Photosensitivity of Optical Materials for Photonics and Integrated Optics

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fabulas

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Functional Glasses:
Properties and Applications for Energy and Information
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Learning To Love the Materials that Make Glass – SAND in Sergipe

Prof. Peter Kazansky learns to love sand

Outline of Talk

- Introduction to Photosensitivity:
  - Historical Perspective:
    - Art, Photography, Photosensitivity
  - Photo Refractive materials
    - Charge generation in Electro Optic Crystals : change in refractive index
    - Grating Formation
- Photosensitive Materials:
    - Defects in glass
      - Two Photon and Single photon excited charge generation: Ge doped Silica
      - Holographic Glass: Silver doped glass, Photothermal Refractive Glass
    - Photoresist, Polymers: Dichromated gelatin (DCG: 1830s), photochromics, Photopolymerisable resins (PR)
    - Chalcogenides: phase transitions
- Femtosecond pulsed laser recording vs CW
  - Imaging of moving biological samples
- Laser Cooling with Quantum Dots in Glass
- Future Prospects

Introduction

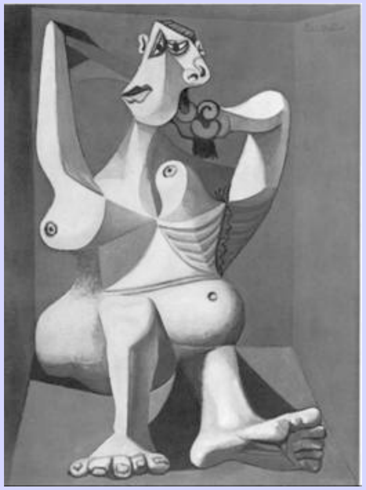
- Our fascination with *Capturing the Image*:

  Since time began.....painting was an inexact art..........has had its advantages!

- Photosensitivity:

  Paintings fade when exposed to light: well known

  Paper colours when exposed to light..c.f. Kodak Museum.



Nude lady combing her hair, Picasso, 1940

  - The **REVERSE** process: *Photo-Darkening*

    Daguerre-type photographic process captures images permanently on glass coated with silver-halide emulsion : 1820

  - Changing absorption into refractive index change by bleaching: Lippmann: 1894……. More later…..

  – However,.....All materials change properties when exposed to electro-magnetic radiation of some frequency!

  – High Energy FEMTOSECOND LASER INTERACTION!

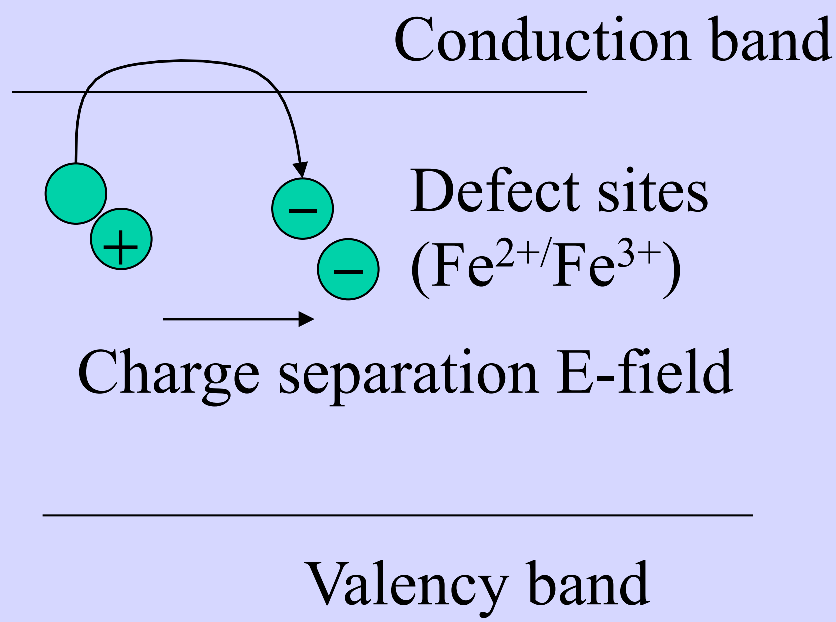
Louis-Jacques Mande Daguerre: Born Cormeilles, Normandie region, 1787: DATA STORAGE: Boulevard du Temple, 1838

Basic Material is Silver Nitrate, **fixed** as Silver Oxide with an **associated Refractive Index change**

Another Material From Sicily can also Change Your Refractive Index

Photorefractivity

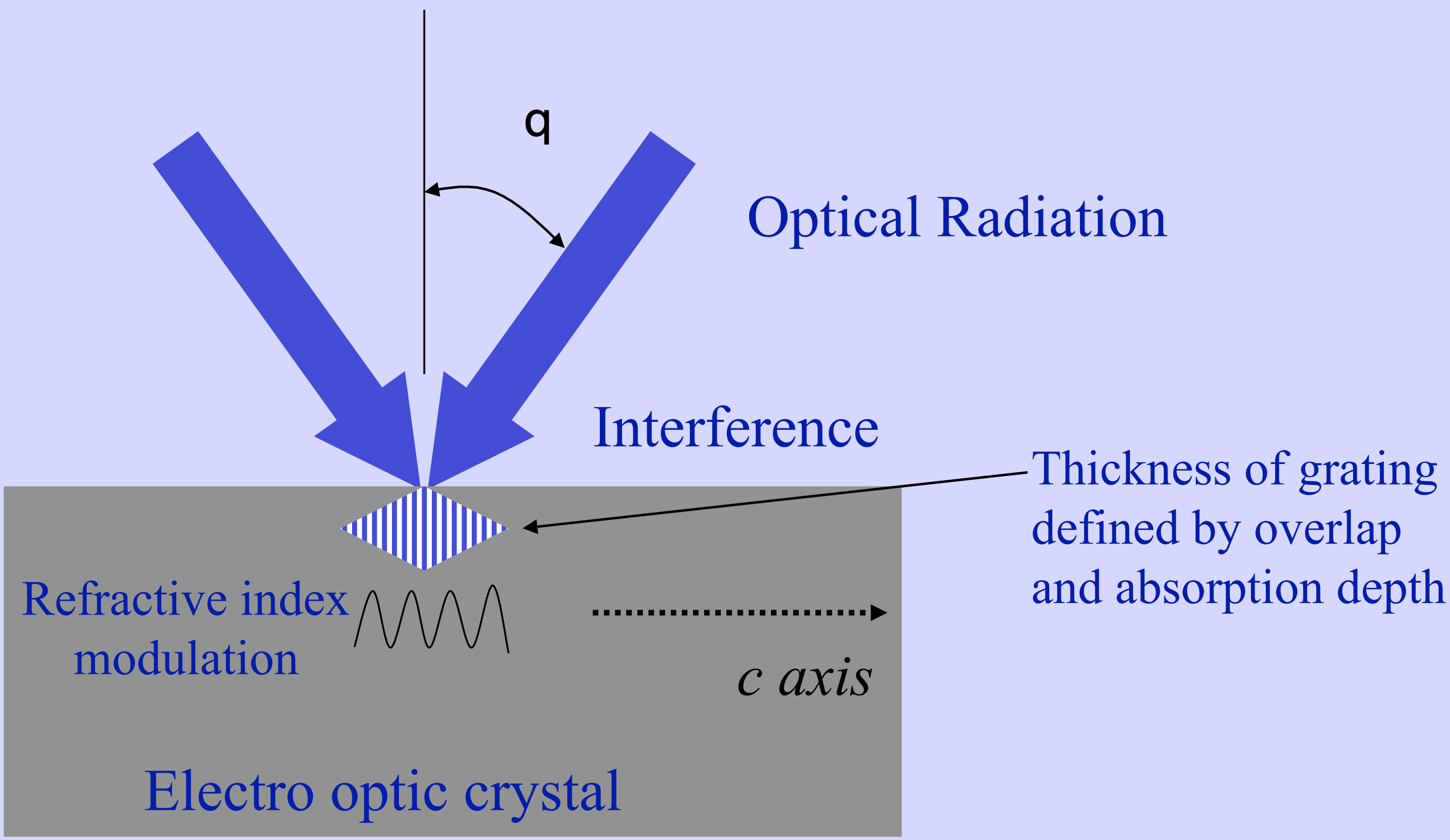
- Photoexcitation of low lying defects in Electro-Optic crystals



- Charge migration:
  - Under external field (enhanced effects)
  - Without external field (weak effect)

- Elevated temperature allows ionic diffusion to neutralise charges
  - Room temp diffusion of ions is slow.
  - Electrons remain in deep traps → quasi permanent E-field.

Process of phase grating formation



•**Development of internal field through charge separation**

Energy requirements for 1% diffraction efficiency: EO photorefractives

Material	1% eff mJ/cm²	Dark Storage time (yr)	Wavelength (nm)	Ext. E-field (kV/cm)
$LiTaO_3$:Fe	**11**	**10**	351	15
$LiNbO_3$:Fe	200 300	1 0.1	351 488	15 0
$Sr_{0.75}Ba_{1.25}Nb_2O_6$:Ce	1.5	0.1	488	0
$Bi_{12}SiO_{20}$	0.3	0.003	514	6
$KTa_{0.65}Nb_{0.35}O_3$	0.05	0.001	530 2 photon absorption	6

Review by: A M Glass, Opt. Eng. 17, 470-9, 1978

Glass Photosensitivity

Photosensitivity

- Definition:
  - *the change in the optical transmission properties of a material on the exposure to light*
  - Transient or *Permanent*

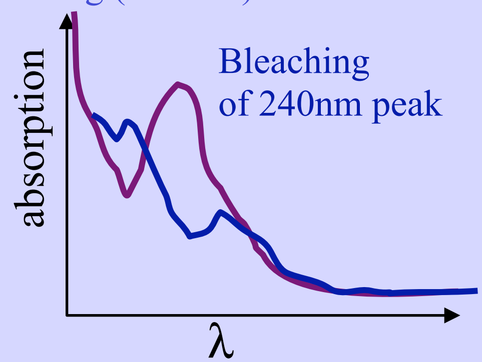
- *Indirect* process
  Charge trapping, self electro-optic induced refractive index change: *Photorefractive, photothermal*

- *Direct* process
  Creation of defects and free charges, breakage of molecular bonds, stress alteration
  > changes in absorption (*photochromic*) and refractive index

•PHOTOSENSITIVITY IS A TOOL FOR CREATING DEVICES

Photosensitive Inorganic glasses:

- **Photo bleaching Glasses:**
- Historical inorganic glasses for phase holograms:
  - Bleaching of color centers by UV radiation: 2 and single photon. 3mm thick, diffraction efficiencies: 1%, up to 6000L/mm*
    - Borosilicate glass (BK-7) also low refractivity (stress/differential etching)
  - Porous silica impregnated photo-polymer† – residual photosensitivity and high scattering (Sol-Gel)
  - **Ge doped silica fibre: bleaching and stress relief**
  - **Excellent stability and low loss:** *Something to Bragg about*!
    - Bulk gratings difficult
    - Hydrogen loading and formation of GeH, GeOH….



- **Photothermal Refractive (PTR) Glass:**

Li-Al-SiO_2:Ce, Na-Zn-Al-SiO_2:Ce

- **Process…aka…Daguerre**
  - **UV exposure and & heat treatment****
  - **Greater than 95% reflection gratings: 10,000L/mm**

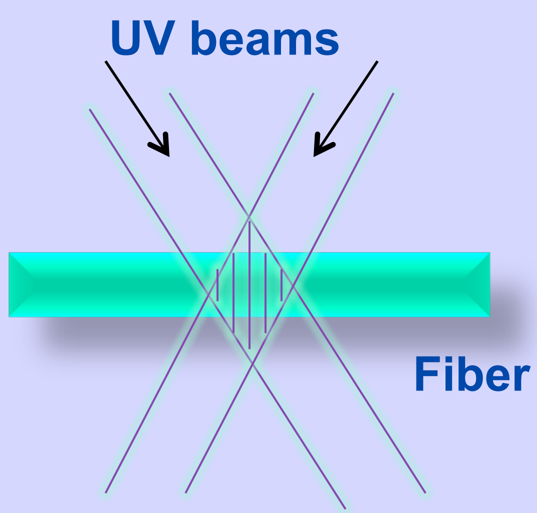
*Kondrashov E B & Tuninamova I V, 'The holographic characteristic curves of photochromic glasses, Sov. J. of Technol., 39, 482-485, 1972.

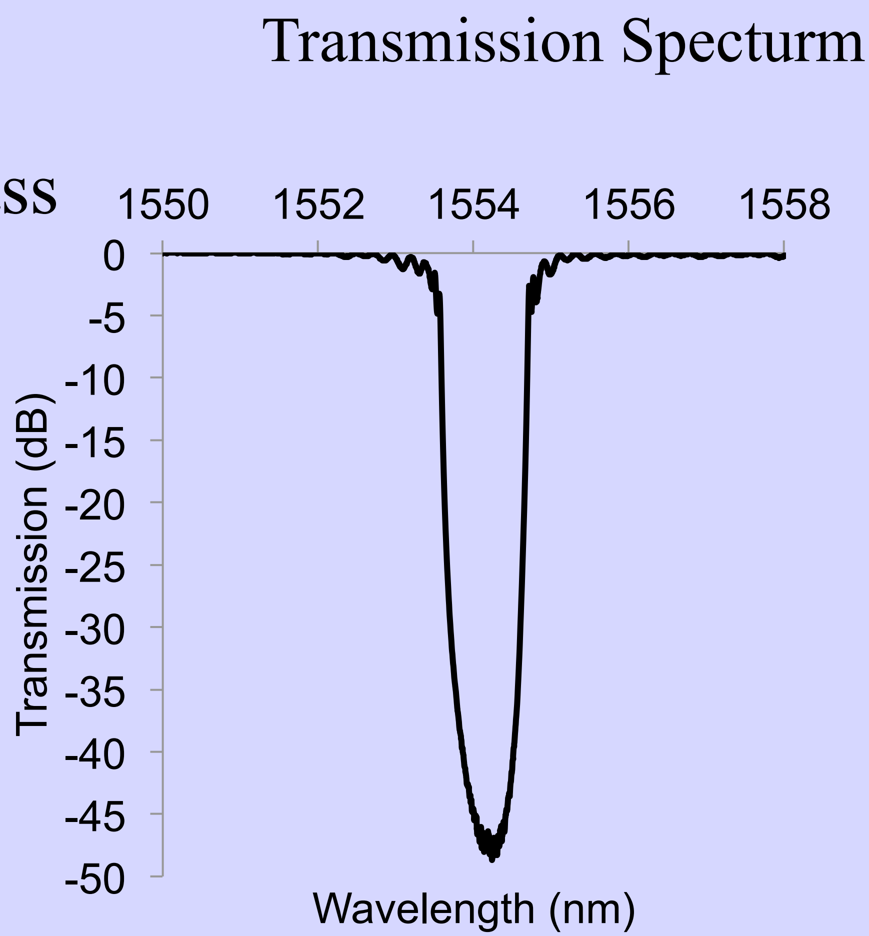
†Cheben P and Calvo M, 'APL78, 1490-1492, 2001

**Borgman V A *et al.*, 'Photothermal refractive effect in silicate glasses', Sov. Phy. Dokl., 35, 878 (1990)
& Glebov et al., SPIE 4724 (2002), pp101-109

Fibre Bragg Gratings Basics

- Most glass is photosensitive to UV laser light
- A diffractive interference pattern can be printed in glass using phase mask





FBG basics

- Fiber Bragg grating: periodic modulation of the index in the core of an optical fiber that allows a Bragg wavelength to be reflected.

Bragg wavelength:

$$\lambda_B = 2 n_e \Lambda$$

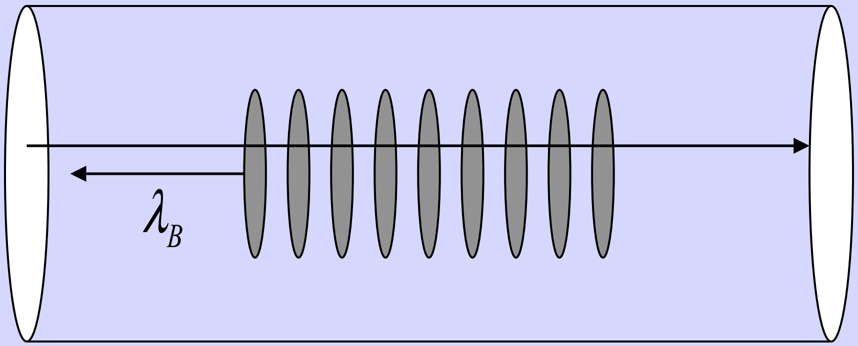
Reflection:

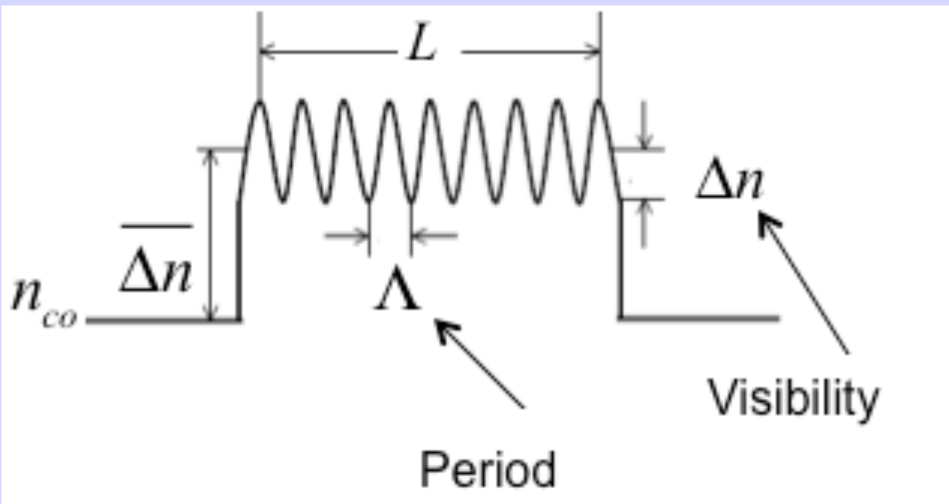
$$R = \tanh^2(k_{ac} L)$$

Bandwidth:

