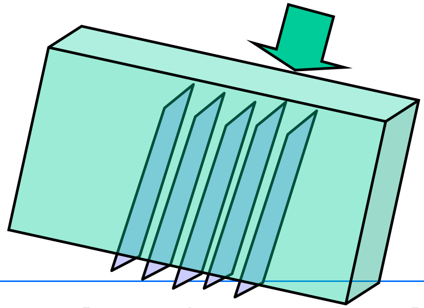
Erraji-Chahid et al. BGPP conf (2010)

Poumellec et al. Opt. Express (2008)

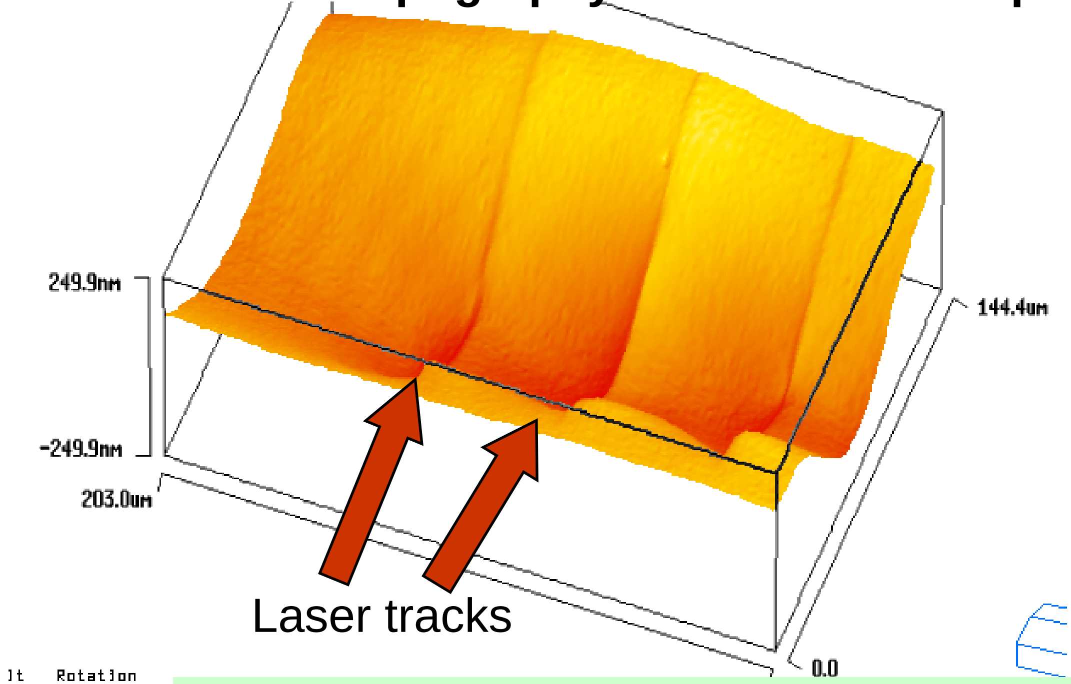
Cut



Phase shift interferometry or AFM



Surface topography of a cleaved sample



*SiO_2, 800 nm, **160 fs**, 100 kHz, 100 µm/s, 0.2 µJ, conf //*

La modélisation des distributions d’indice

On a une variation de volume spécifique localisée i.e. une déformation isotrope libre de contrainte qui engendre un champ de contrainte.

$$r(\vec{r})\ Þ\ e^p(\vec{r})\quad Þ\ s(\vec{r})\quad ou\quad e^e(\vec{r})$$

et une variation d’indice qui provient du champ de contrainte

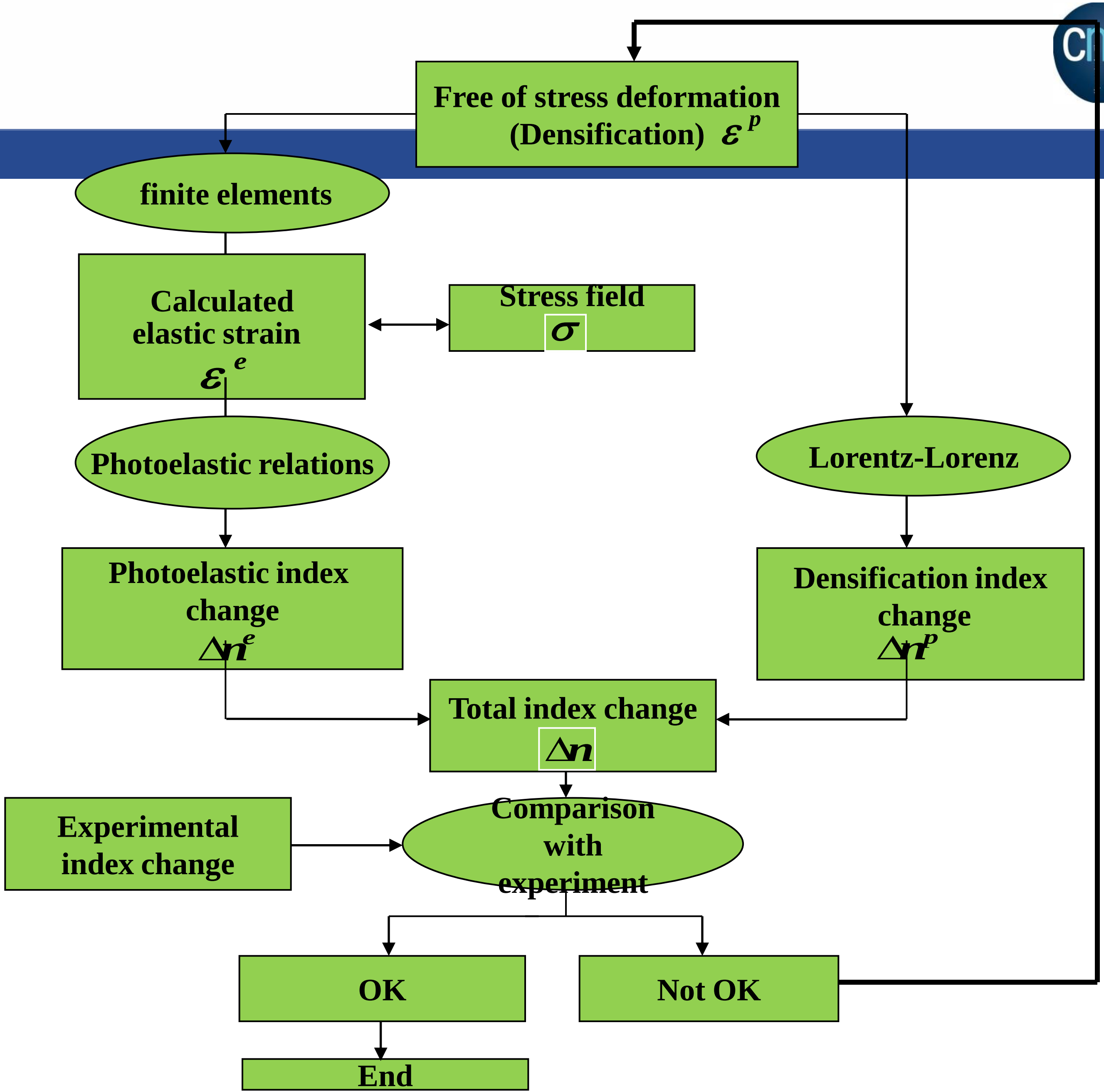
$$Dn_{ii}^p = -\frac{\left(n^2-1\right)\left(n^2+2\right)}{2n}\left(1-W\right)e^p$$

On a une variation de volume spécifique localisée qui engendre une variation d’indice (Lorentz-Lorenz)

$$\begin{cases}
\Delta n_{xx}^e = -\frac{n^3}{2}\left(p_{11}\varepsilon_{xx}^e + p_{12}\varepsilon_{yy}^e + p_{12}\varepsilon_{zz}^e\right) \\
\Delta n_{yy}^e = -\frac{n^3}{2}\left(p_{12}\varepsilon_{xx}^e + p_{11}\varepsilon_{yy}^e + p_{12}\varepsilon_{zz}^e\right) \\
\Delta n_{zz}^e = -\frac{n^3}{2}\left(p_{12}\varepsilon_{xx}^e + p_{12}\varepsilon_{yy}^e + p_{11}\varepsilon_{zz}^e\right) \\
\Delta n_{xy}^e = -\frac{n^3}{2}\left(p_{11} - p_{12}\right)\varepsilon_{xy}^e \\
\Delta n_{yz}^e = -\frac{n^3}{2}\left(p_{11} - p_{12}\right)\varepsilon_{yz}^e \\
\Delta n_{xz}^e = -\frac{n^3}{2}\left(p_{11} - p_{12}\right)\varepsilon_{xz}^e
\end{cases}$$

Pb: calculer le champ de contrainte à partir de la déformation libre de contrainte, mais quel est le bon champ de déformation?

