LASER ET PROCÉDÉS DANS LES VERRES

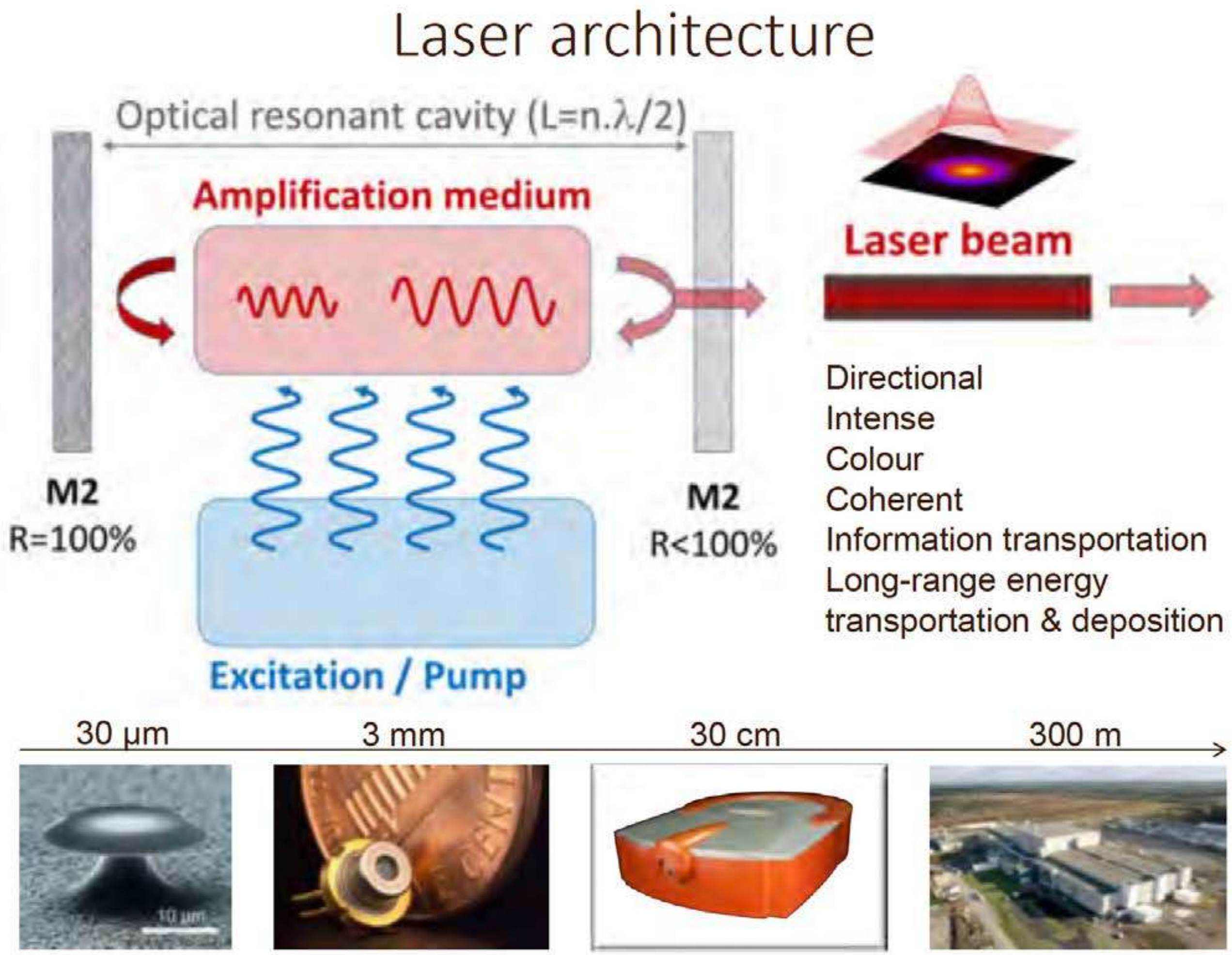
Matthieu Lancry

université PARIS-SACLAY

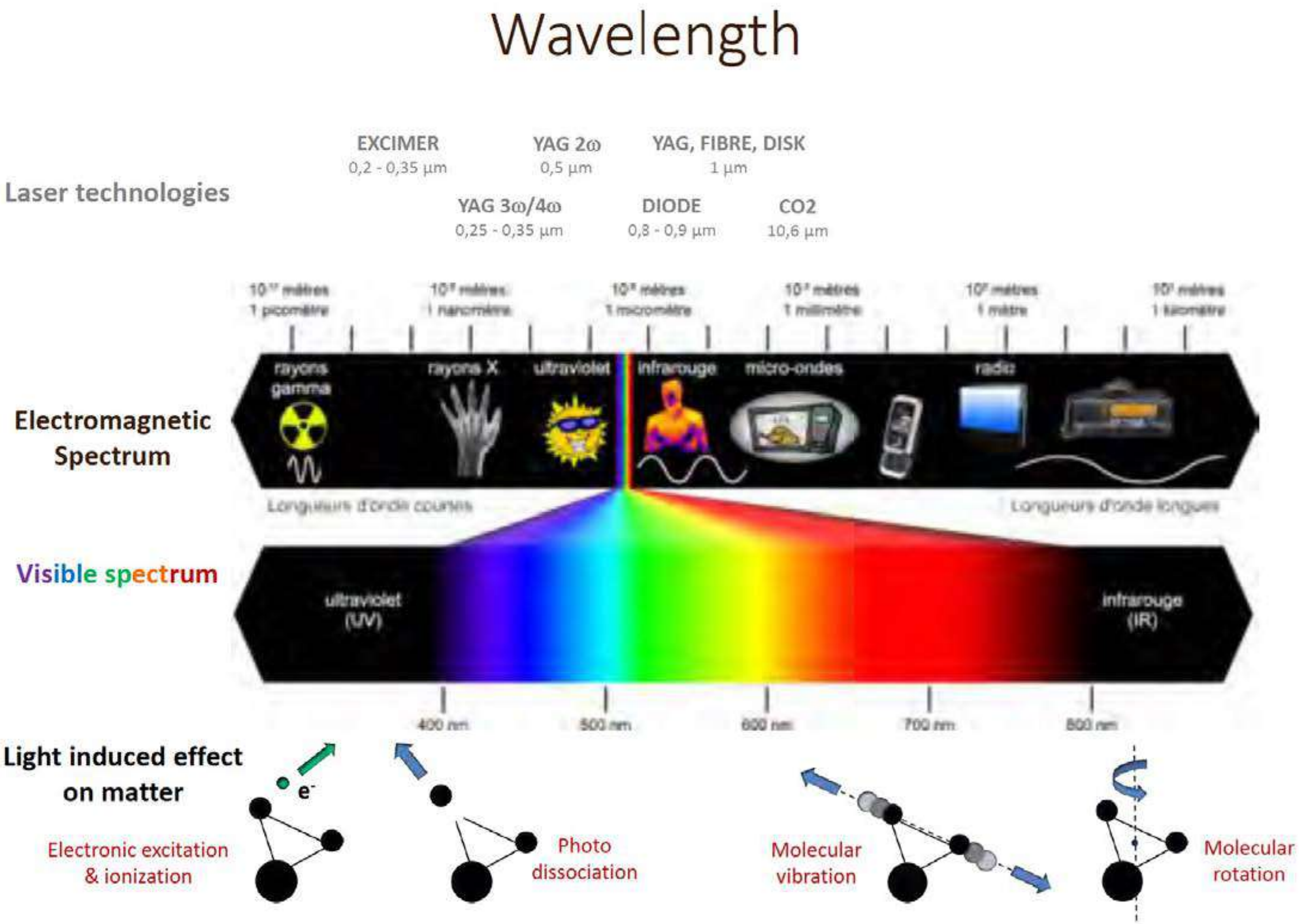
OUTLINE

- **Introduction**
- **Basic concepts**
- CO_2 laser
- Surface processing
- Volume processing
- Conclusions

CONTEXT AND INTRODUCTION

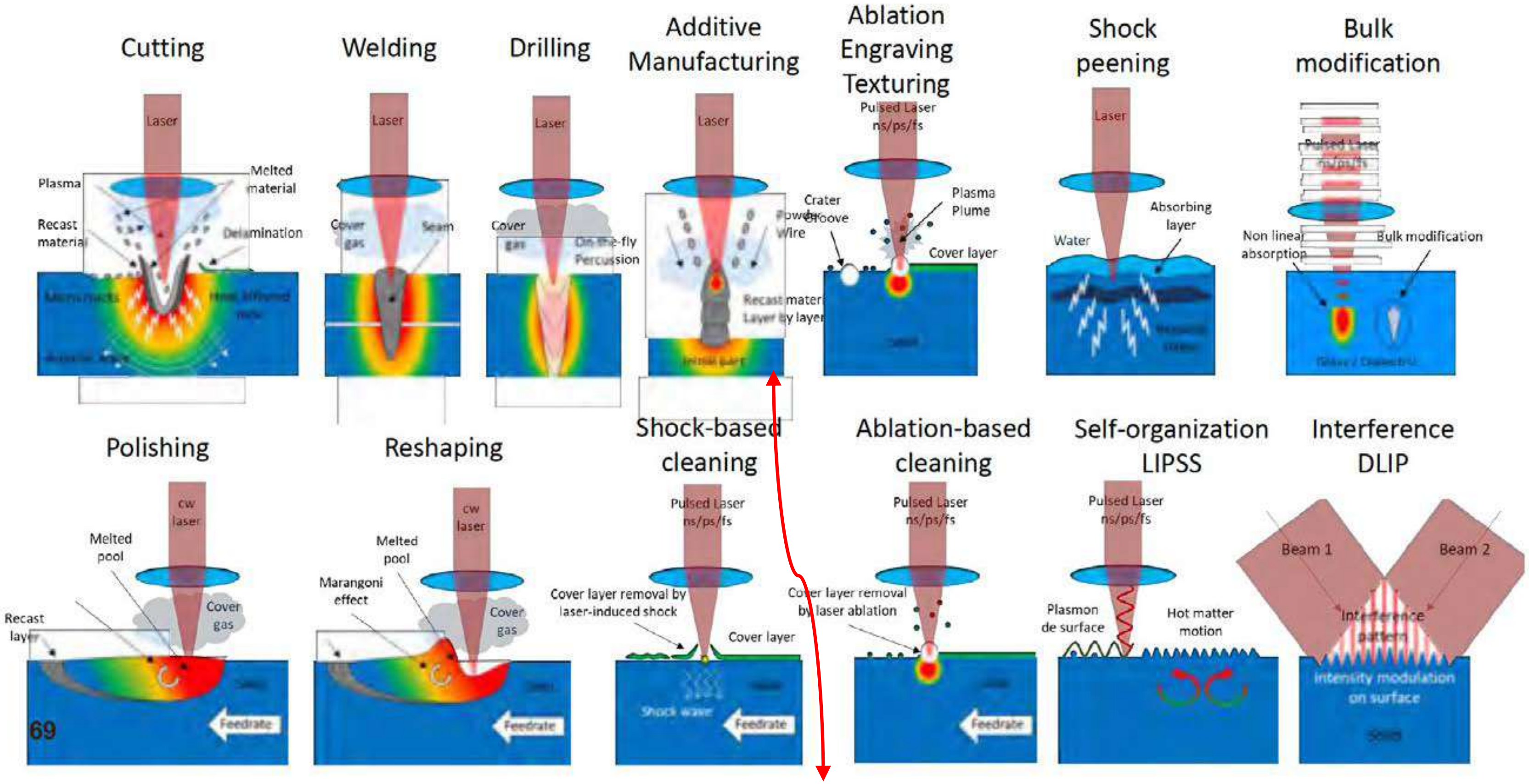


CONTEXT AND INTRODUCTION



CONTEXT AND INTRODUCTION

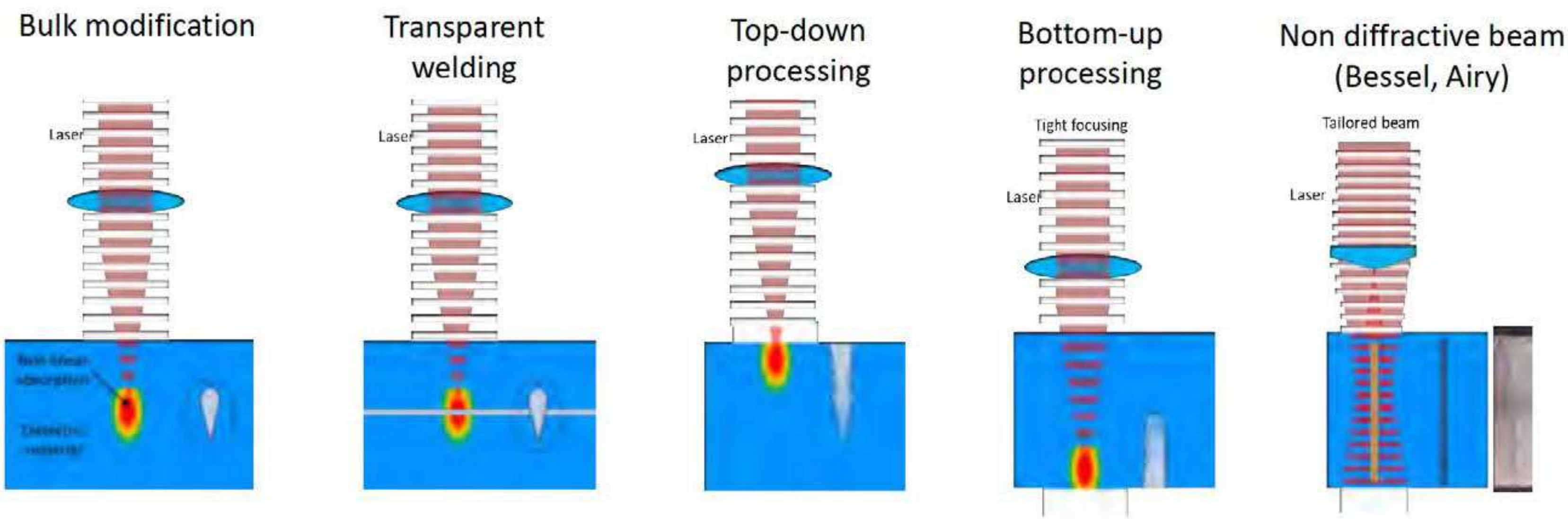
An universal tool for material processing…



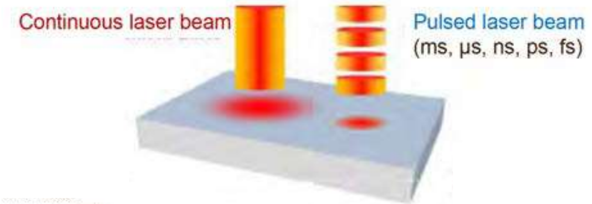
Cours de Yves Quiquempois

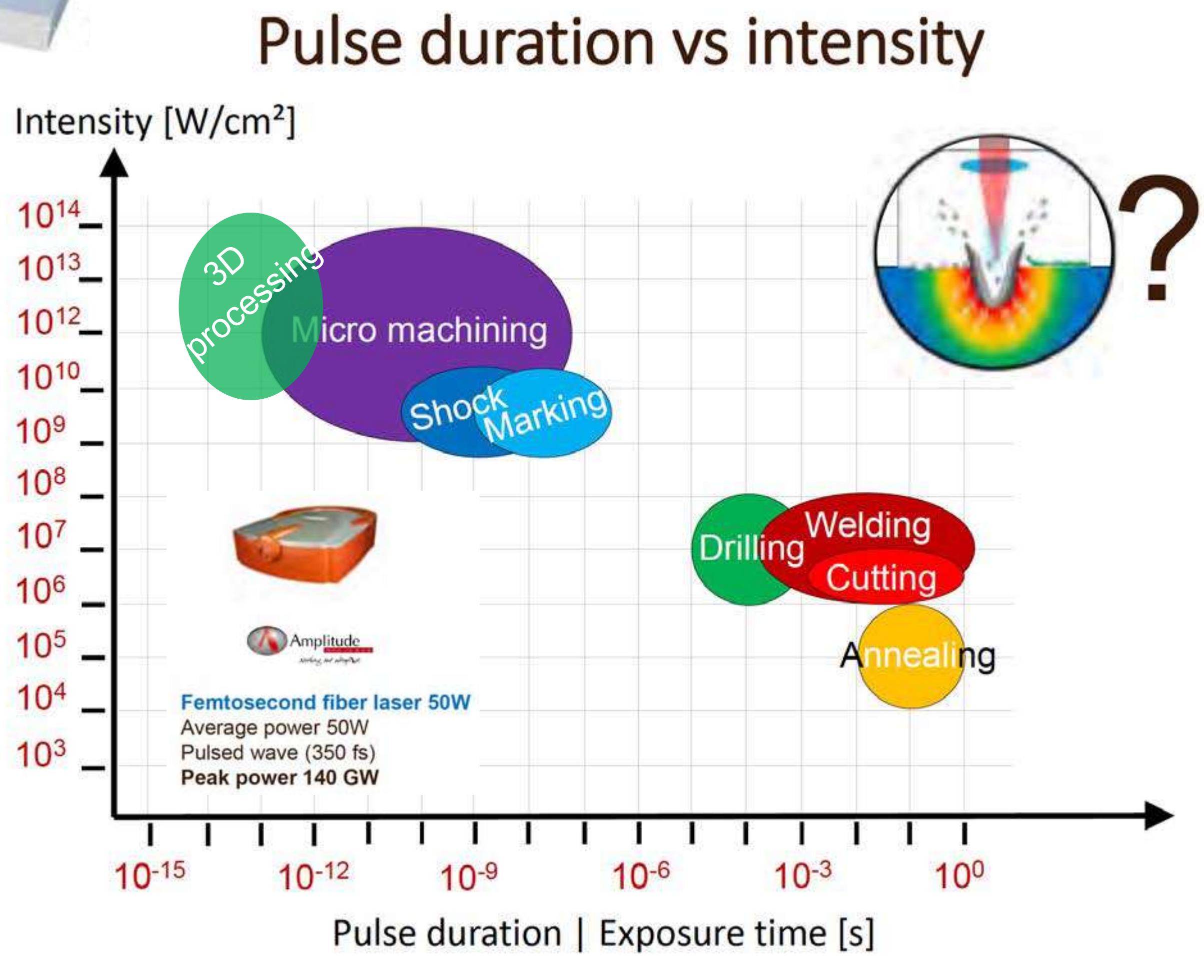
CONTEXT AND INTRODUCTION

… even for transparent materials



CONTEXT AND INTRODUCTION





Fiber laser 100kW
Average power 100 kW
Continuous wave
Peak power 100 kW

Cours de Maxime Cavillon

OUTLINE

- Context and introduction
- **Basic concepts**
- CO_2 laser
- Surface processing
- Volume processing
- Conclusions

BASIC CONCEPTS

- **Indice de réfraction (n) et biréfringence**
  - Lien avec la constante diélectrique : $\varepsilon = \varepsilon_1 + i\varepsilon_2$, $N = n + i\kappa$,
  - Milieu isotrope : n unique (scalaire).
  - Milieu anisotrope : n devient un tenseur → indices propres selon les axes principaux.
  - Biréfringence : $\Delta n = n_e - n_o$ (uniaxe) ; deux ondes orthogonales se propagent avec vitesses/indices différents → déphasage ou retard
  - Retard : $\delta = (2\pi\,\Delta n \cdot e) / \lambda$ (e = épaisseur).
- **Absorption (α) et dichroïsme linéaire**
  - Coefficient d'extinction κ lié à l'absorption : $\alpha = 4\pi\kappa / \lambda$
  - Isotrope : κ scalaire. Anisotrope : κ tenseur → absorption dépend de la polarisation.
  - Dichroïsme linéaire (DL) : $\Delta\alpha = \alpha\| - \alpha\perp$; absorption différentielle entre polarisations orthogonales.

Matériau isotrope
(n ; κ)

Matériau anisotrope
(n_o, n_e ; κ‖, κ⊥)

$N = n + i\kappa$,

$\alpha = (4\pi\,\kappa / \lambda)$,

Biréfringence : $\Delta n = n_e - n_o$

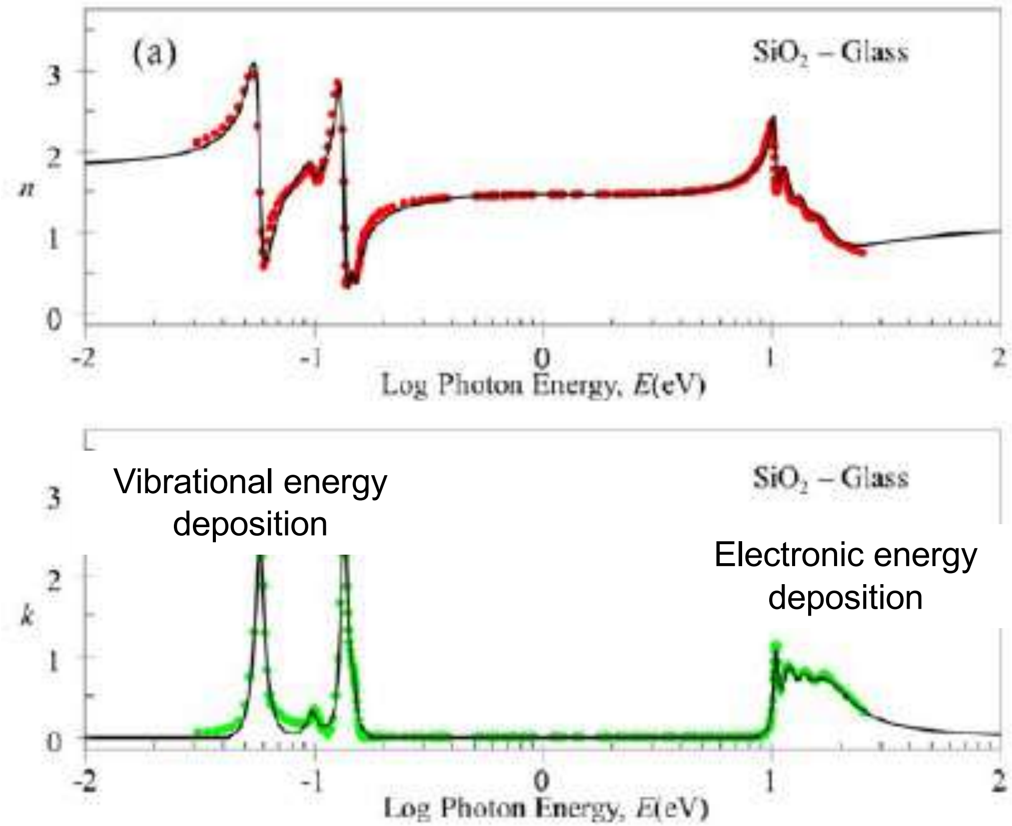
Retard $\delta = (2\pi\,\Delta n\, e)/\lambda$

Dichroïsme : $\Delta\alpha = \alpha_{\|} - \alpha_{\perp}$

Lien cours de Wilfried Blanc

BASIC CONCEPTS

Everything start with light absorption



$N = n + i\kappa$,
$N^2 = \varepsilon_1 + i\varepsilon_2$

Partie réelle ⟶ Indice de réfraction n

Partie imaginaire ⟶ Indice imaginaire k

➡ **SPECTRE D' ABSORPTION**

$$\alpha = \frac{4\pi k}{\lambda}$$

Type de laser	CO_2	Ti:Sa, Nd:YAG, Yb :YVO_4	Excimère
Longueur d'onde	10.6 um	266nm-1064nm	157-351nm
Energie des photons	0.12eV	4.6-1.2eV	7.8-3.5eV
Régime	Continu	Continu, pulsé ns-fs	Pulsé 10ns

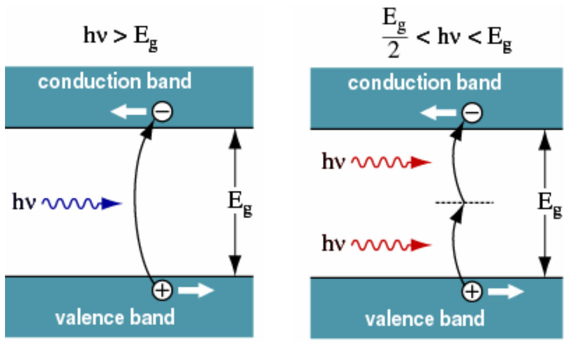
BASIC CONCEPTS

Everything start with light absorption

BANDGAP excitation

Two cases

Single photon create (e-h) pair	Multiphotons create (e-h) pair
Linear absorption	*Two-photons absorption*



M. Lancry et al. Phys Reports 523 (2013)

But multiphotons absoption (MPA) needs high peak power >MW/cm^2 and thus ns-ps-fs lasers

REAH (Rare Earth Atom Heating)

R. Sato et al. J. Non-Cryst. Solids 289 (2001)

Sm^{3+}, Dy^{3+}, Nd^{3+} …
>5mol% Sm_2O_3, Dy_2O_3

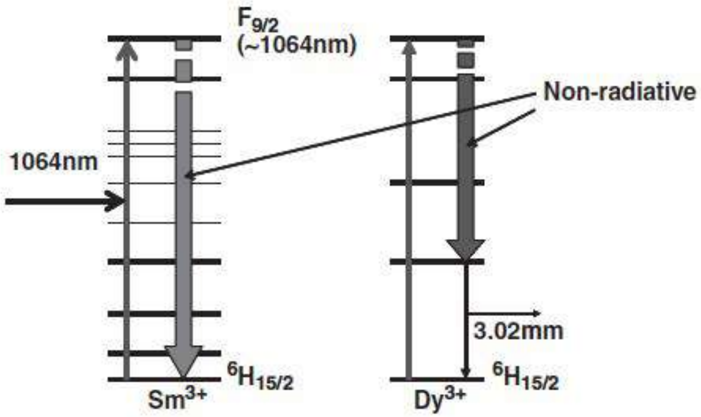


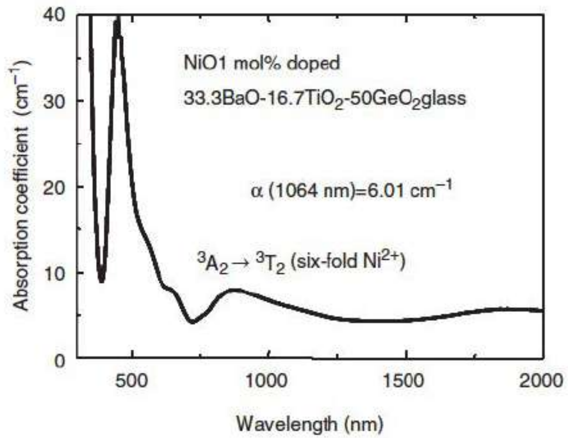
Fig. 1. Electronic energy levels of Sm^{3+} and Dy^{3+} ions.