$$2\Delta\lambda = \frac{\lambda^2}{\pi n_e L}\sqrt{(\kappa_{ac} L)^2 + \pi^2}$$

Length Coupling constant

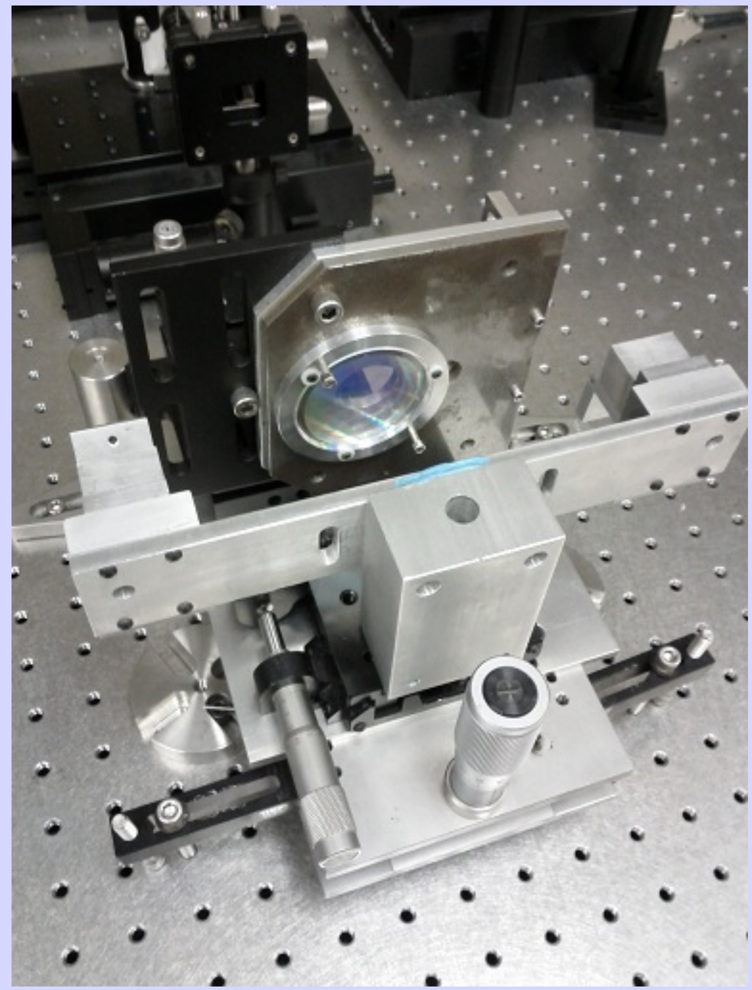




Raman Kashyap, Fiber Bragg Gratings, Academic Press, 2009

Phase mask technique

Diffractive phase mask



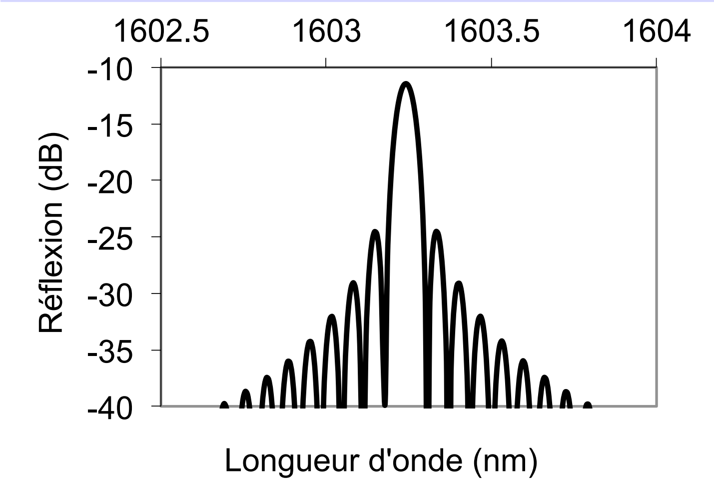
- Grating period fixed by phase mask

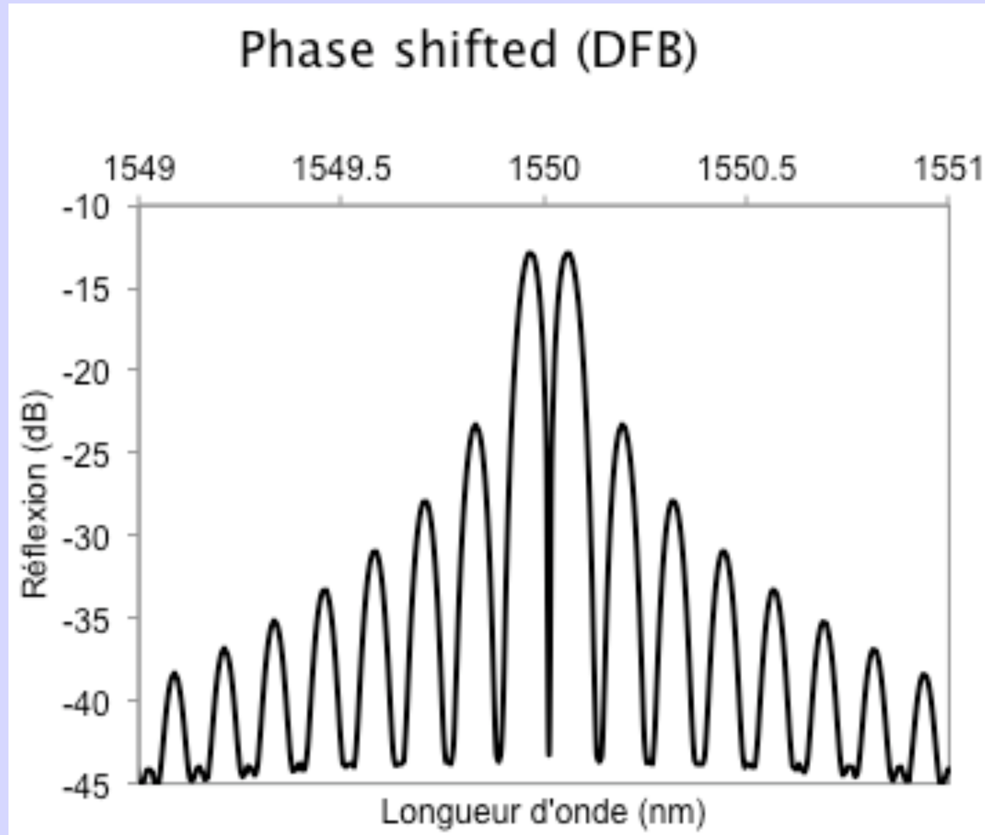
$$\Lambda_g = \frac{N\lambda_{Bragg}}{2n_e} = \frac{\Lambda_{pm}}{2}$$

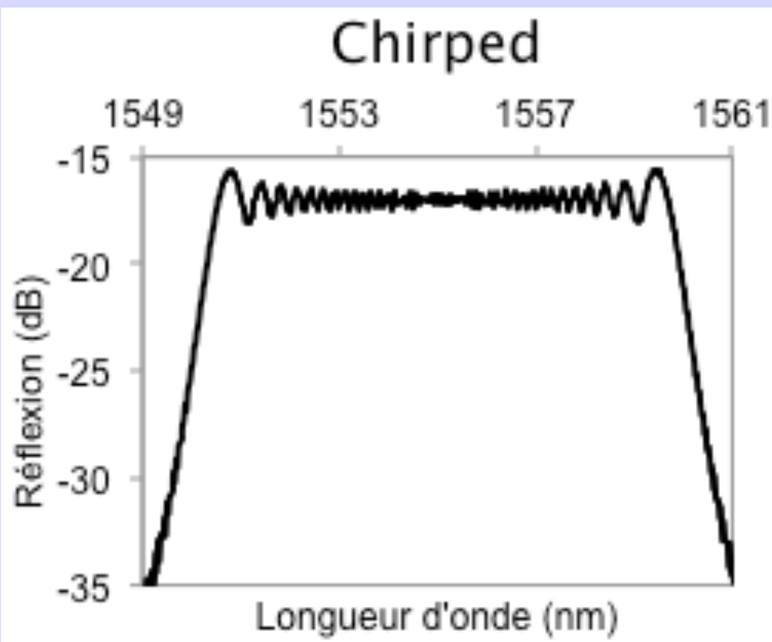
- Very simple to align
- Length is limited by phase mask (10cm)

Reflection Spectra: FBG types

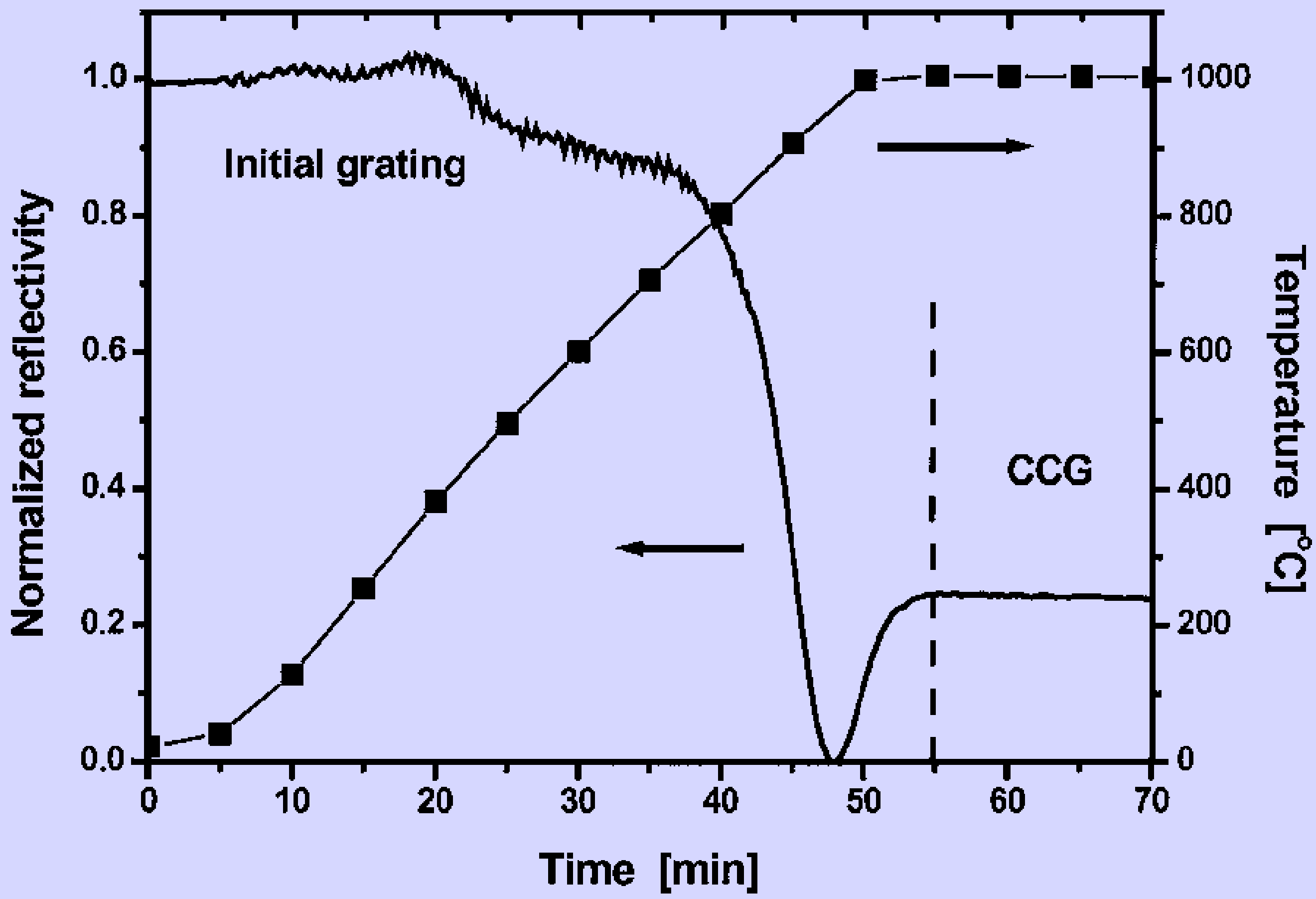
Uniform





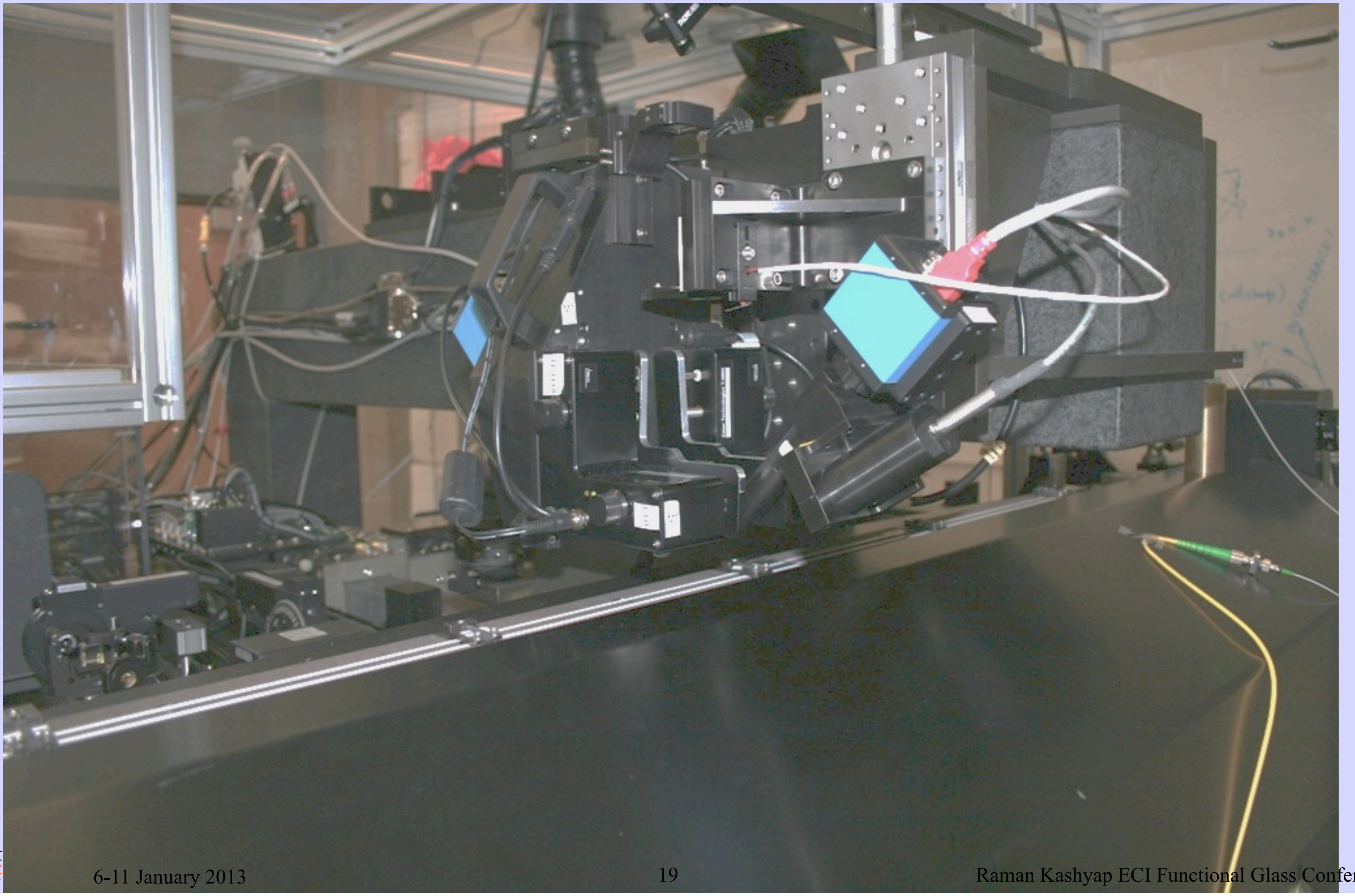


High Temperature Chemical Composition Gratings in F:Ge: Silica

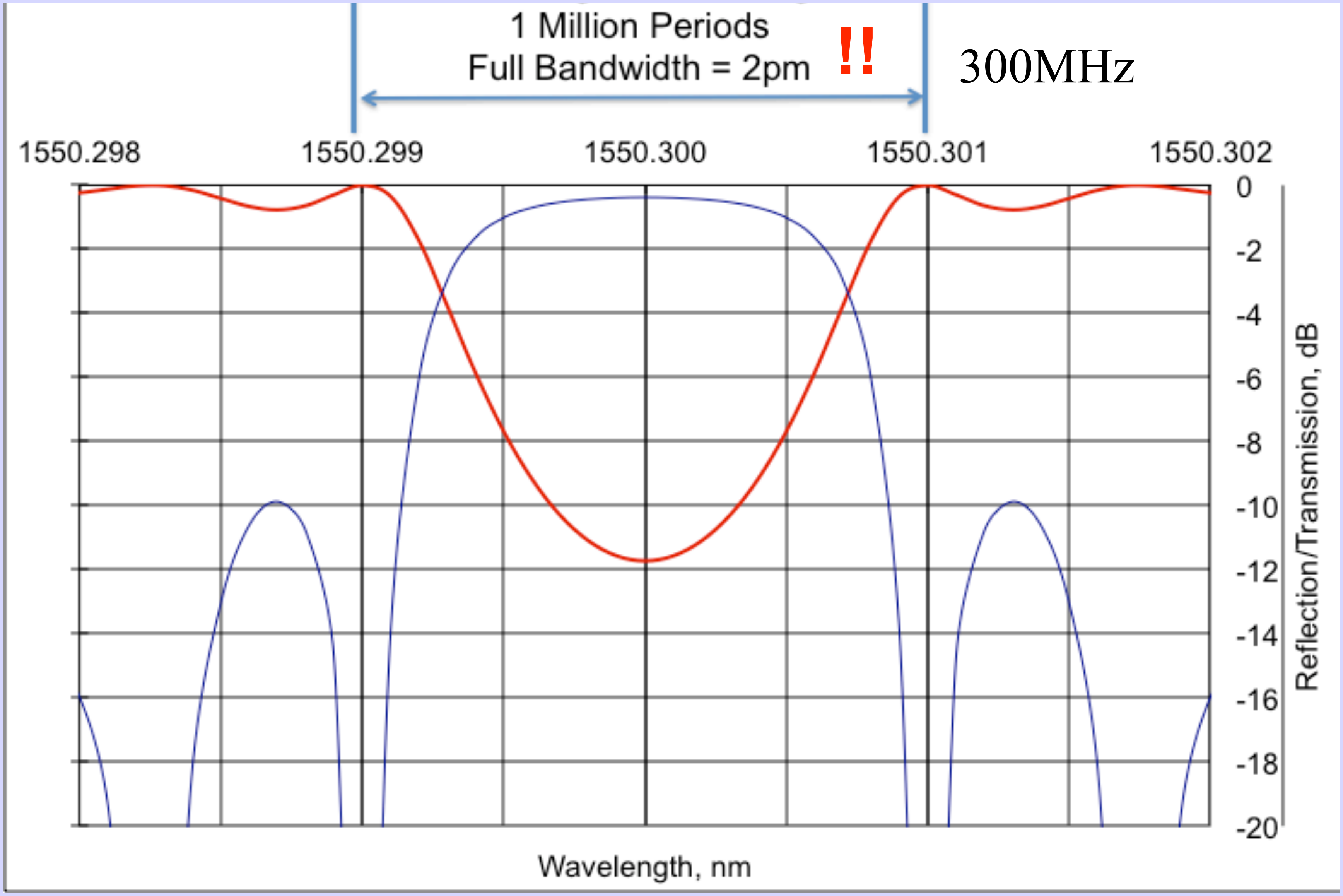


Michael Fokine, "Formation of thermally stable chemical composition gratings in optical fibers," J. Opt. Soc. Am. B 19(8), 1759-1765, August 2002.