La modélisation des distributions d’indice



Free of stress deformation (Densification) ε^p

finite elements

Calculated elastic strain ε^e

Stress field σ

Photoelastic relations

Lorentz-Lorenz

Photoelastic index change Δn^e

Densification index change Δn^p

Total index change Δn

Experimental index change

Comparison with experiment

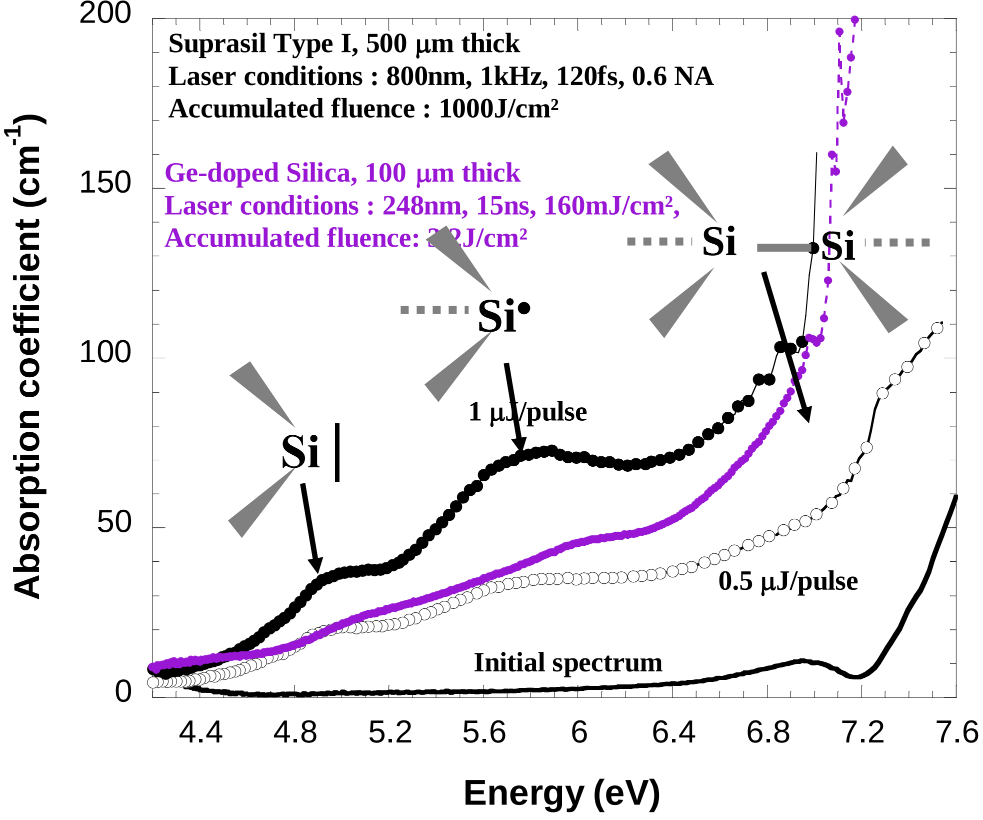
OK

Not OK

End

Defects creation … one of the refractive index changes origin

UV-VUV absorption

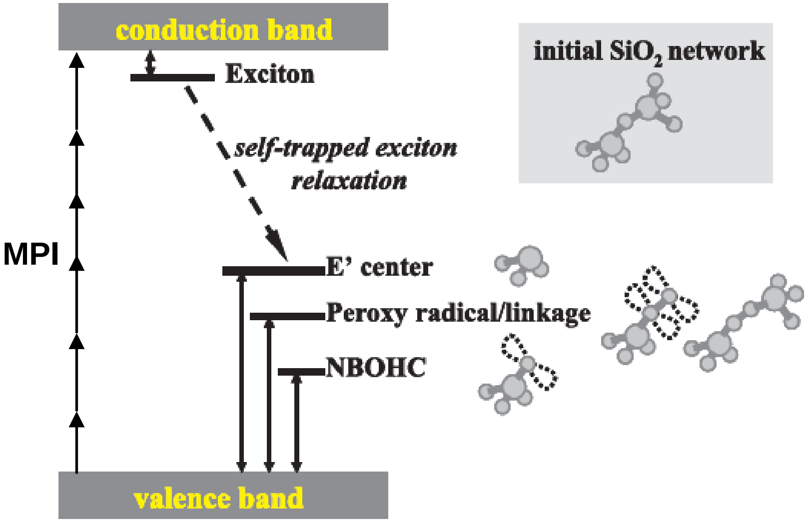


- **Defects centers**

Hosono et al. NIM PRB 191 (2002) 89

Sun et al. J. Phys. Chem. B 104 (2000) 3450

Lancry et al. SiO_2 conf (2010) , Accepted in Optical Material Express (2012)



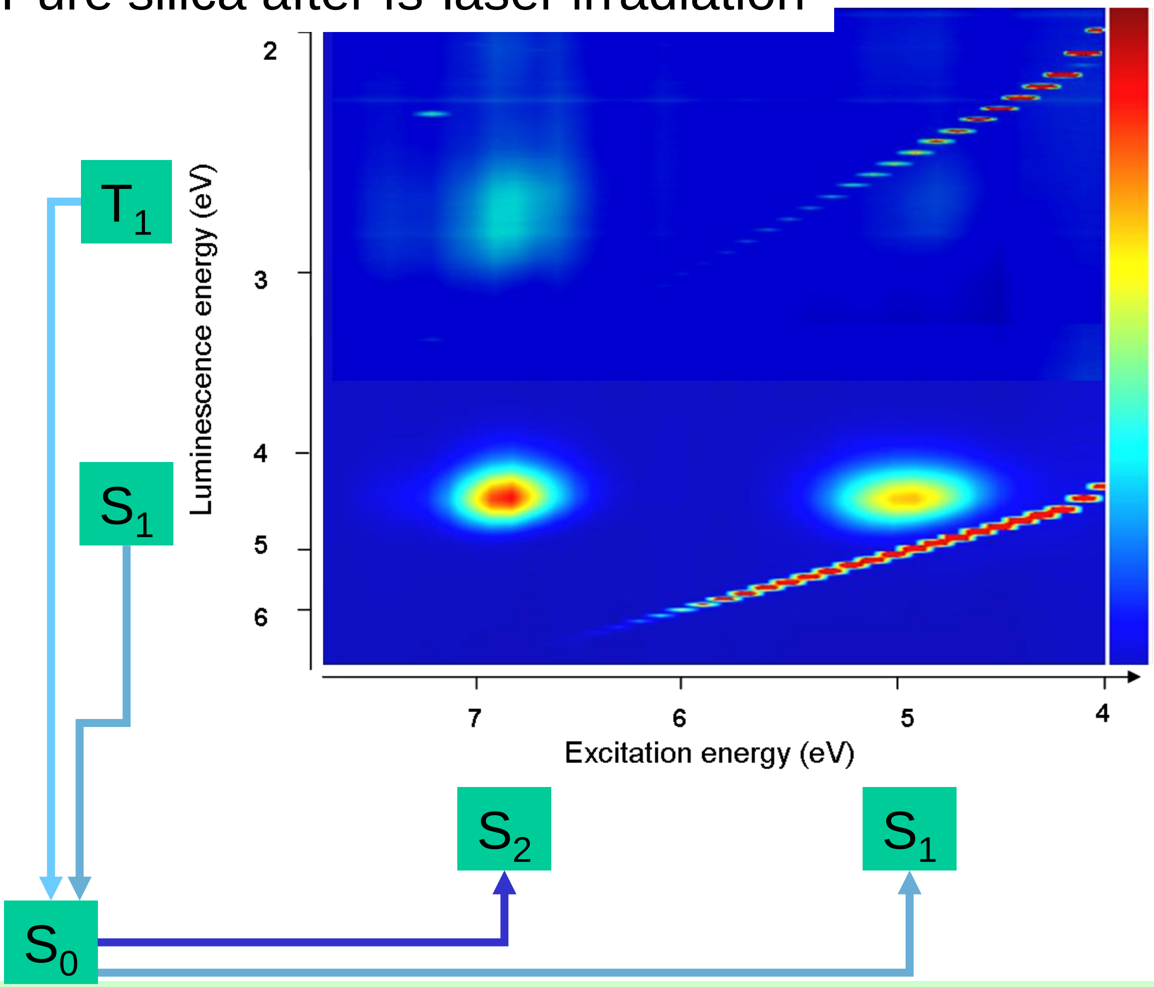
800nm, 1kHz, 120fs, 0.6NA, 0.5 and 1μJ/pulse, 10μm/s, linear polarization