T. Komatsu et al. J. Am. Ceram. Soc., 90 [3] 699–705 (2007)

TMAH (Transition Metal Atom Heating)

T. Honma et al. Appl. Phys. Lett. 88 (2006)

Ni^{2+}, Fe^{2+}, Cu^{2+}, …
Typ. 0.01-1mol%

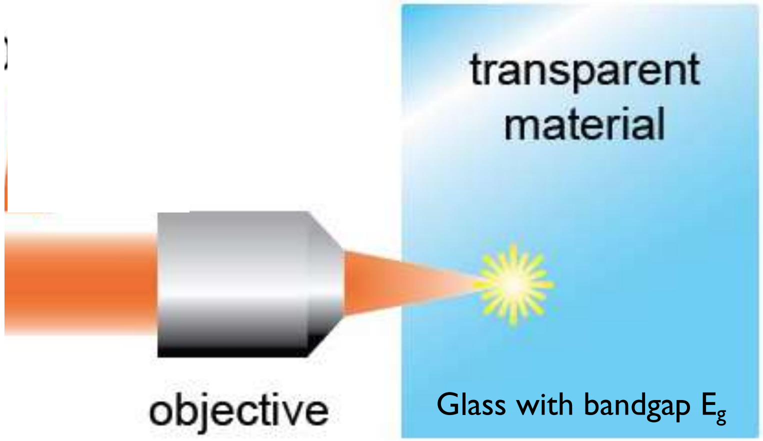


T. Komatsu et al. J. Am. Ceram. Soc., 90 [3] 699–705 (2007)

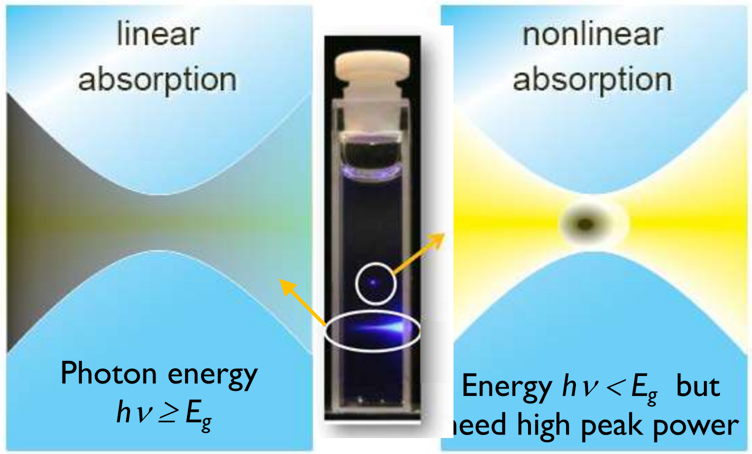
Cours « verres et couleurs » Laurent Cormier, Gérald Lelong

BASIC CONCEPTS

Everything start with light absorption



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



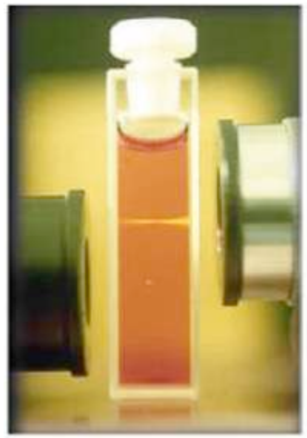
Amount of absorbed power in a thin layer of the medium is proportional to the I^n square of the light intensity (n is the number of photons).

Provide a 3D bulk confinement in a voxel of few µm³

Example: 2 photons absorption (TPA)

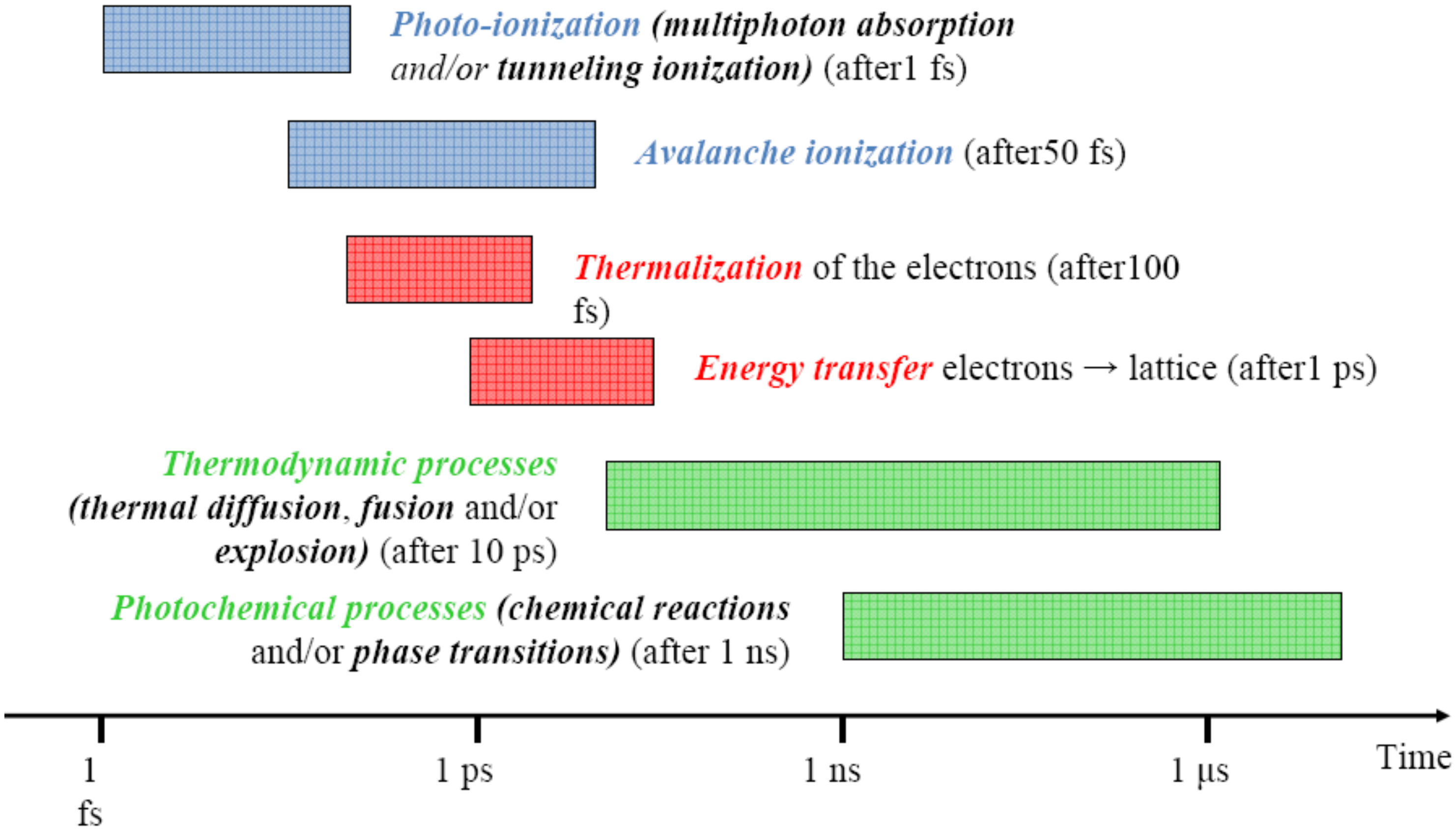
$$\beta = \frac{1}{I^2}\frac{dI}{dz} = \frac{3\omega}{2\epsilon_0 n^2 c^2}\mathrm{Im}(\chi^{(3)}_{zzzz})$$

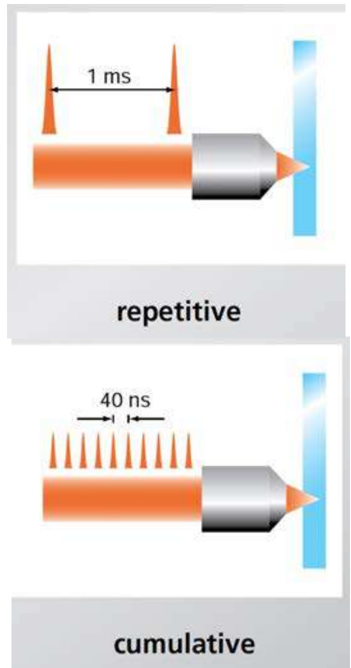
Absorption coefficient is proportional to the intensity of the light !



BASIC CONCEPTS

Light absorption followed by many relaxation pathways



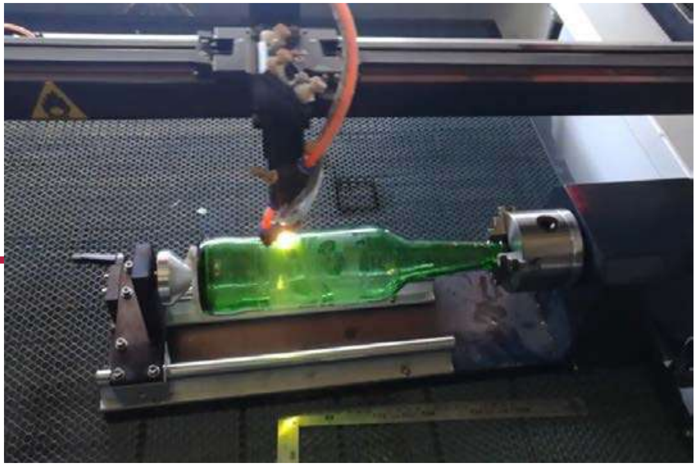


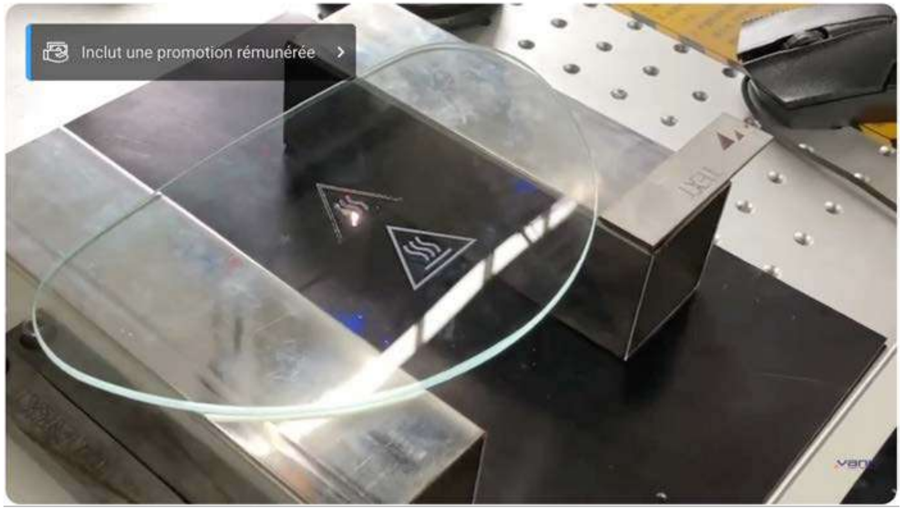
Schematics of main physical processes involved in the ultrashort (fs, ps) pulse laser processing of oxyde glasses

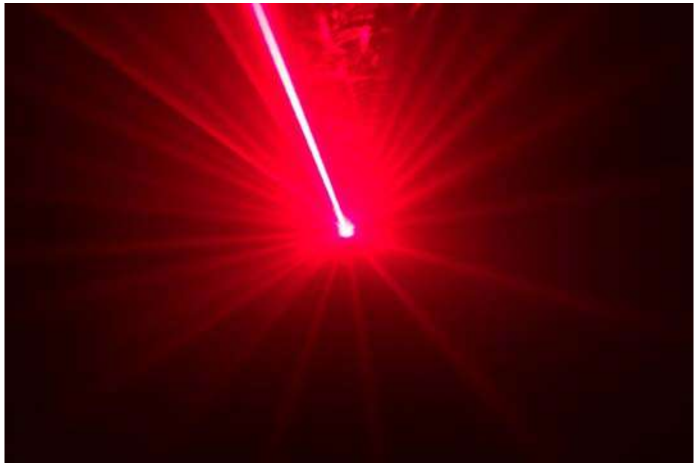
OUTLINE

- Introduction
- Basic concepts
- **CO_2 laser**
- Surface processing
- Volume processing
- Conclusions

CO_2 LASER HEATING

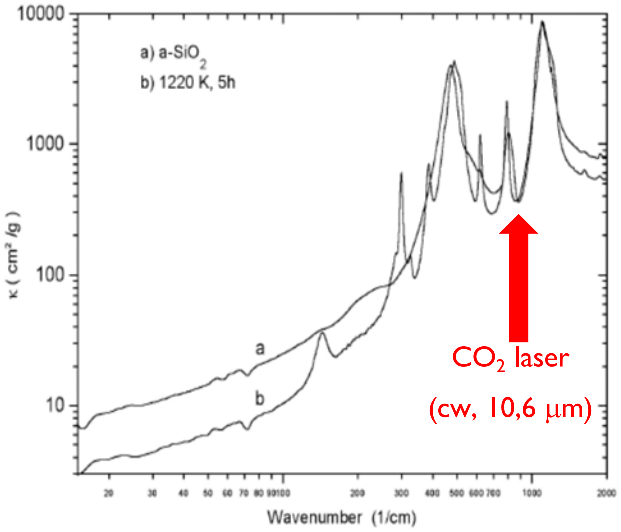






CO_2 LASER HEATING OF GLASS — FUNDAMENTALS

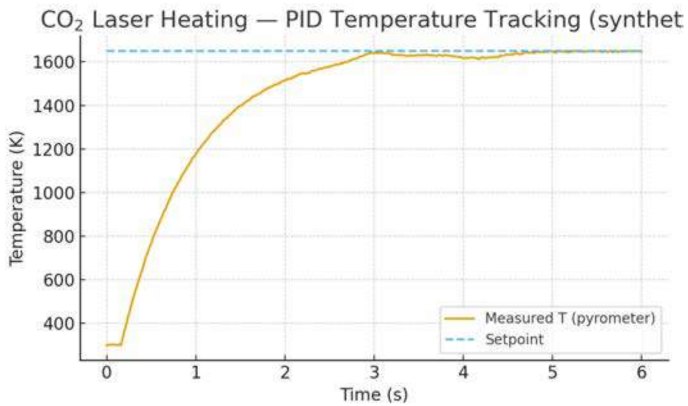
- Strong absorption at 10.6 µm → volumetric/surface heating
- Above T_g, viscosity drops → stress relaxation & surface flow.
- Then control cooling rate to set fictive temperature T_f and residual stress state.



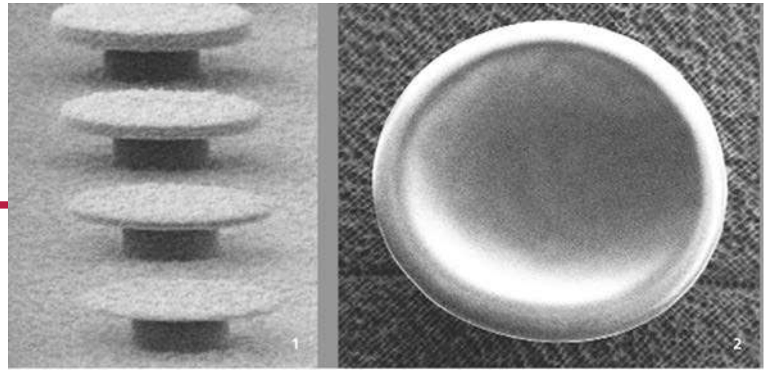
Strong linear absorption: α =100-1000 cm^{-1}

i.e. 63% (1/e) of light absorbed within 10µm ($\sim 1/\alpha$)

- ΔT set by application (anneal vs morphing/polishing).
- Closed-loop control: pyrometer (e.g., 1300–2000 K) and bound thermal budget (avoid crystallization/devitrification).
- Process window : spot size (100–300 µm typical), irradiance W/cm², dwell 0.1–5 s (scan speed, duty cycle); environment (air/He/N_2).



PROCESSES & APPLICATIONS

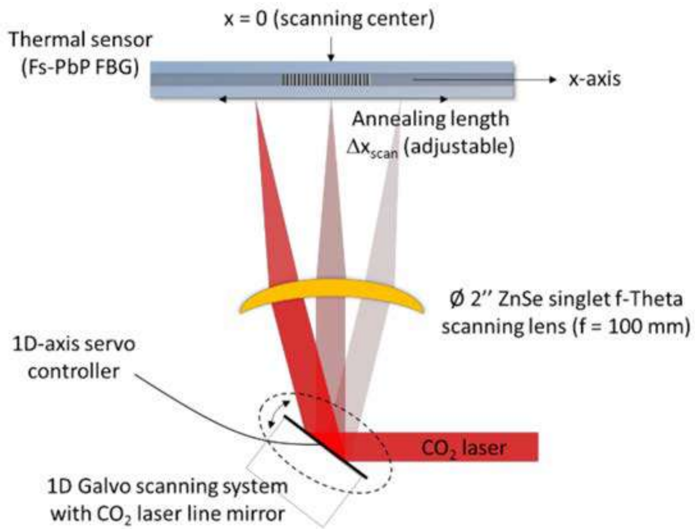


Microresonator (diameter of 50–200 µm, height of 2–10 µm)
Roughness is reduced to Ra ~ 50 nm

- Surface morphing: forming spheres and sealed cavities;
- Polishing of flats, micro-optics, and resonators: adaptable to molds and lens arrays.

- CO_2 pretreatment of fibers (few-mode, single-mode): relaxes frozen-in stresses → rapid cooling (higher T_f).
- CO_2 annealing of Fiber Bragg Gratings (=fiber sensors): → thermal stabilization; slower decay at 1050 °C

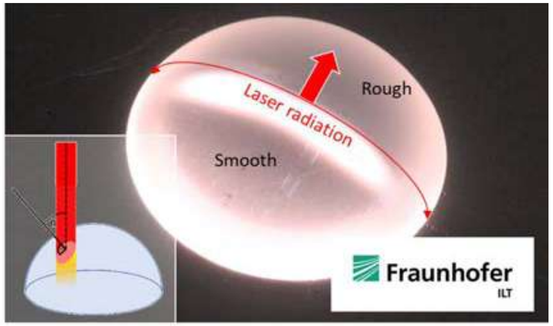
Cf Cours fibres de Maxime Cavillon



Fiber Bragg Gratings (FBG) heating

CO_2 LASER GLASS POLISHING

- Mechanism: surface tension (σ) driven smoothing in the viscous regime; $\tau \sim \eta . R/\sigma$
- Peaks flow faster than valleys (curvature-dependent), lowering Rugosity (R_q). $\sigma = \sigma_0 \left(1 - \frac{2\delta}{R}\right)$
- Regimes: (i) sub-melting viscous flow for ultra-low roughness; (ii) near-melting reshaping for recontouring; (iii) overexposure → crack risk.



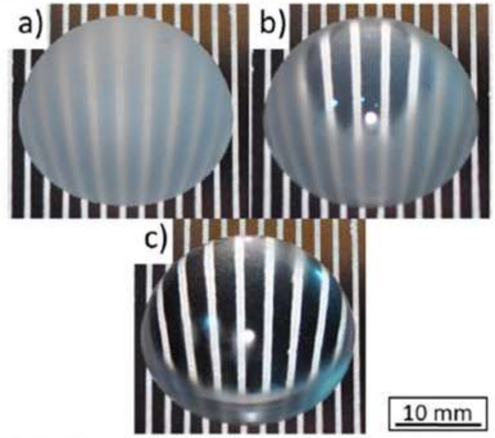
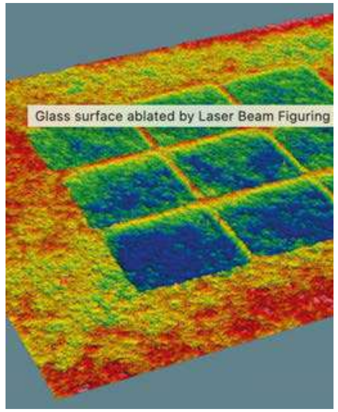


Fig. 8. Left: Images of samples with initial state (a), laser polished without correction (b) and with the presented model-based correction (c).

- Optimization: choose dwell/overlap to hit R_q minimum; raster or spiral scan (1 - 10 cm^2/s), multi-pass, cooling intervals.
- Metrology: white-light interferometry/AFM for Rq; profilometry for form error; scattering/reflectance; micro-crack inspection; refractive-index homogeneity.



Roughness rms < 5 nm in SiO_2

Micro roughness rms < 0.4 nm

CO_2 LASER ENGRAVING ON GLASS

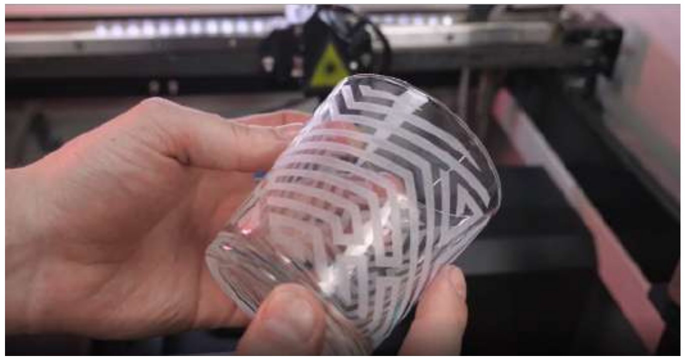
Mechanism — 10.6 µm absorption → localized heating; micro-fracturing / frosting/glazing of surface yields white contrast.

Typical settings — Spot 100–300 µm; 5–25 W at part; 200–1200 mm/s; multi-pass to deepen without cracks.

Best materials — Soda-lime, borosilicate, lead crystal; avoid tempered glass (risk shatter). Masking improves edge quality.

Tips — Wet or dish soap to reduce chipping; large beam for smoother frost..

Example: personalized flute (text + symbol).

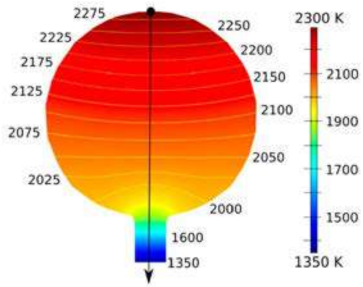


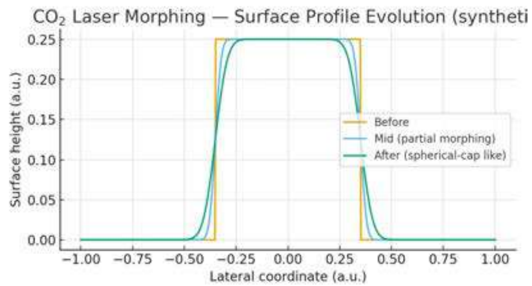
Example: patterned frosting on tumbler (rotary engraving).

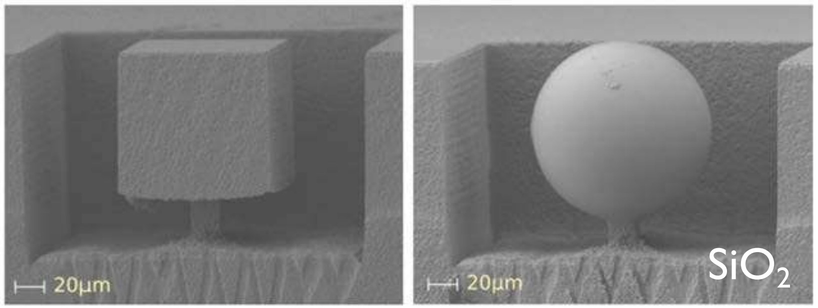
- Notes: ranges are indicative and depend on optic size, coating/contamination, pyrometer emissivity calibration, and desired outcome (anneal vs morphing vs polishing)..

CO_2 LASER MORPHING — SURFACE TENSION DRIVEN SHAPING

- Principle — Above T_g, viscosity drops and surface tension σ drives curvature-dependent flow → features relax toward spherical caps. $\Delta P \approx 2\sigma/R$
- Process window — λ = 10.6 µm; spot 100–300 µm; 2–20 W at part; dwell 1–60s s; scan (raster/spiral), multi-pass with cool-down.
- Applications— Recontouring micro-optics, sealing cavities, shaping microspheres, smooth polishing.
- Metrology — Interferometry/AFM for R_q & form error; check n homogeneity; watch for crystallization, ripple, microcracks (over-exposure).