1 m long FBG Writing Station



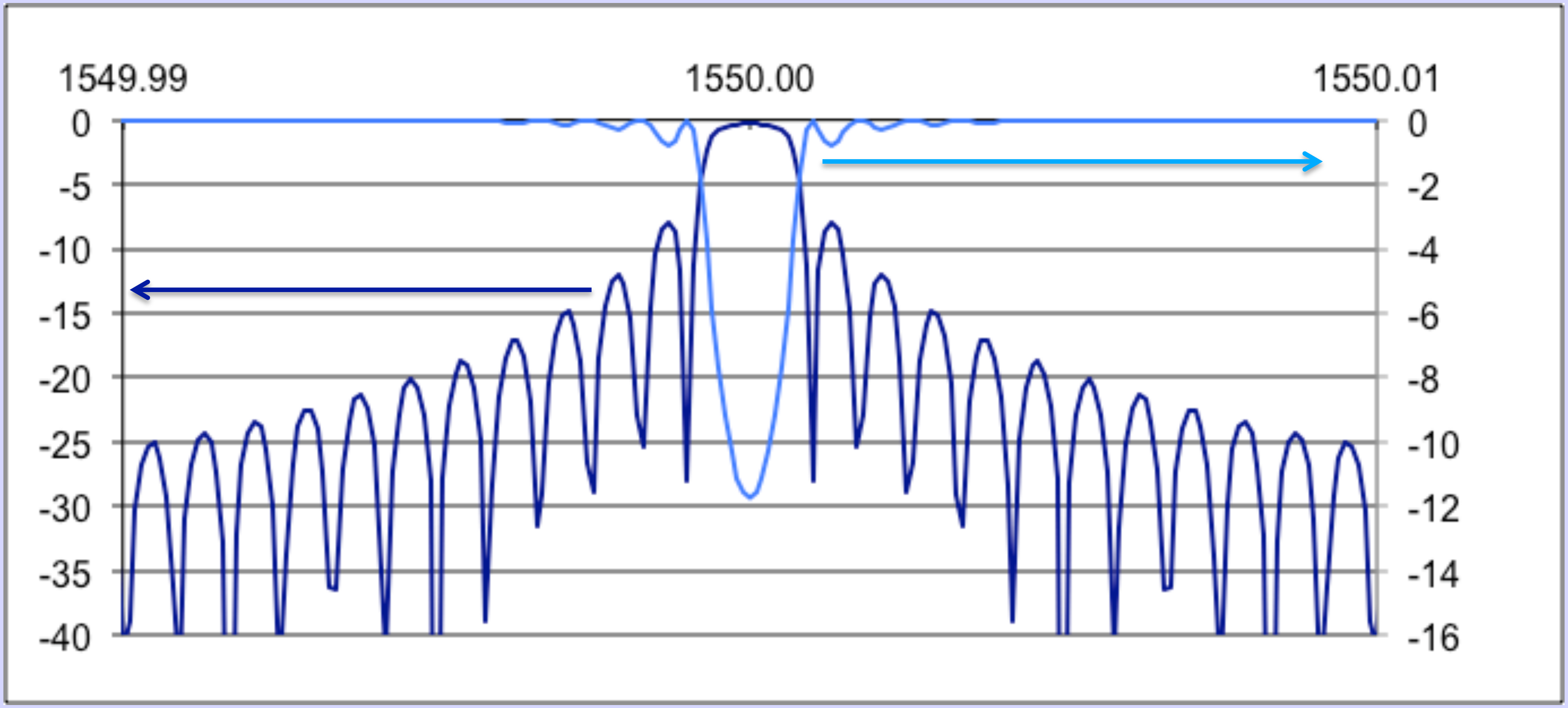
1 Meter Long FBG: Simulation



Impact of non-uniformities

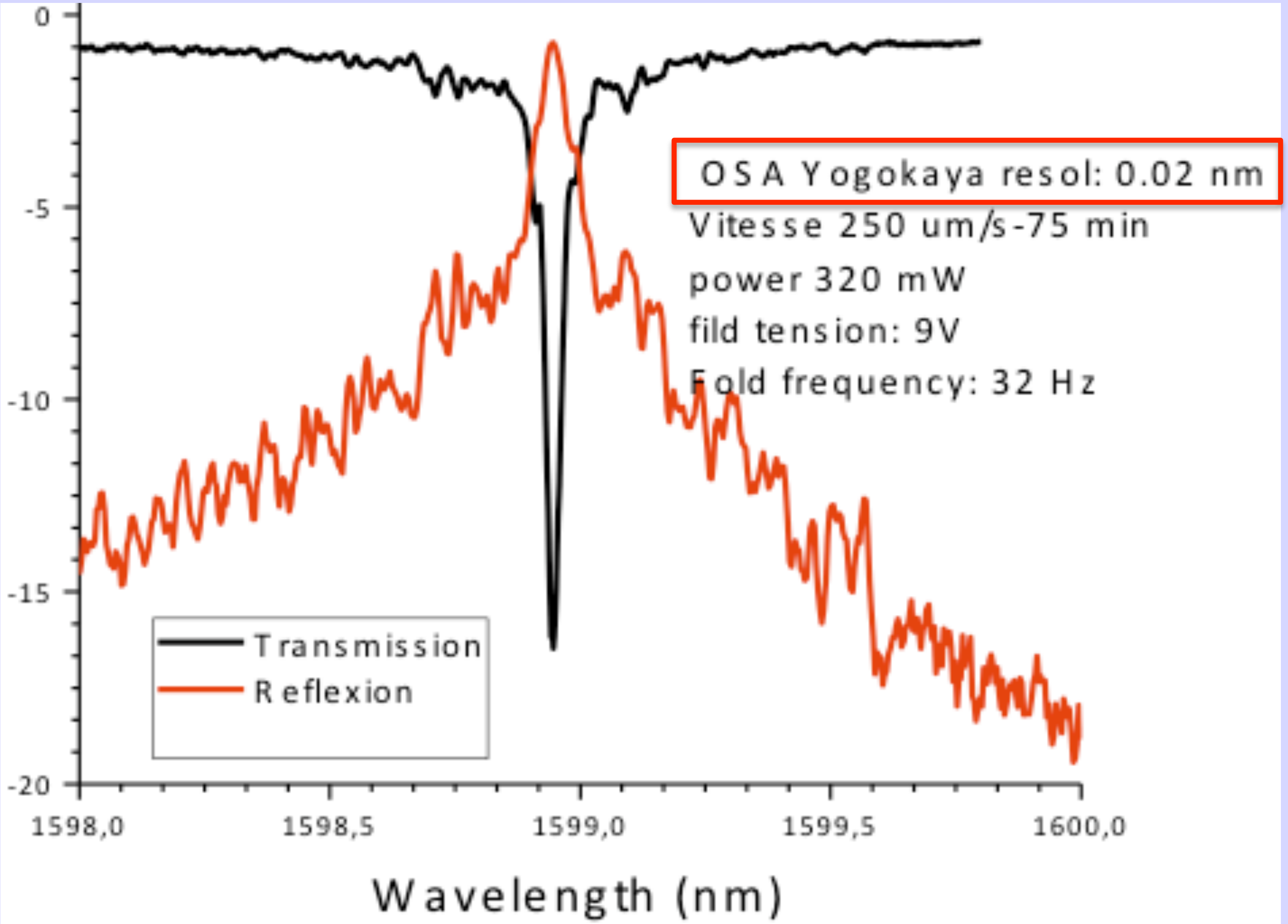
- Can we achieve Perfect Device characteristics?
- What is an acceptable random variation?
- How uniform does a material have to be?

Reflection & Transmission of 1M periods: dn = 10^{-6}



Wavelength

1m Long FBG (Bandwidth < 80pm)

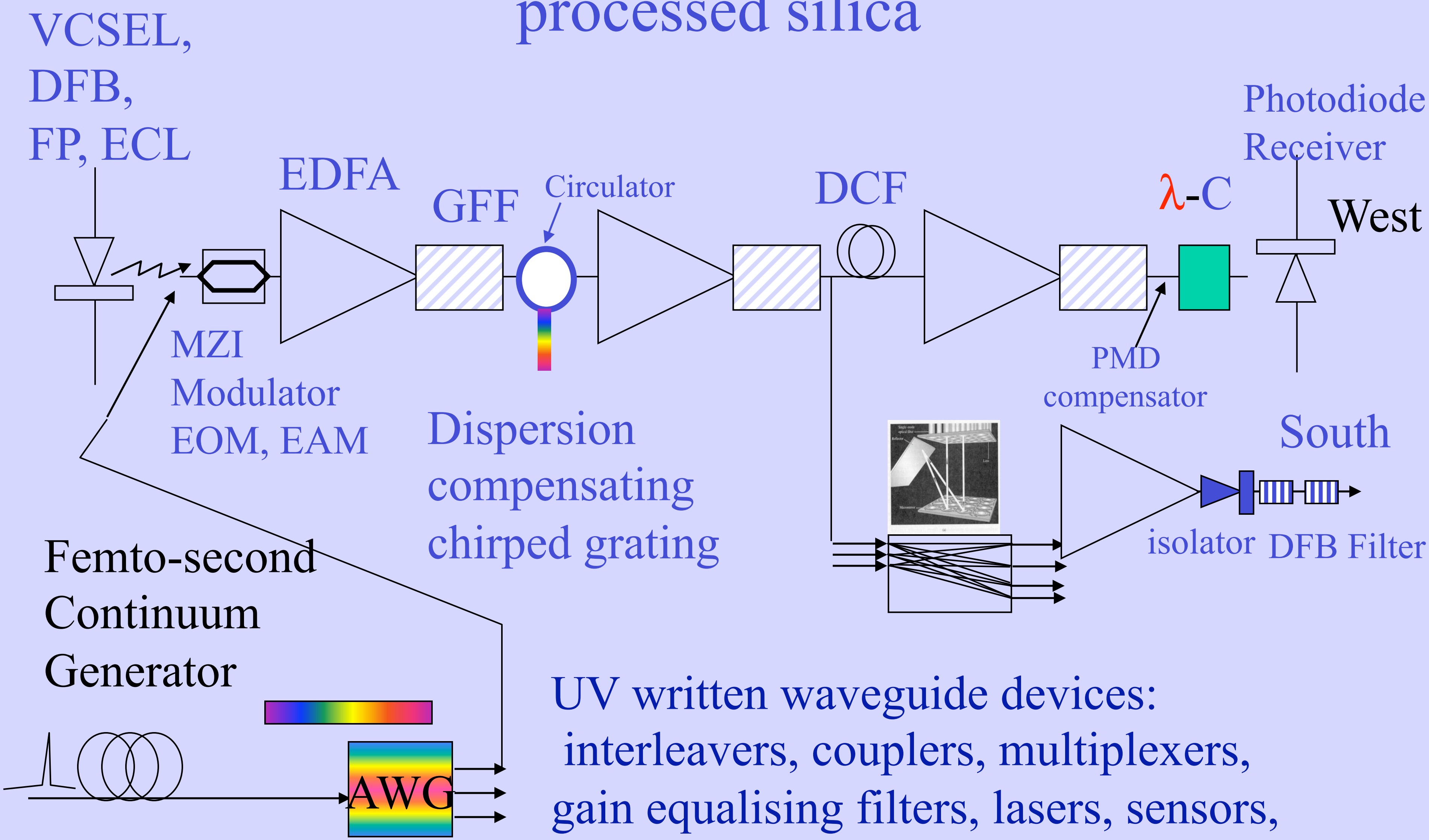


Summary on Uniformity

- A refractive index modulation of only10^{-6} is needed for meter long gratings….
- However
  - 10^{-6} random change in refractive index visibly affects performance
  - 0.1% variation in the core diameter is equivalent to a change of ~1.5×10^{-6} in refractive index!
  - SO ??????

Photosensitivty & Materials Requirements

Photonics in Action: Applications of UV processed silica



UV written waveguide devices:
interleavers, couplers, multiplexers,
gain equalising filters, lasers, sensors,
ASE rejection filters…etc

Photosensitive Material Issues For Photonics Applications

- High Transparency in region of interest
- Low Scatter loss
- **Zero** Absorption loss
- Resistant to Bleaching
- **Large** controllable refractive index change
- High Optical Damage Threshold
- Low Dispersion
- High Stability with temperature and time
- Good Reliability & Lifetime (10-20 years)
- Durability
- Process **Repeatability** and **Adjustability**
- Low Reversability
- Ease of Handling
- Long Storage & large operating temperature range

Photosensitivity: Challenging Device Issues

- Uniform characteristics
- Guided wave devices with CONSTANT properties: Ultra-low variation in dimensions ~ **few nm over meter lengths…0.1% …. ~ 5nm in 5 micron!**
- Low variation in refractive index with distance:

  < 10^{-7} over meter lengths: ~0.01% in waveguide refractive index difference

- Increase Change in Refractive Index to 0.1

Some words about Ge:Silica

- Fascinating material!

If you thought you knew everything about silica….wait|

It has ALL the properties one would lust after!

Makes:

- Near perfect waveguides…..but we are at the limit
- Dope with all sorts of materials: lasing
- Make complex near-perfect grating filters optically in waveguide core
- Infinitely adaptable for device fabrication
- Stable >500ºC
- High Quality and…………..well……er…….understood?

So…..why do we need other materials?

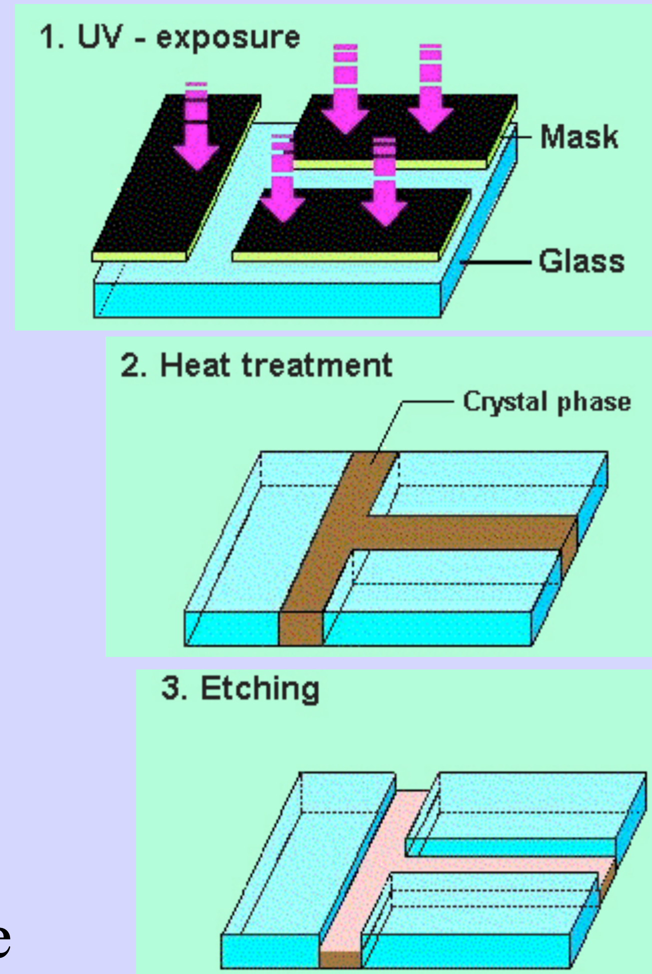
Lets consider some other materials & applications……..

Photosensitive Glass: Foturan ® Schott: Silver loaded silicate

1. UV radiation between 290-330nm @ 2 Joule/cm^2

2. Silver atoms formed in illuminated regions. Heat treatment between 500^{o} and 600^{o}C crystallizes glass around silver atoms.

3. Room temperature etch in 10% HF:
➢ Etching rate of crystalline 20 x higher than vitreous regions.
High aspect ratios: 25 micron feature size with micron size roughness.



Main application: Masking and feature formation: NEW APPLICATIONS??

Foturan Glass

- Excellent processability
- Excellent aspect ratios
- Durable
- Transparent

- But not acceptable as Optical glass….loss due to scattering

- Is there anything else……????

PhotoThermal Refractive (PTR) Glasses

- Probably most promising material
  Properties:
  - Inorganic glass
  - Stable to greater than 400° C
  - Index change 0.001 ….on low end of scale
  - Low loss
  - Bulk processing
  - High optical damage resistance
  - Volume phase holograms
  - Commercial applications in lasers and beam combiners

Photo-Thermal Refractive Process

- Na-Zn-Al-SiO_2: Ag, Ce, F
  - Precipitation of dielectric micro-crystals in the bulk of glass exposed to UV radiation.
  - Electron released by

    $Ce^{3+} = Ce^{4+} + e^{-}$

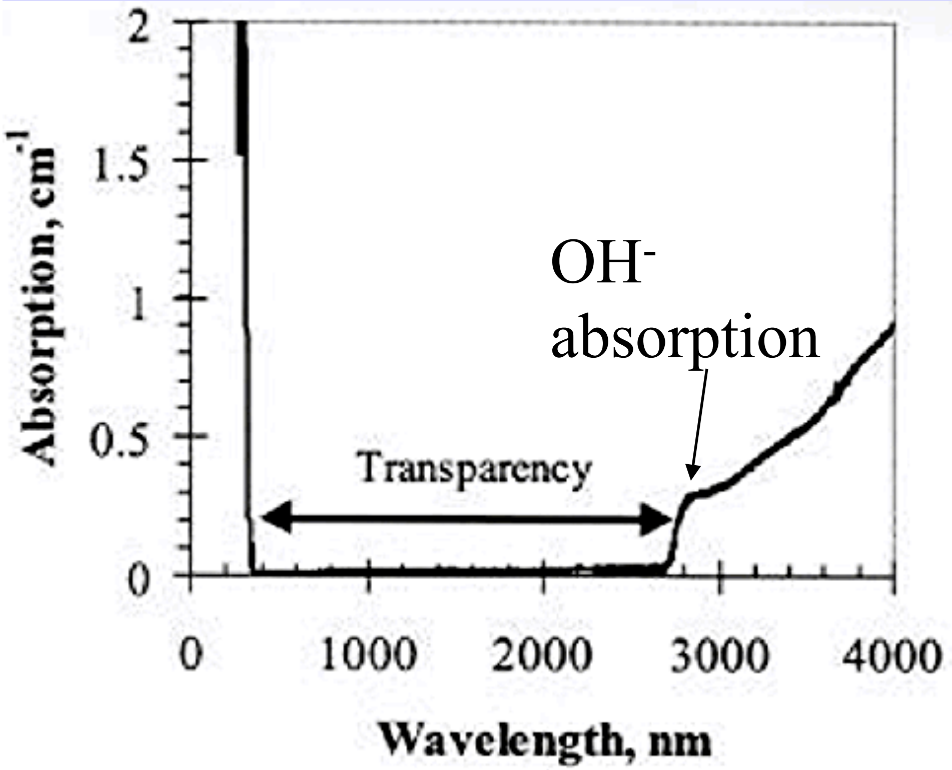
    is trapped at nearby Ag ion ➔neutral atom (latent image)

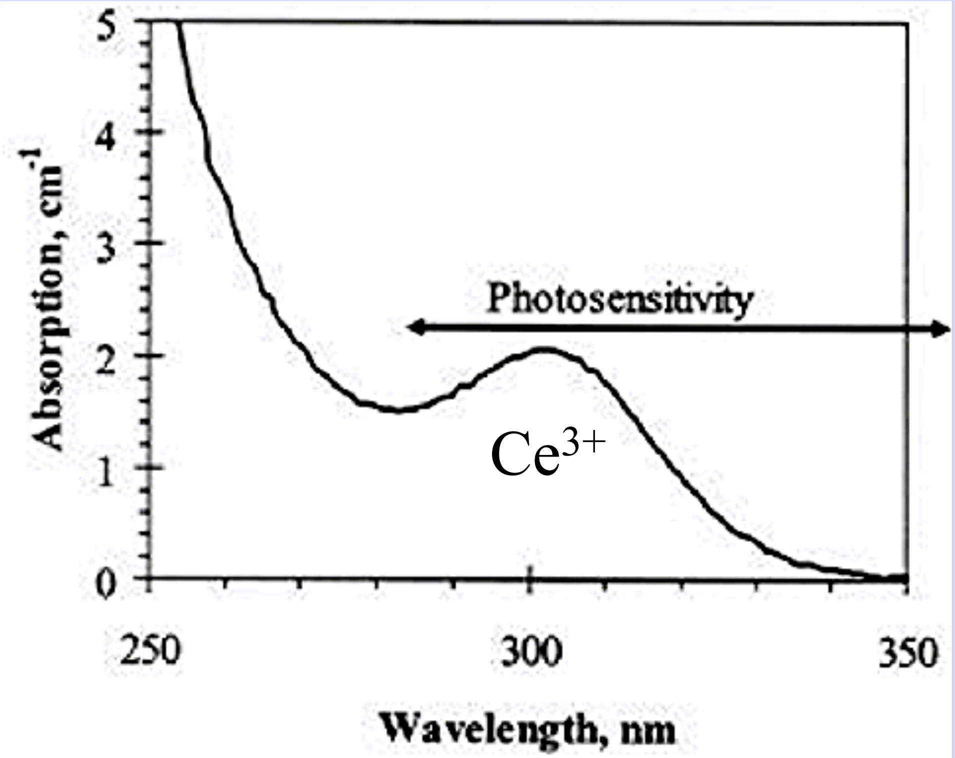
    - But NO significant change in refractive index or coloration....
- UNTIL HEATING:
  - 3 Hrs at 450-550°C ➔ diffusion of Ag atoms to form tiny crystals ➔ nucleation site for NaF crystal growth