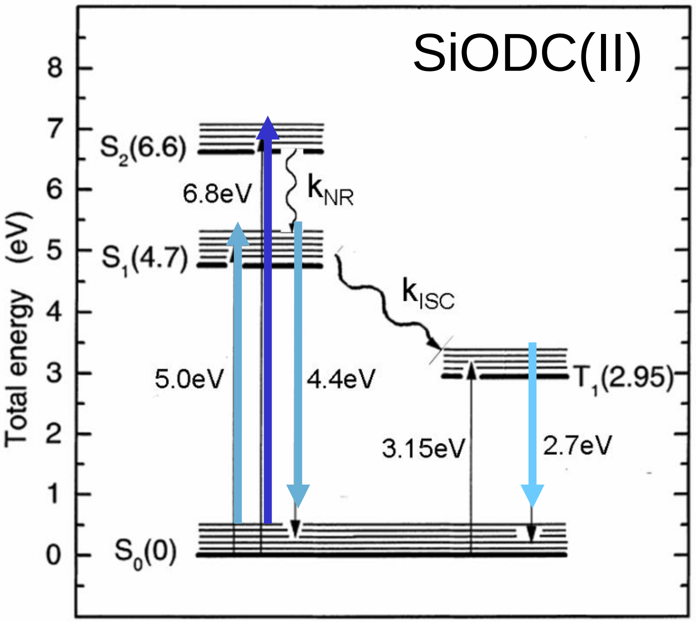
Lancry et al. OME (2012, in Proof)

Defects creation … one of the refractive index changes origin

UV-VUV excitation spectroscopy

Pure silica after fs-laser irradiation





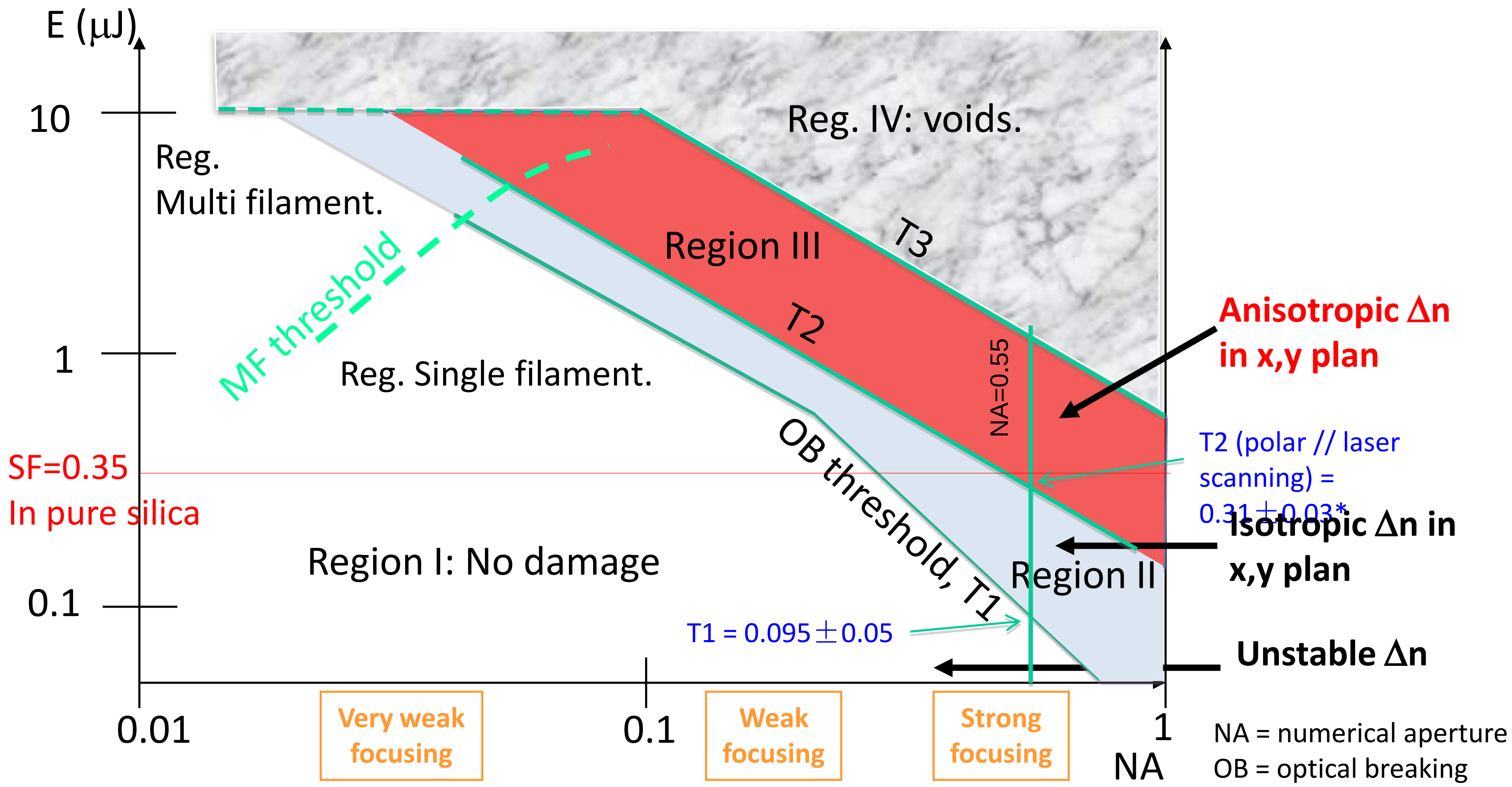
Optical transition scheme in Si-related oxygen deficient center SiODC(II). After L.Skuja, JNCS 239, (1998), 16-48.

800nm, 1kHz, 120fs, 0.6NA, 0.5µJ/pulse, 10µm/s, linear polarization

Lancry et al. OME (2012, in Proof)
Poumellec et al. SUM (2011)

Fs laser processing in silica-based glasses
Region III i.e. above T2

SiO_2, *800 nm, **160 fs,** 100 kHz, 100 μm/s, conf //*



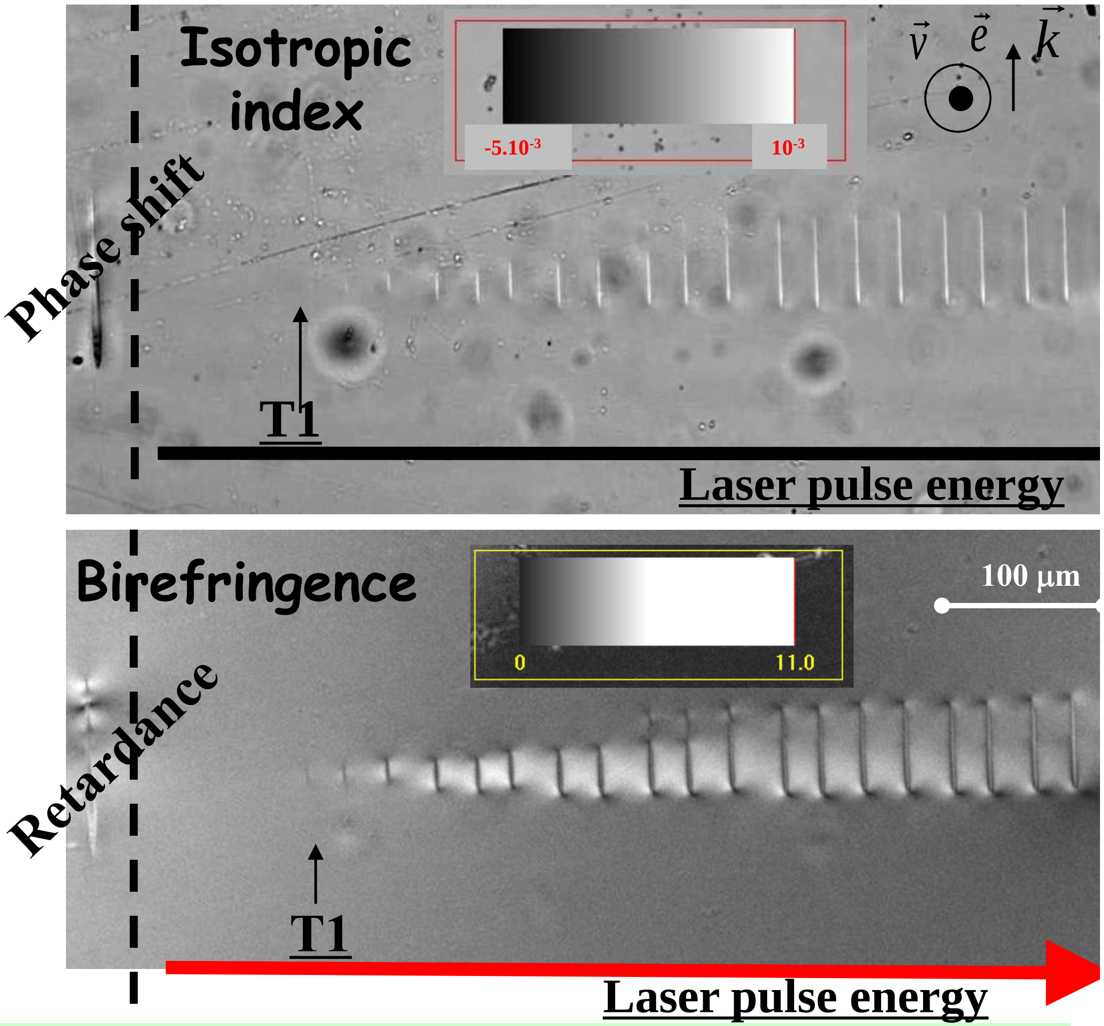
NA = numerical aperture
OB = optical breaking
SF = self focusing
T1,T2,T3 = thresholds