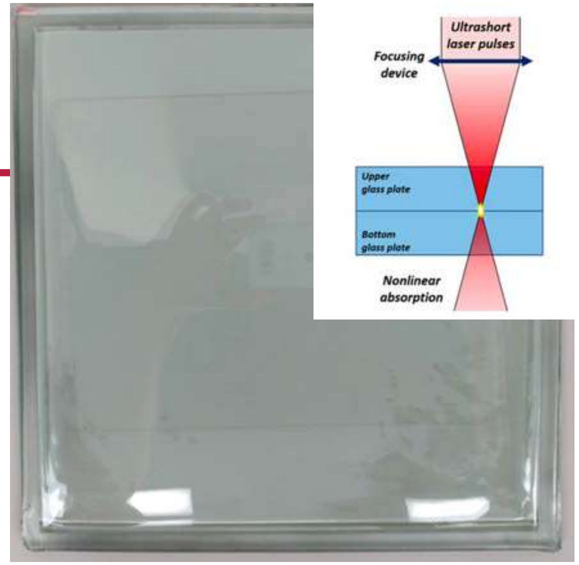


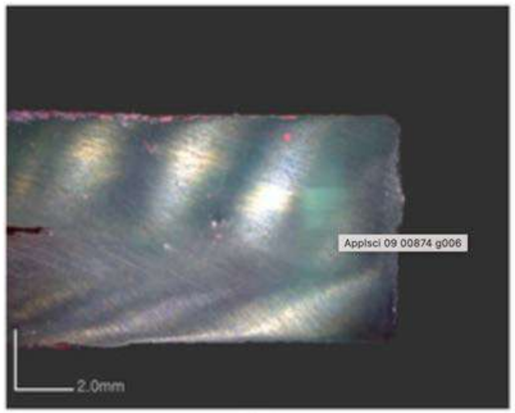
Jakub Drs, Opt. Express **23**, 17355-17366 (2015)

CO_2 LASER WELDING OF GLASS — EDGE/SURFACE SEALING

$\tau \sim \eta . R / \sigma$

- Principle — Strong absorption at 10.6 µm heats the surface/edge above $T_{softening}$ + controlled cooling forms a welded seam.
- Process window — Spot 100–300 µm, 5–30 W, 0.1–5 mm/s; multi-pass
- Criticals — Contact (gap < few µm), clean interfaces, CTE mismatch → cracks (mitigate by preheat).
- Applications — Cover-glass sealing, edge joints on plates/tubes, simple glass-glass assemblies (not internal bulk welding).
- Metrology— He or liquid leak test; polarimetry (residual stress); check light scattering (bubbles/voids);





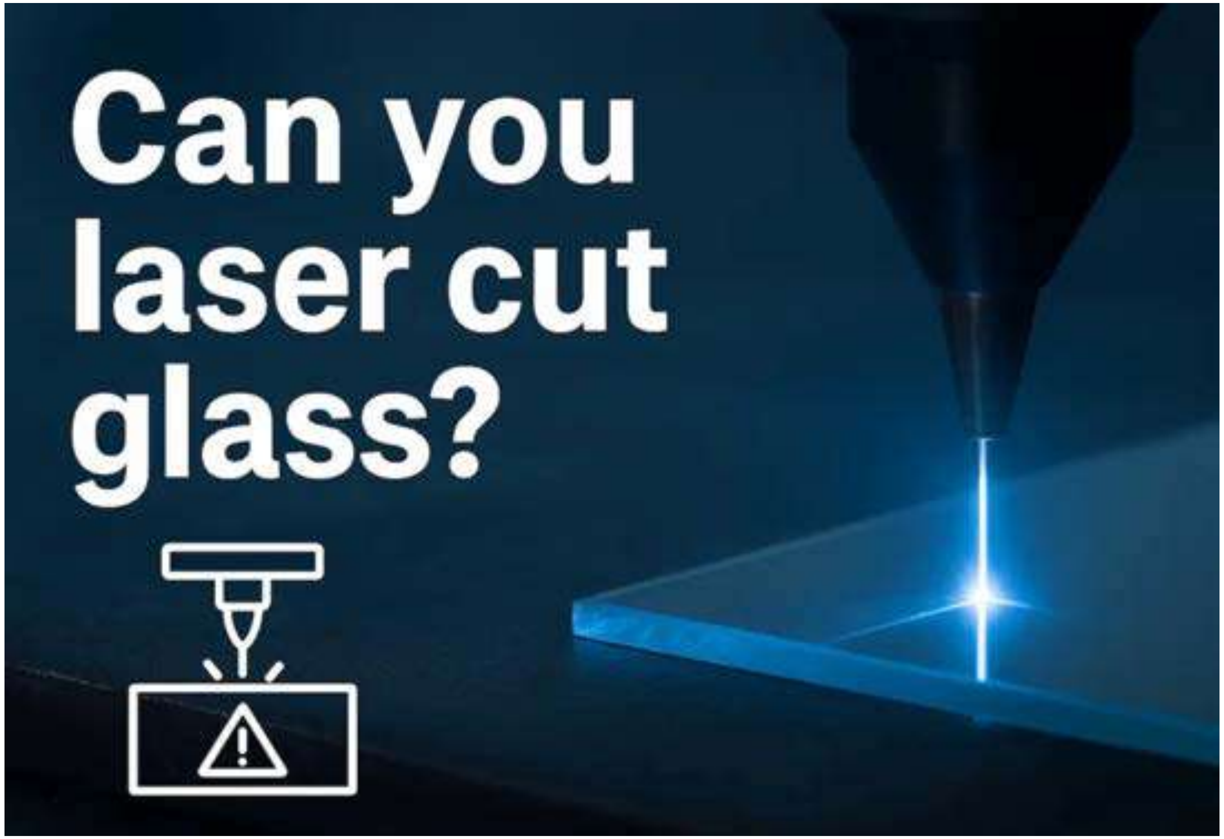
Schematic (not to scale): two glass plates clamped; CO_2 beam scans along the edge → molten seam; cool down under control.

OUTLINE

- Introduction
- Basic concepts
- CO_2 laser
- **Surface processing (en Français)**
- Volume processing
- Conclusions

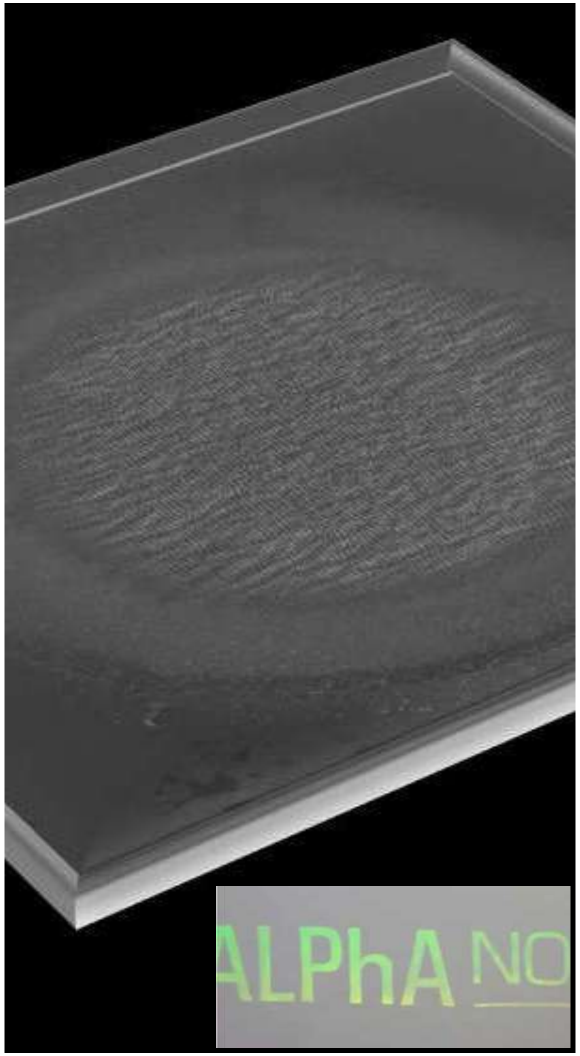
MODIFICATION DE SURFACE DES VERRES PAR LASER

MARQUAGE • ABLATION • DÉCOUPE • TEXTURATION • SOUDAGE



PANORAMA

- Procédés visés
  - Découpe
  - Usinage / ablation
  - Marquage (contraste/couleur)
  - Texturation fonctionnelle (mouillabilité, optique, antibactérien)
- Atouts du laser
  - Procédé sans contact
  - Précision µm–nm, faible HAZ (heat affected zone) with ps/fs
  - Moins d'étapes / pas de chimie (e.g. mask + chemical etching)
  - Intégrable en ligne de production (m^2/min)
- Matériaux cibles
  - Silice fondue, borosilicate (Borofloat, EagleXG..) verres alcalins
  - Saphir, ou dérivée, couches minces sur verre (ITO/Ag/oxydes)

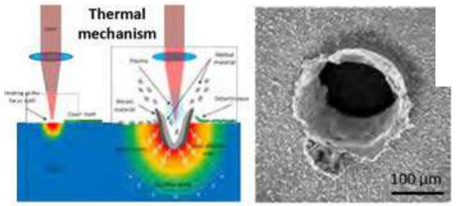


HAZ = Heat Affected Zone

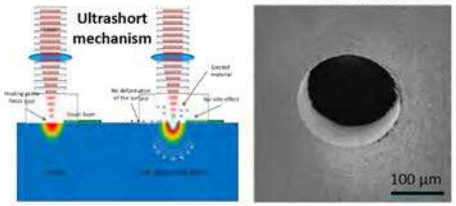
PHYSIQUE ESSENTIELLE (VERRES, IMPULSIONS NS/PS/FS)

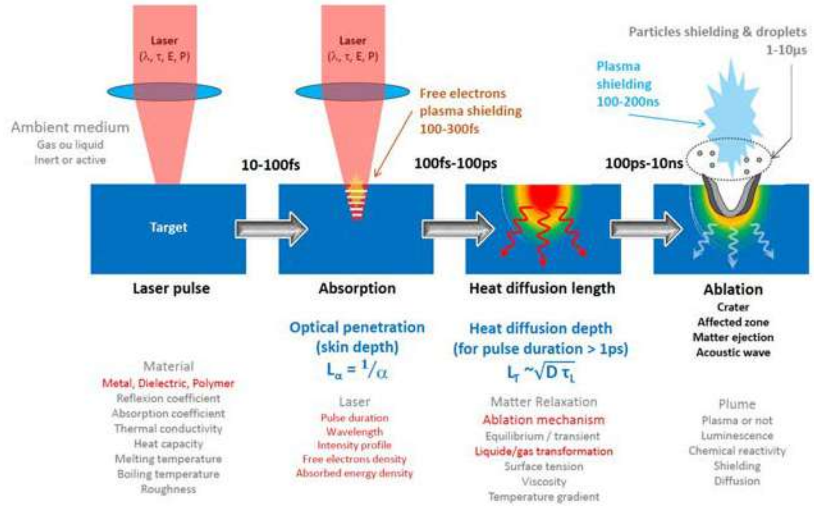
- Absorption non linéaire
  - Ionisation multiphotonique / tunnel (cf Keldysh)
  - Avalanche (impact) → plasma électronique transitoire
- Dépôt d'énergie – transfert au réseau vitreux
  - Électrons chauds → réseau (modèle à deux températures: $T_{electronique}$, $T_{ionique}$)
  - Élévation locale de T, densification/expansion, ondes de choc, ondes de pression
- Phase explosion + effets de bords
  - Cratère d'ablation
  - Onde de pression, chaleur résiduelle, …

ns laser Thermal vs ultrafast



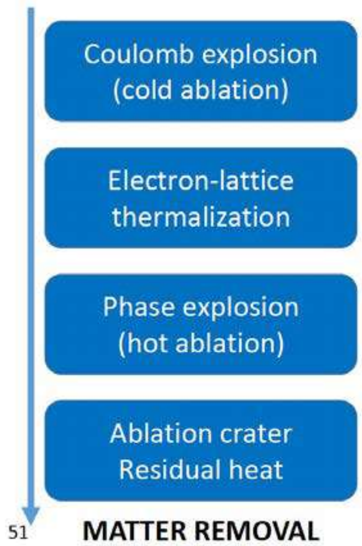
ps, fs laser





PHYSIQUE ESSENTIELLE (VERRES, IMPULSIONS NS/PS/FS)

Mécanismes



Dielectric materials (non organic

Semi conductor	Gap (eV)
Ge	0,7
Si	1,1
InP	1,35
GaAs	1,4
GaP	2,3
SiC	3,3
GaN	3,4
BN	5-6
Diamond	6,0
AlN	6,2
SiO_2 quartz	8,8
Al_2O_3 sapphire	9,0

Guides de choix λ

Higher photo ionization with shorter λ

Higher electrons heating with longer λ

UV : smaller penetration depth, precise ablation depth, marquage “sans chauffage”

Vert/IR : couches métalliques (décoating propre)

Paramètres

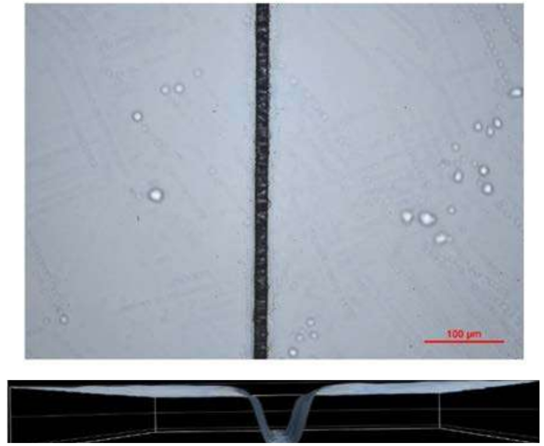
Fluence proche du seuil, durée/recouvrement

Défocus léger ou NA modérée pour marquage « doux »

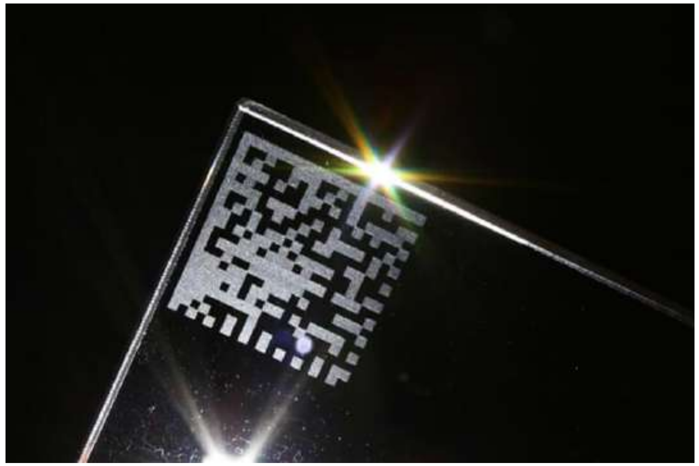
Matrices de trames (multicouches) pour niveaux de gris

MARQUAGE / ABLATION SUPERFICIELLE

- Ablation fs/ps
  - Enlèvement couche par couche (5nm - 10 µm; mm^3/s), faible HAZ
- Rafales GHz (nouveaux laser fs)
  - Efficacité d'enlèvement ↑ (accumulation contrôlée)
- Paramètres clés
  - Fluence par pulse & par rafale
  - Nb de pulses/rafales, cadence (MHz–GHz)
- Applications
  - Scribing fin (0,1–10 µm de large /passe)
  - Cavités peu profondes (logos, QR, microstructures)

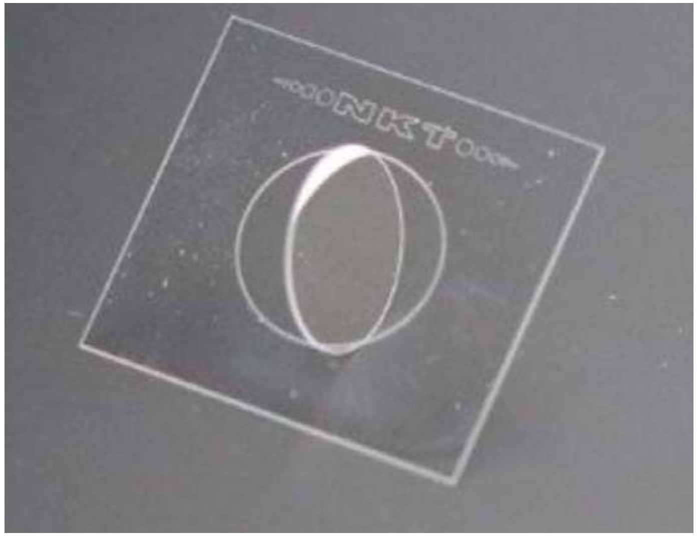


V-shape channel with a 15 µm width and a 20 µm depth.

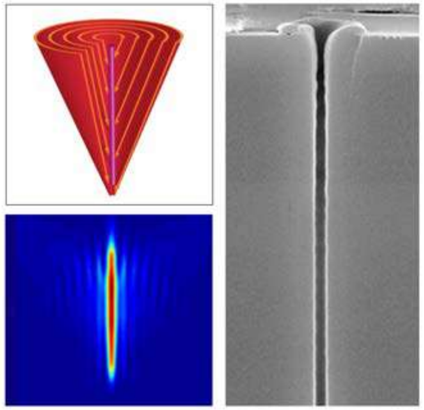


HAZ = Heat Affected Zone

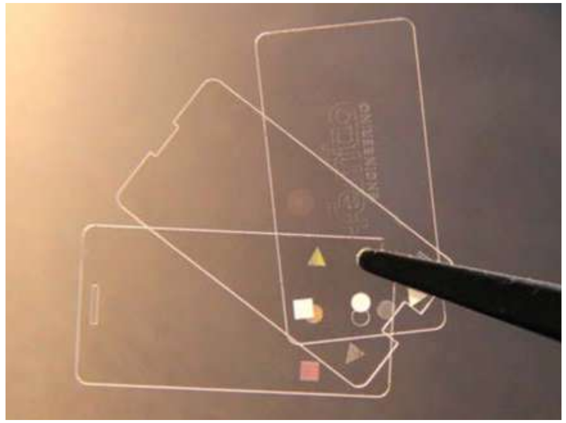
DÉCOUPE / SÉPARATION DU VERRE (FS)



- Approche surface
  - Scribe / ablation (chaud ou froid) + choc (jet, ultrason, flexion)
- Écriture en volume + clivage
  - Focalisation fs dans le bulk (NA adaptée, Bessel-Gauss beam)
  - Lignes de faiblesse (densification/vides) → clivage contrôlé
- Points de réglage
  - Profondeur focale vs épaisseur
  - Polarisation & vitesse de scan

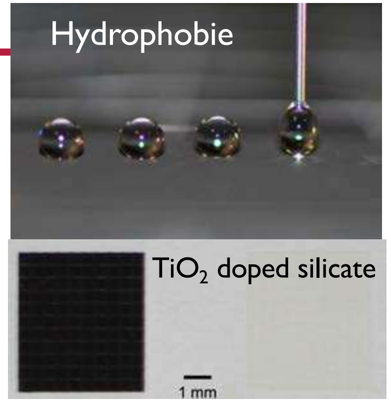


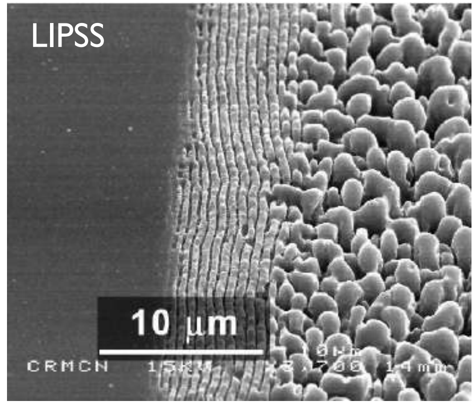
Bessel-Gauss beam

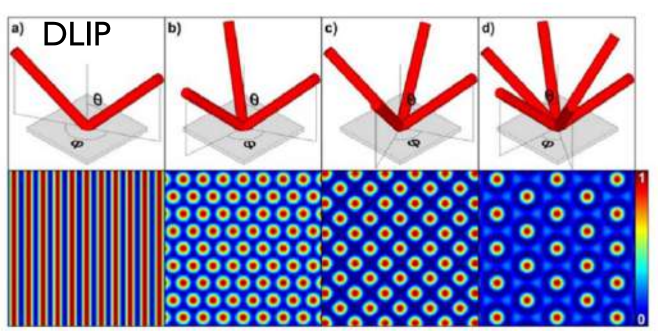


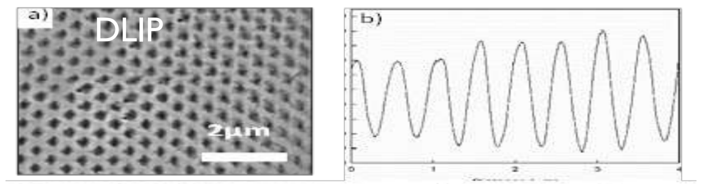
TEXTURATION FONCTIONNELLE (LIPSS & DLIP)

- LIPSS - Laser-Induced Periodic Surface Structures . (auto-organisation)
    - Périodicité ~λ/2…λ et sous-λ
    - Contrôle par polarisation, fluence, dose
    - Propriétés : super-hydrophobie, anti-givre, noir profond (e.g. sub-λ ripples + nano-features trap light)
- DLIP - Direct <u>Laser Interference </u>Patterning
    - Réseaux 1D/2D en 1–2 tirs
    - Pas Λ typiques 0,5–50 µm
    - Très productif (grande surface)
- Intégration industrielle
    - Lignes prod kW, m²/min
    - Réplication par moulage









SOUDURE (CW, FS)

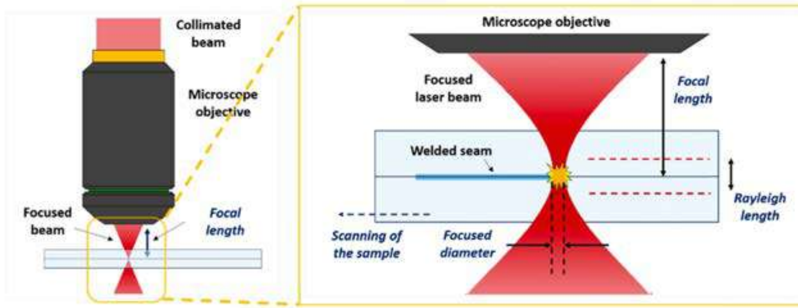
- Principe — L'absorption locallisée augmente T > T_{soft} ou T_{fusion} ; le refroidissement contrôlé crée une liaison permanente à l'interface.
- Plusieurs chemins d'absorption possibles —

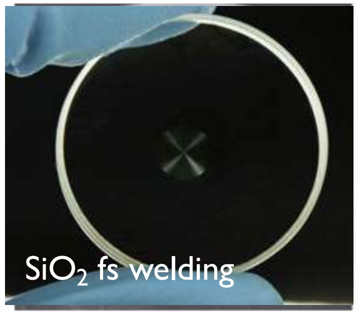
(i) CO_2 à 10.6 µm (surface);

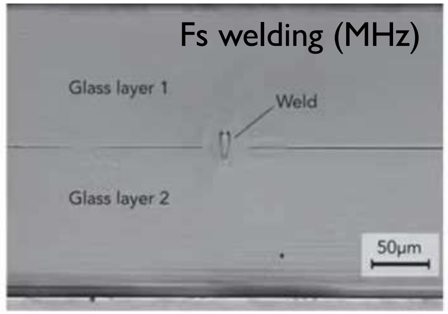
(ii) Proche-IR Cw avec couches absorbantes (métal, C);

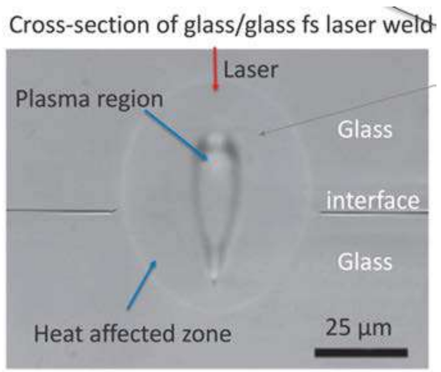
(iii) Ultracourt (fs/ps): absorption non-linéaire à l'interface

- Contrôle de l'interface (écart, planéité), CTE induit des contraintes : le préchauffage et/ou la statégie de scan atténuent cracks ou la biréfringence résiduelle.
- Applications — Fermeture hermétique (capteurs, MEMS, PICs), puce microfluidique, assemblages verre–verre/Si, emballage



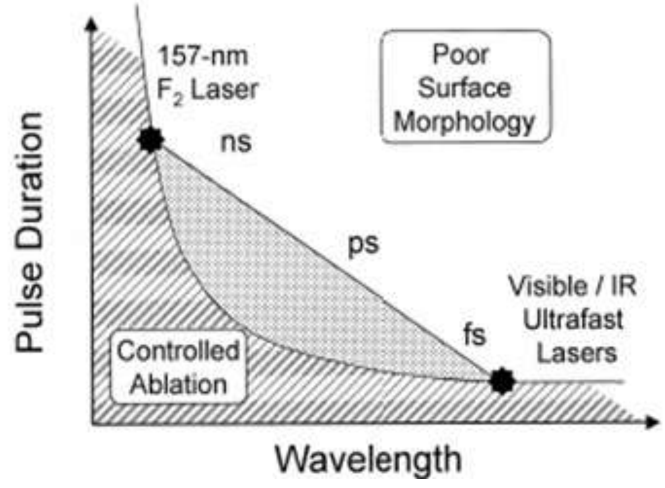


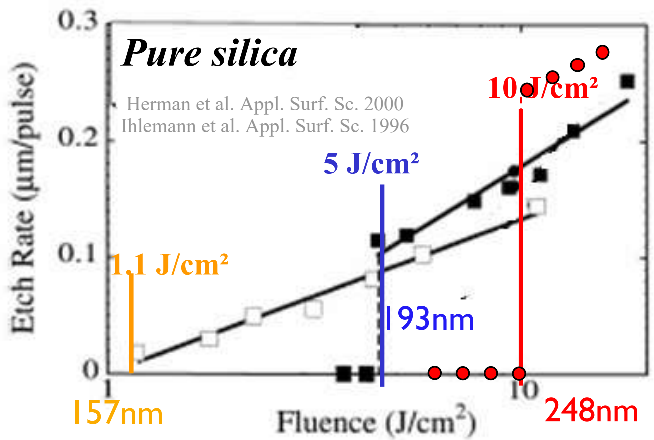




FENÊTRES PROCÉDÉ — ORDRES DE GRANDEUR

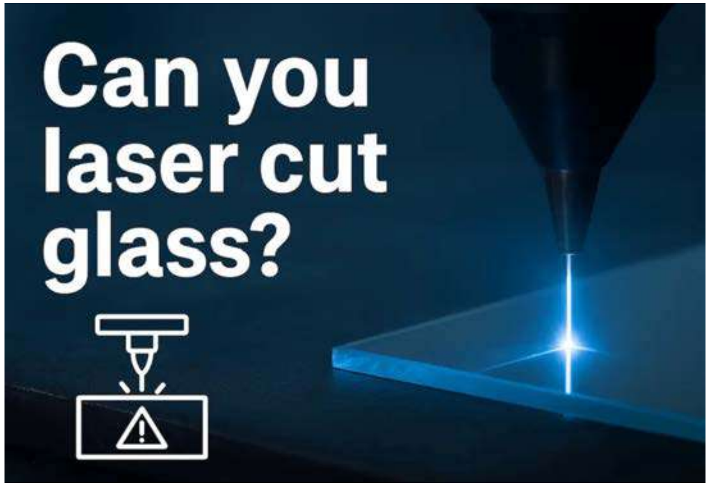
- Durées d'impulsion
  - 100 fs – 10 ps (qualité, HAZ ↓)
  - 5-10ns : économique mais HAZ ↑
- Fluences
  - Proche du seuil d'ablation (0.5–10 J/cm², selon matériaux et longueur d'onde)
  - Plus bas pour contraste/marquage sans enlèvement
- Optique / Focalisation
  - NA 0.1–0.4 (marquage classique, soudure, …)
  - NA ≥ 0.4 ou Bessel (écriture en volume)
- Cadence
  - 100 kHz – multi-MHz
  - Rafales GHz pour ablation efficace (nouveaux lasers fs!)