➔ dn

From: Glebov L B, *Glastech. Ber. Glass Sci. Technol.* 71C, 85-90, 1998

Transparency and Photosensitivty windows in PTR Glass

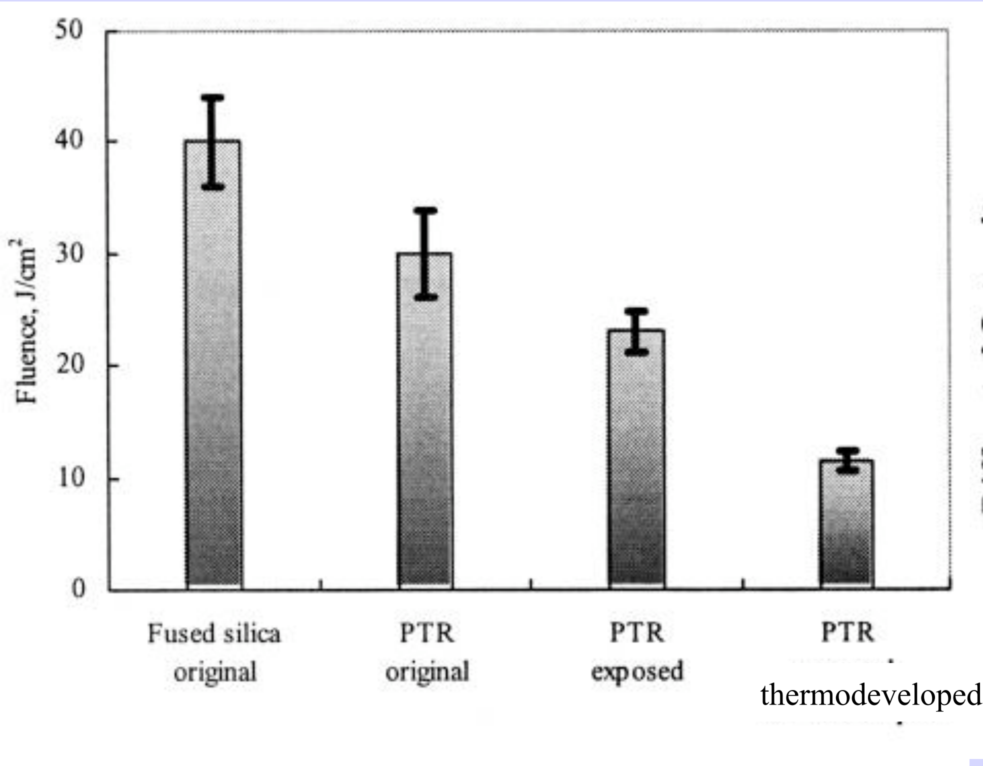


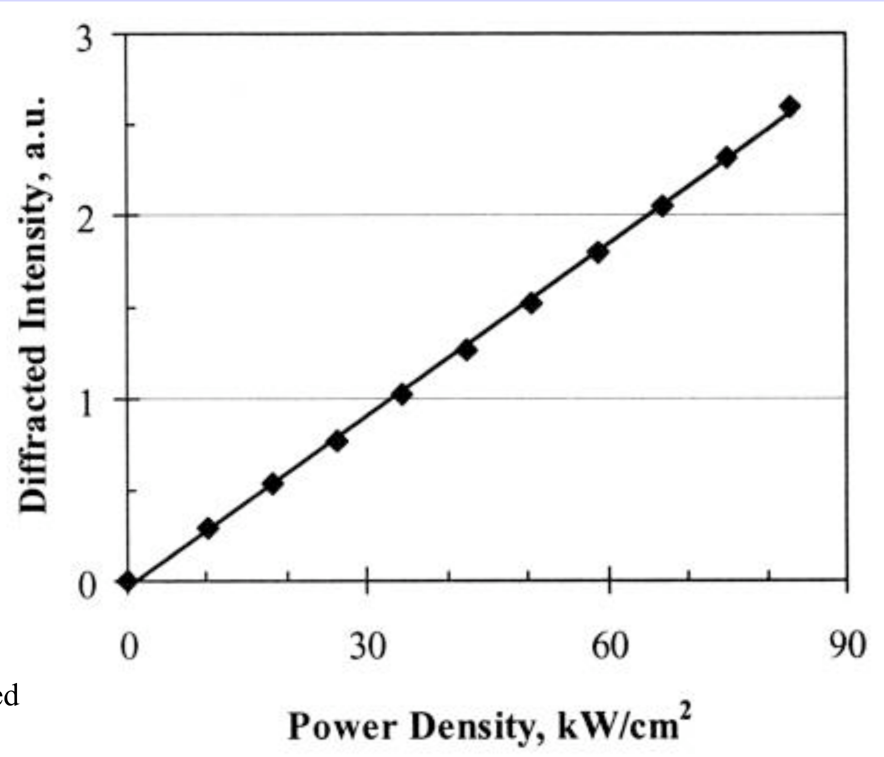


Absorption in Unexposed PTR Glass

From: Glebov L B *et al.*, SPIE 4724, pp101-109

Optical damage and diffraction in PTR glass



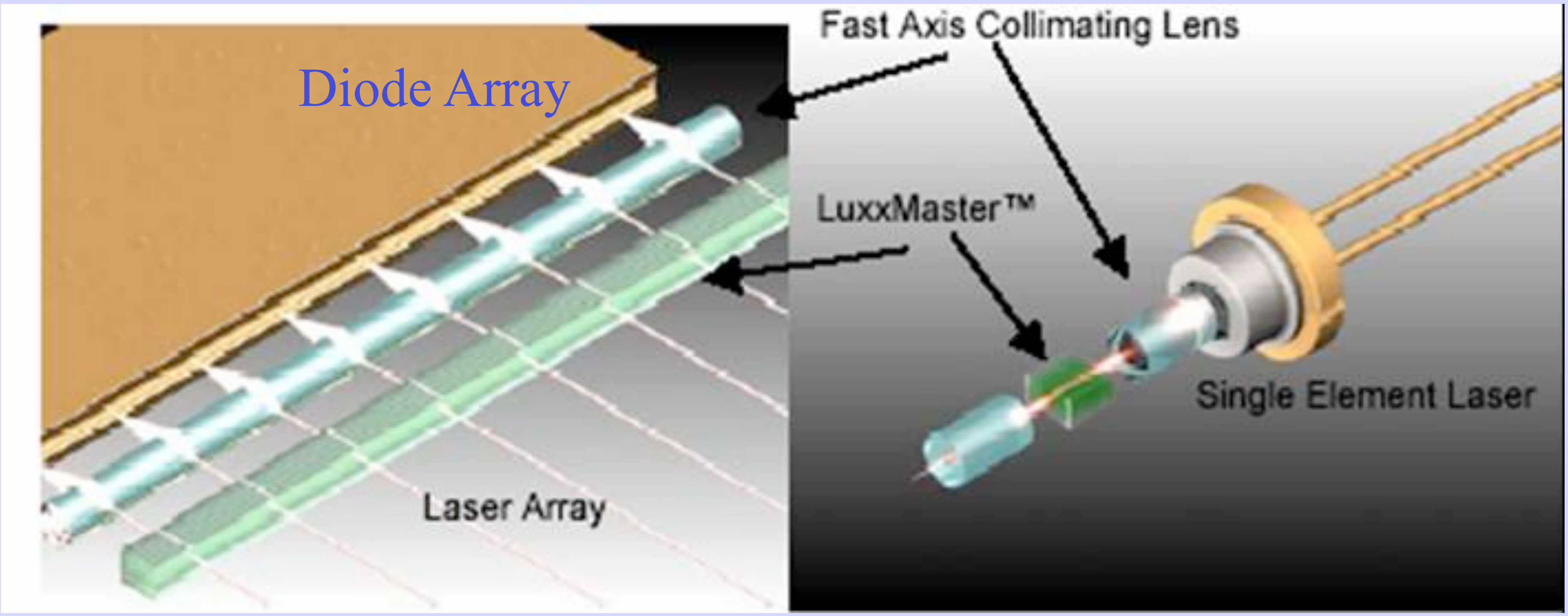


From: Glebov L B *et al.*, SPIE 4724, pp101-109

Summary: Processed PTR Glass

- Transparent between 350 – 2700nm (contamination: OH^- group)
- Extra loss in UV due to mixtures of Ce & Ag
- Fluoride crystals are transparent but scatter light :
  - Additional absorption < 0.3cm^{-1} in blue region
  - < 0.03 cm^{-1} in red region
- Index change ~ 10^{-3}
- Ideal for PLANE WAVES

Photosensitive glass: Application



• Laser mirror for locking semiconductor diode arrays

FROM. PDLD website

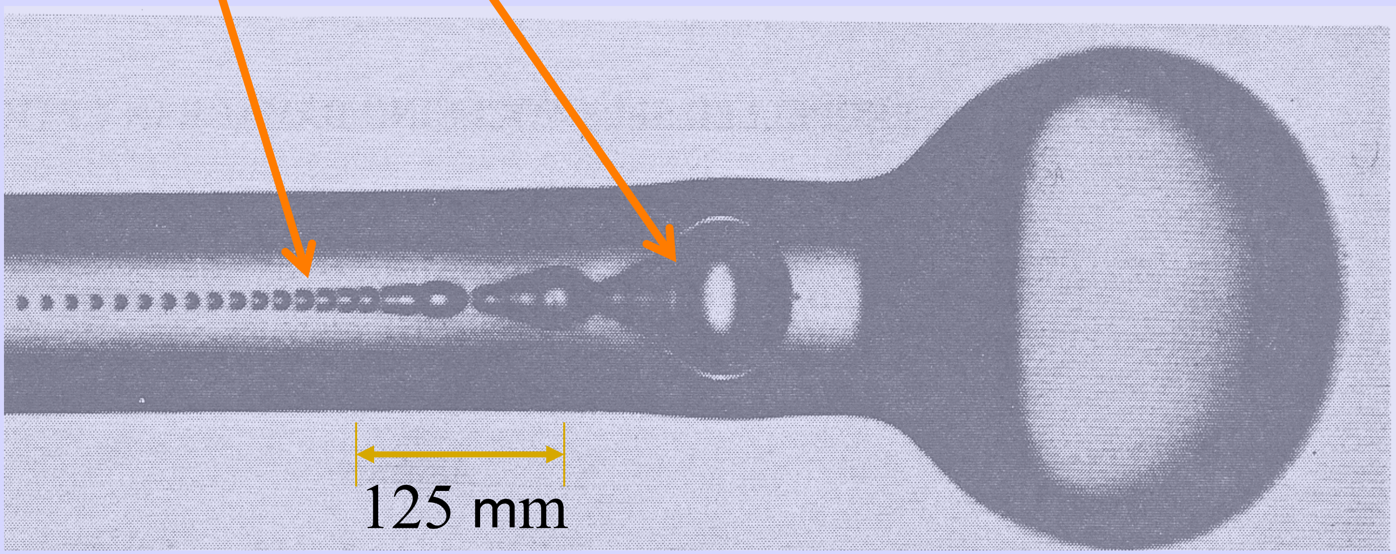
Waveguide Fabrication by Direct Laser Writing

But First……
Optical Fibres…25 years ago…..

Plasma Generation in Glass

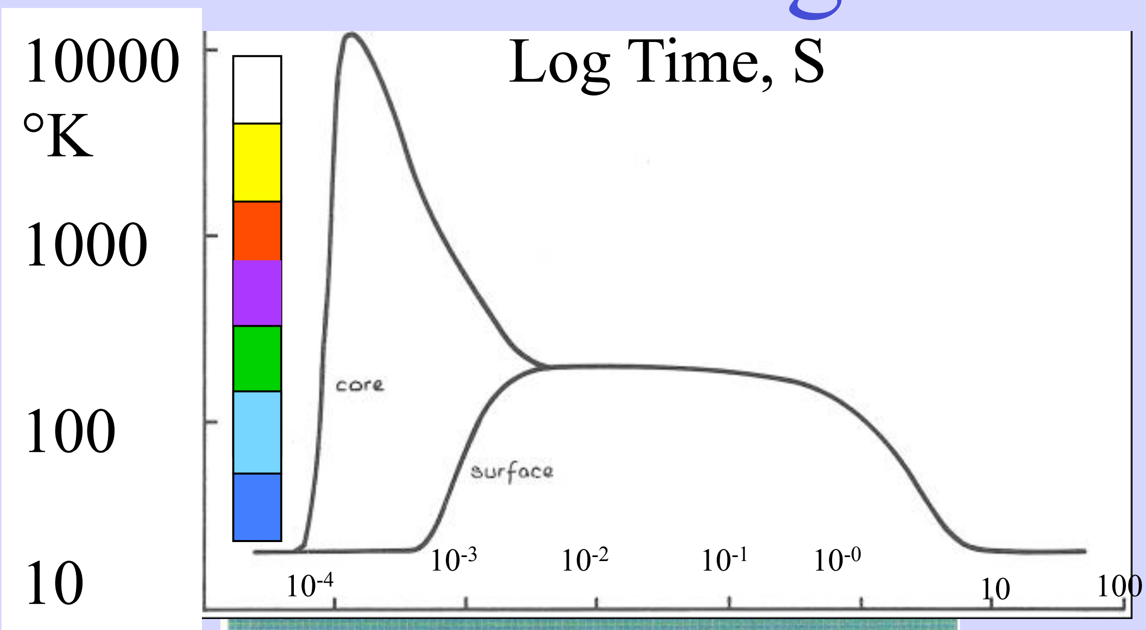
…Optical Fibre Damage at Low Powers*: 'Fibre End'

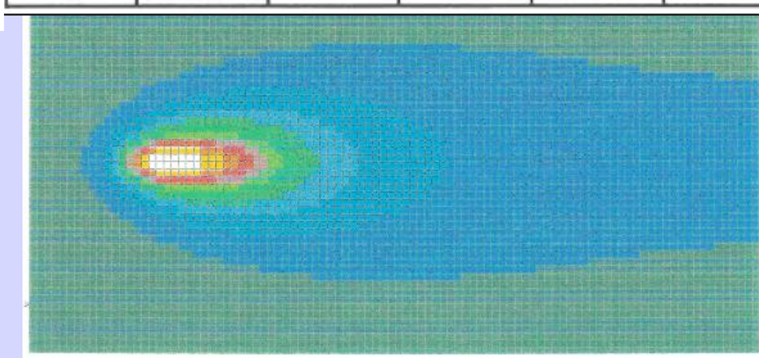
Molecular oxygen in cavities



*Kashyap R and Blow K J, "Observation of catastrophic self-propelled self-focusing in optical fibres", *Electron. Lett. 29* (1), pp. 47-49, 7 January 1988.

Stationary Temperature Profile of Damage Filament





Self-Propelling Damage

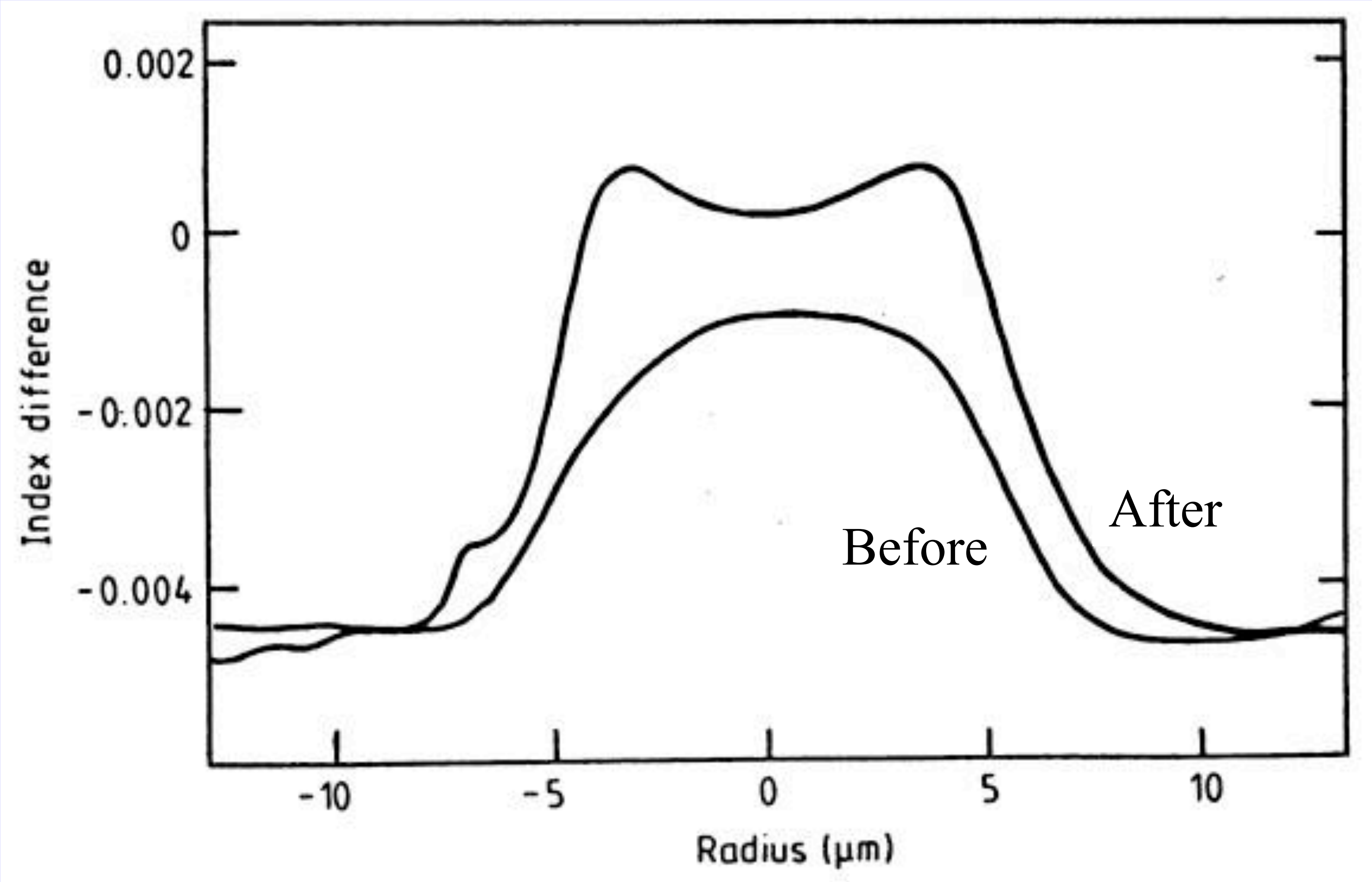
Absorption of light by glass at elevated temperatures

- Thermal runaway

Calculated using a heat diffusion model

Kashyap R, Sayles A & Cornwell G F, 'Heatflow modeling and visualisation of catastrophic self-propelled damage in single mode optical fibres', *Special Mini-Symposium at the Optical Fibres Measurement Symposium, Boulder, October 1996, SPIE Vol. 2966, pp. 586-591.*

Refractive Index Increase After Damage



E.M.Dianov et al. "Change of refractive index profile in the process of laser-induced fibre damage." Sov. Lightwave Commun. vol.2, (1992) 293-299.

*Damage Summary

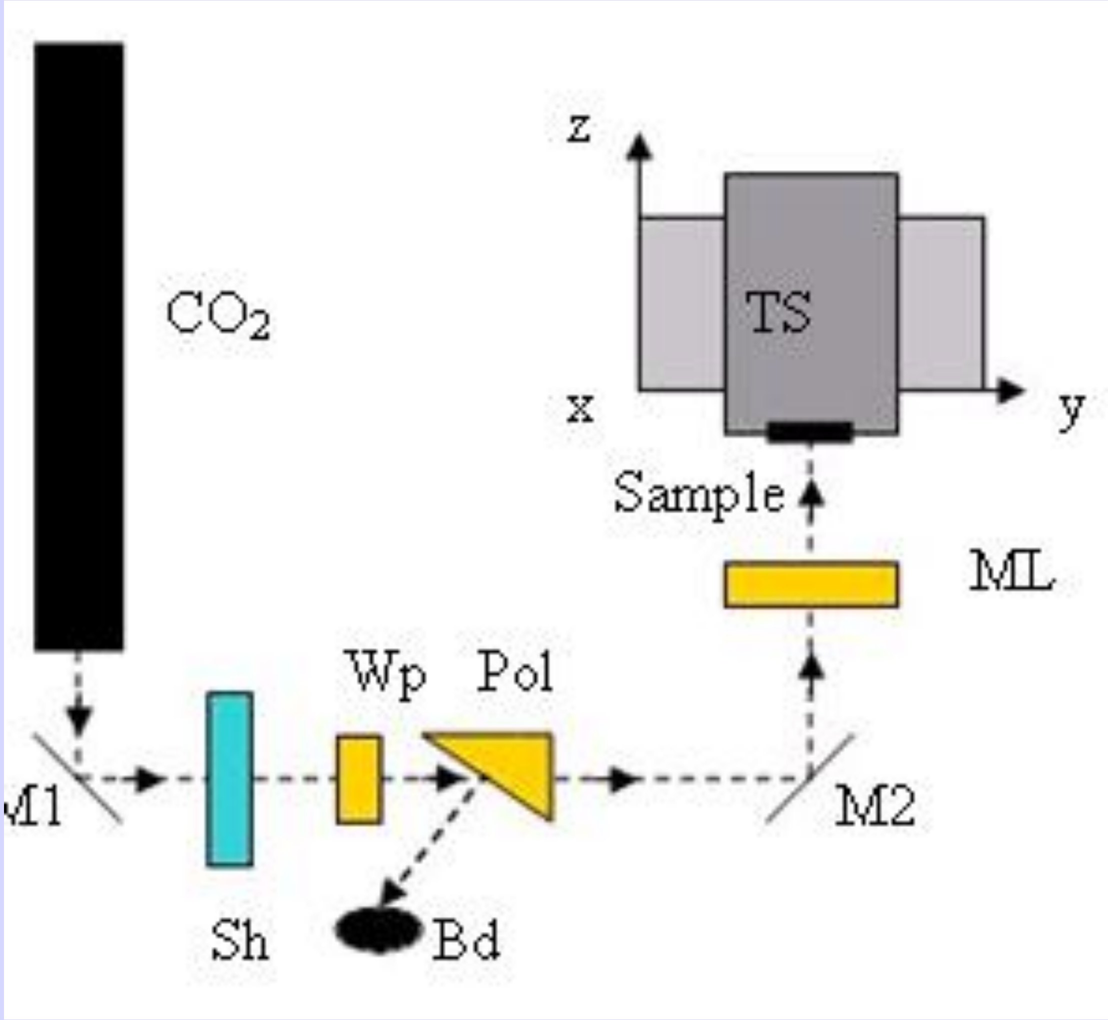
- Wild Temperatures…10,000K!
- Almost no heat loss: Only Conductive Heat
- Creates Sub Oxide of Ge/Si
- Refractive index modification….
- Catastrophic Damage….
- Similarities to fs laser processing.