Poumellec et al. BGPP conf (2010)

*T2 (polar perpendicular to laser scanning = 0.17±0.05

Strong Birefringence and negative index change (Type II)

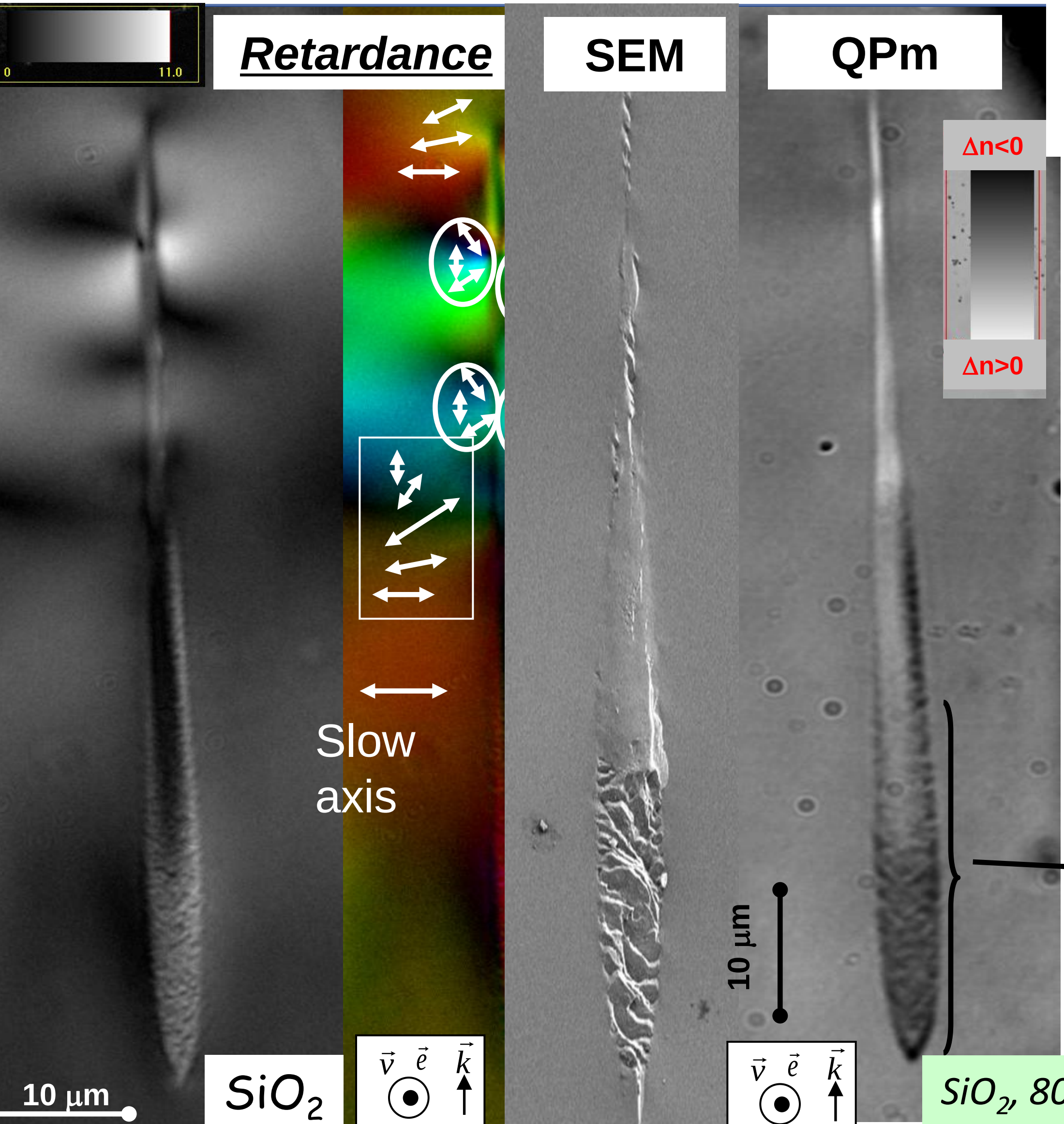
Laser track cross section



*SiO_2, 800 nm, **160 fs,** 100 kHz, 100 µm/s, 0.05-1.2µJ, conf //*

Strong Birefringence and negative index change (Type II)

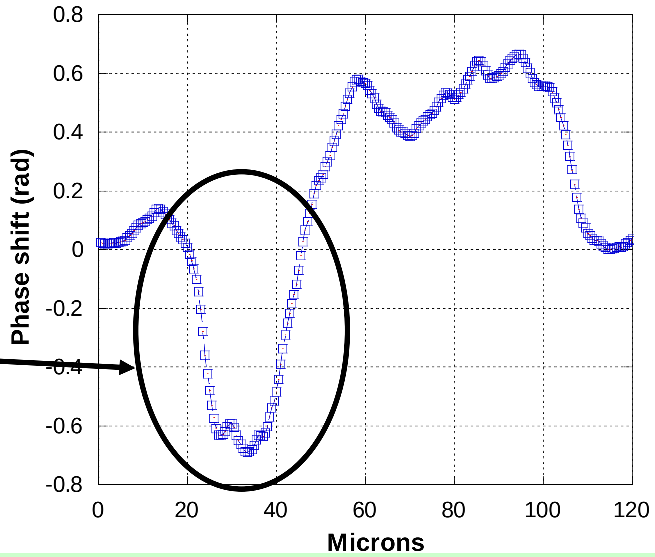
Laser track cross section



Strong birefringence (up to 1.2 10^{-2} or 250 ± 3 nm retardance in one layer)
+ "residual" stress birefringence

Lancry et al. AIOM conf (2009)

Non-uniform Δn :
–Δn < 0 (≈ - 5.10^{-3}) in the head
- Δn > 0 in the tail (**up to $2.2.10^{-2}$**)