HAZ = Heat Affected Zone

CHECK-LIST



1) Définir l'objectif : contraste, profondeur, débit, rugosité

2) Choisir λ (UV/Vis/IR) et durée (fs/ps) selon matériau/couches/épaisseurs, HAZ

3) Balayer : fluence, recouvrement, cadence, pulses/rafale

4) Optimiser polarisation (LIPSS/DLIP) et la focalisation (NA, defocus, Bessel)

5) Métrologie : interférométrie, profilométrie, MEB/AFM, angle de contact, endurance, indice, absorption

HAZ = Heat Affected Zone

APPLICATIONS « PRÊT-À-PRODUIRE »

Marquage noir profond sur verre (LIPSS, oxide + slight melt, nanoparticules photoreduction (Ag ou TiO_2)

Décoating sélectif (ITO/Ag/oxydes) pour vitrages fonctionnels

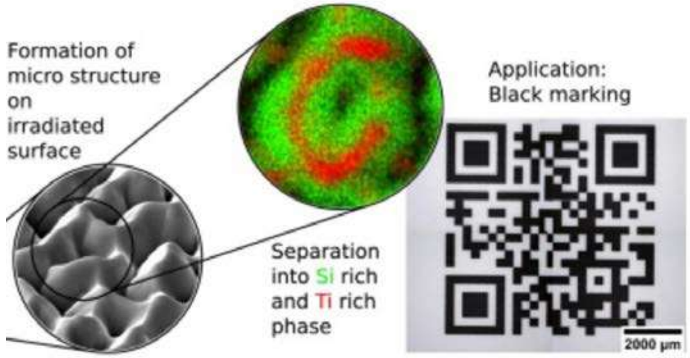
Marquage blanc, coloré: QR code & microgravure haute lisibilité,

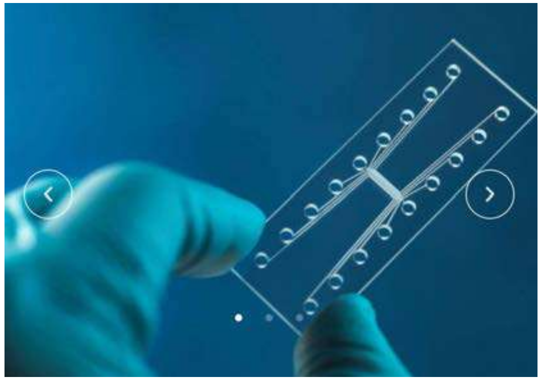
Scribing & découpe via lignes Bessel + clivage

Fonctionnalisation de larges surfaces (hydrophobe, anti-givre, anti-bactérien)

Soudure : Scellage hermétique (capteurs, MEMS, PIC), puces microfluidiques, assemblages verre-verre/Si, soudures d'emballage

Schott SF11, N-SF11 (TiO_2 doped silicate)





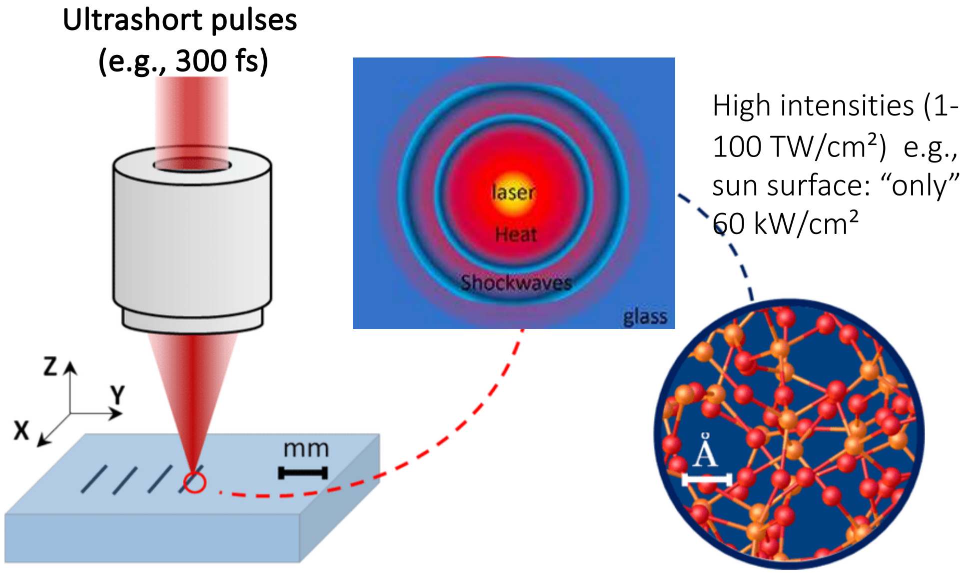
OUTLINE

- Introduction
- Basic concepts
- CO_2 laser
- Surface processing
- **Volume processing**
- Conclusions

Femtosecond laser direct writing (FLDW)

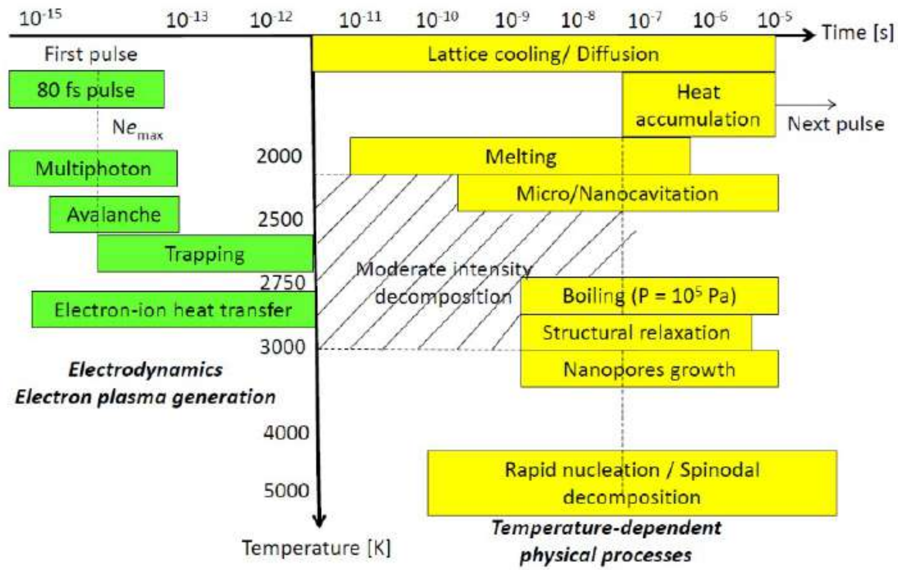
3D laser processing in glasses

Ultrashort pulse : 3D confined HP-HT micro-reactor



- High Temperatures (1000's K)
- High Pressures (>100's GPa)
- Each pulse contain E > glass formation enthalpy
- Strong gradients (T, P, I, E_{dc})

Few words on fs – matter interaction

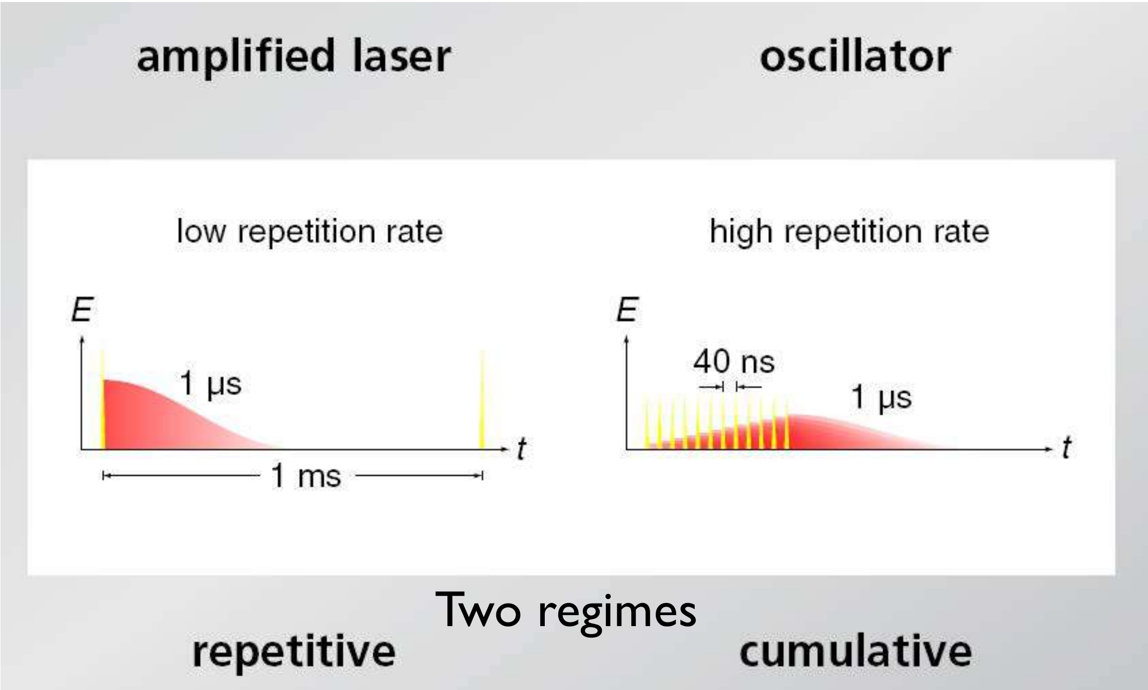


A plasma mediated process

Femtosecond laser direct writing (FLDW)

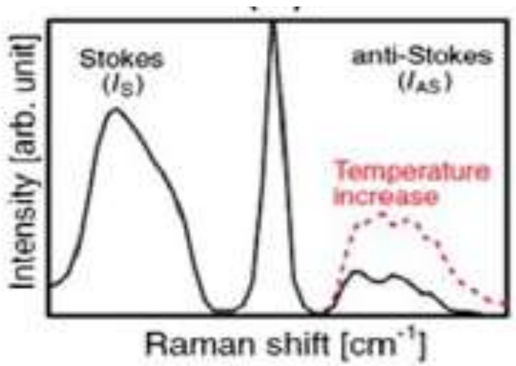
Femtosecond-materials interactions: Temperature effects

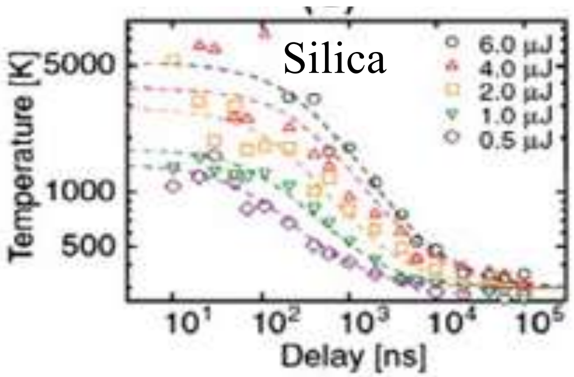
Thermal effects are somehow decoupled from optical one



Heat diffusion time a few µs in silica
So, relaxation time has to be taken into account

Single pulse

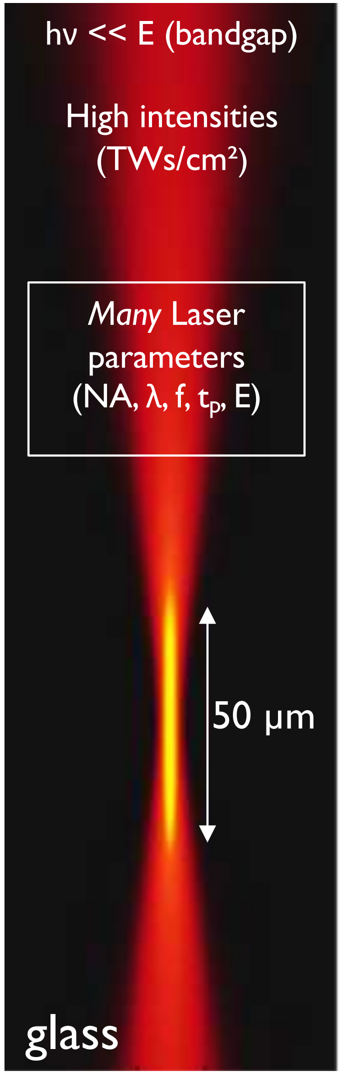


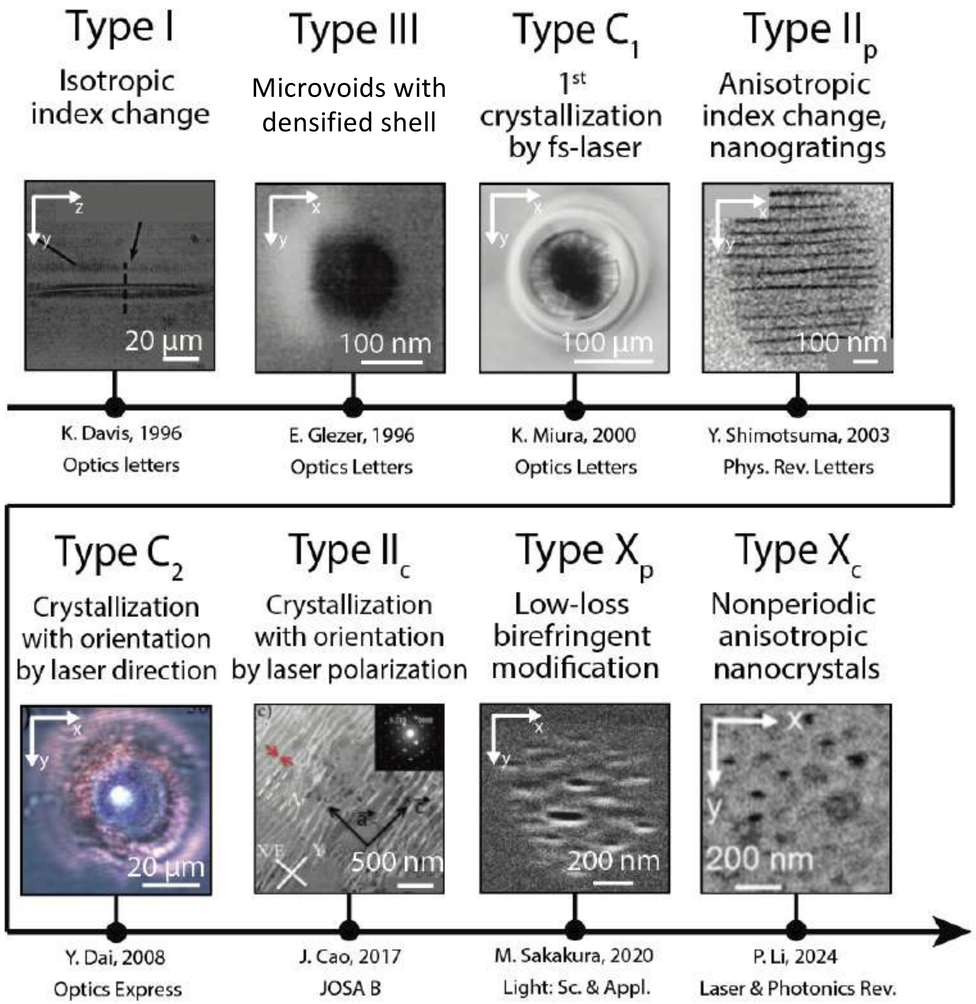


Fernandez, T. T. et al. (2018). Progress in Materials Science 94
Tomoki, Yoshino et al. (2012). Japanese JAP 51(10R)

Femtosecond laser direct writing (FLDW)

So many possibilities for glass microstructuration





*SiO_2, 800 nm, **160 fs,** 100-500 kHz **(below heat accumulation)**, 100 µm/s, Xx writing configuration*

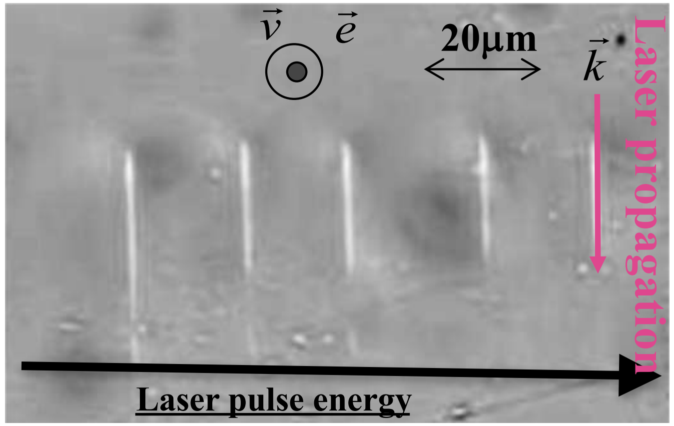
TYPE I: 3D ENGINEERING OF « ISOTROPIC » INDEX CHANGES

- Definition — Smooth, permanent refractive-index changes (Δn) with no cracks or voids, minimal stress birefringence

- Nonlinear absorption (multiphoton, avalanche) → free carriers; sub-ns relaxation.
- 3D localization (up to cm below the surface)
- "Voxel" longitudinal size (typ. 5-100 μm) but depends on pulse duration, NA, aberrations, pulse shaping (e.g. Bessel beam)…

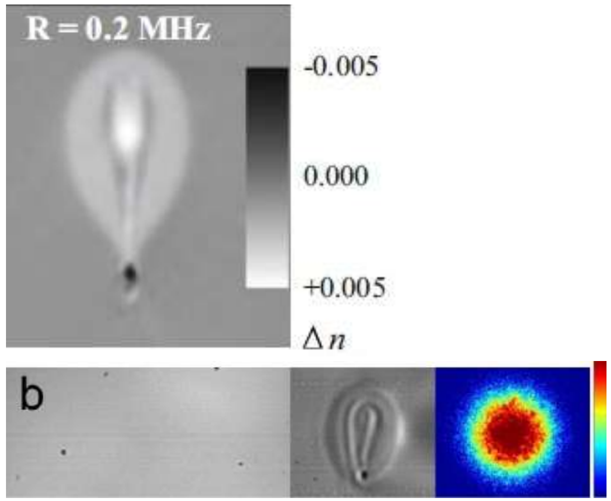
- Heat accumulation at high rep-rates can increase Δn but must avoid damages, bubbles, …

Cross section (xz) - Repetitive regime

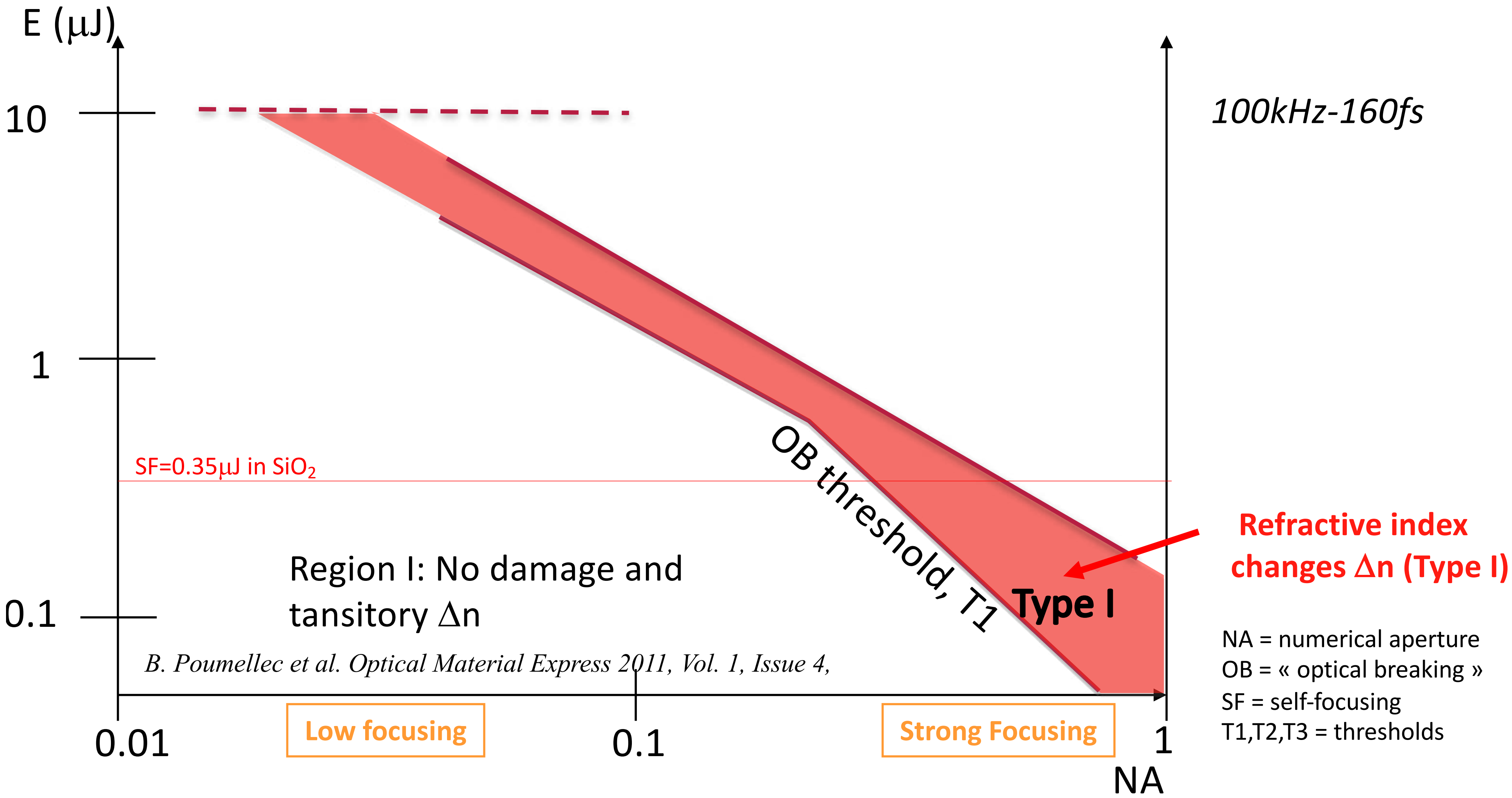


Lancry et al. OME (2011)

Cumulative regime



TYPICAL WRITING WINDOW (MATERIAL-DEPENDENT)



Pulse: 50–300 fs | λ: 800–1100 nm | NA: 0.3–0.65 (buried focus).
Rep-rate: 100 kHz–5 MHz | Scan: 0.1–20 mm/s |

TYPE I: MECHANISMS

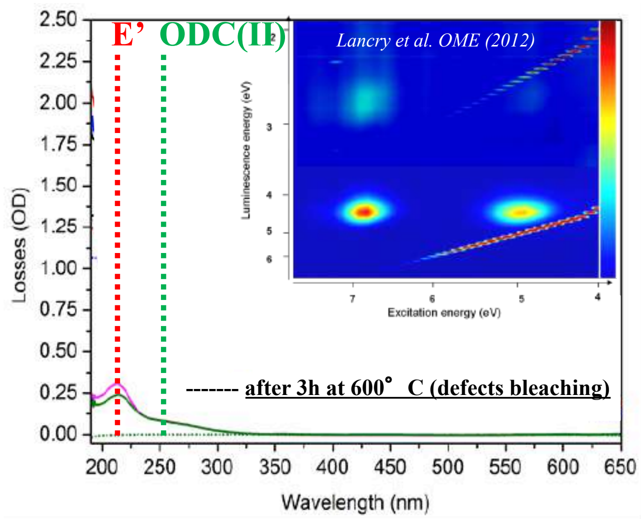
Point/color centers → Δn

- Defects centers so called colors centers
  - NBOHC, (Non Brigding Oxygen Hole center) ODC (Oxygen Deficient center), E'
  - seen by PL (UV excited photo-luminescence) and OA (optical absorption)

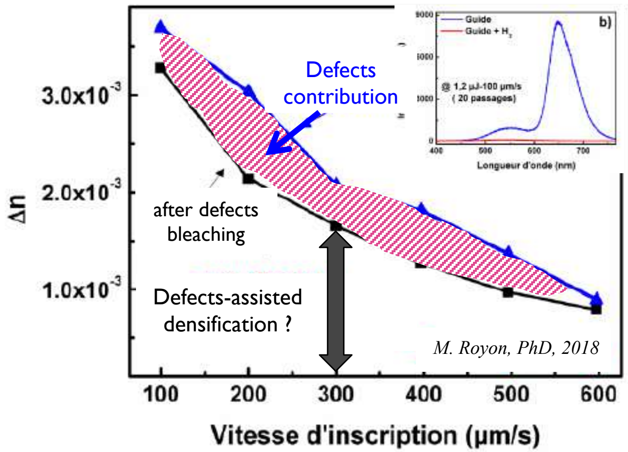
- Points defects (color centers) contribution : < 5.10^{-4}.