*Raman Kashyap, "**The Fiber Fuse - from a curious effect to a critical issue: On the 25th year of its discovery** ", Submitted Op. Exp.

So what else can we do?

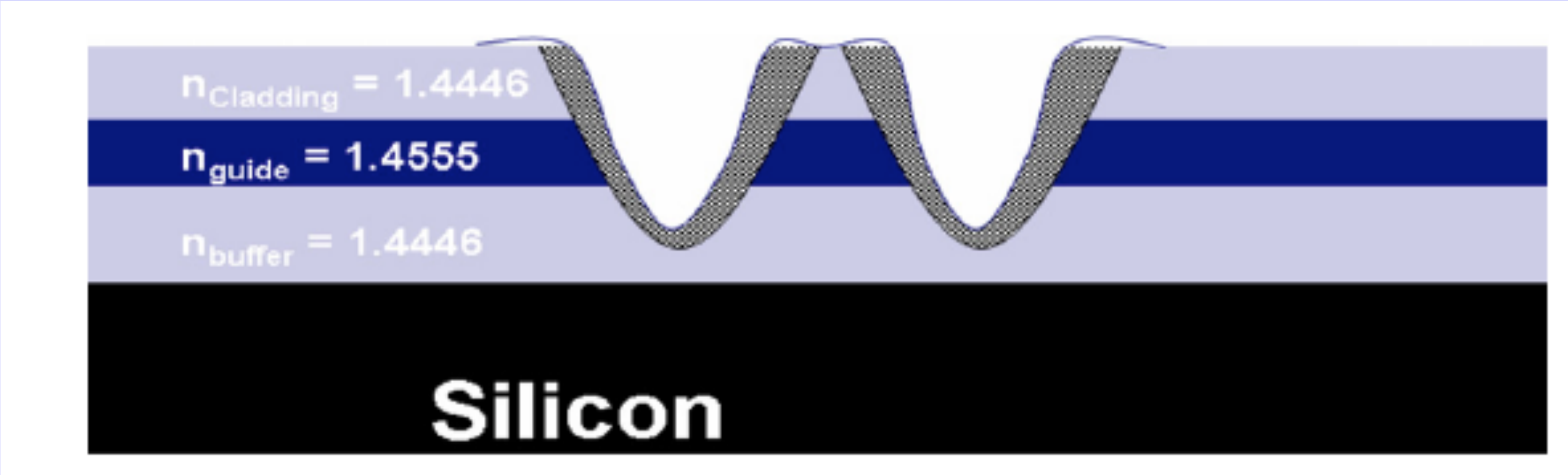
……Laser Ablation

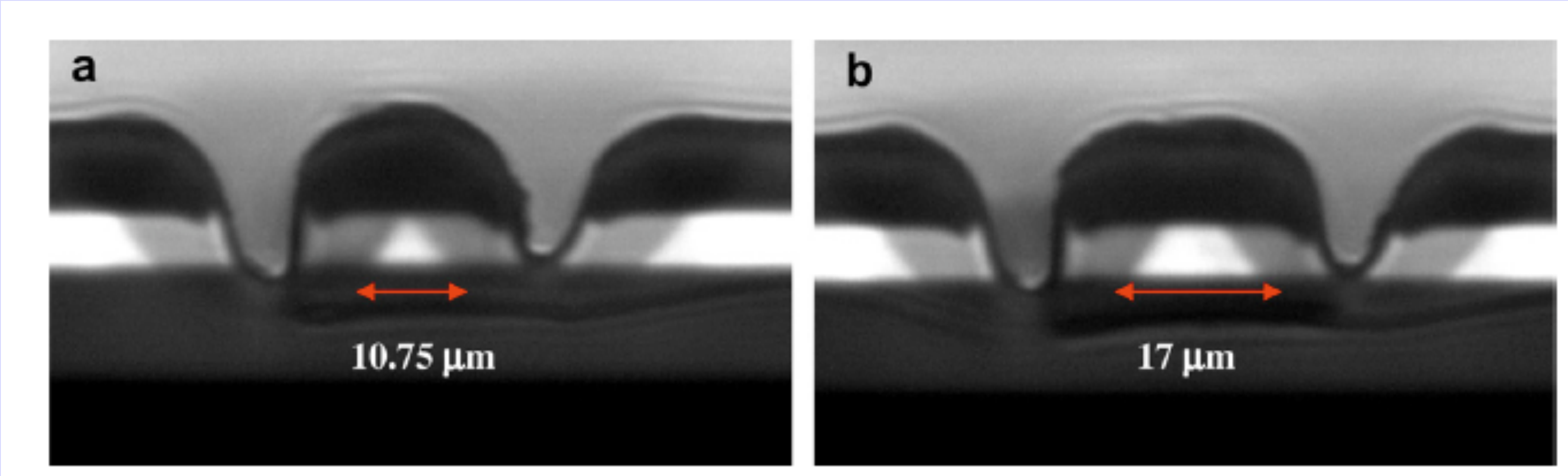
Laser Written Waveguides*



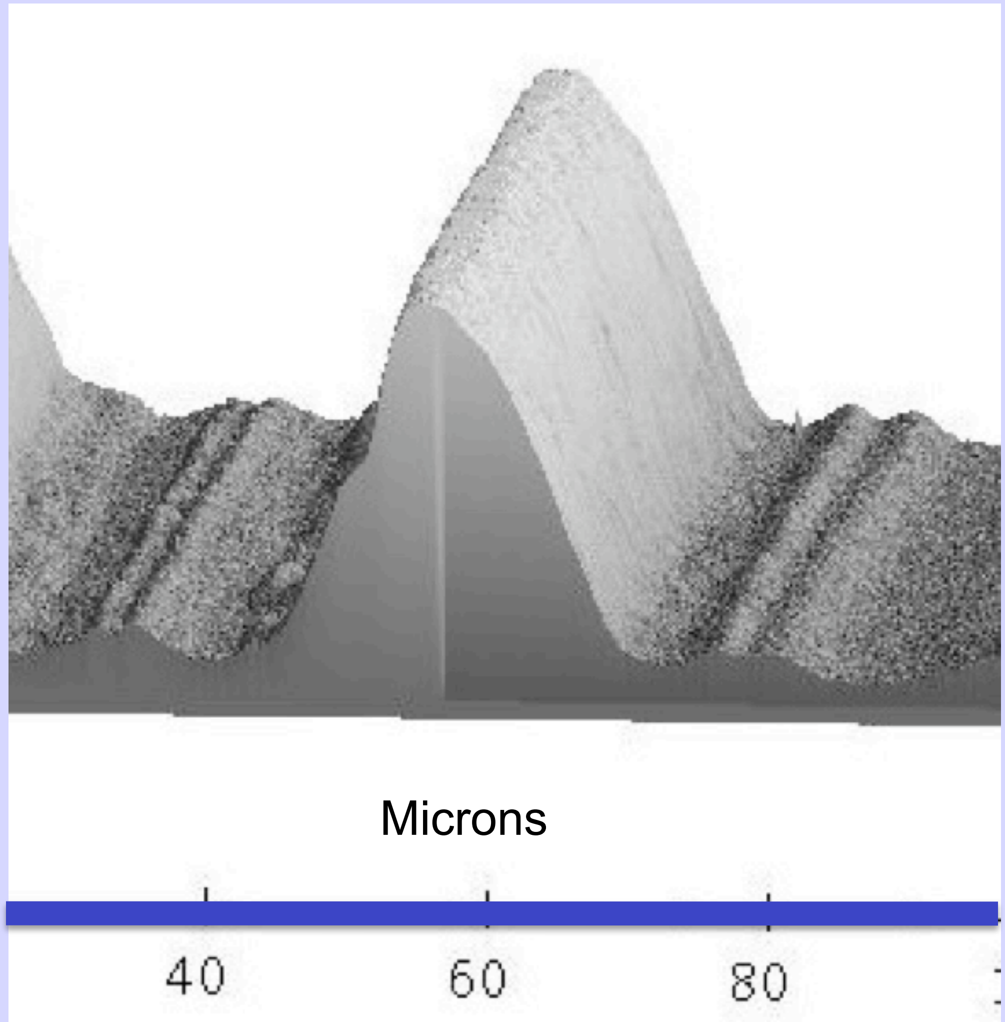
2 x NSERC I2I

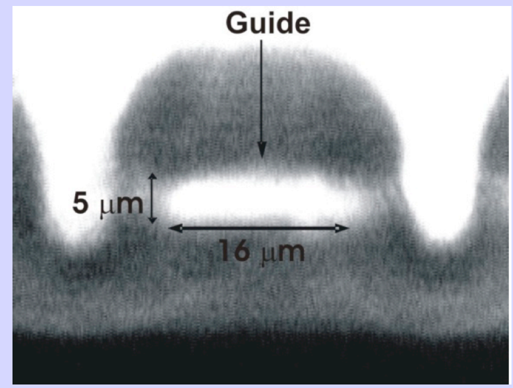
***Ozcan L C**, **Guay F**, Kashyap R, and Martinu L, "Investigation of refractive index modificaiotn in CW CO_2 laser written planar optical waveguides", Optics Communications 281, 3686–3690, 2008, DOI:10.1016/j.optcom.2008.03.074. . (Erratum to "Investigation of refractive index modifications in CW CO_2 laser written planar optical waveguides" [Optics Communications 281 (2008) 3686])


$n_{Cladding}$ = 1.4446
n_{guide} = 1.4555
n_{buffer} = 1.4446
Silicon


a
10.75 µm
b
17 µm

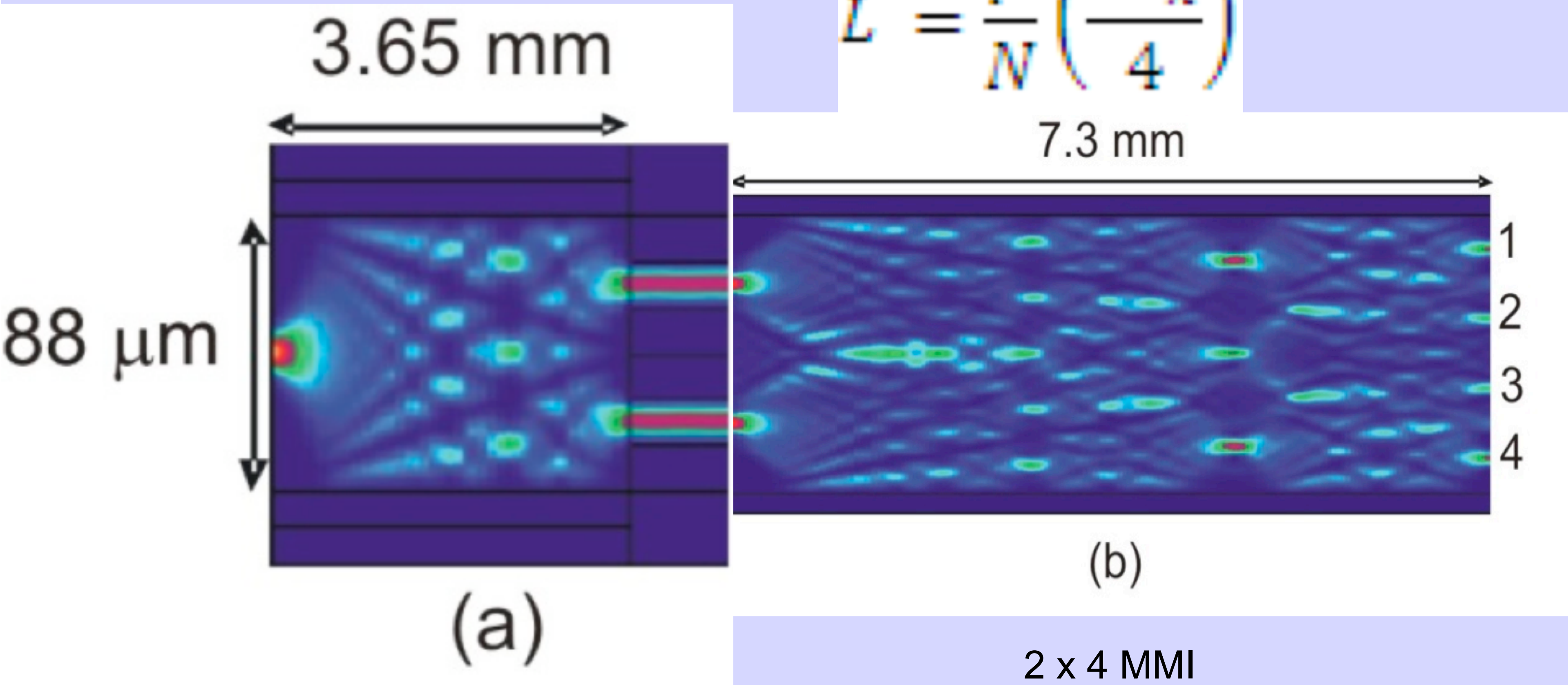
High magnification picture of ablated waveguide





Cascaded Multimode Interference Filters (Six Ports)

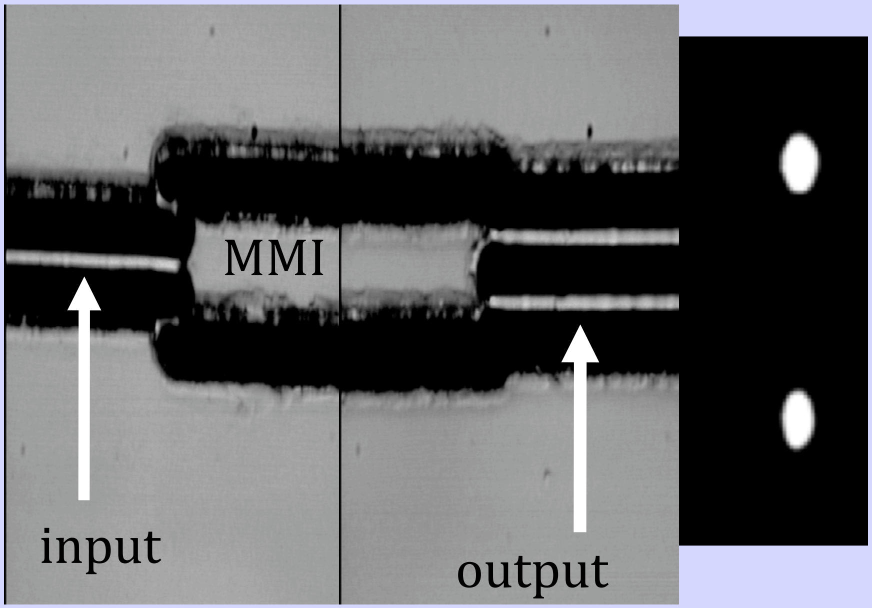
$$L = \frac{p}{N}\left(\frac{3L_\pi}{4}\right)$$