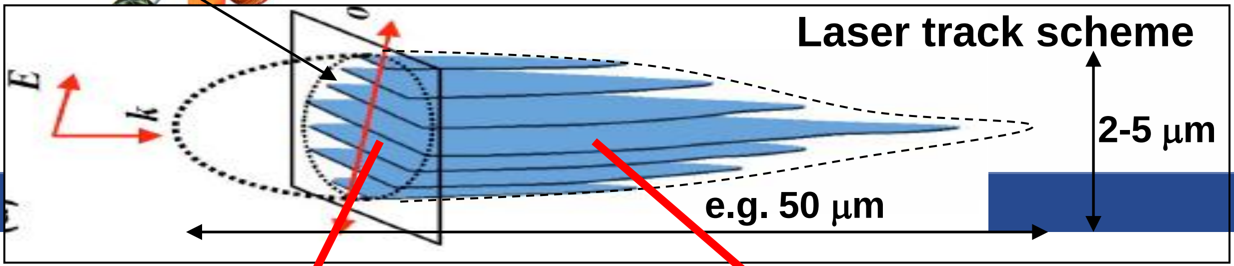


*SiO$_2$, 800 nm, **160 fs,** 100 kHz, 100 µm/s, 1 µJ, conf //*

Birefringence and negative index changes origin

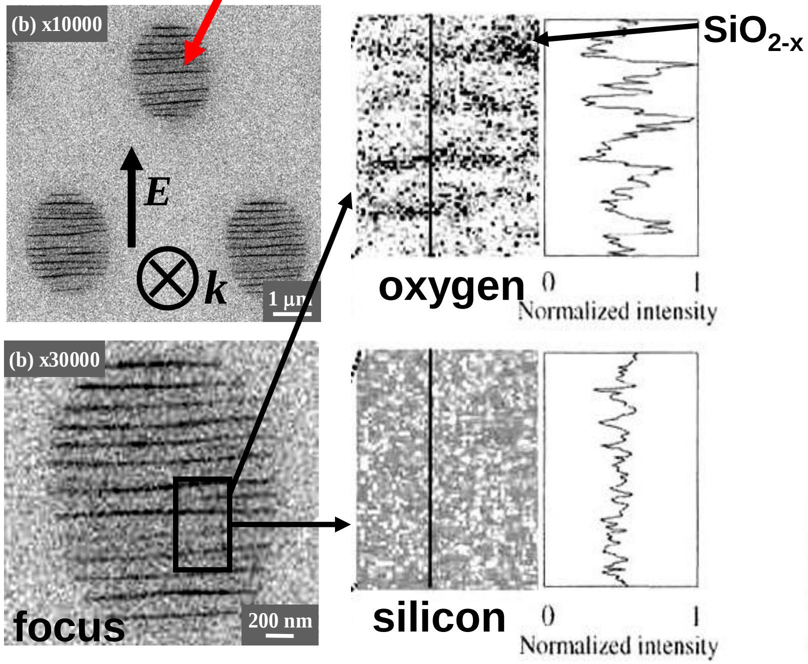
Λ ~ 300nm

Laser track scheme



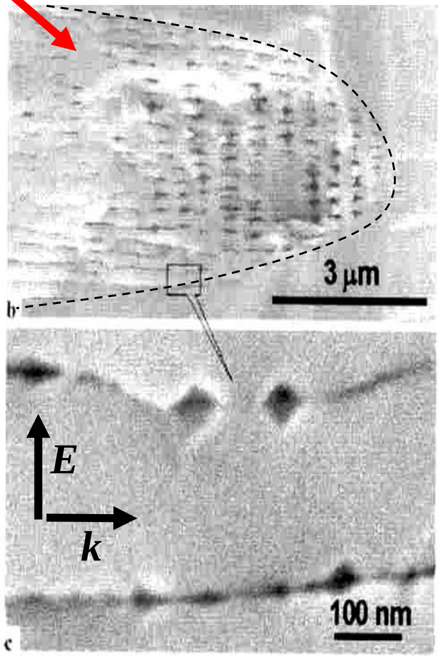
Nanogratings at the roots of form birefringence

Backscattered e⁻ | **Auger photoemission** | **Cut, polish, SEM** | **HF Etching, SEM**

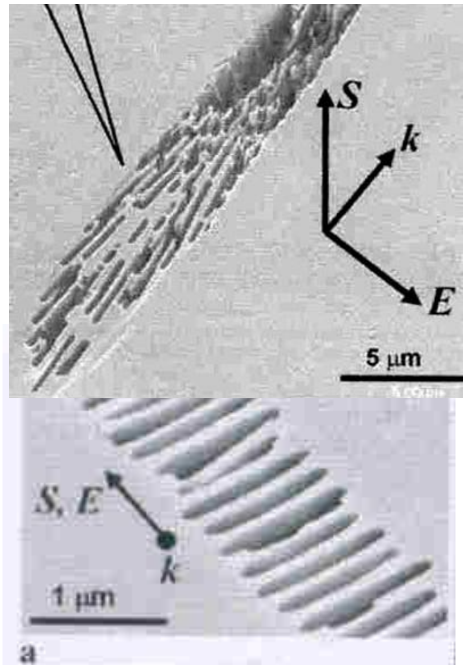


Shimotsuma et al. Phys. Rev. B 91 (2003)

800nm, 150fs, 1-3 μJ/pulse, 200 kHz, NA=0.95



Hnatovsky Appl. Phys. Lett. 87 (2005)



Hnatovsky Appl. Phys. A 84 (2006)

800nm, 150fs, 0.3 μJ/pulse, 100 kHz, NA=0.65

Oxygen segregation ?

Nanocracks ?

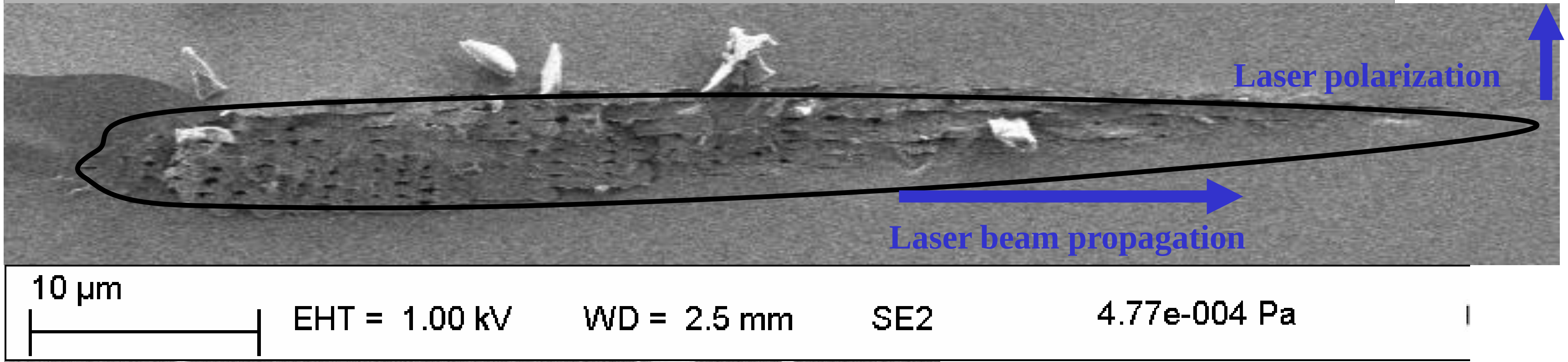
weakening of the structure

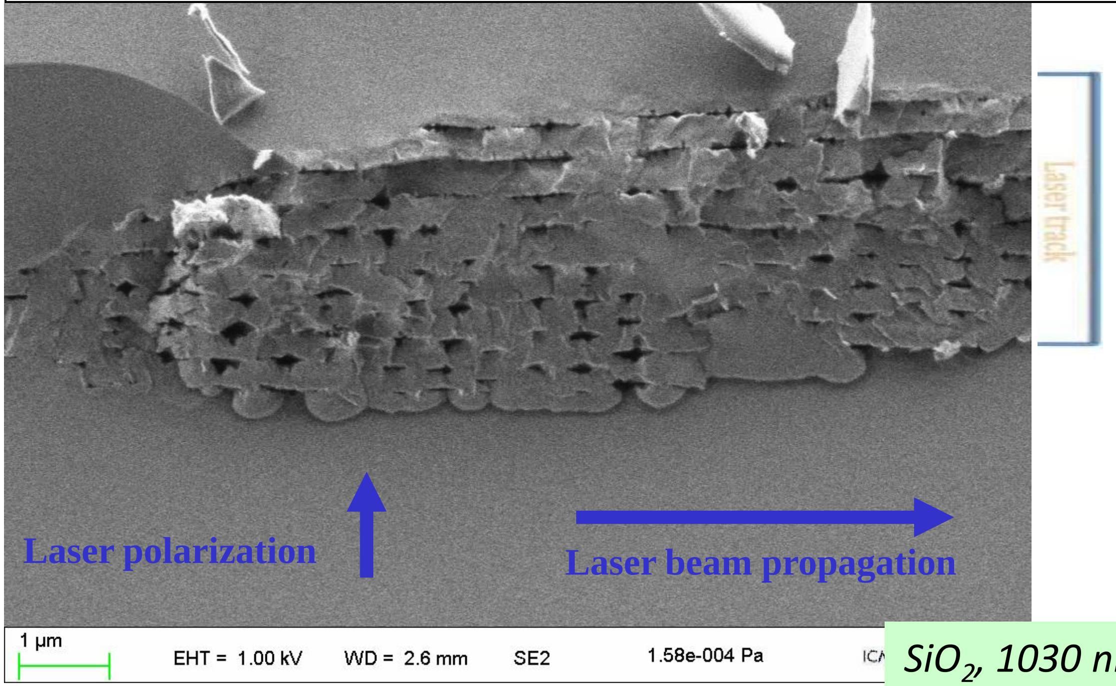
So what is the intimate structure of these nanoplans and how to probe it ?

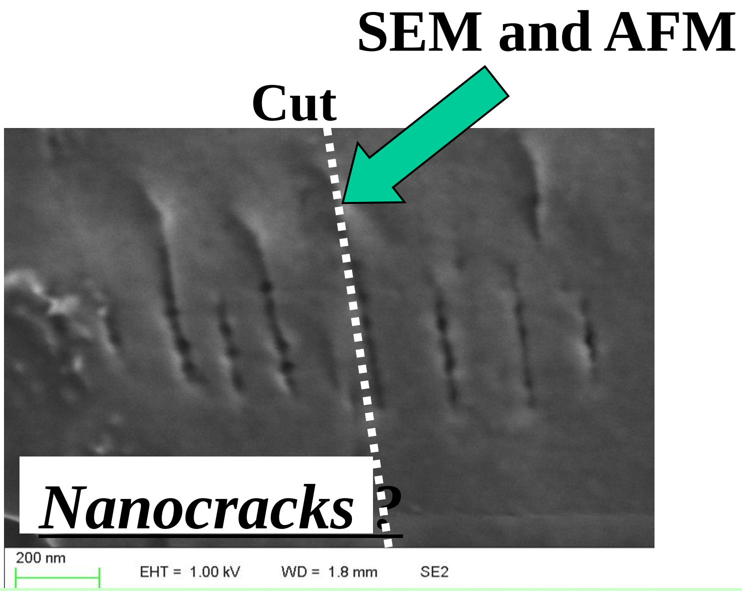
Birefringence and negative index changes origin

polarisation perpendicular to the scanning direction

SEM images of a whole laser track written in perpendicular configuration.