(nearly like in UV ns laser glass photosensitivity)

- Main contribution: « Defects-assisted » densification



Cf Cours N. Ollier



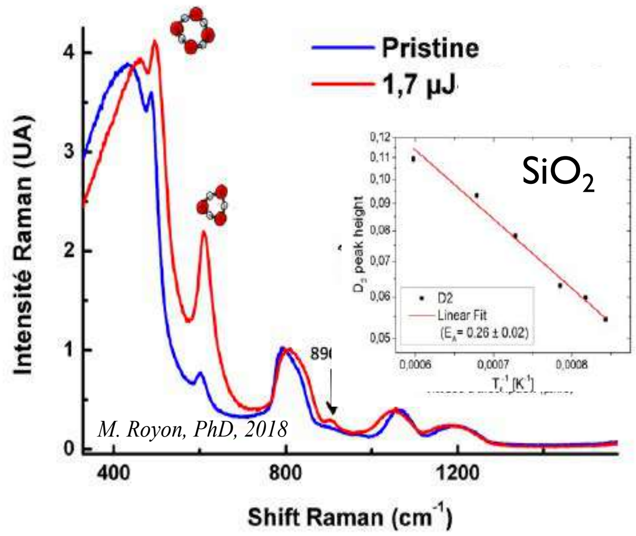
SiO_2, 800 nm, 160 fs, 100 kHz, 100 µm/s, 0.05-0.4µJ,

TYPE I: MECHANISMS

Densification → Δn

- Vibrational (Raman or FTIR) signature of a permanent densification in SiO_2

cf cours de N Ollier



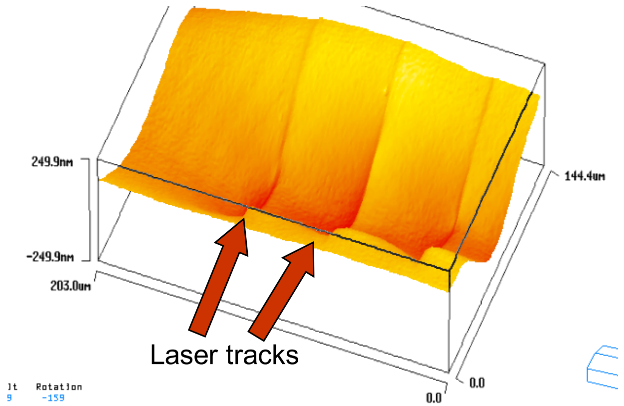
M. Lancry et al. Opt. Material Express, Vol. 1, (2011)

- Mechanical signature of glass densification (AFM, PSI, profilometer)

$$\Delta n_{\alpha\alpha} = -\frac{n^3}{2}\left[p_{11}\varepsilon^e_{\alpha\alpha} + p_{12}\left(\varepsilon^e_{\beta\beta} + \varepsilon^e_{\gamma\gamma}\right)\right] - \frac{\left(n^2-1\right)\left(n^2+2\right)}{6n}.(1-\Omega).Tr\left(\varepsilon^p\right)$$

Photo-elastic relation *Lorentz-Lorenz*

Densification and stress field

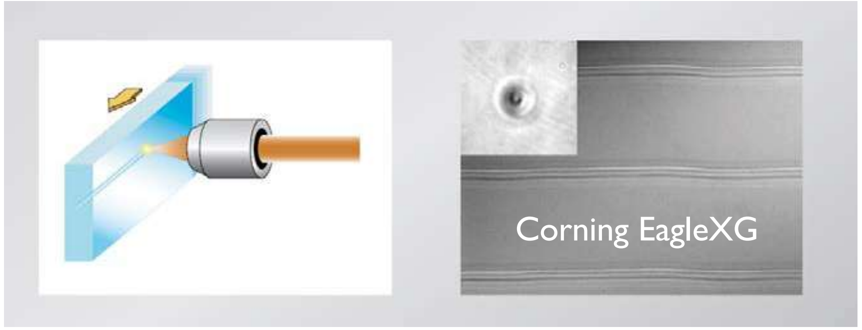


Poumellec et al. Opt. Express (2008)

- Type I origin: defects assisted densification likely assisted by heat effects (fictive temperature increase)

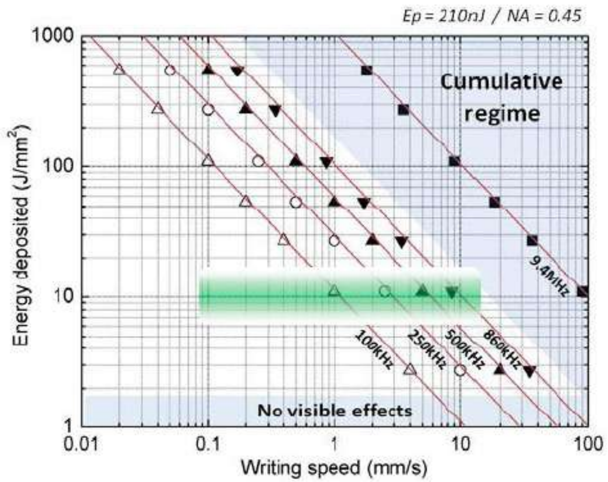
SiO_2, 800 nm, 160 fs, 100 kHz, 100 µm/s, 0.05-0.4µJ,

TYPE I: TECHNOLOGICAL ASSETS



- $\Delta n \approx 10^{-4}$–10^{-2}; (m-lines, near field refractometry, QPM, DHM, QPI, Brewster …)
- Waveguides with low loss (<0.5 dB/cm in fused silica).
- Ultralow losses down to 0,04dB/cm in SiO_2; 0,052dB/cm in Gorilla glass (Corning)

J. Lapointe,, "Making smart phones smarter with photonics," Opt. Express 22, 15473-15483 (2014)

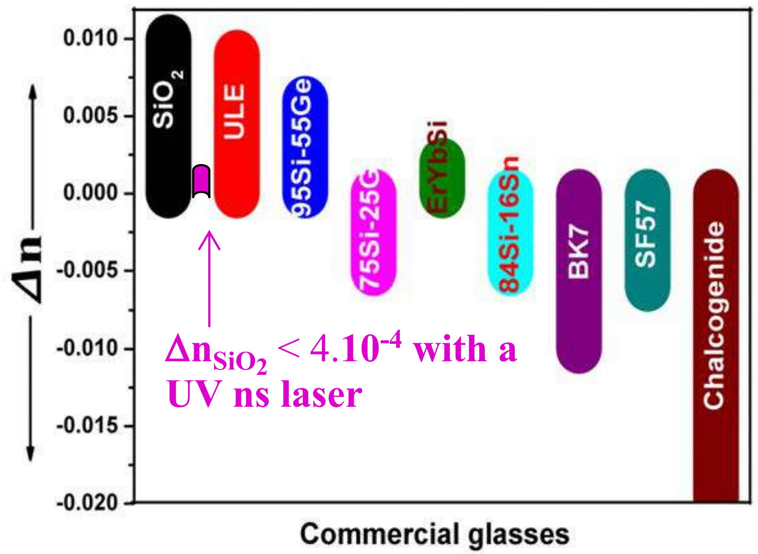


- Industrial potential - single mode 3D waveguides :
  - ➢ 1 cm/s (repetitive regime)
  - ➢ 10 cm/s (cumulative regime)
  - ➢ 1m long – 30 cm/s reported in Gorilla glass

QPM (Quantitative Phase Measurements), DHM (Digital Holohraphy Microscope), QLSI (Quadriwave Lateral Shearing Interferometry)

TYPE I: GLASS MATERIALS
VIS, NEAR-IR SPECTRAL RANGE

- Works in all glasses (contrarily to UV ns or cw light)
- Δn ≈ up to 1×10⁻²; (even more in mid-IR glasses)
- Nearly polarization-insensitive (low stress)



- Δn positive / negative vs composition (T_f related)
- Best Δn>0 : high-purity fused silica but also mid-IR (see next slide).
- Network modifiers (Na, K) or B, P lower thresholds but may raise losses; « optimize trade-off.»

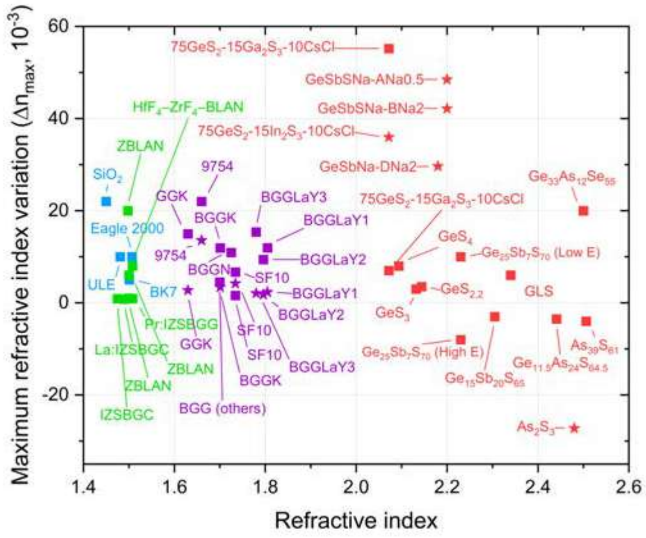
QPM (Quantitative Phase Measurements), DHM (Digital Holohraphy Microscope), QLSI (Quadriwave Lateral Shearing Interferometry)

TYPE I: GLASS MATERIALS
TOWARDS IR SPECTRAL RANGE

- Best Δn/ high reflection loss in chalcogenide
- $\Delta n > 5 \times 10^{-2}$; in some Chalcogenide (GeS$_2$ based)
- Δn up to 2×10^{-2}; in Fluoride
- Δn up to 2×10^{-2}; in Heavy Oxide (BGG = Barium Gallo-Germanate) or Alumino-germanate

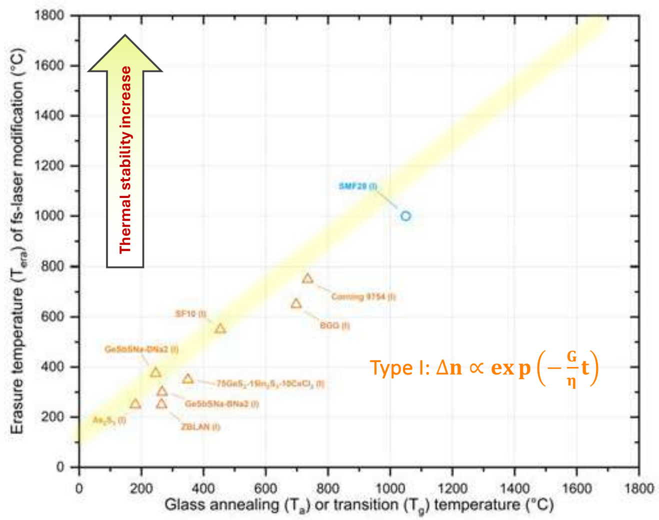
cf cours verres IR de Laurent Calvez

- Thermal stability mostly driven by glass structural relaxation $\eta(T)/G(T)$
- High thermal stability in heavy oxide glasses (Corning 9754 or BGG)
- Fluoride and Chalcogenide owns quite limited thermal stability (typ. below 300°C).



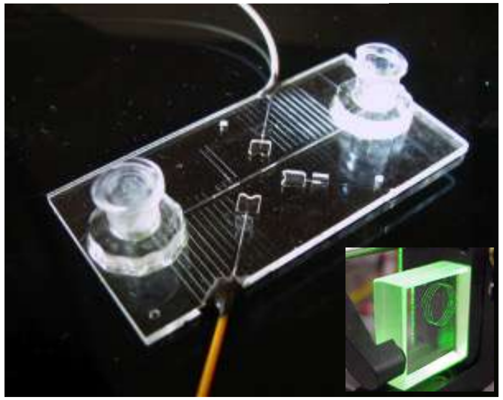
J Ari et al., Optical Materials (2025)

Compilation of results – isochronal annealing experiments (Δt = 30 min)

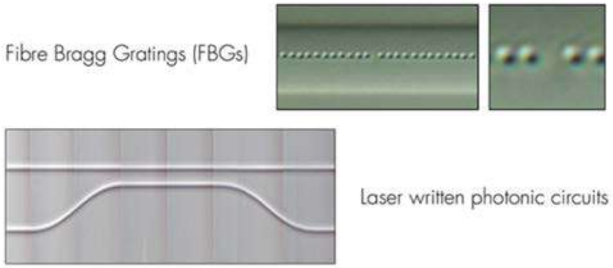


TYPE I: commercial applications

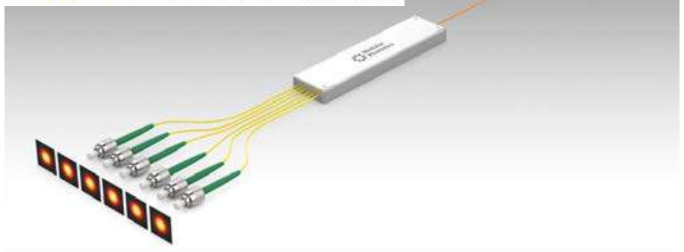
Translume
Guiding Optical Solutions



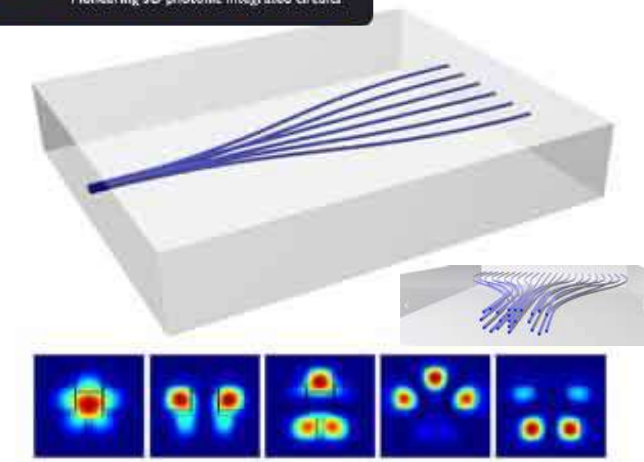
Optofab ANFF



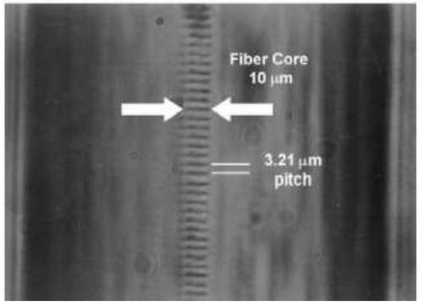
Modular Photonics



OPTOSCRIBE
Pioneering 3D photonic integrated circuits



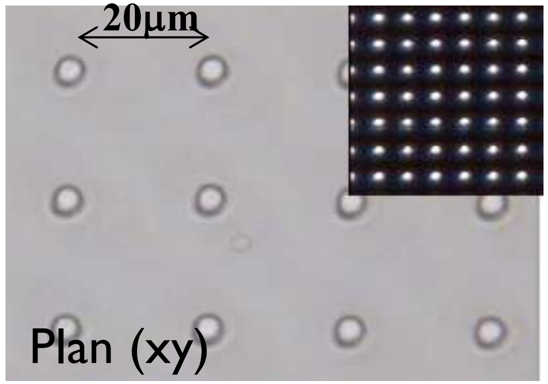
TeraXion



- 3D buried waveguides, splitters/ couplers, MZIs, laser waveguides.
- Optofluidic chips, lab-on-chip;
- Sensors (RI, temperature) via Δn control or Bragg grating period.
- Lenses (GRIN, Fresnel)
- Phase mask

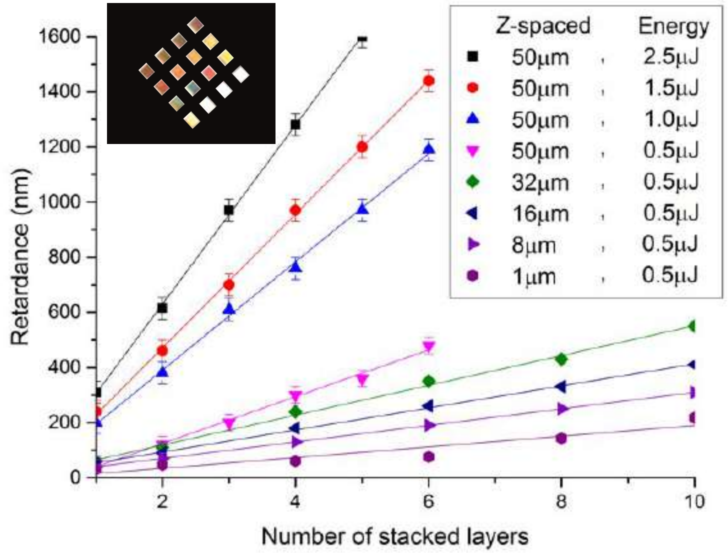
TYPE II: 3D ENGINEERING OF « ANISOTROPIC » INDEX CHANGES

- Definition — Self-organized, sub-wavelength periodic index modulation (nanogratings), producing strong birefringence



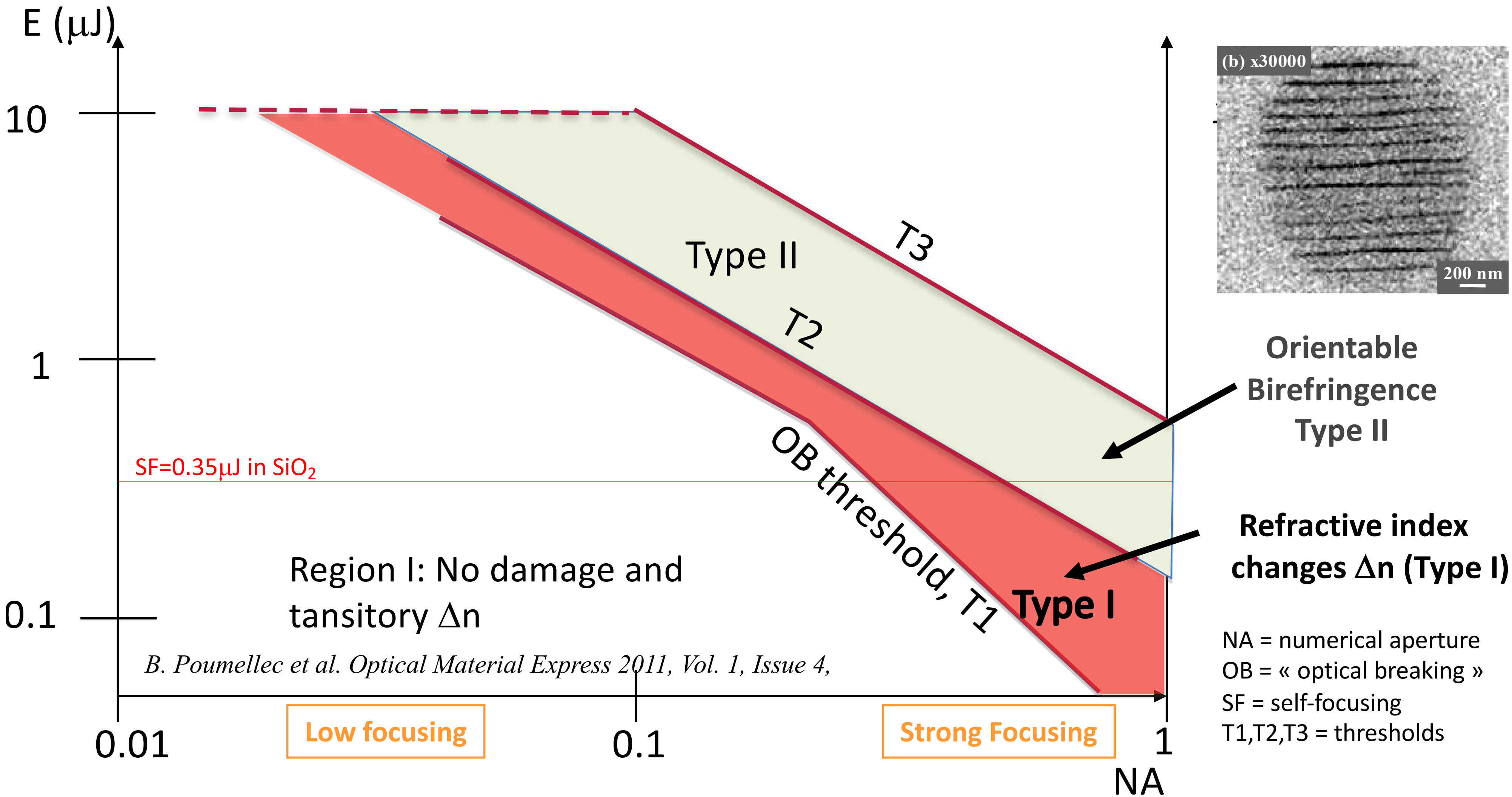
Main Features:

- Negative uniaxial birefringence (n_e-n_o) up to -10^{-2} in SiO_2
- Retardance (n_e-n_o).L up to 600nm for a single layer
- On demand slow/fast axis orientation
- High laser damage threshold (>23 J/cm²@1064nm, 5ns)
- High thermal stability (years at 800° C)
- Medium writing speed (up to 1cm/s)



M. Lancry et al. Micromachines (2014)

TYPICAL WRITING WINDOW (MATERIAL-DEPENDENT)

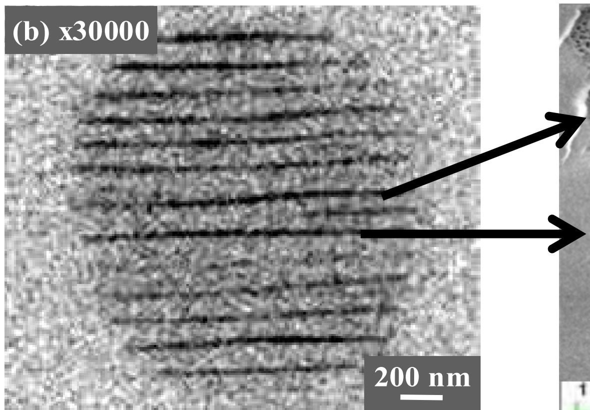


NA = numerical aperture
OB = « optical breaking »
SF = self-focusing
T1,T2,T3 = thresholds

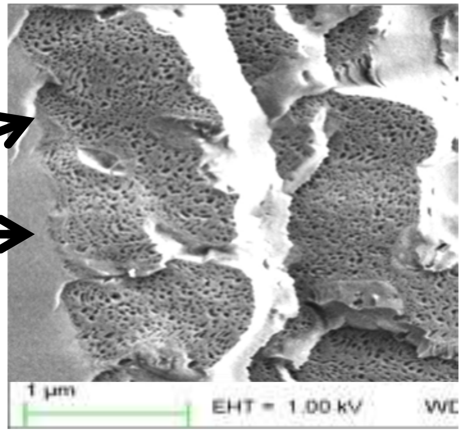
Pulse: 50–2000 fs | λ: 800–1100 nm | NA: 0.1–0.65 (buried focus).
Rep-rate: 100 kHz–1 MHz | Scan: 0.1–10 mm/s |

TYPE II: MECHANISMS

- The smallest « self-organized » nanostructures created by light in the glass bulk (first observed in SiO_2)
- Ultrafast decomposition into $x.O_2$ + $SiO_{2(1-x)}$ in less than 1 µs
- Need multiple pulses (from few pulses to thousands and more)
- Polarization oriented

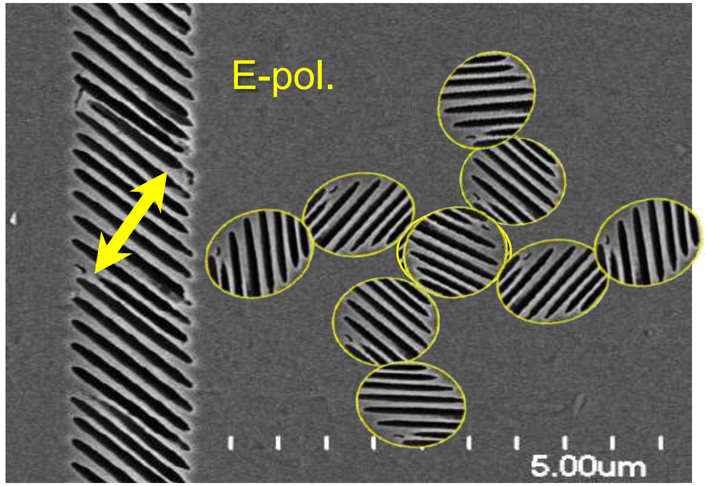


Shimotsuma et al. Phys. Rev. B 91 (2003)