2 x 4 MMI

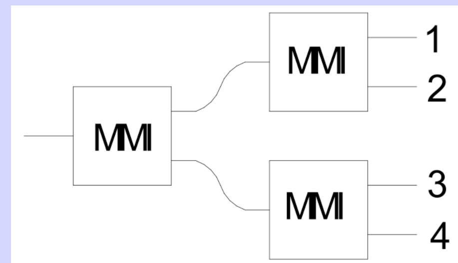
1 x 2 MMI

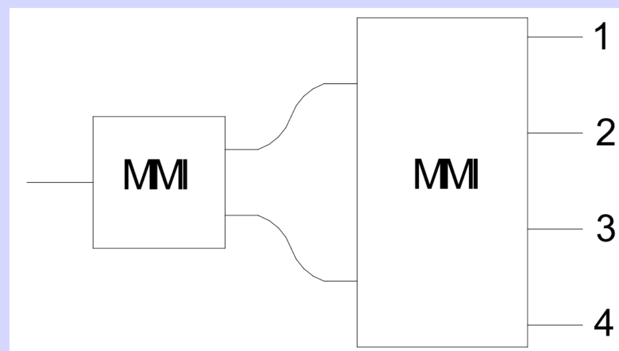
5 port devices using 2 configurations

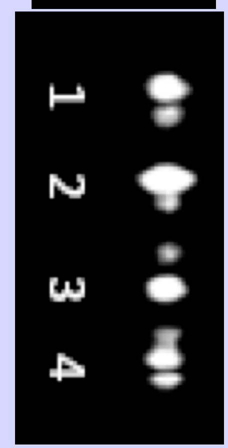


Straight Waveguide Loss: 0.36dB/cm

1 x 2 + 1 x 2



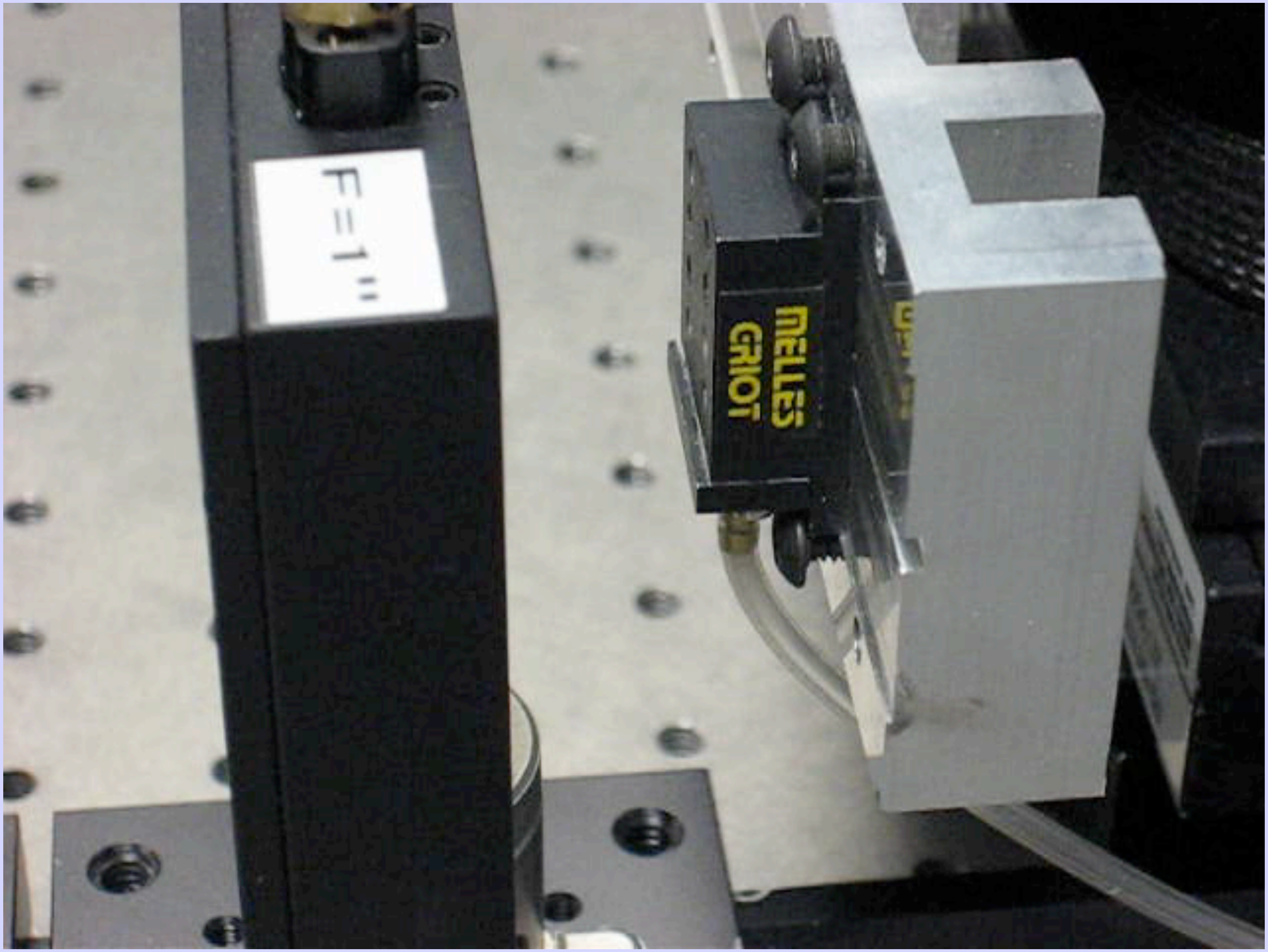




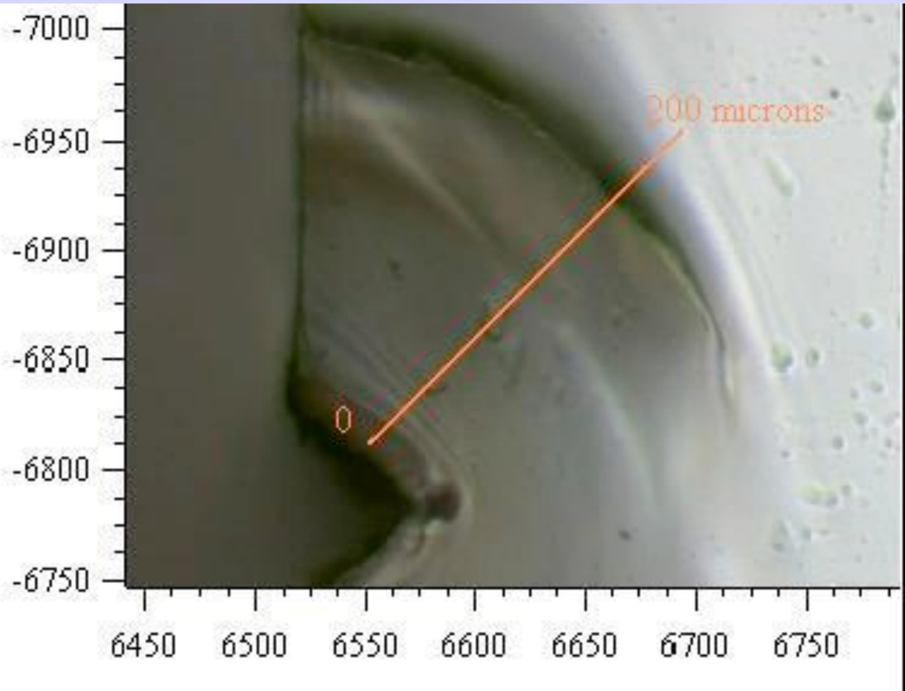
1 x 2 + 2 x 4

G. V. Vázquez, A. Harhira, R. Kashyap and R. G. Bosisio, Micromachining by CO_2 Laser Ablation: Building Blocks for a Multiport Integrated Device, *Accepted in Optics Communications*

Movie of MMI Fabrication

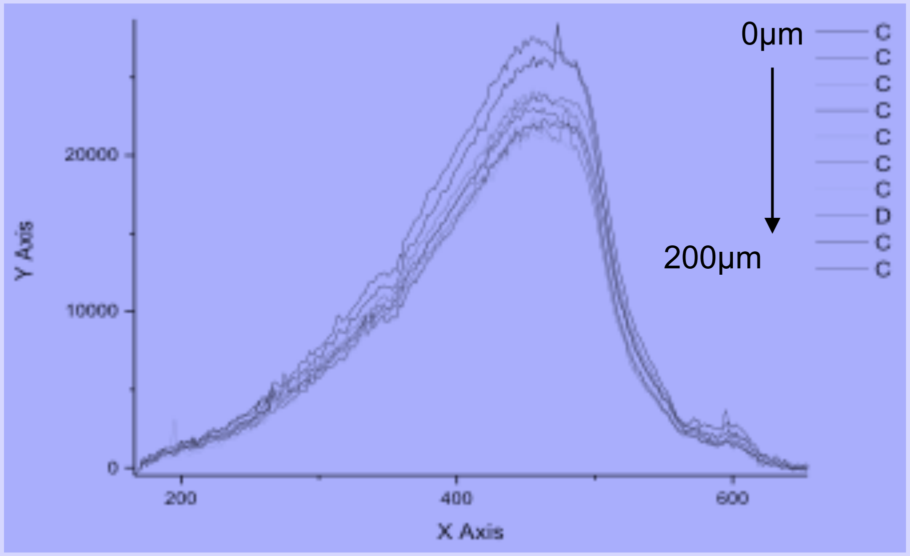


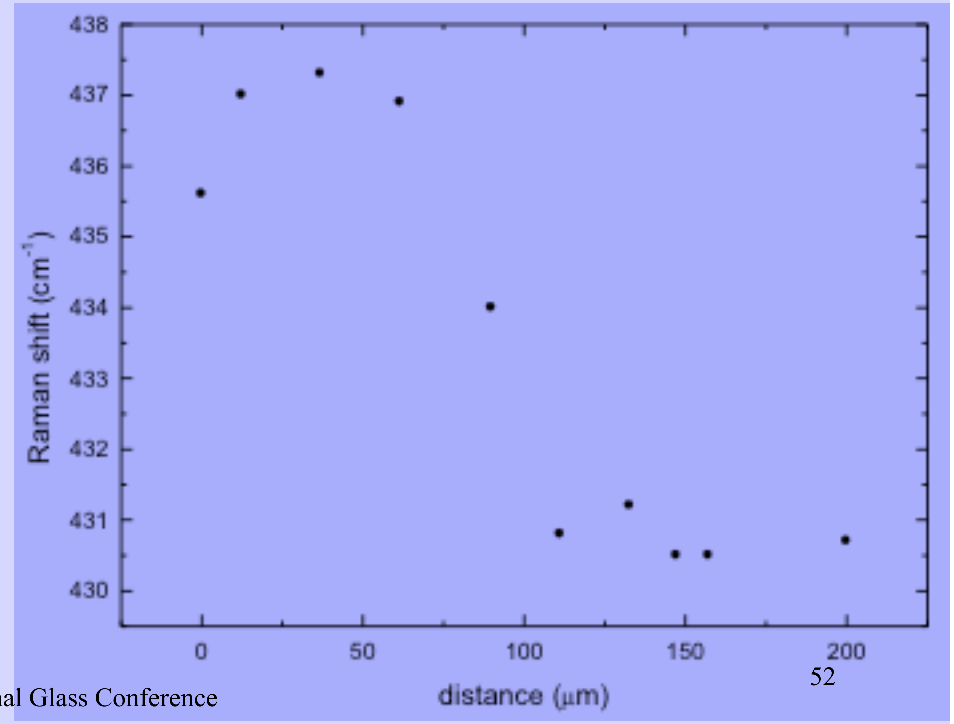
T.Deschamps - Prof. B.Champagnon
LPCML Universite Lyon



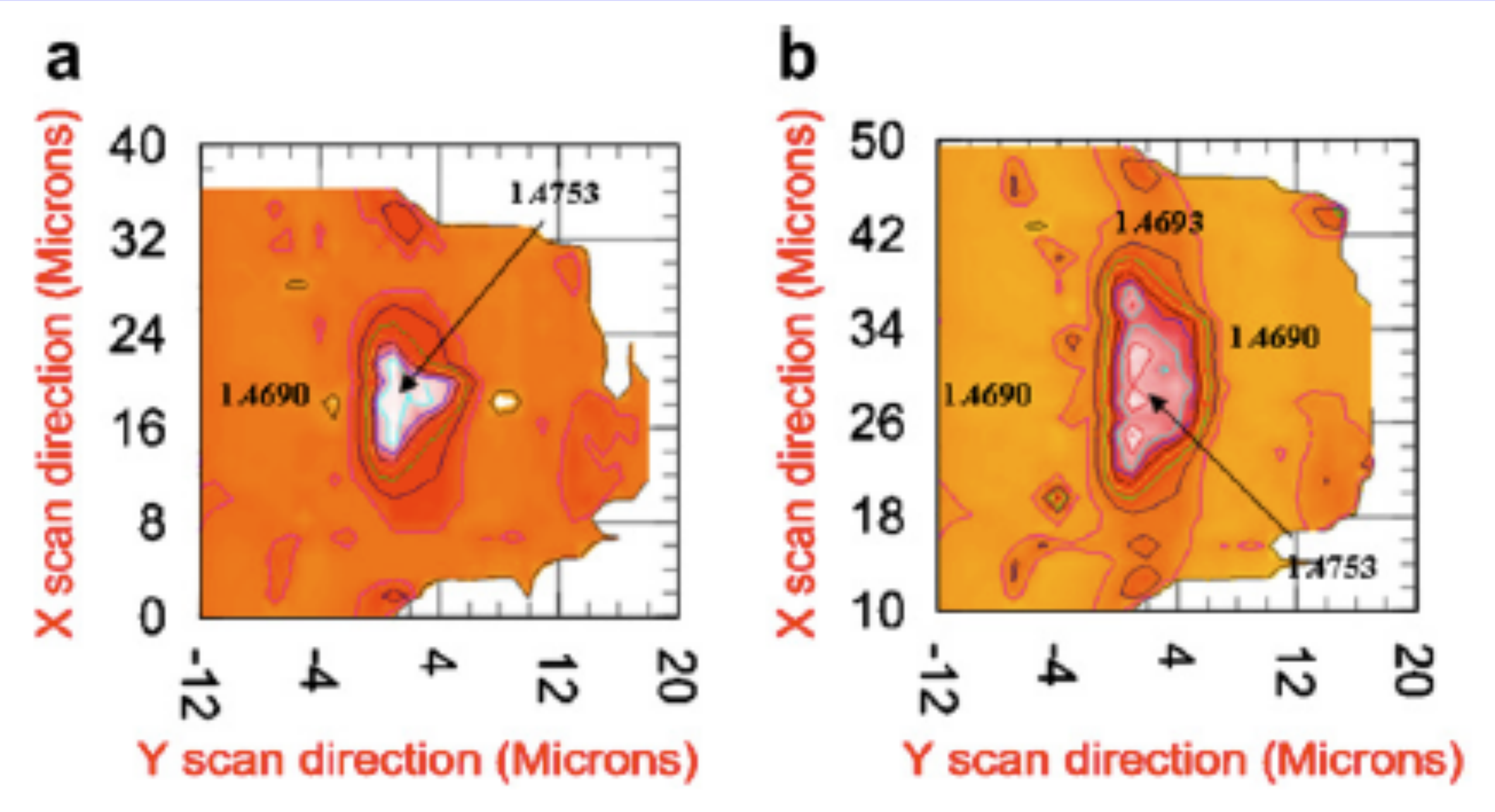
L'impact est du à un laser CO2 (P=1,05W) . Le shift est déterminé par le shift du centroïde.
Les spectres sont enregistrés le long de la ligne ci-dessus a partir du centre de l'impact. La densité du verre de silice dopé germanium augmente lorsque le Raman shift augmente

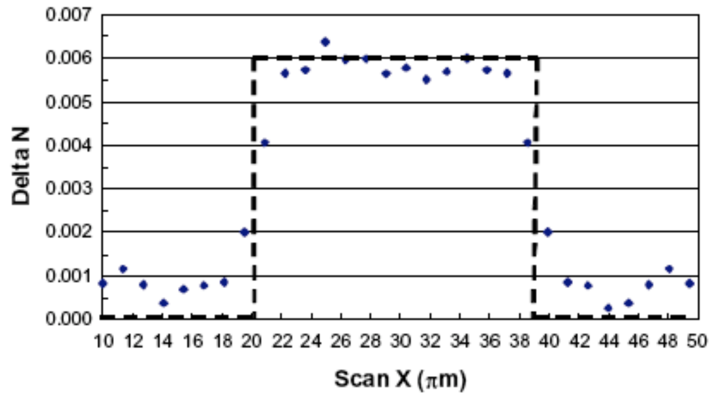
Raman Spectra





Refractive Index Change (Reflectometry)





Annealing!

- Waveguide is ***buried*** due to Heat Affected Zone Lowering Refractive Index!

- THEREFORE:

Pre-annealed planar samples **do not work**!

CHANGE OF PACE FROM CW ILLUMINATION…

Femtosecond pulse photoinduced effects in glasses

Acknowledgement: Prof Hirao, Ravi Bhardwaj

Question of Maximum Optical Power Limitation

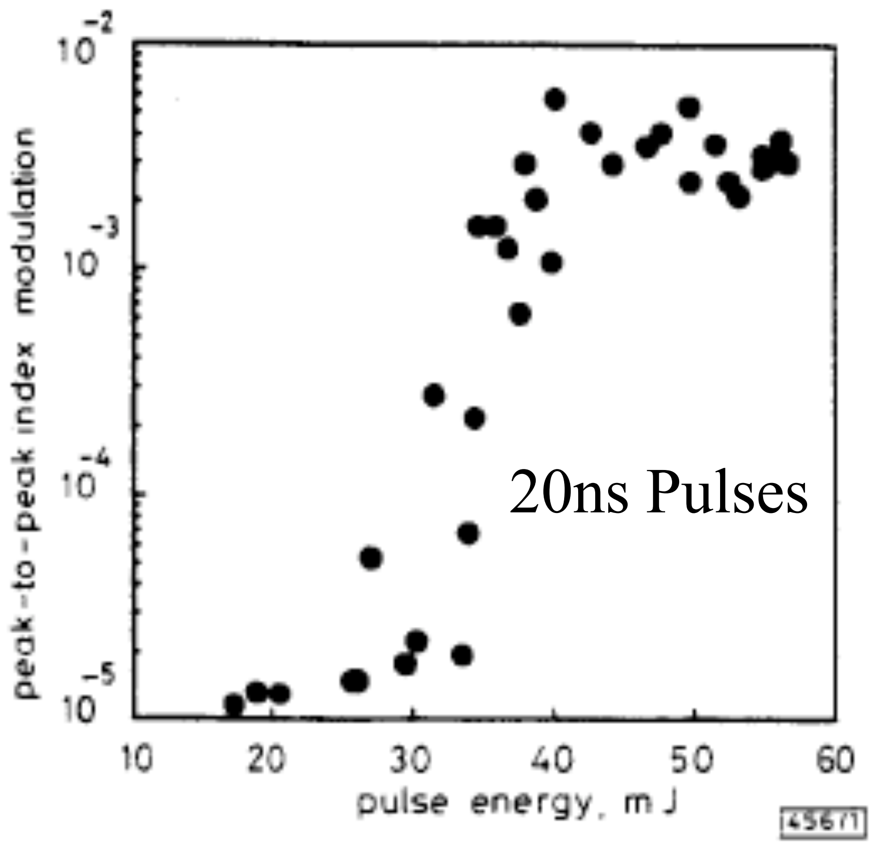


Fig. 1 *Peak-to-peak modulation of refractive index for different pulse energies*

Commensurate with fs modification: 30mJ/20ns OR 60nJ/100fs

J-L Archambault, L Reekie & P. St. J. Russell, "100% reflectivity Bragg reflectors Produced in optical fibres by a single excimer laser pulse", El. Lett. 29(5), 453, 1993.