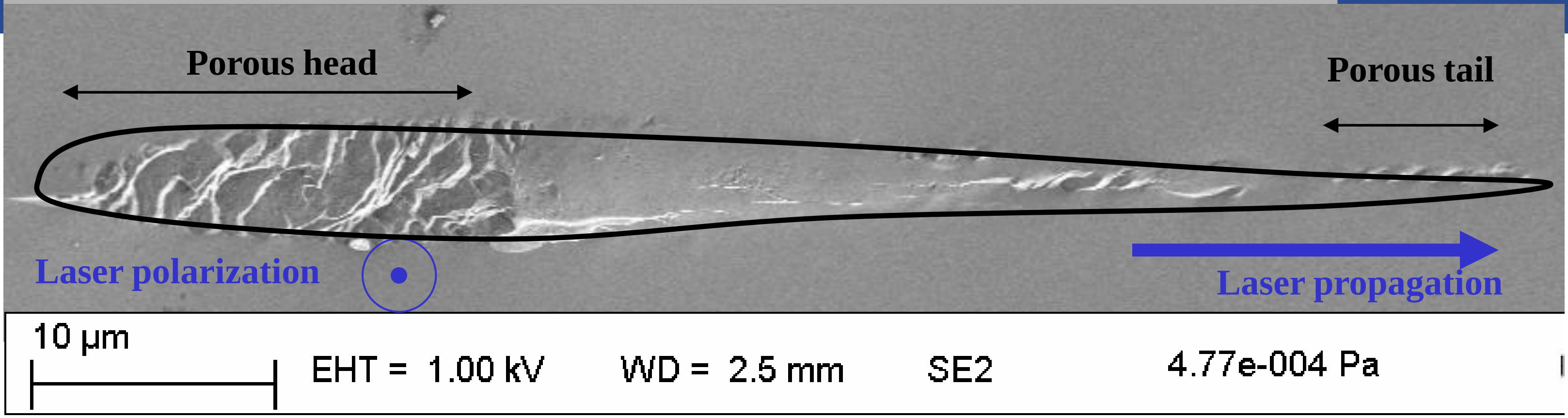


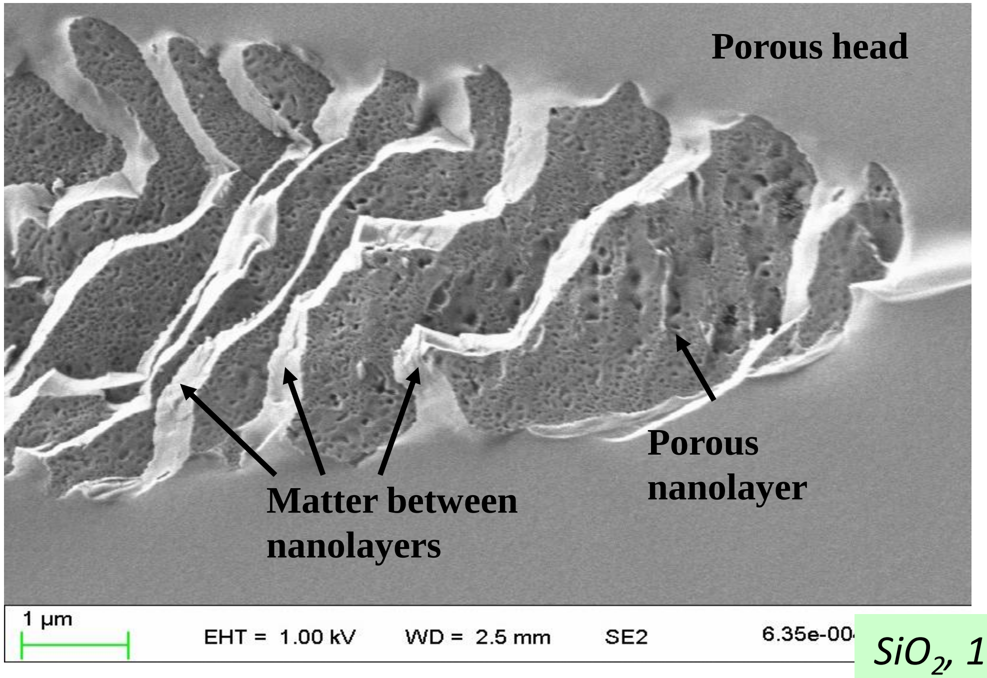
*SiO$_2$, 1030 nm, **250 fs,** 100 kHz, 100 μm/s, 0.5 μJ, 0,6 NA*

Birefringence and negative index changes origin

<u>polarisation parallel to the scanning direction</u>

SEM images of a whole laser track written in parallel configuration.



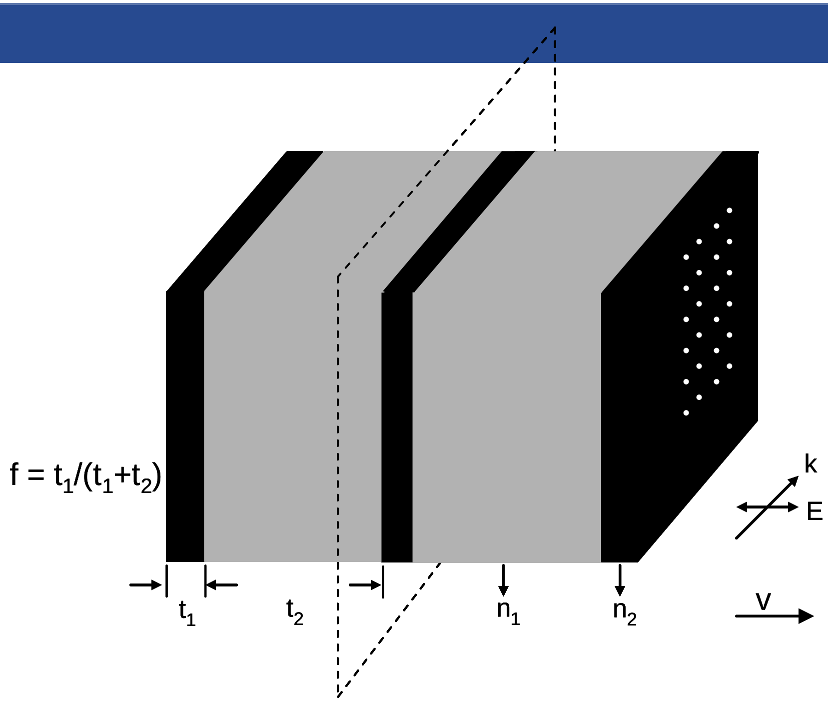


Observation repeatable over more than 200 laser tracks written with various laser parameters !!!

Decomposition of SiO_2 into x.O_2 + $SiO_{2(1-x)}$ initiated by 200fs photo-excitation !!!

*SiO_2, 1030 nm, **250 fs,** 100 kHz, 100 µm/s, 0.5 µJ, 0,6 NA*

The nanoplans produces form birefringence



Bricchi, E., B. G. Klappauf, et al. (2004). "Form birefringence and negative index change created by femtosecond direct writing in transparent materials." Optics Letters 29(1): 119-121.

Nanogratings filling factor (deduced from SEM observations): $f = t_1/(t_1+t_2) = 0.2$

$$\Delta n_e = \left[\sqrt{\frac{n_1^2 n_2^2}{f n_2^2 + (1-f) n_1^2}} - n_{bg} \right],$$

// writing polarization

$$\Delta n_o = \left[\sqrt{f n_1^2 + (1-f) n_2^2} - n_{bg} \right]$$

material between the nanoplans unchanged i.e. pure silica $n_1=1.45$ → Then, for a birefringence of 10^{-2}, we deduce a decrease of index by 0.2 in the nanoplanes

---

Large interest: birefringence is large 10^{-2}, orientable and local and extremely stable

→ Many possibilities for elaborating optics with unpreceeding thermal resistance, but « only in pure silica » at this date.

A few words about chemical composition dependence

Lancry *et. al*, OSA, AIOM 2009, AWB4

Birefringence

Samples	IR-fs Isotropic Δn	IR-fs Birefringence	UV-ns, Isotropic Δn (±)
Pure SiO_2	up to $+2.2\ 10^{-2}$	Yes, up to 8.10^{-3}	Up to 4.10^{-4} but very high cumulated fluence
GeO_2-SiO_2 (GeO_2 up to 20w%)	up to $+10^{-2}$, but narrow processing window	Yes, up to $1.2.10^{-2}$	Up to 4.10^{-3} (H_2-loaded)
F-doped SiO_2	up to $+8.10^{-3}$, wide processing window	Yes, up to 5.10^{-3}	Up to 3.10^{-4}
P-doped SiO_2	up to $+8.10^{-3}$	Yes, up to 8.10^{-3}	Up to 4.10^{-3} (H_2-loaded)

Only isotropic Δn !