M. Lancry et al. Laser Photonics Rev. 7 (2013)

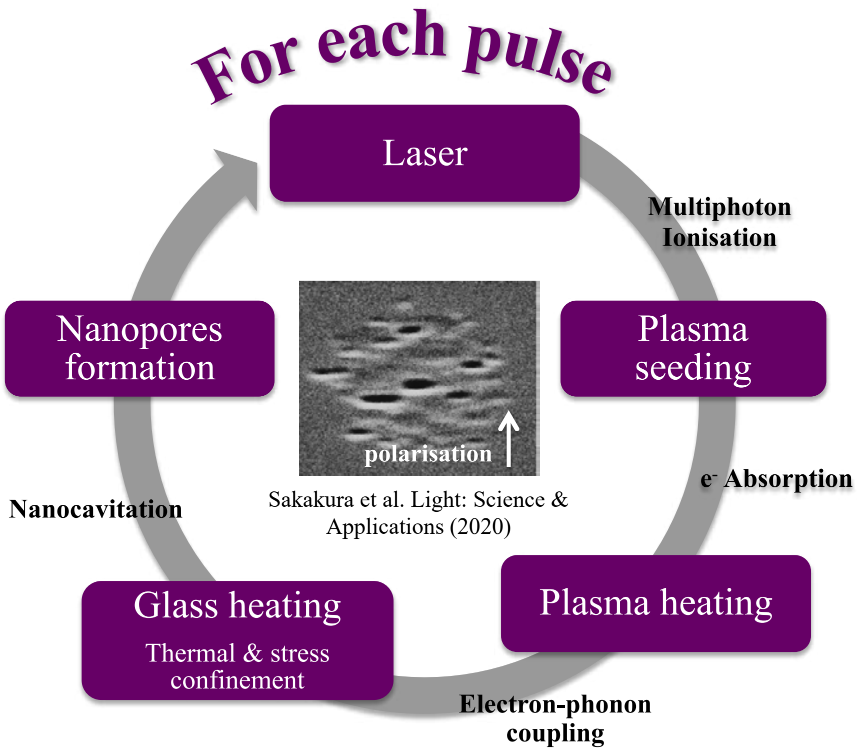
Controllable orientation (in 3D)



S. Juodkazis, Sci Report 7 (2017) *J. Lu et al. APL (2023)*

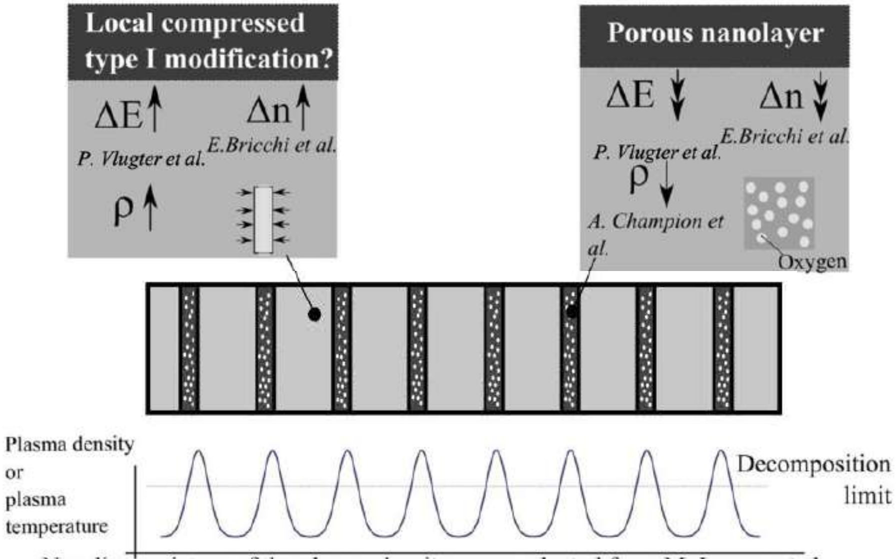
TYPE II: MECHANISMS

Nonlinear absorption → dense free-electron plasma spatial structuration



Sakakura et al. Light: Science & Applications (2020)

Interference/scattering of the writing field and plasma mediated nanocavitation process

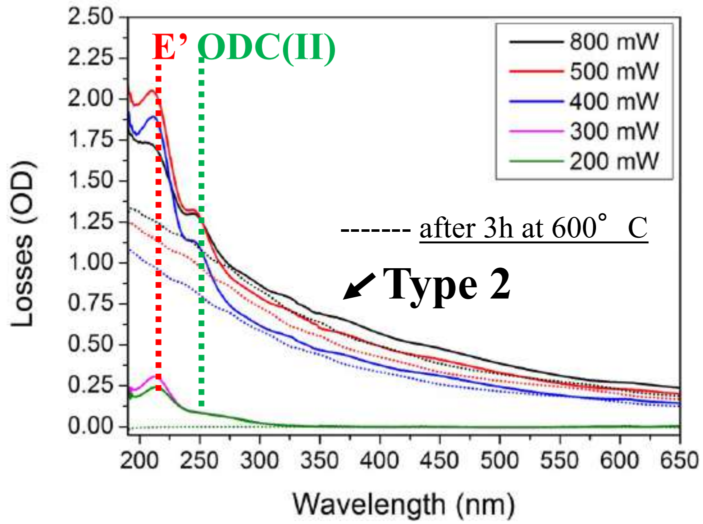


Non-linear picture of the plasma density wave, adapted from M. Lancry et al.

P. Vlugter et al. Phys Rev materials 4, (2020)

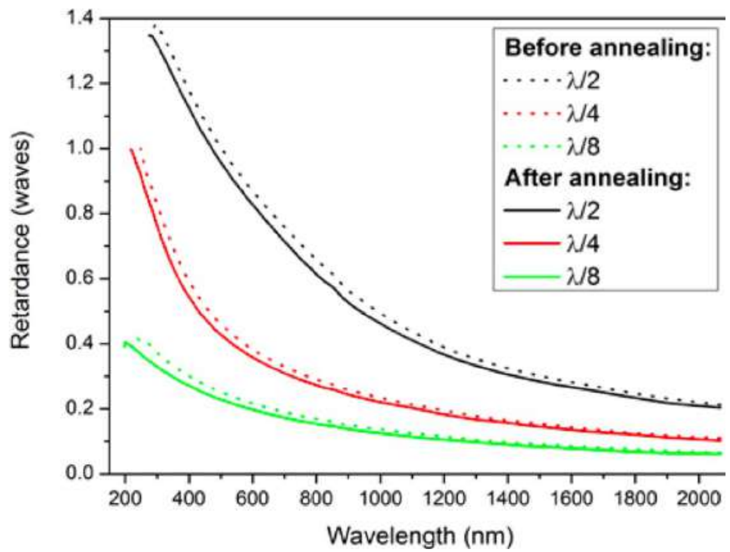
TYPE II: TECHNOLOGICAL ASSETS

- Strong light scattering remains e.g. 75% transmission for λ/2 @ 532nm but 90-95% in the near-IR
- Anisotropic and oriented light scattering
- Better Transmission after heat treatment at 600°C: erasure of points defects/color centers



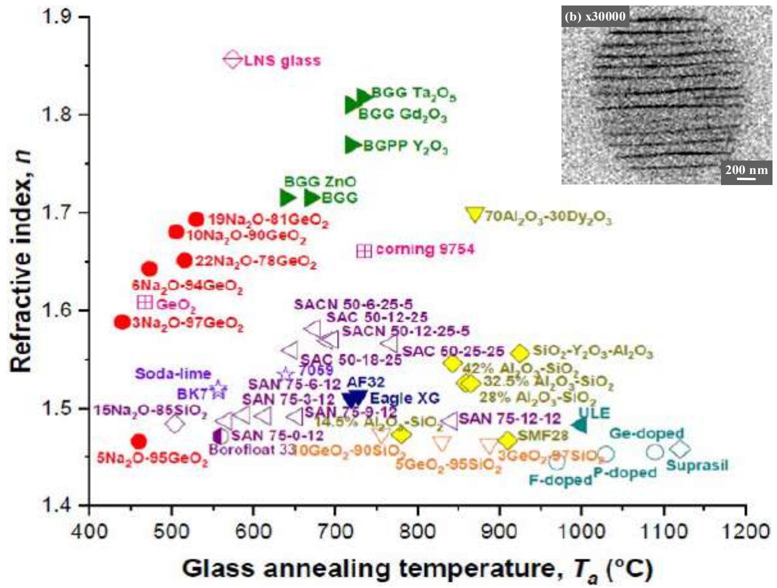
M. Beresna et al Apl Phys Lett **103** *(2013)*

- Broadband birefringence,
- Strongly chromatic
- Only slight birefringence decrease after heat treatment (typ 3%)
- Defects play a role in the "seeding mechanisms" but low contribution to the birefringence



TYPE II: GLASS MATERIALS

- Initially only in silica / doped silica
- Nanogratings can be achieved in any oxyde glasses !
- Looking forward to see them in Fluoride, chalcogenide etc… ???

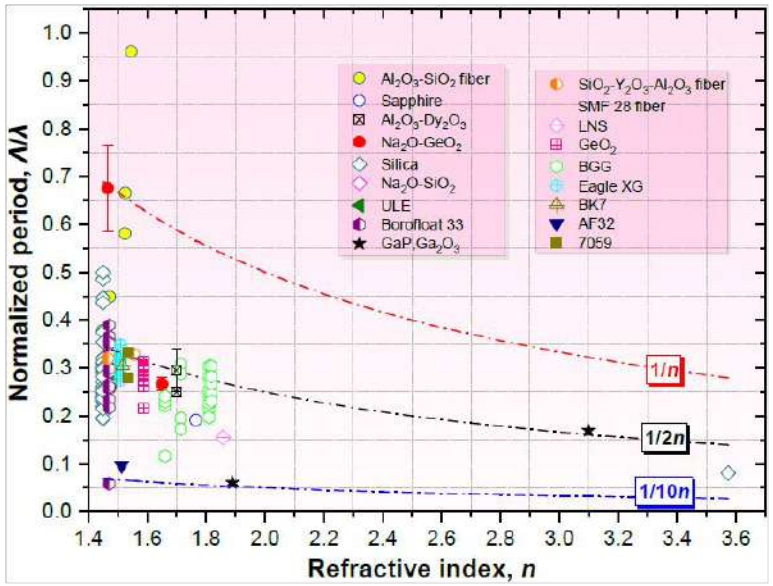


- Nanogratings period Λ/λ_{laser}

$$\lambda/n < \Lambda < \lambda/10n$$

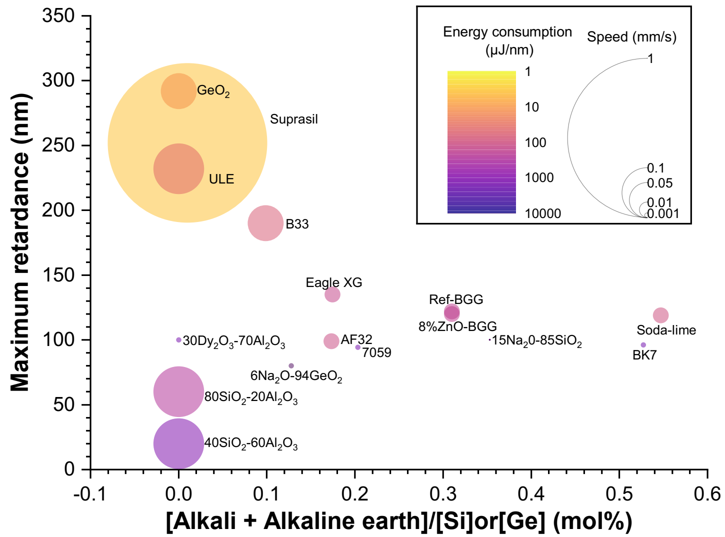
- Period Λ depends on the concentration C_i of "inhomogeneities" (thus glass composition i.e. AF32, B33)
- Higher pulse, number higher C_i shorter Λ !

A Rudenko et al. Phys Rev B (2016)

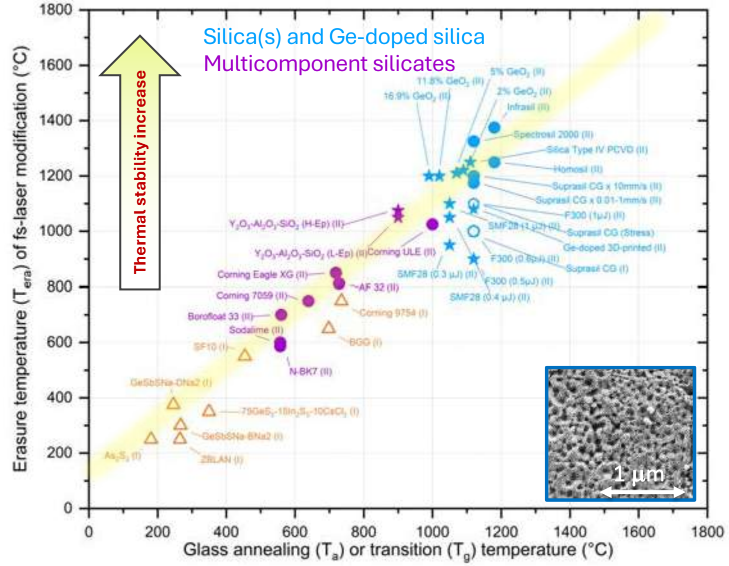


TYPE II: GLASS MATERIALS

- Up to now, SiO_2 best candidate to unlock industrial potential (low energy consumption, high writing speed, high retardance)
- Alkali and alkaline earth are detrimental for nanogratings formation.
- Alumino-borosilicate: 1:1 cationic ratio between Ca and Al is better (charge compensation) : viscosity(T) driven !



- Thermal erasure can be modeled using a Rayleigh-Plesset model
- Viscosity driven (mostly) but also related to σ and "Φ" init
- So SiO_2 would be the best performer ? Not fully true ;)

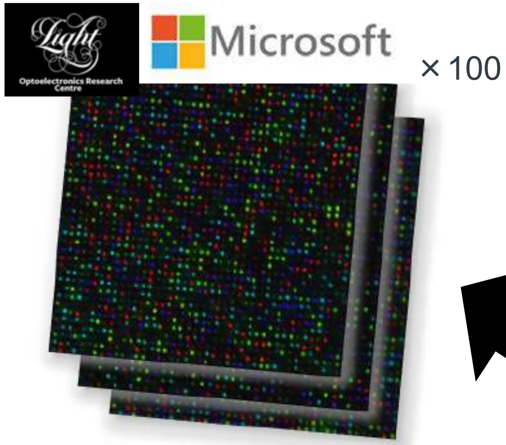


cf cours fibres de Maxime Cavillon

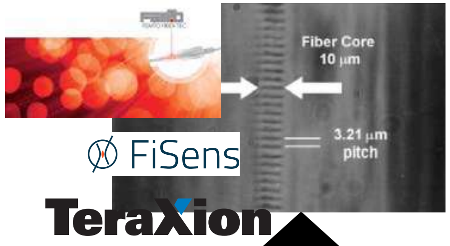
Xie et al., Applied Optics (vol. 62, 2023), Shuen et al., Sensors (vol. 20, 2020)

TYPE II: commercial applications

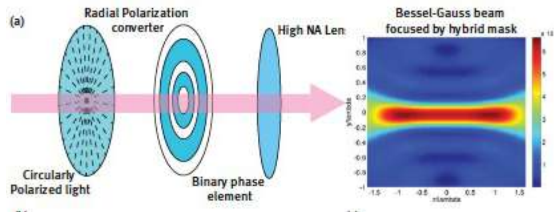
5D optical data storage

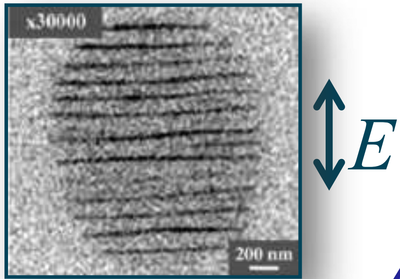


High T fiber sensors

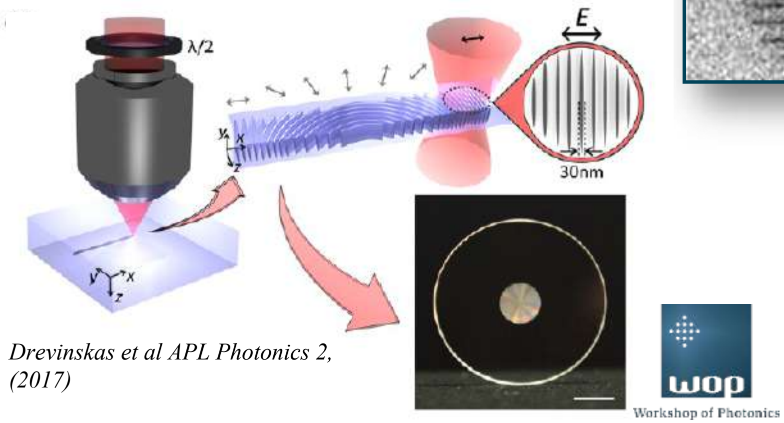


2D- 3D geometric phase elements





3D space variant birefringent devices

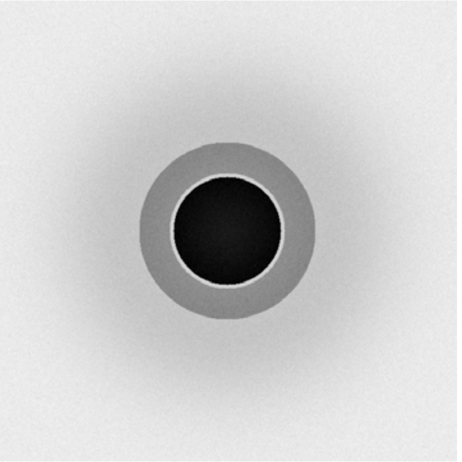


Drevinskas et al APL Photonics 2, (2017)

Optomechanics and optofluidics using selective laser etching

TYPE III — VOIDS & 3D ENGINEERING OF LIGHT SCATTERING

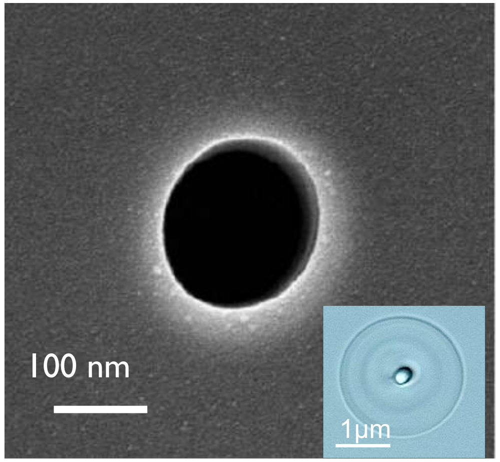
- Definition — Nanoscale to microscale voids/cavities formed by micro-explosions; surrounded by densified shell and stress.



Schematic cross-section: central cavity with densified shell and stress halo

Main Features:

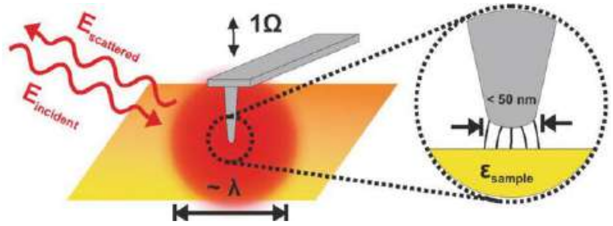
- Single or chains ("pearl strings")
- Very high index changes (Δn decreases -0,5 in SiO_2 !)
- Strong light scattering
- High writing speed (typ. up to few m/s)
- Residual stress-birefringence and possible microcracks



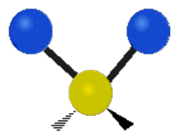
Gamaly et al. PHYSICAL REVIEW B 73, 214101 2006

TYPE II: MECHANISMS

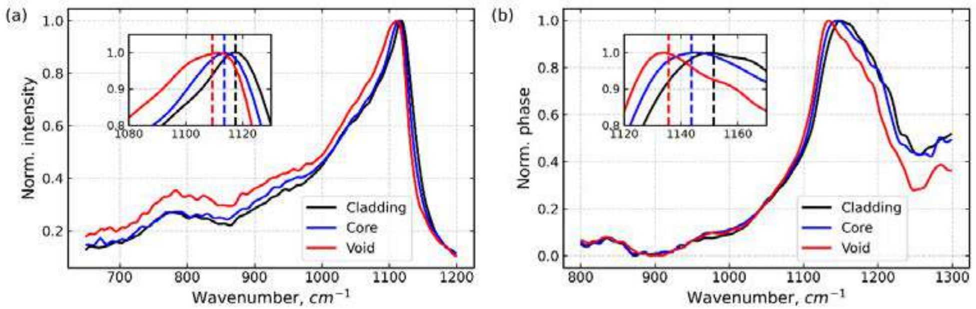
s-SNOM scattering-type scanning near field optical microscopy made at SOLEIL Synchrotron (SMIS)



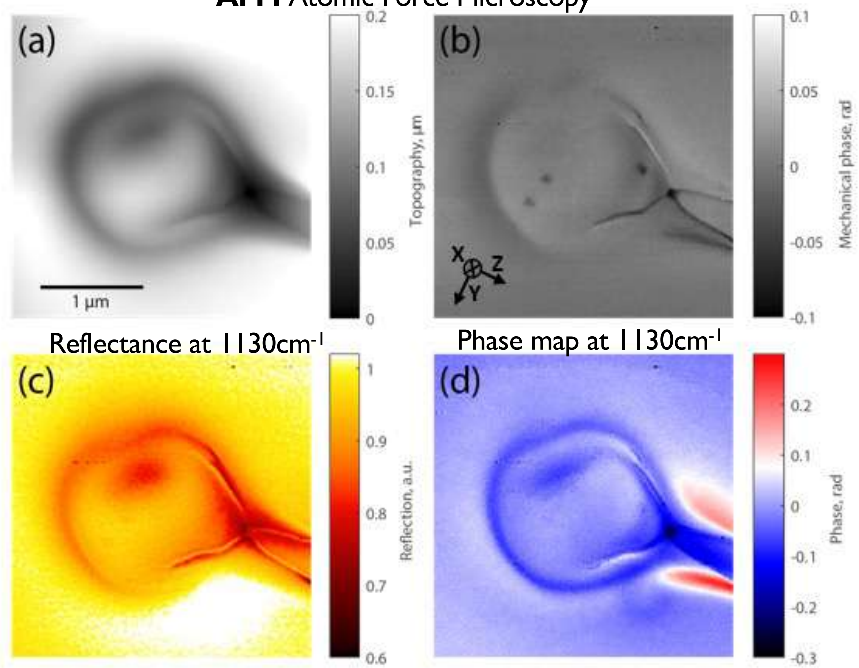
- Surface topography (e.g. AFM) depression : mechanical signature of densification
- Vibrational signature of densification using IR s-SNOM at σ=1130 cm^{-1} (Si-O-Si asym stretching),
- Phase contrast at 1130cm^{-1} : Δn increase



N. Shchedrina 2025, https://doi.org/10.1111/ijag.16706



AFM Atomic Force Microscopy

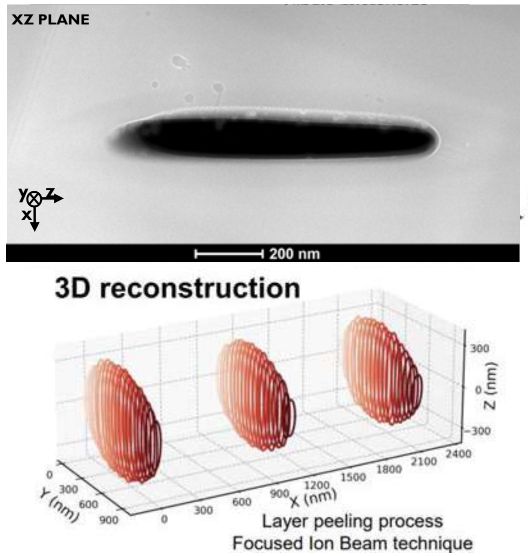


M. Sosa et al. Nanomaterials 2024, 14, 1228.

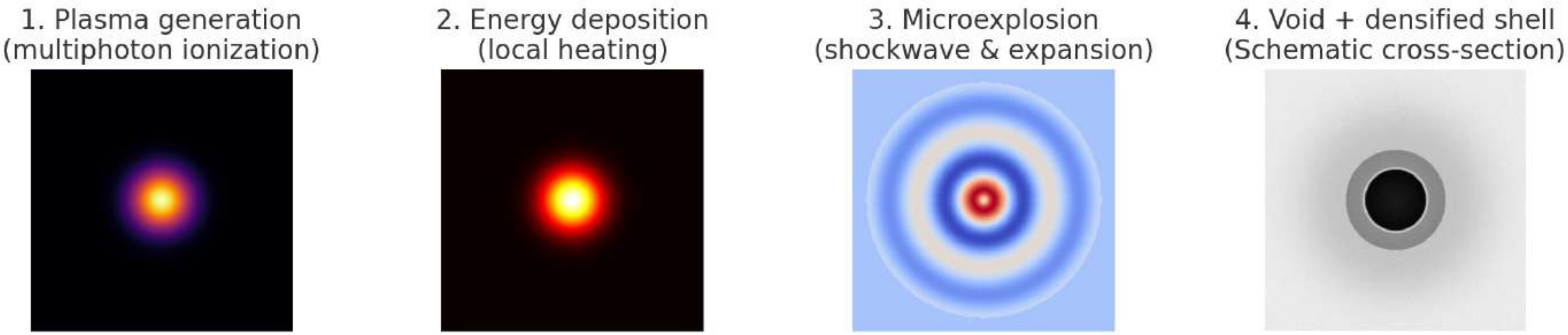
- Densification is estimated 6% which involved High Pressure (>10 GPa) mechanisms

TYPE II: MECHANISMS

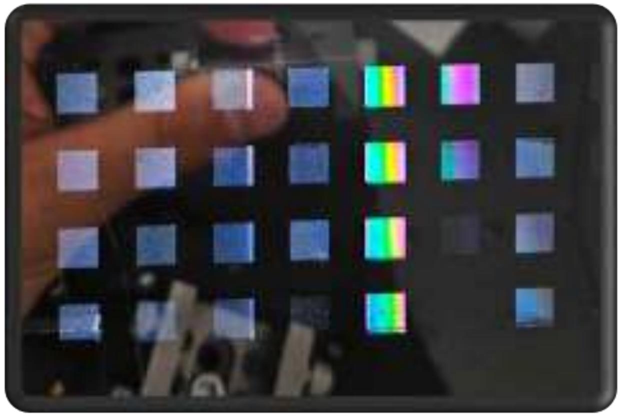
- Generation of a dense plasma (multiphoton ionization), with an electron density near or above the critical density (~10^{21} electrons/cm^3).
- Localized energy deposition (ultrafast heating, 1–10 ps).
- Supersonic material expansion (CTE-driven) creating a shock wave.
- Void formation (a cavity with a densified surrounding shell).