Fabrication platform

Laser parameters

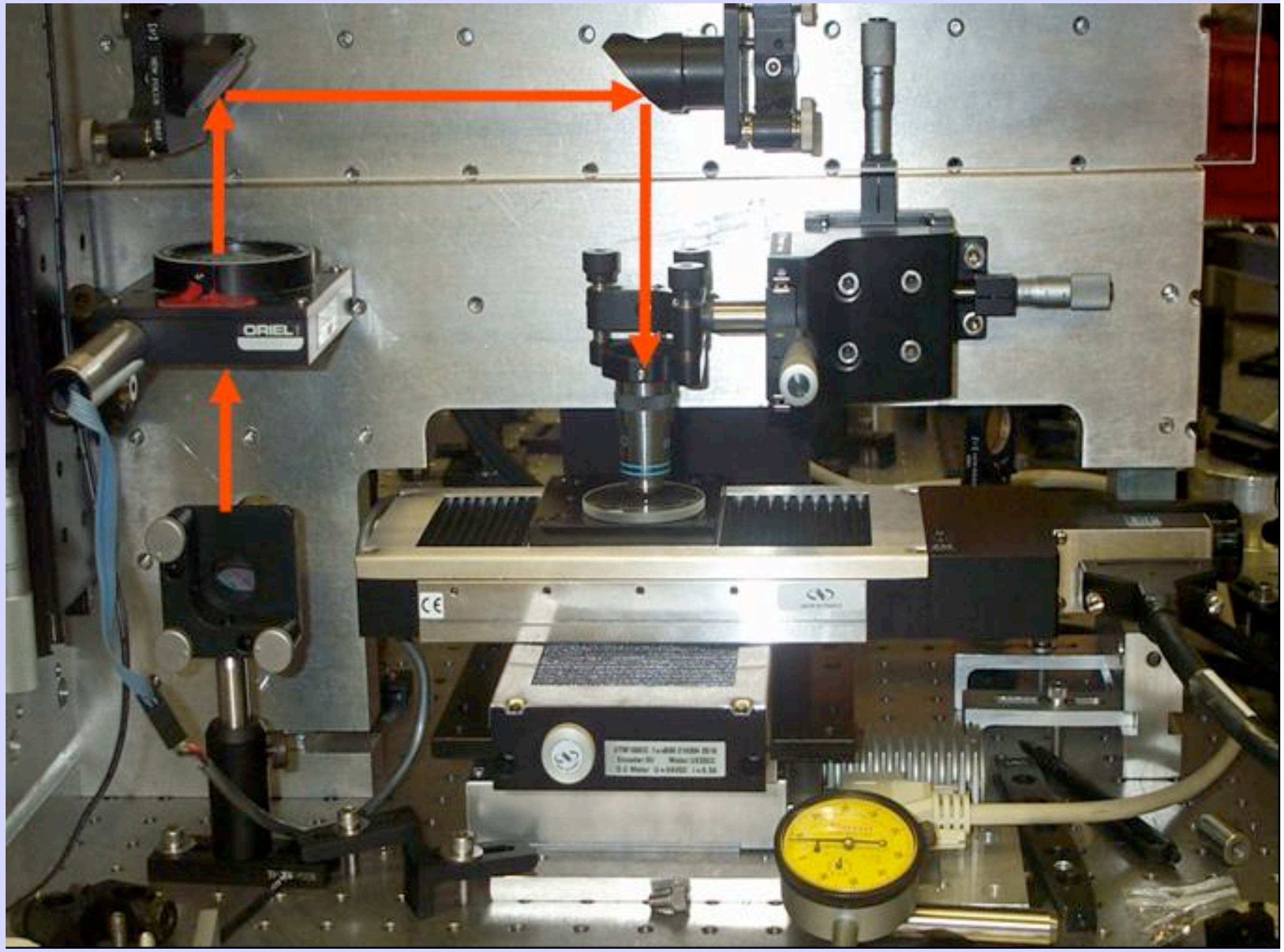
Power : 300 mW

Wavelength: 800nm

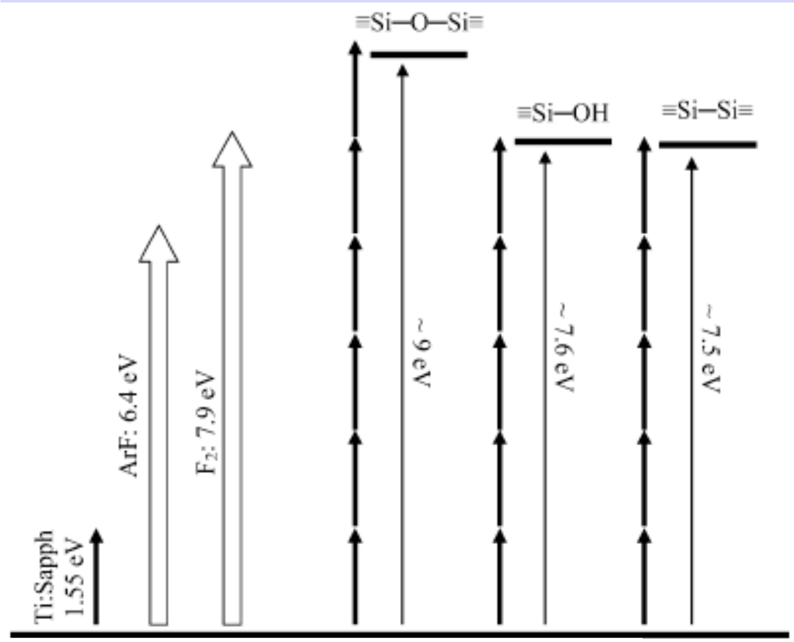
Pulse duration: 40-50 fs

Rep rate: 10 – 250 KHz

Scan rate: 10 – 500 μm/s



Fs laser induced refractive index changes



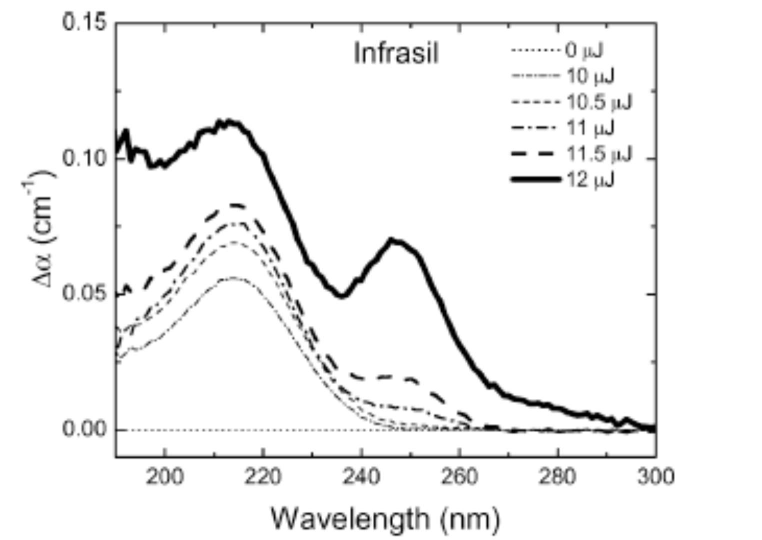
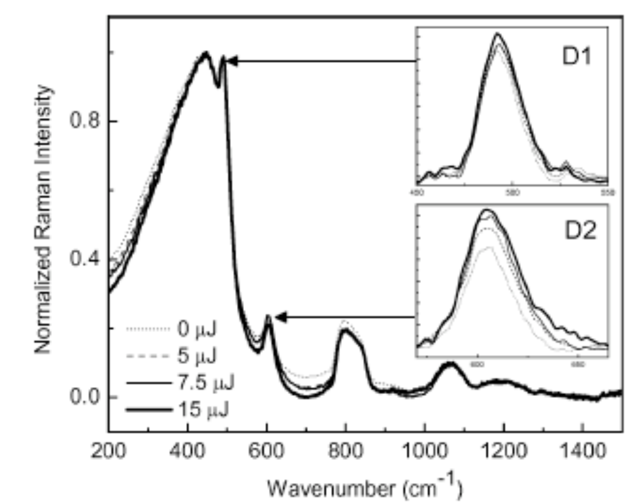


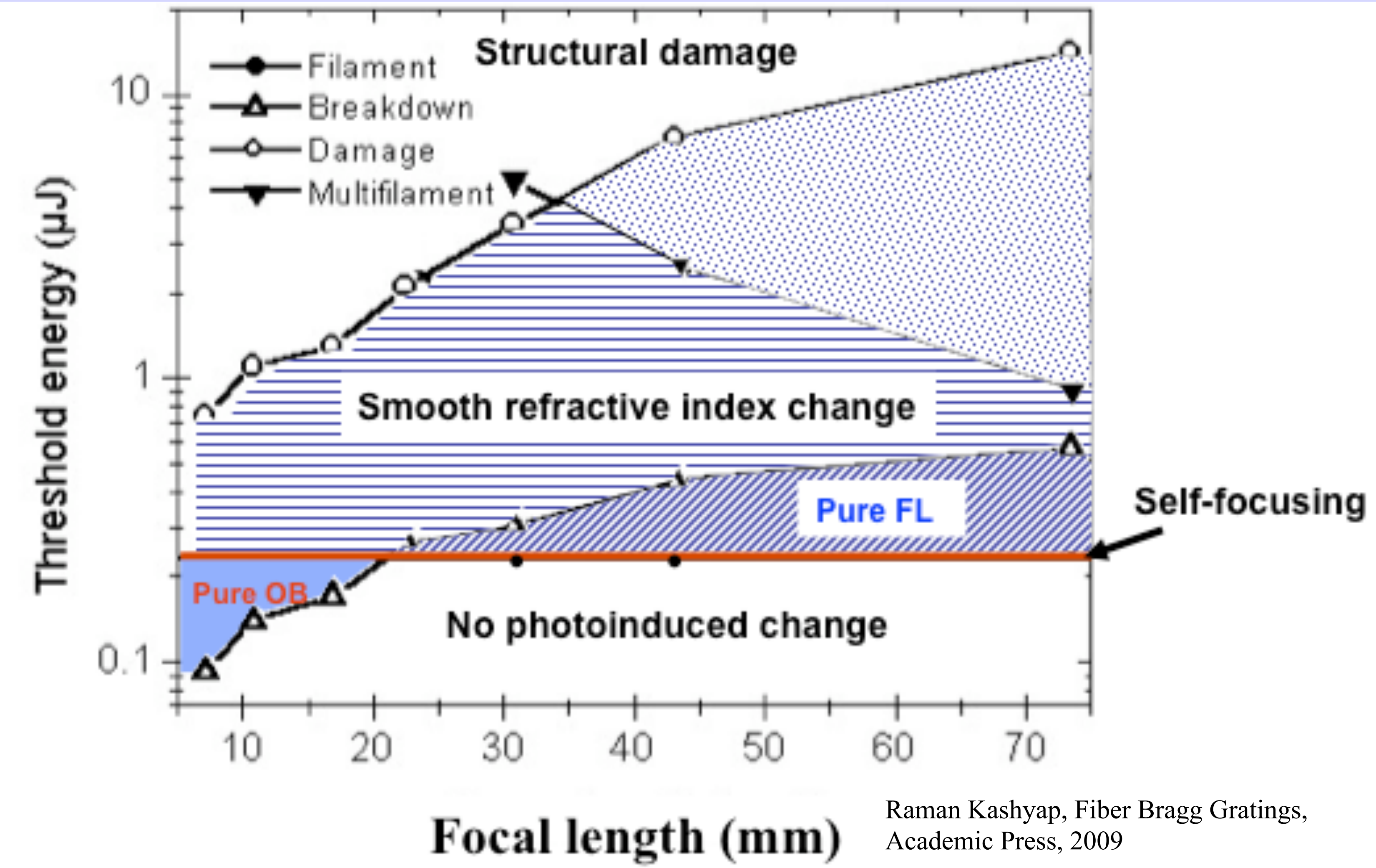
FIG. 4. Absorption change spectrum in Infrasil with smaller pulse energy increment showing the sequential development of Si E' centers (214 nm) and NBOHC (248 nm).



Laser induced generation of ODC (II) generation and optical damage in the form of scattering centers in the volume of the sample, whereas the generation of Si E' only left the samples scatter free. Finally, Raman spectroscopy confirmed the generation of threefold and fourfold rings and revealed a decrease in the Si-O-Si angle distribution as a result of the photoinduced disruption of strained bond upon IR femtosecond laser irradiation.

Zoubir et al., PR B 73, 224117, 2006.

Material Modification with fs lasers

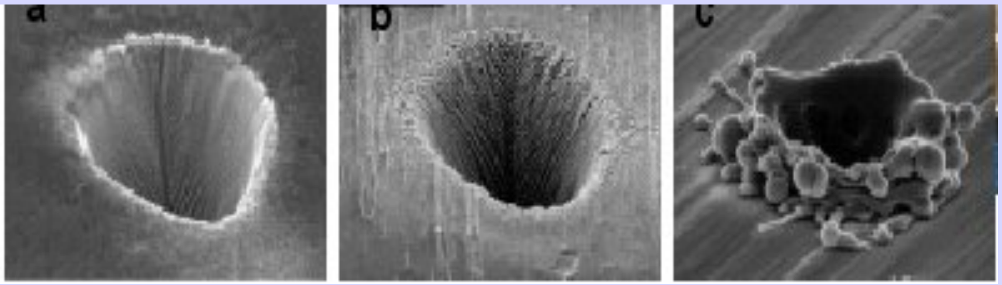


Raman Kashyap, Fiber Bragg Gratings, Academic Press, 2009

Provided by courtesy of Dr. Réal Vallée, U Laval

Femtosecond Interaction with solids: Originally demonstrated by Prof. Hirao

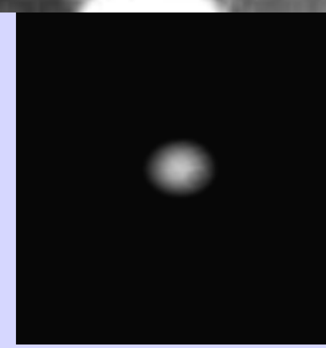
fs laser　　fs　　ns laser



On solids

- Material ablation
- No heat diffusion
    - Rapid solid to vapour transitions
- Micromachining

Waveguide inside glass



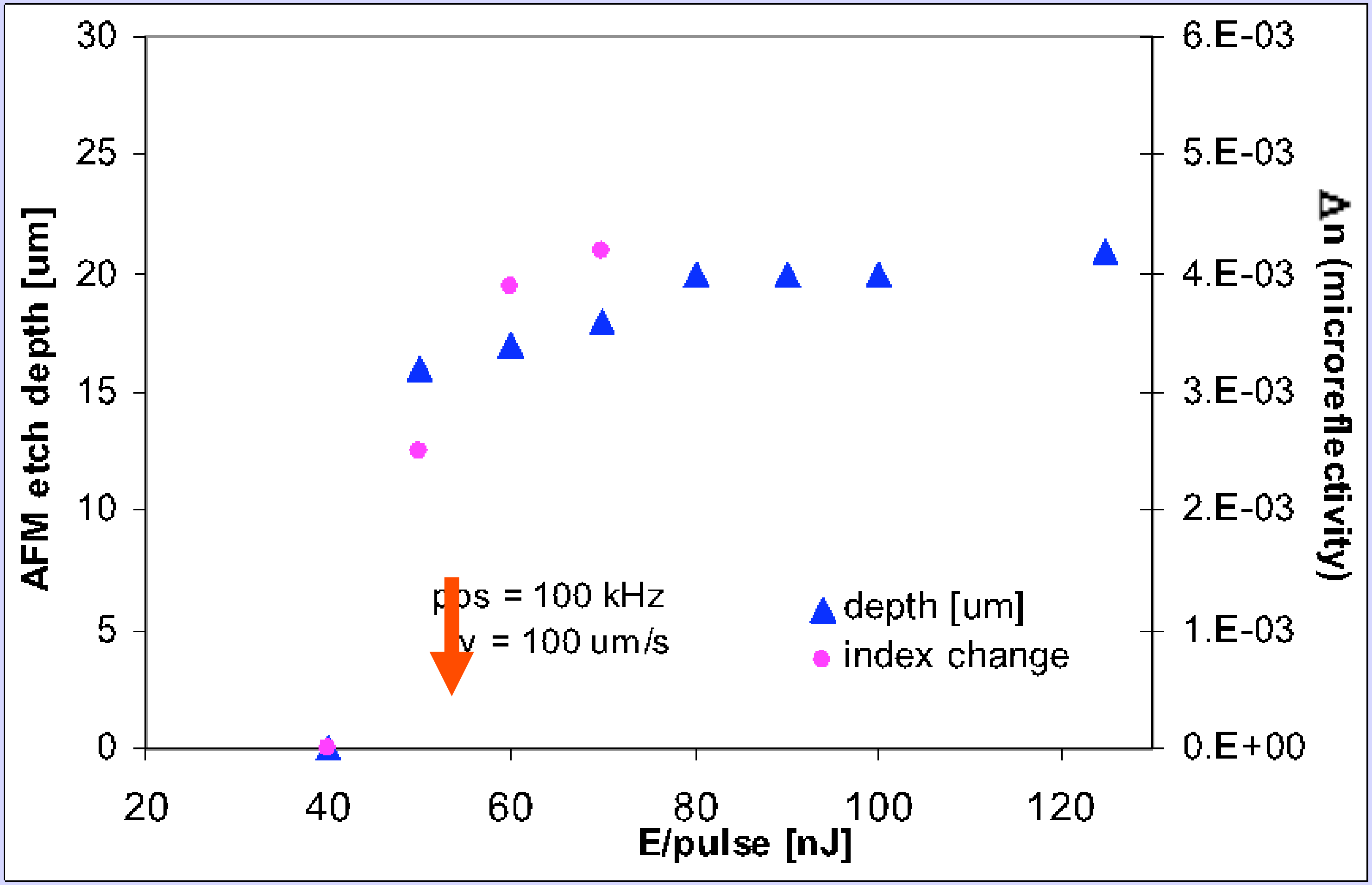
Output mode

Inside glass

- No material ablation
- Localized refractive index change
    - only at the focal spot
    - IR photosensitivity
- Integrated optics

Bhardwaj *et al* Proceedings of SPIE, **TD01** (2002) 211

Threshold for refractive index modification

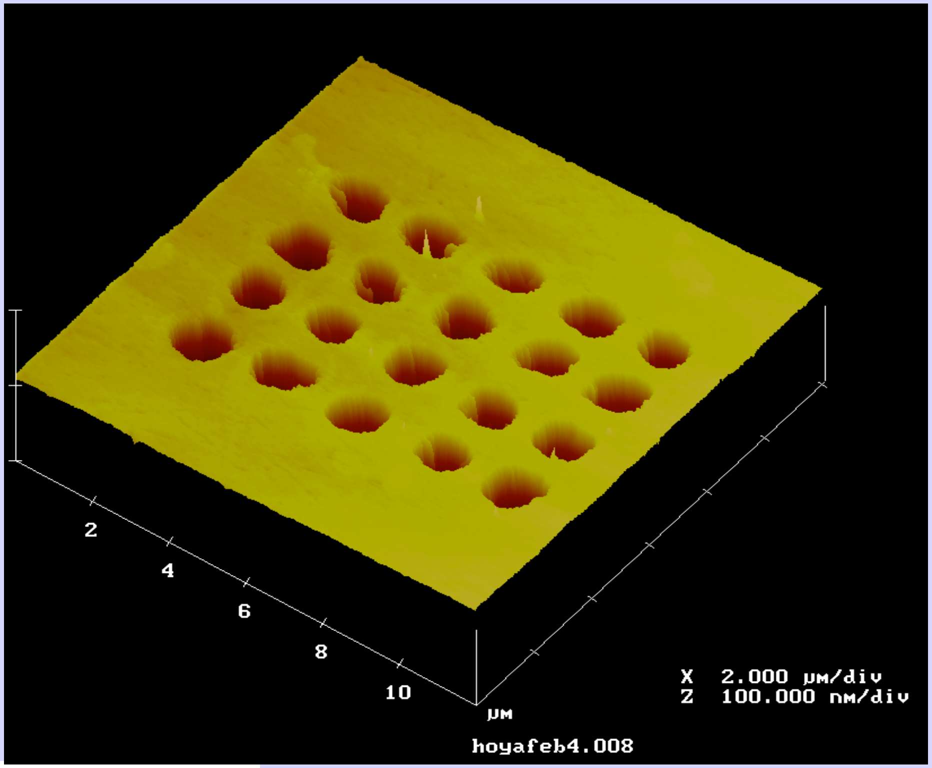


Threshold agrees with the atomic ionization energy

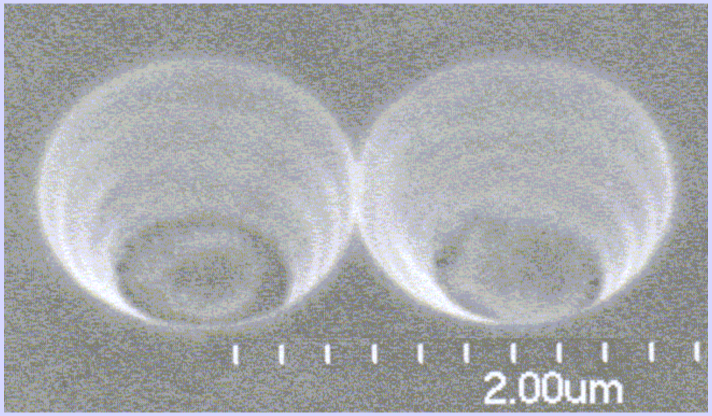
Fabrication of nanostructures

Closely spaced microwells in fused silica

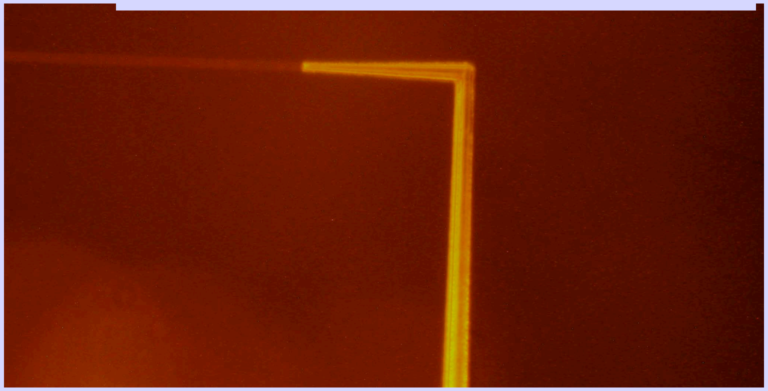
Well densities ~ 33 million/cm^2 !!!



R.S. Taylor *et al,* Optics Letters **28,** 1043 (2003).