SiO_2-SnO_2 (16 mol%)	up to -5.10^{-3}, $+4.10^{-3}$	No	Up to 3.10^{-3} but strong scattering loss
Boro-silicate (BK7)	up to $+/-10^{-2}$	No	A few 10^{-4}
Lead-silicate (SF57)	up to $+2.10^{-2}$	No	Up to 9.10^{-2} but surface relief gratings
Bi_2O_3 based glass	up to $+5.10^{-3}$	No	?
Soda-lime	up to $+3.10^{-3}$	No	A few 10^{-4}

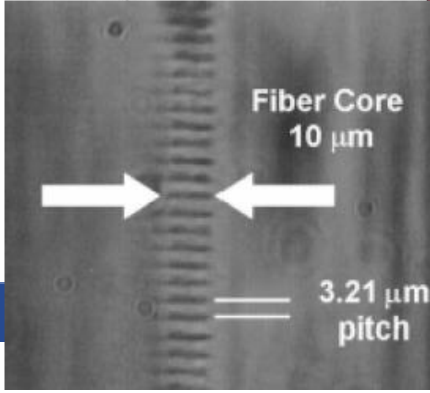
800nm, 160-200fs, E = 0.05- 2.2 µJ, 100kHz, 0.1-0.5 NA, 100 µm/s, 10 – 500 TW/cm²

Femtosecond laser 3D processing in silica-based glasses

Part 3

Applications

Applications I



Mihailov et al., Opt. Lett. 28 (2003

Réseaux d’indice de réfraction:

- **FBG (Fiber Bragg Gratings) stables > 1000° C**
- **FBG à travers le revêtement polymères**
- **FBG pour laser fibrés (stabilisation λ)**
- **Bragg en Volume pour lasers (CPA, égalisation gain)**

<u>Propriétés utilisées</u>: fort Δn (qq 10^{-2}), biréfringence (pour maintien de polarisation), trous en volume, stabilité thermique, peu sensible à la composition chimique, localisé spatialement

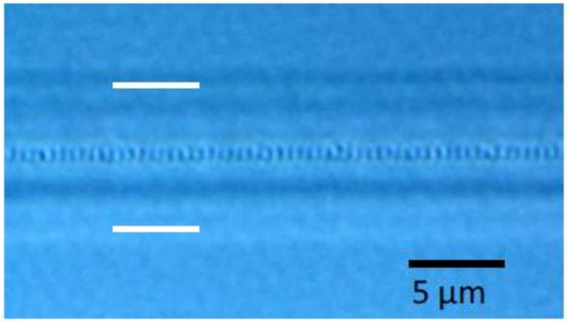
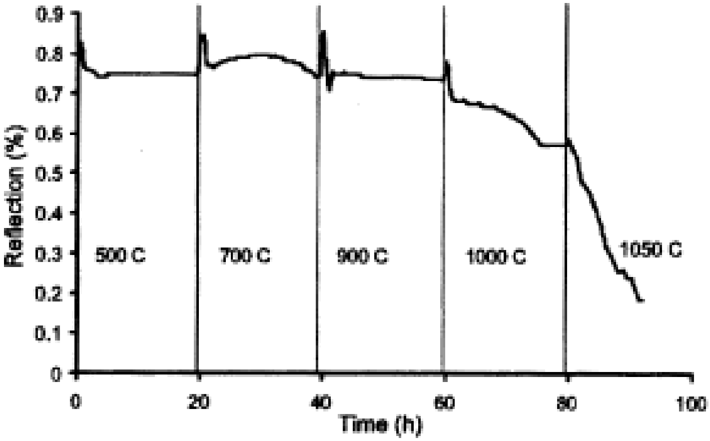


Fig. 5. Microscope image of the WBG. The small pitch of 0.52 µm can clearly be seen. The white bars mark the full width of the waveguide.

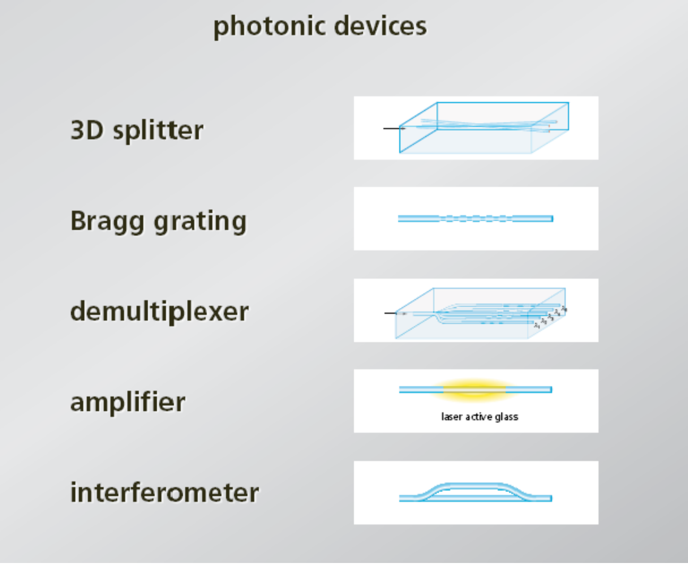
Miese et al. OME (2011)

Contrat FP7-PEOPLE-IRSES (2010-2014) en collaboration avec OFTC Sydney, UO-FSU Jena et ORC Southampton.
Collaborateurs industriels : Thales RT, Thales laser, 3S Photonics

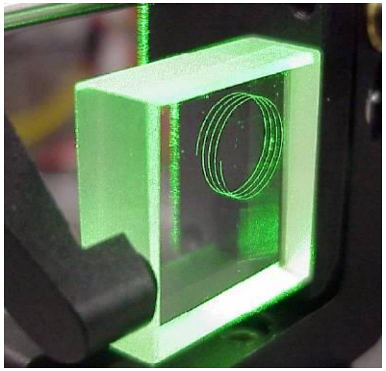


Applications II

Guides optiques monomodes en 3D présentant une atténuation compatible avec les télécoms (<0.1dB/cm): coupleurs, séparateurs, polariseurs etc … (puces biophotoniques, microfluidique)



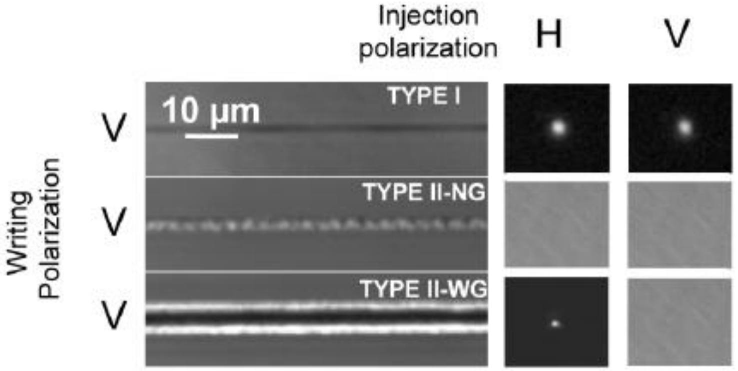
<u>Propriétés utilisées</u>: fort Δn isotrope (qq 10^{-2}), Δn anisotrope pour guides d'onde enterré, biréfringence, stabilité thermique, localisé spatialement, vitesse élevée (qqcm/s).



Guide d'onde courbe

Translume compagny (USA)

Guides optiques doubleurs de fréquence



Guide d'onde (C. Mishchik PhD)

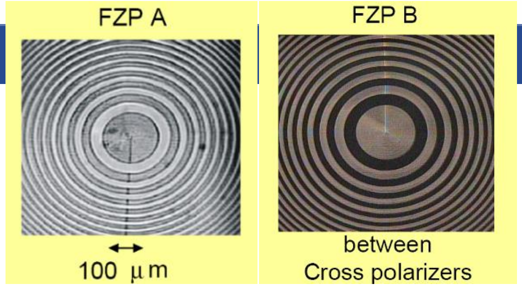
Contrat FP7-PEOPLE-IRSES (2010-2014) en collaboration avec Macquarie University and Sydney University

Applications III

Composants optiques (où la biréfringence et son orientation sont maîtrisées) pour la mise en forme des faisceaux lasers et l'imagerie.