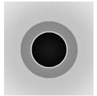


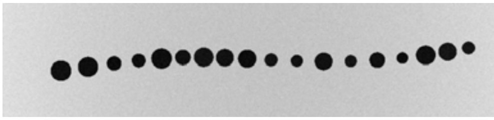
M. Sosa et al. Nanomaterials 2024, 14, 1228.



TYPE III: TECHNOLOGICAL ASSETS



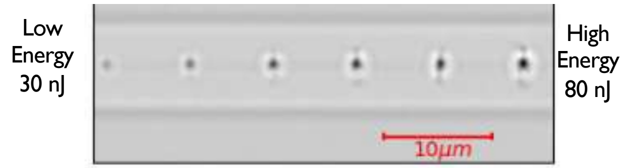
- High NA >1 (oil immersion objective): single void 
- Low NA : voids chain

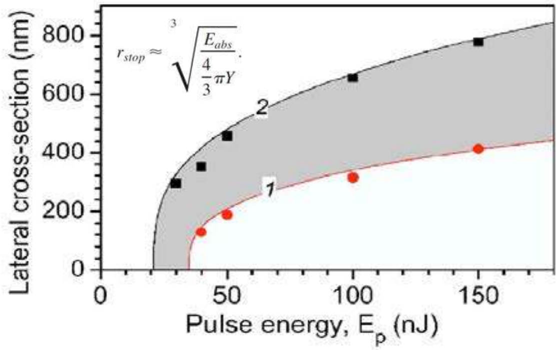


- Single pulse writing → high writing speed e.g. 100 mm/s using 100 kHz laser repetition rate
- Strong light scattering (Mie regime) → forward scattering by voids: $\lambda/10 <$ size $< \lambda$

- Void radius and shock-affected zone scale up with absorbed energy (and elastic modulus)
- High Δn shell (few 10^{-2}) : densified shell (6% $\Delta\rho/\rho$)

QPM quantitative phase microscopy





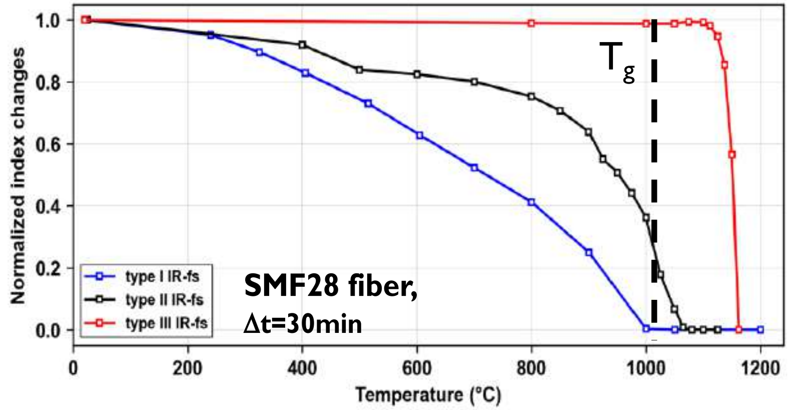
Gamaly et al. PHYSICAL REVIEW B 73, 214101 2006

TYPE III: TECHNOLOGICAL ASSETS

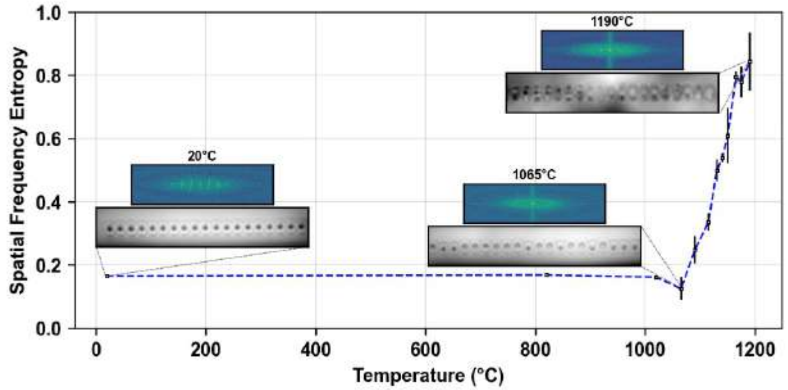
Thermal stability

Around T_g

- Type I: Δn erased (defects, densification relaxation).
- Type II: Nanogratings collapse → major birefringence loss., small nanopores radius closes faster (e.g. Rayleigh-Plesset).
- Type III: Voids still stable i.e. larger voids persist longer at the same T.



- Below T_g (~1050 °C). ⇒ voids remain stable
- Near T_g: viscous flow becomes significant → voids round and shrink; smaller R closes faster ($\Delta P \approx 2\gamma/R$),
- Above T_g: partial/total closure vs regrowth can occur depending on voids shape and internal pressure (PO_2)



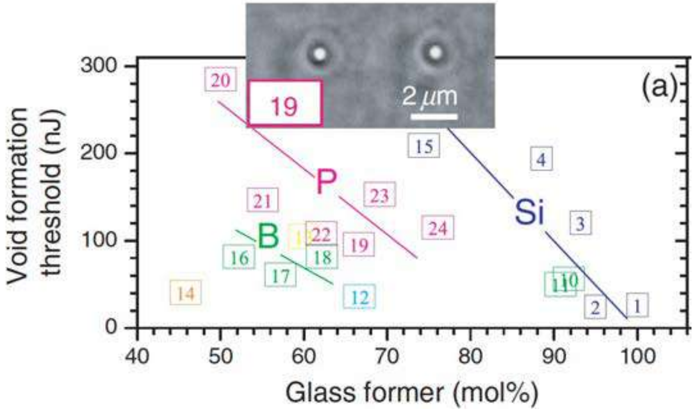
M. Sosa et al., Micromachines (2025)

Scaling: $\tau \approx \eta(T) \cdot R / \gamma$ (η: viscosity; R: void radius; γ ~ 0.3 $N \cdot m^{-1}$)

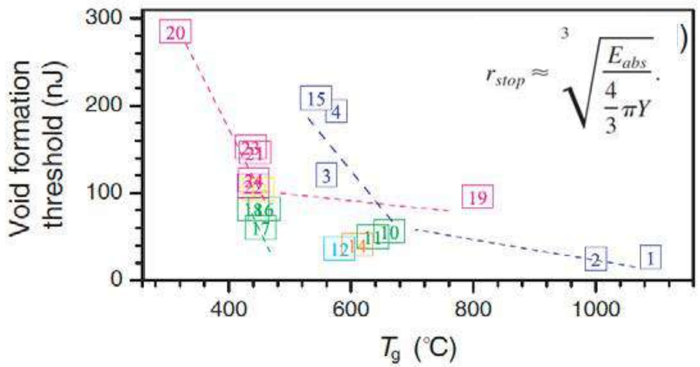
TYPE III: GLASS MATERIALS

- **Lower threshold** with higher network-former fraction ($SiO_2/P_2O_5/B_2O_3$), T_g, and Young's modulus (trend across 20+ glasses)
- **n & n_2 increase** (e.g. heavy oxides) → stronger self-focusing → less confined energy due to filamentation and clamping
- **Shell nature depends on chemistry**:
  - SiO_2 or GeO_2 shell mimics high-P high-T amorphous phase (fictive T and fictive P changes),
  - Al_2O_3-SiO_2 shell is partly crystallized

- **Clean, "spherical", voids** — choose network-former rich glasses (high-purity silica, some phosphates/borates), use high NA to counter self-focusing; low-energy (just above threshold)

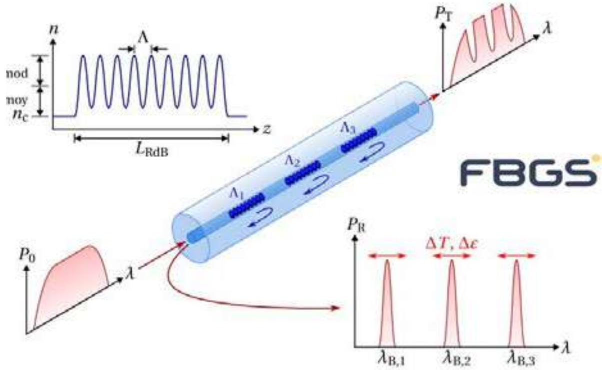


Hashimoto et al. New Journal of Physics 9 (2007) 253



TYPE III: towards applications

Optical Fiber Sensors

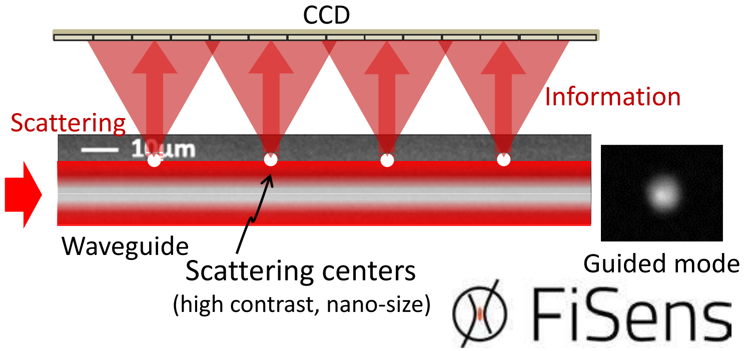


λ_B sensitive to temperature (or σ, ε)

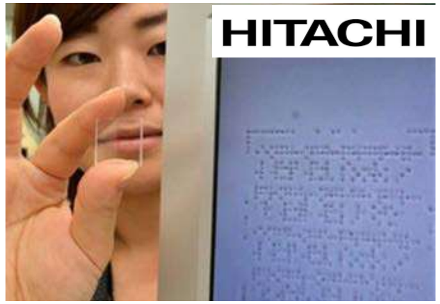
Sensibility : $\frac{d\lambda B}{dT} \approx 11{,}2pm/°C$ at $\lambda \approx 1550\ nm$

cf cours fibres de
Maxime Cavillon

Spectrometer function embedded on a glass chip!

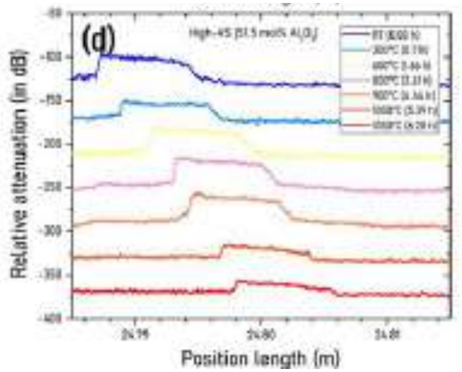


3D marking/QR-like, optical Data Storage



Rayleigh/Mie enhanced scattering, directional scattering

Vision glazing applications



Scattering based sensors

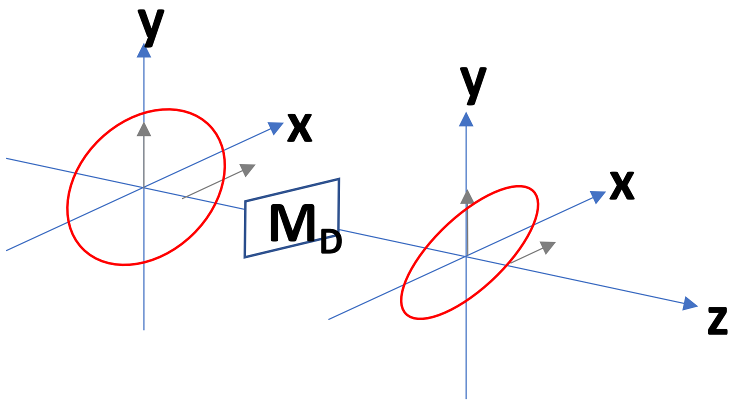
OTHERS OPTICAL MODIFICATIONS IN VOLUME

DICHROISM • NANOPARTICULES • CRYSTALLIZATION • OTHERS

DIATTENUATION – DICHROISM (LD, CD)

Definitions

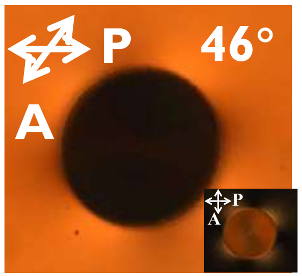
- Linear dichroism: different absorption for two orthogonal linear polarizations.
- Circular dichroism: different absorption for left vs right circular polarization.

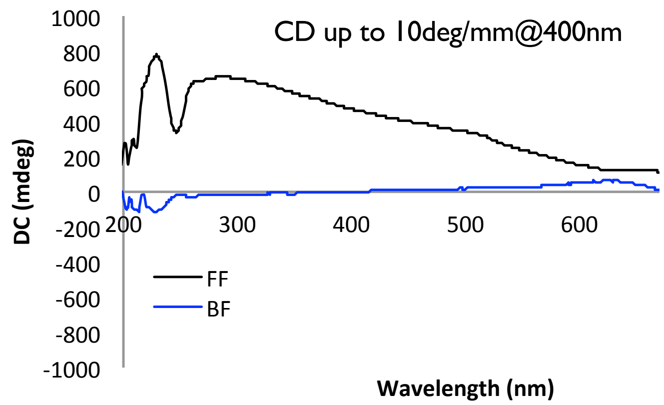


Potential applications:

- All integrated optical isolator
- Achromatic polarization rotator
- Chiral sensitive sensors
- Magneto-optics crystal photoprecipitation

Circular dichroism and optical rotation in silica





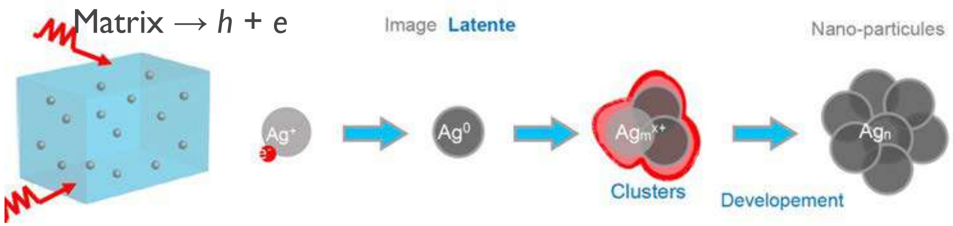
PRECIPITATION, DISSOLVING AND SHAPING OF METAL NANOPARTICLES IN GLASSES

Surface plasmon resonance

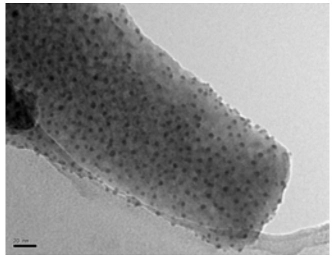
Photochromic glasses, Photo Thermo Refractive Glass

- **Approach:** Laser rradiation + Heat treatment
- Size and space, density control
- Color control with doping ions: Au^{3+}, Ag^{+}, Pb^{2+}, Pd^{2+} Cu2+ ions etc..

cf cours de L. Cormier

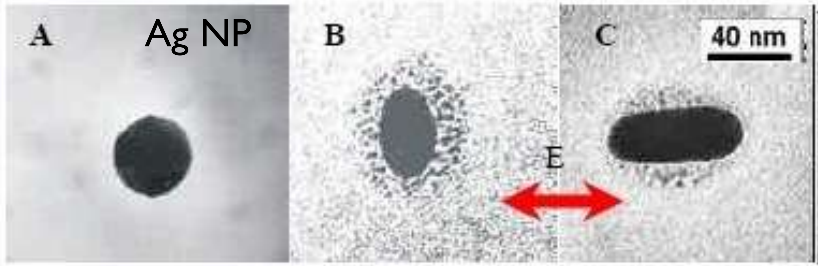


- Nonlinear interaction of laser with glass:
  Matrix → *h* + e (*option: add* $Ce^{3+} \rightarrow Ce^{4+} + e^{-}$)
- Formation of metal atoms + colors centers:
  $Au^{3+} + 3e \rightarrow Au^{0}$, $Ag^{+} + e \rightarrow Ag^{0}$, $Pd^{2+} + 2e \rightarrow Pd^{0}$
- Aggregation of metal atoms under heat treatment:
  $Au^{0} \rightarrow Au_n$, $Ag^{0} \rightarrow Ag_n$, $nPd^{0} \rightarrow Pd_n$



Note PTR glass : add Ce^{3+} as electron donor + formation of NaF or Li_2SiO_3 nanocrystals (e.g. Schott Foturan, alkaline alumino silicate)

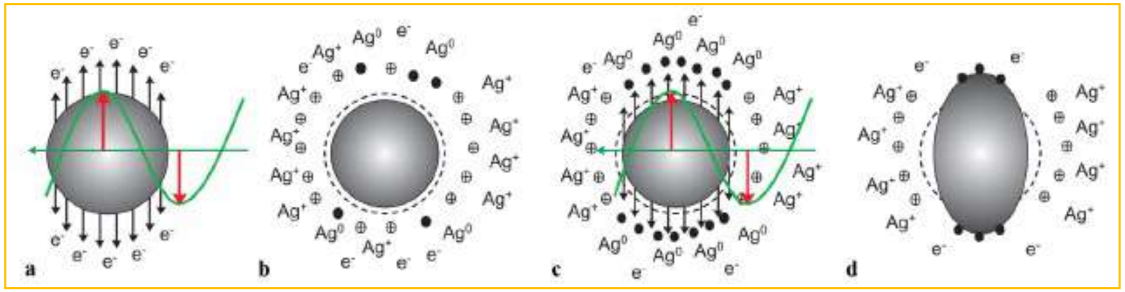
SHAPING OF METAL NANOPARTICLES IN GLASSES



Fs: 400nm, 150fs, 1kHz, 0,5-2 TW/cm²

Modification in low intensity mode

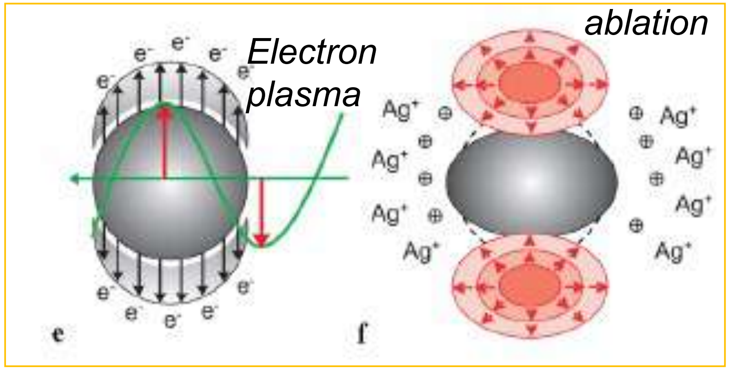
- 1: e^- emission parallelly to laser polarization
- 2: Ag^+ trap electrons forming Ag^0
- 3: Ag^0 is amplified by the next pulse
- 3: **Spherical NP grows in the polarization direction → elongated (prolate)**



A. Stalmashonak, Opt. Lett. 32(2007) 3215

Modification in high intensity mode

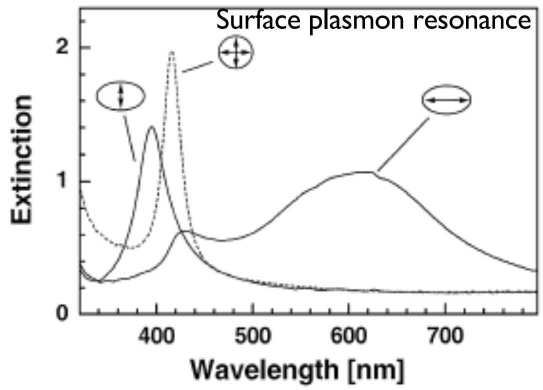
- 1: High intensity → high plasma density at the nanoparticle-matrix interface
- 2: **Local ablation of NP → oblate**



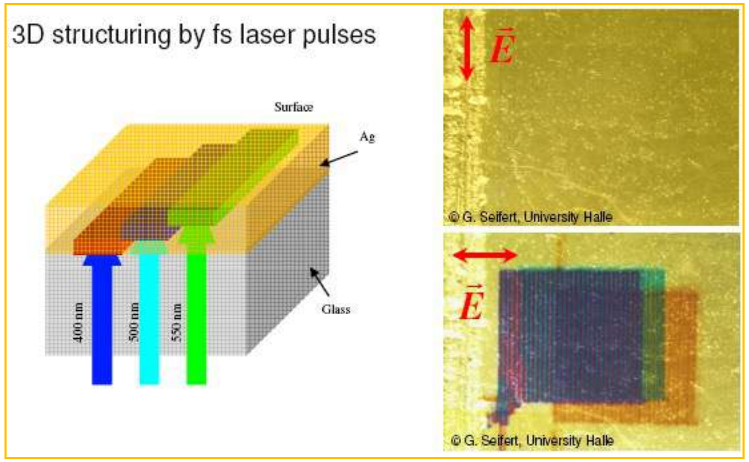
Interest ? Strong linear dichroism in the visible !

PRECIPITATION, DISSOLVING AND SHAPING OF METAL NANOPARTICLES IN GLASSES

- Polarization dependent absorption: linear dichroism in the visible
- Tunable in wavelength / wavelength dependent reading
- Polarization dependent light scattering
- Polarization dependent emission (Fluorescent Ag clusters Ag_m^{x+}.)
- Optical contrast controlled (multilayers, etc…)



A. Stalmashoneak, Opt. Lett. 32 (2007)



Seifert et al Univ. Halle, Germany

NANO-MICRO CRYSTALLIZATION

Main Features:

- 2D (cw) / 3D (fs/ps) crystallization
- Size control (10's nm up to 10's mm)
- Oriented crystallization
- Polar axis parallel to laser scanning direction but not only (polarization controlled as well)
- β-BaB_2O_4, Ba_2TiGe/Si_2O_8, $LiNbO_3$, $LaBGeO_5$, etc…

Some applications:

- SHG waveguides, Optical switch
- Acousto-optic modulators
- Phase modulation waveguides
- Saturable absorption

Cf Cours ONL de M Dussauze

Cw laser crystallization

$LaBGeO_5$ (Ferroelectric, congruent crystallization)

A. Stone et al. / JNCS 356 (2010)

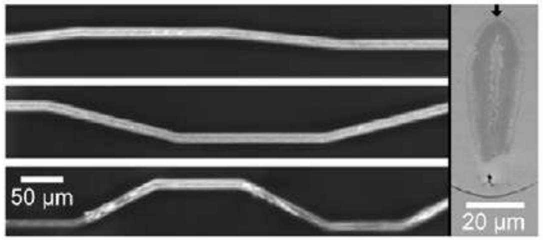
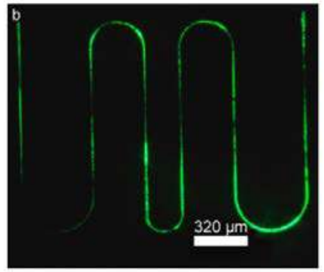


Fig. 2. Left: Polarized light micrographs of fs laser-crystallized $LaBGeO_5$ lines written in XY plane with bends of 6°, 14°, and 27°. Right: SEM backscattered electron image of a line cross-section. Arrow indicates incident beam direction.