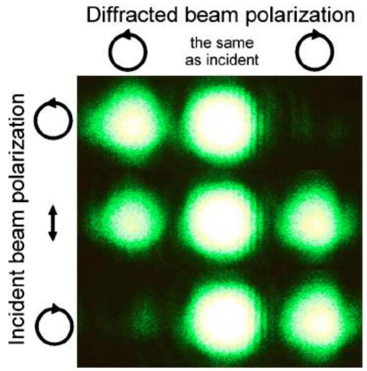
<u>Propriétés utilisées</u>: forte biréfringence

Optiques 2D/3D: lentilles de Fresnel ou lame de phase annulaires, convertisseurs de polarisation, lames d'onde UV-Vis-IR ($\lambda/4$, $\lambda/2$ et plus…), polariseurs, films compensateurs pour écrans LCD, micro-lentilles (50µm focale), …



Lentille de Fresnel (collab ORC southampton)

Radial or azimuthal polarization converter (collab ORC southampton)



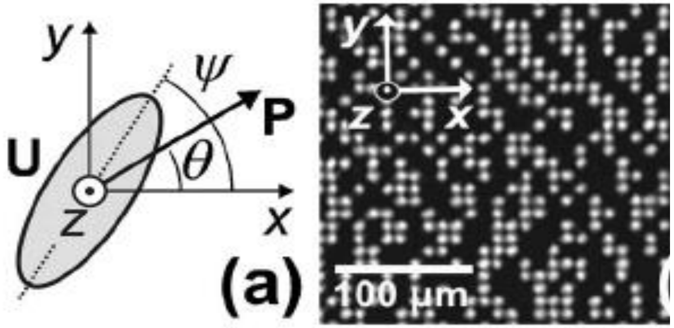
Contrat FP7-PEOPLE-IRSES (2010-2014) en collaboration avec UO-FSU Jena et ORC Southampton.

Collaborateurs industriels : Thales RT , Thales laser, Jobin Yvon

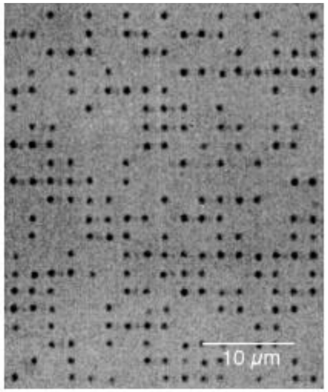
Applications IV

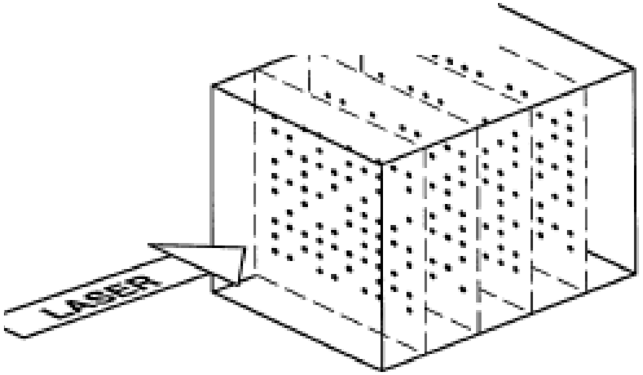
Stockage optique d’information en 3D

<u>Propriétés utilisées</u>: « fort » Δn ou la luminescence, stabilité thermique (durée de vie élevée et possibilité de faire de la prédiction !!), localisé spatialement (capacité de stockage).



Papazoglou et al., Opt. Lett. 28 (2003)





E. N. Glezer et al., Opt. Lett. 1996

Collaborations: Gilles Pauliat (Institut d’optique), Glazt compagny

The different color of each letter is corresponding to the different orientation of the slow axis of the birefringence

Conclusion and perspectives

In contrast to what is observed with UV lasers, ***fs Vis-IR lasers*** provide a powerful tool to direct-write ***strong permanent (isotropic AND anisotropic) Δn up to*** 10^{-2} in "***any glasses"***, without the need for any photosensitization process and ***with superior thermal stability (up to 1000° C) !!!***

Ultrafast Vis-IR laser also has one substantial advantage over UV lasers – the ***internal structuring of 3D index profiles*** in transparent glasses. This presents interesting prospects for shaping 3D photonic structures for optical telecommunication, high power laser, optical data storage, LCD, sensors, …

Ultrafast Vis-IR laser implies a ***slower processing*** (to overcome using high power 100's kHz and 10's MHz laser), but one that ***offers more flexibility*** in patterning and trimming applications.

But also :form birefringence, nanostructures, linear dichroism, circular dichroism, metallic nanoparticules precipitation and shaping, nano/micro-crystallization and so more …

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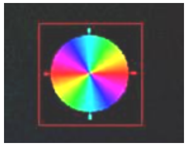
iPL/USyd, MQ, ORC Southampton/UK, Friedrich-Schiller-Uni/Jena

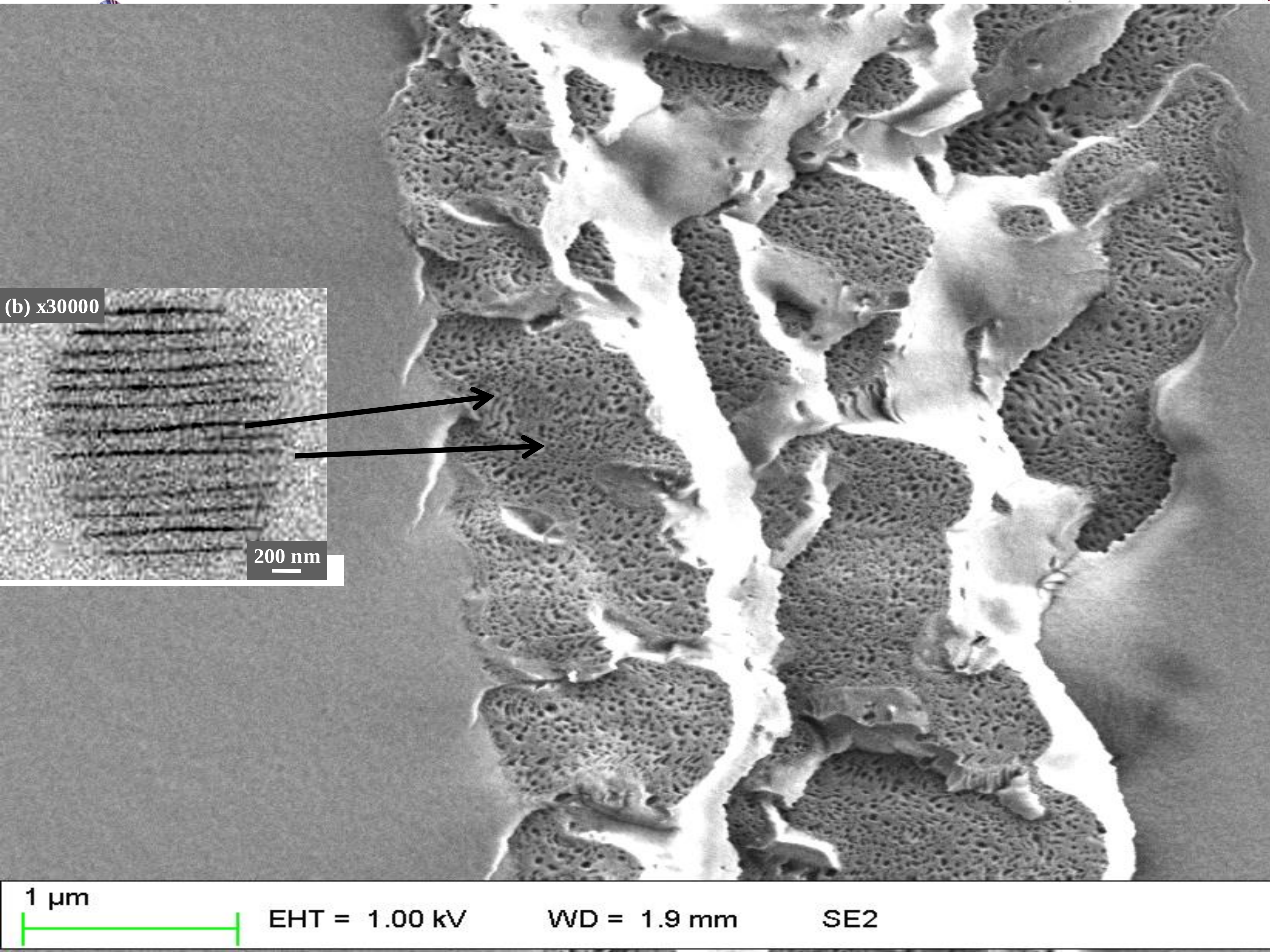
Femtosecond Laser for Appplications in Glasses

Supported by

FP7-PEOPLE-IRSES
Agence Nationale pour la Recherche
RTRA Triangle de la Physique
Département de l' Essonne



The different colors of each letter correspond to different orientations of the slow axis of the birefringence (due to different nanograting orientation).


(b) x30000
200 nm
1 µm
EHT = 1.00 kV
WD = 1.9 mm
SE2