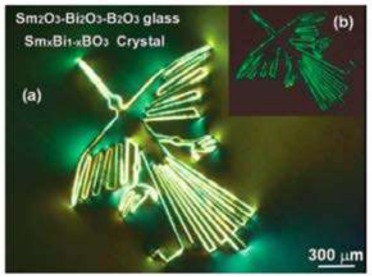
Gupta et al. J. Am. Ceram. Soc., 91 (2008)



Fs laser crystallization

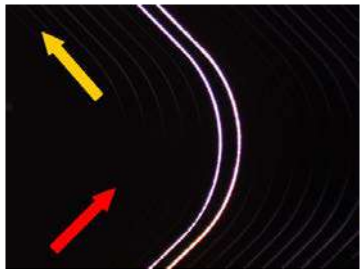
$SmBiBO_3$

T. Komatsu et al. J. Am. Ceram. Soc., 90 (2007)



$LiNbO_3$ High $\chi^{(2)}$

C. Fan et al. Opt. Lett. 37 (2012)



Polarized optical image of the written curved waveguides

NANO-MICRO CRYSTALLIZATION

Thermal treatment during the irradiation process

$$T_{00} = \frac{A \cdot E_p}{\pi^{\frac{3}{2}} \rho C_p w^3}$$

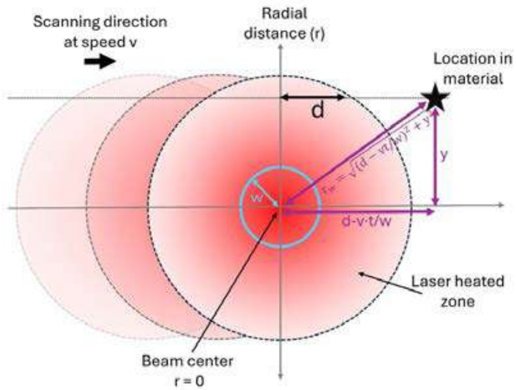
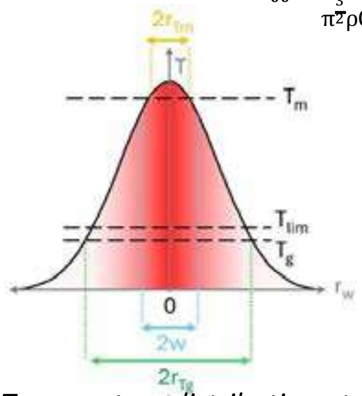
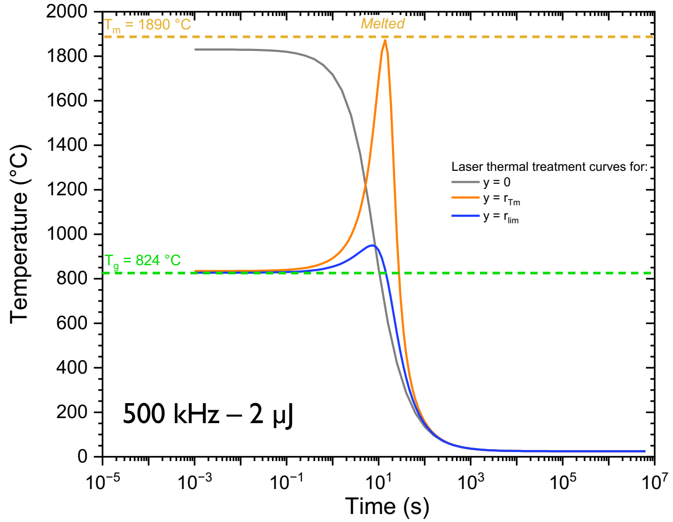


Illustration of laser beam scanning



Temperature distribution at a given time in the material

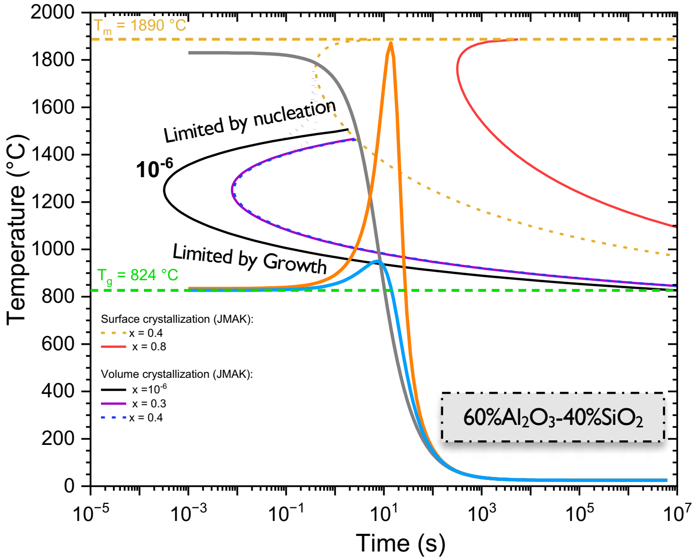
Cw laser or high repetition rate approach



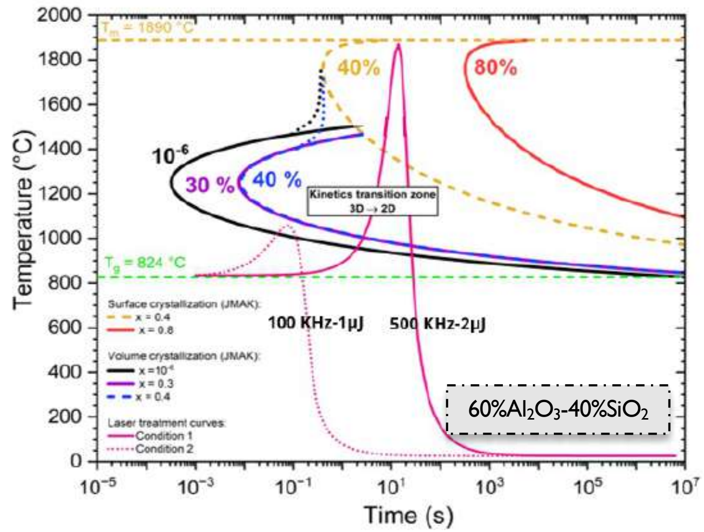
- Computation of healing-cooling curves vs laser conditions
- Initial energy deposition $T_{00} = \frac{A \cdot E_p}{\pi^{\frac{3}{2}} \rho C_p w^3}$ Note: $C_p(T)$, $\kappa(T)$, $\rho(T)$
- Solving Fourier heat equation $\rho T\left(\frac{\partial C_p}{\partial T}\frac{\partial T}{\partial t}\right) + \rho C_p \frac{\partial T}{\partial t} - \frac{\partial}{\partial r}\left(k\frac{\partial T}{\partial r}\right) = 0$ $D_{th} = \frac{\kappa}{\rho \cdot C_P}$

NANO-MICRO CRYSTALLIZATION

Thermal treatment during the irradiation process



Time-Temperature-Transformation (TTT) domain

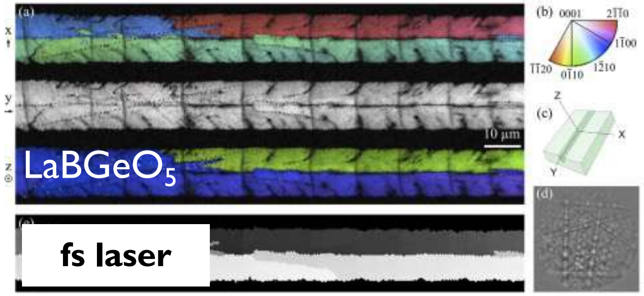


- Comparison of T variation (induced by laser) as a function of time (with the TTT diagram)
- Managing glass to crystal transformation (liquid-solid or solid-solid crystallization depending on T_{max})
- Example: 30% crystallization for 1 µJ – 100 kHz vs 60% for 2 µJ - 500 kHz

ORIENTED CRYSTALLIZATION

- Probing crystallization orientation : Second-harmonic generation, Raman, or EBSD.
- Polar axis parallel to laser scanning direction with cw laser (gradient of T)
- Polar axis ⊥ to fs laser polarization (controlled by $E_{\omega} \wedge P_{\omega}$)

EBSD (electron backscatter diffraction)



A. Stone et al. Sci. Rep 5 10391 (2015)

Polarized microscopy

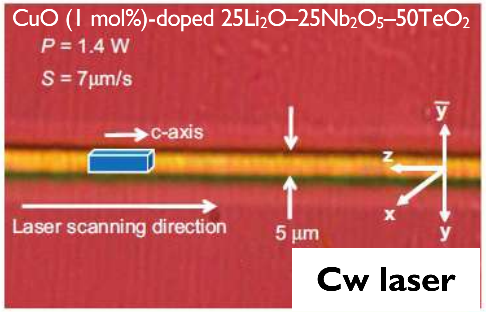


Fig. 9. Polarized optical microscope photograph for the sample obtained by Yb:YVO$_4$ laser (λ=1080 nm) irradiations with P=1.4 W and S=7 µm/s in the Cu–LNS glass.

H. Sugita et al. / Solid State Communications 143 (2007) 280–284

Polarized SHG
(second harmonic generation)

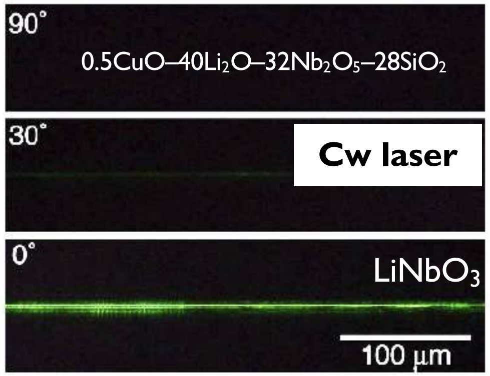
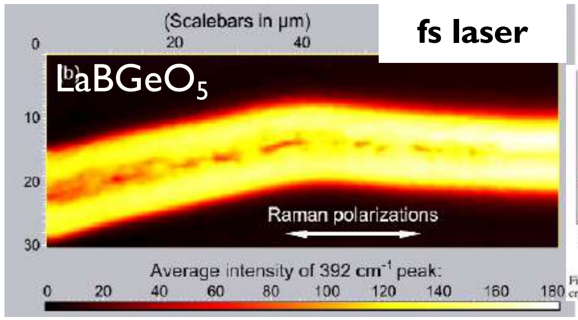


Fig. 6. Second harmonic (SH) wave images (532 nm) at different configuration (H-H mode) for the crystal line which written in the sample No. 2.

T. Honma et al. / Optical Materials 31 (2008) 315–319



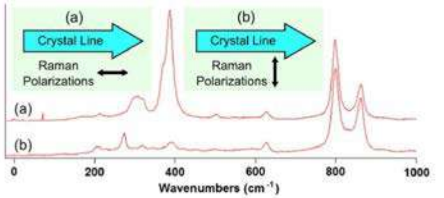
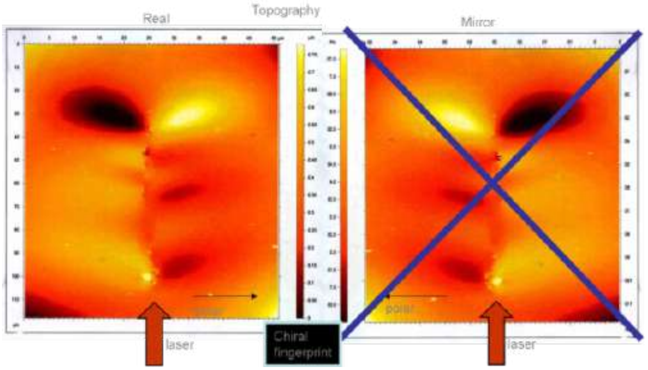


Fig. 3. Typical Raman spectra when excitation and emission polarizations are (a) parallel to a crystal line, and (b) orthogonal to a crystal line.

A. Stone et al. Optics Express 17(25):23284-23289 (2009)

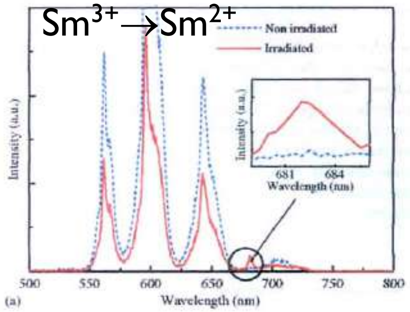
MANY OTHERS

Chiral mechanical structures



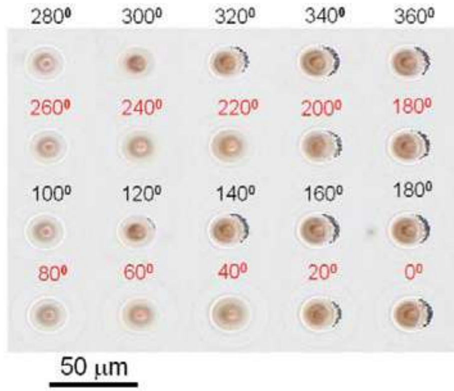
Poumellec et. al, Opt. Express 2003 & 2008

Oxydo-reduction



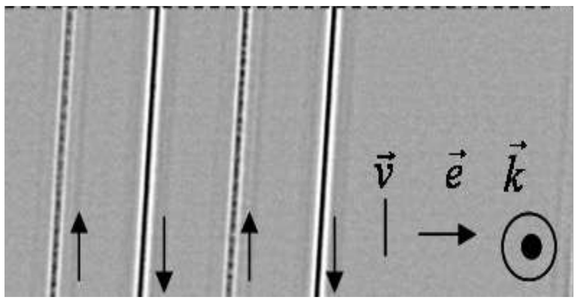
You et al. JNCS, Vol 352 (26–27), 2006

Photothermal effect



Zhang, F., et al. (2016). Optics Express, 24(19)

Orientational dependent writing



Poumellec et al. (2013). Optical Materials Express, 3

Kazansky et al. APL 2006

Oriented chemical migration

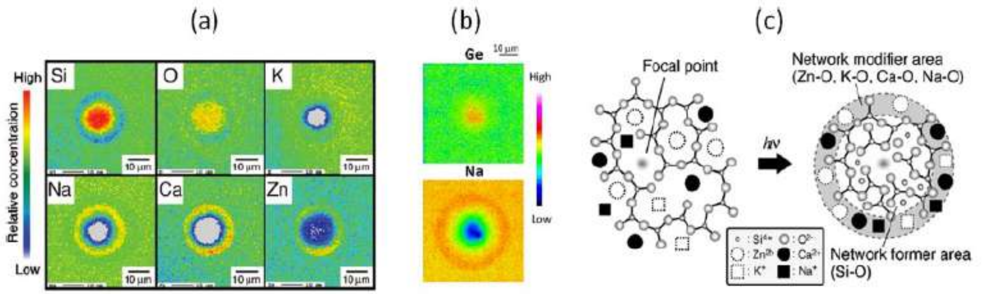


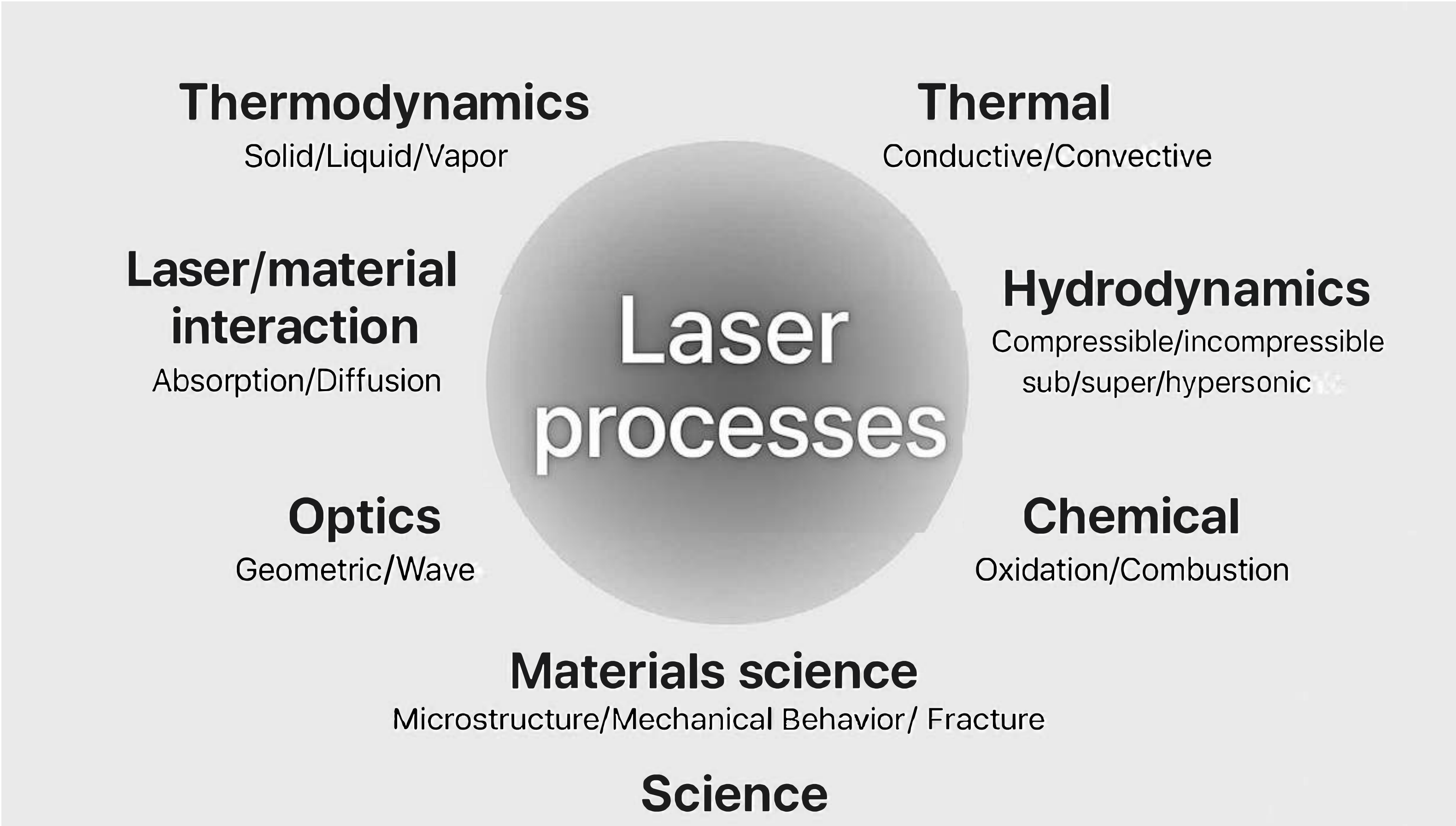
Fig. 3-15. EPMA mapping perpendicular to femtosecond laser irradiation at 200 kHz repetition in (a) $67SiO_2$-7CaO-$9K_2O$-$9Na_2O$-4ZnO glass and (b) GeO-Na_2O glass. (c) Schematic of the tendency of femtosecond laser induced ion migration (perpendicular to laser irradiation direction) inside a silicate glass, as proposed by Kanehira et al.

Fernandez, T. T., et al. (2018). Progress in Materials Science, 94, 68

Outline

- Context and introduction
- Basic concepts
- CO_2 laser
- Surface processing
- Volume processing
- **Conclusions**

CONCLUSIONS – MECHANISMS



CONCLUSIONS - APPLICATIONS

Modulators, optical switch, SHG waveguides

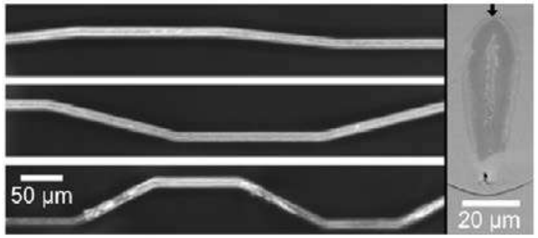
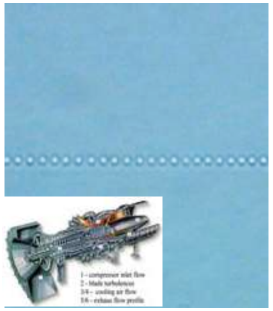
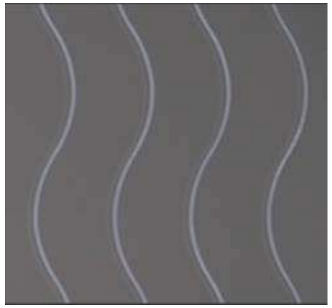


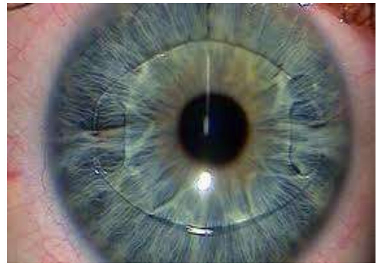
Fig. 2. Left: Polarized light micrographs of fs laser-crystallized $LaBGeO_5$ lines written in XY plane with bends of 6°, 14°, and 27°. Right: SEM backscattered electron image of a line cross-section. Arrow indicates incident beam direction.

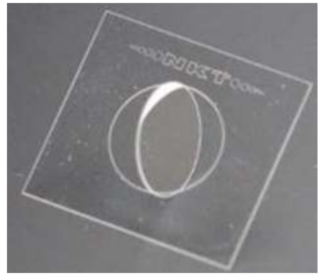
Fiber Bragg gratings, waveguides, Sensors, photonics integrated circuits





Fresnel or graded index Lens

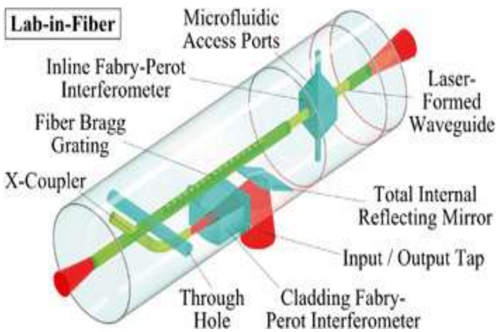




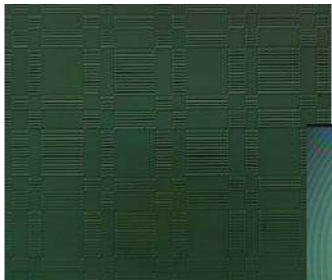
Cutting, ablating, polishing

Polarizers, SPR

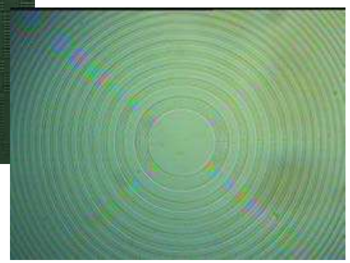
3D marking and optical data storage,



Lab-on-chip and Lab-in-fiber

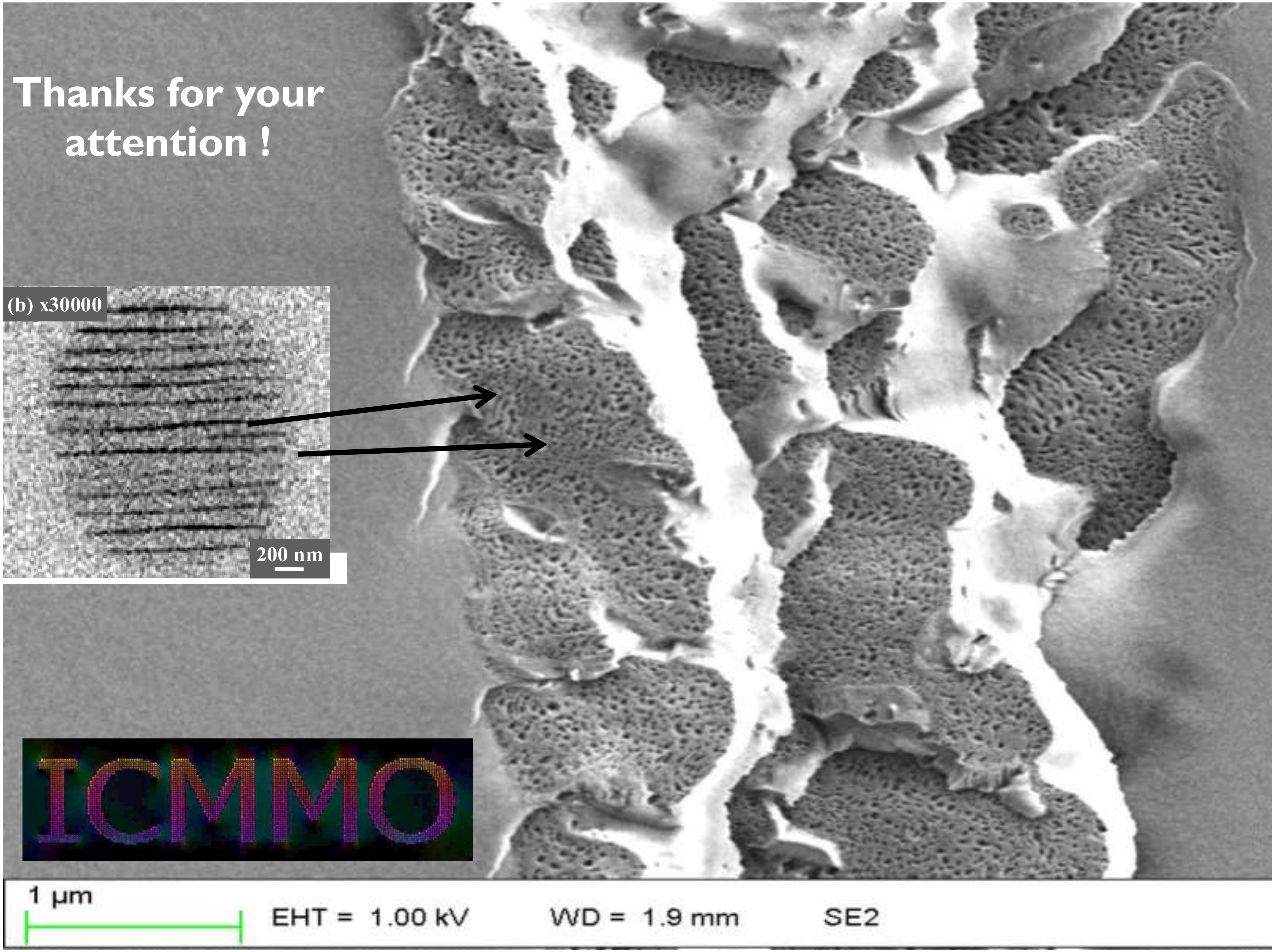


2D- 3D Gratings



Micro-optics

Welding, sealing


Thanks for your attention !
(b) x30000
200 nm
ICMMO
1 µm
EHT = 1.00 kV
WD = 1.9 mm
SE2