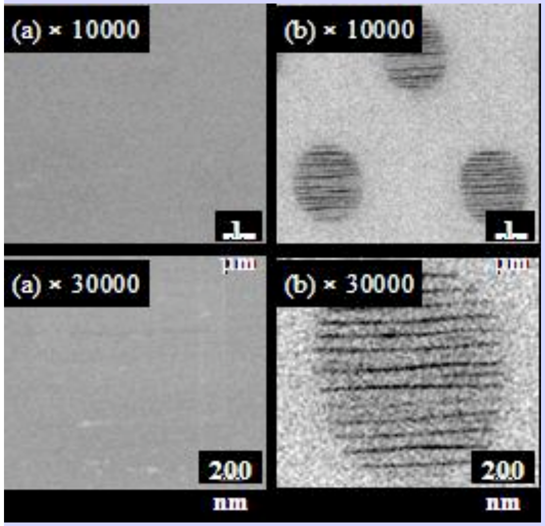


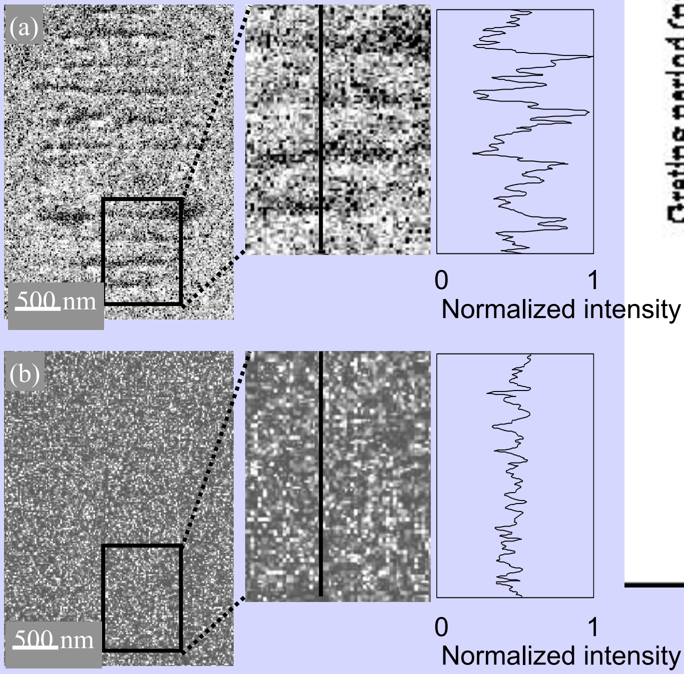
Mixing biological fluids in 3D microfluidic channels

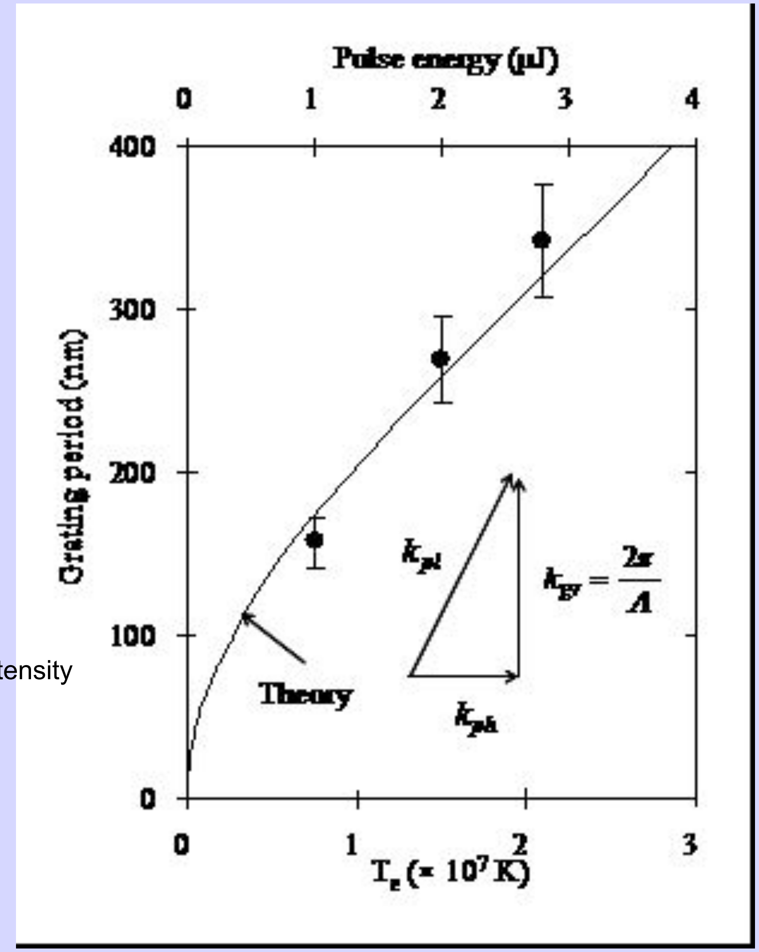


50 [?]m

Femtosecond pulse interaction with glass

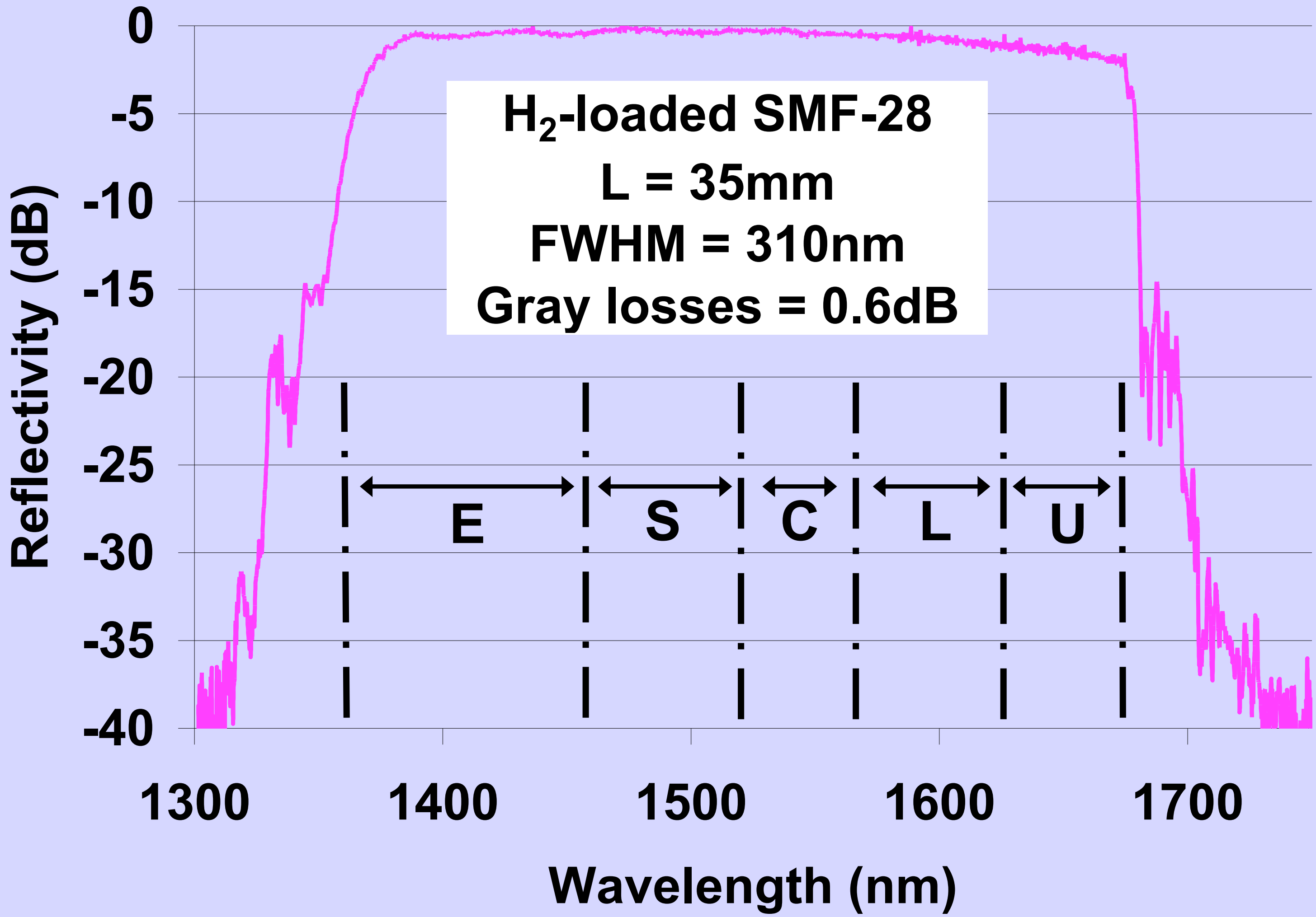






Courtesy: Prof. Hirao

Broadband reflectors



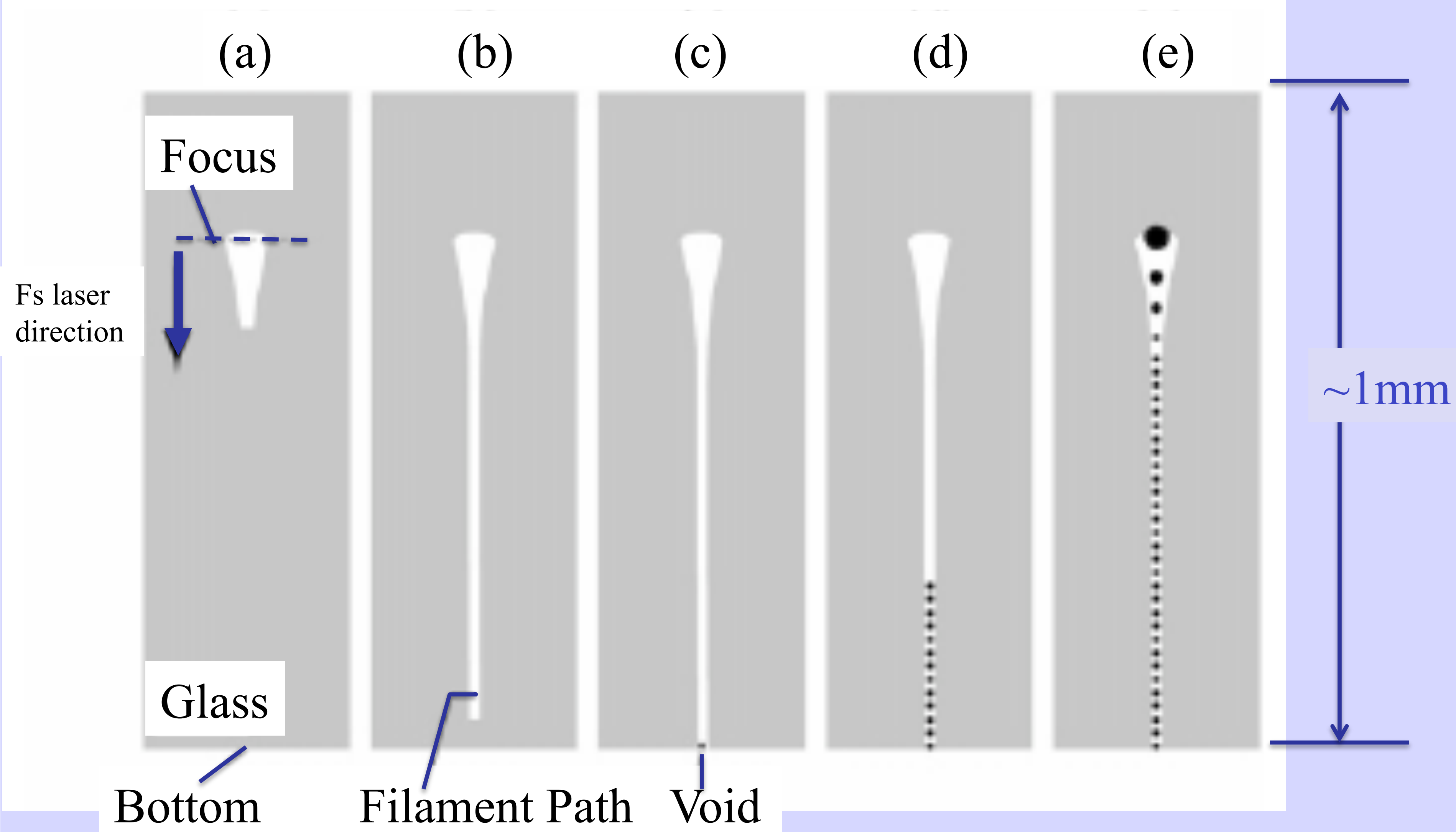
M. Bernier, Y. Sheng, R. Vallée, "Ultrabroad fiber Bragg grating using femtosecond pulses", Opt. Express, 17(5), 3285-3290 (2009).

Novel Observations with fs lasers

- Preferential crystallisation in Ge: glass (*c.f.* A. Stone *et al.* , "New advances and current challenges in femtosecond laser-induced crystallization for 3D precision patterning of nonlinear optic structures inside glass" [Poster, This Conf.])

- Refractive Index Modification and Self Structuring

Fs Laser Generated Void Formation: Similar to Optical Fibre



Shingo Kanehira, Jinhai Si, Jianrong Qiu, Koji Fujita, and Kazuyuki Hirao, "Periodic Nano void Structures via Femtosecond Laser Irradiation", NANO LETTERS 2005, 5 (8), 1591-1595

ISSUES in fs structuring

- High propagation Loss
- Control of waveguide shape
- Birefringence
- Better understanding of glass chemistry
- Relationship and similarity to low power damage
- ……

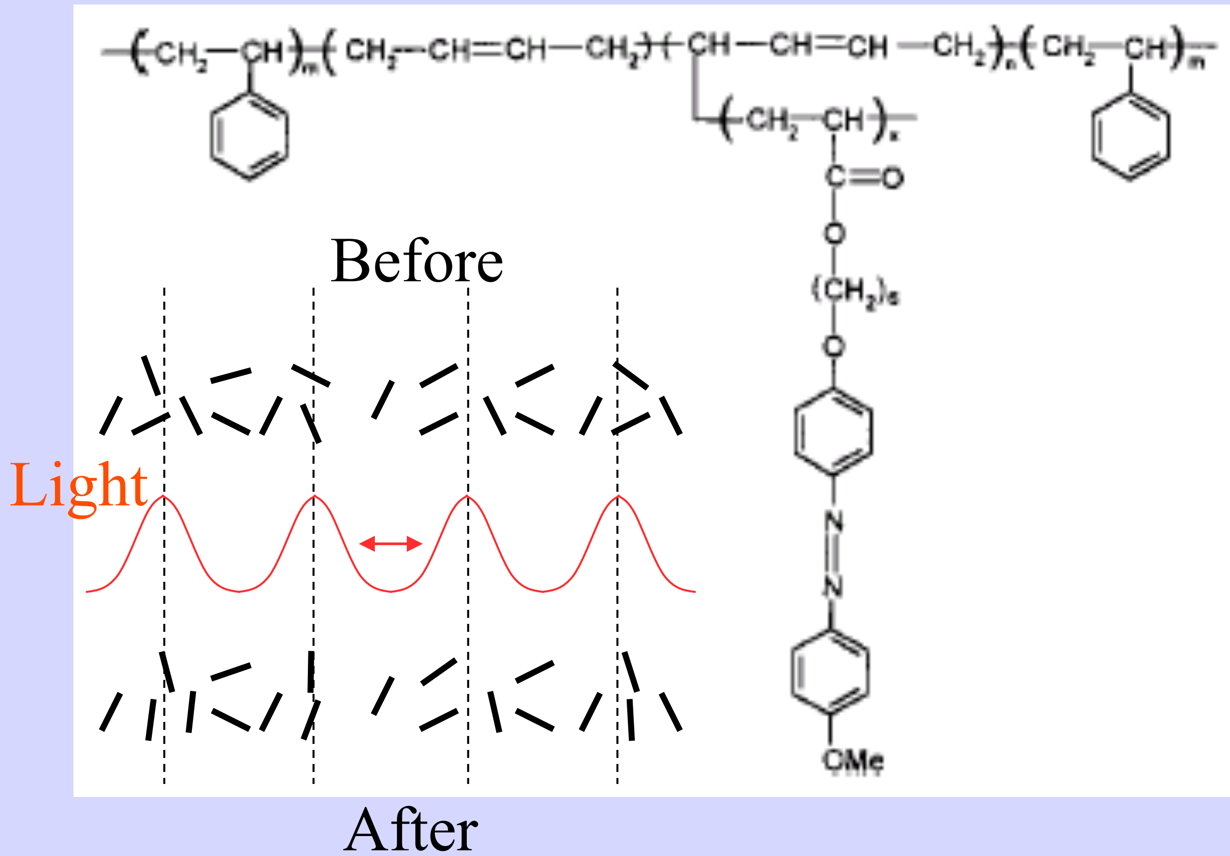
Other Photosenistive Materials of Potential Interest for Photonics Applications:

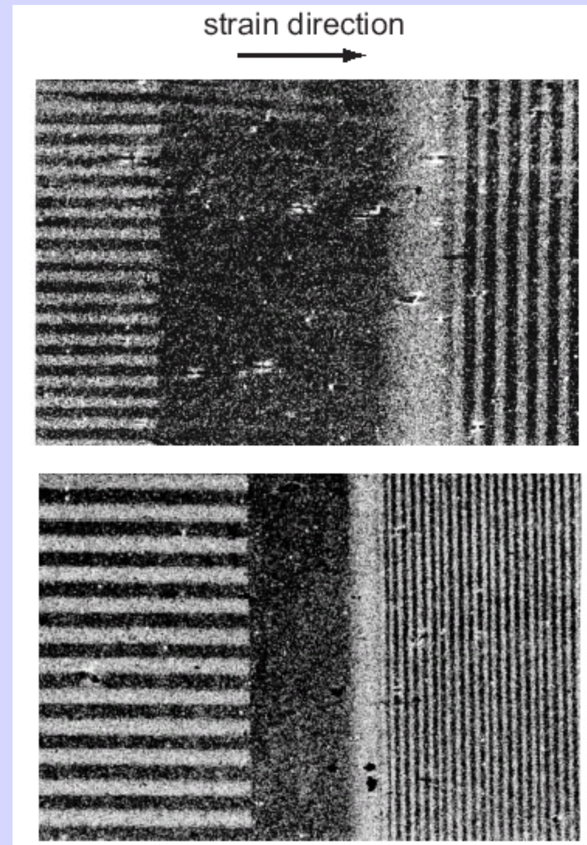
Photopolymers
Chalcogenides

PhotoPolymers: Issues for devices

- Low Energy for cross-linking
- Once fixed: high reversal energy
- Low scatter….multiple gratings
- Polarisation sensitivity
- Transparency
- Relaxation
- Stability……

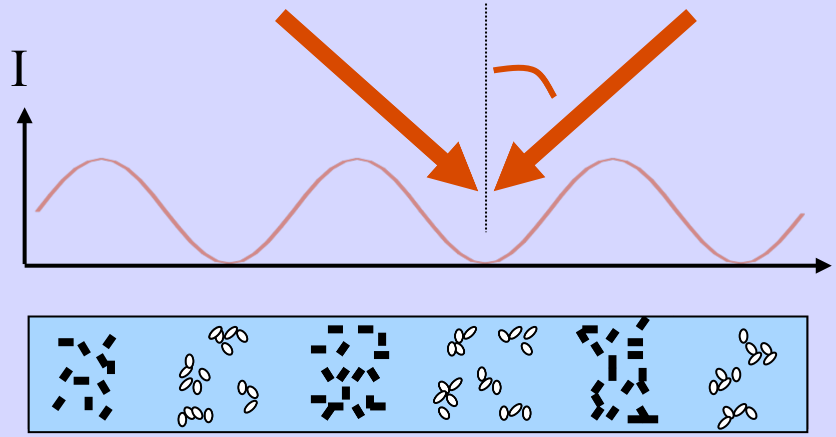
Optically recorded mechanically tunable gratings on azo-elastomers





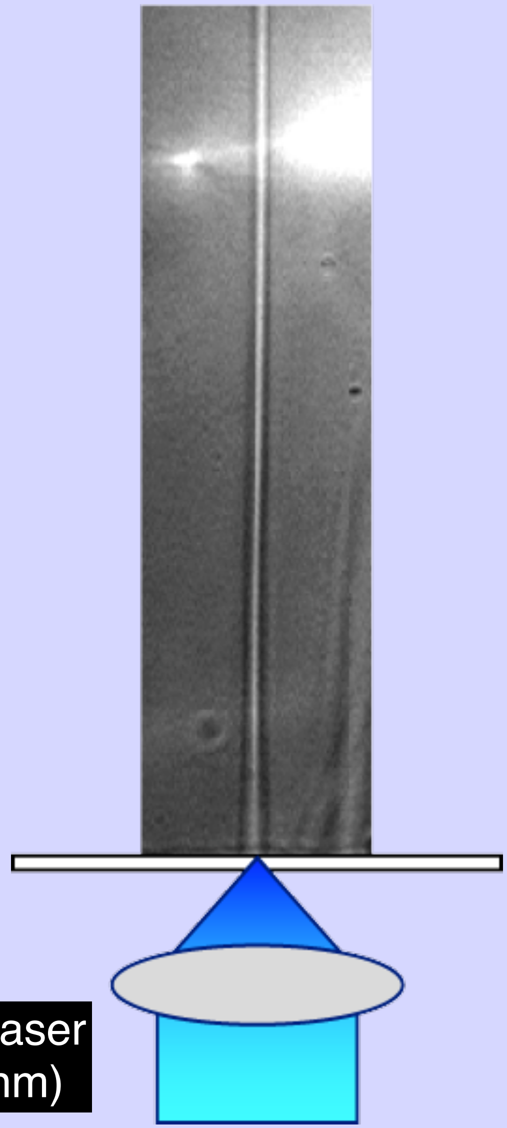
Collaboration *T.Galstian & Y. Zhao*

High diffraction efficiency (>95%) photopolymers sensitive to 850 nm light



• Infrared photo-polymerization

Self-growing of a single waveguide in photopolymerizable resin



He-Cd laser
(441.6 nm)

photopolymerizable resin:
SCR500 (JSR Co., Ltd.)

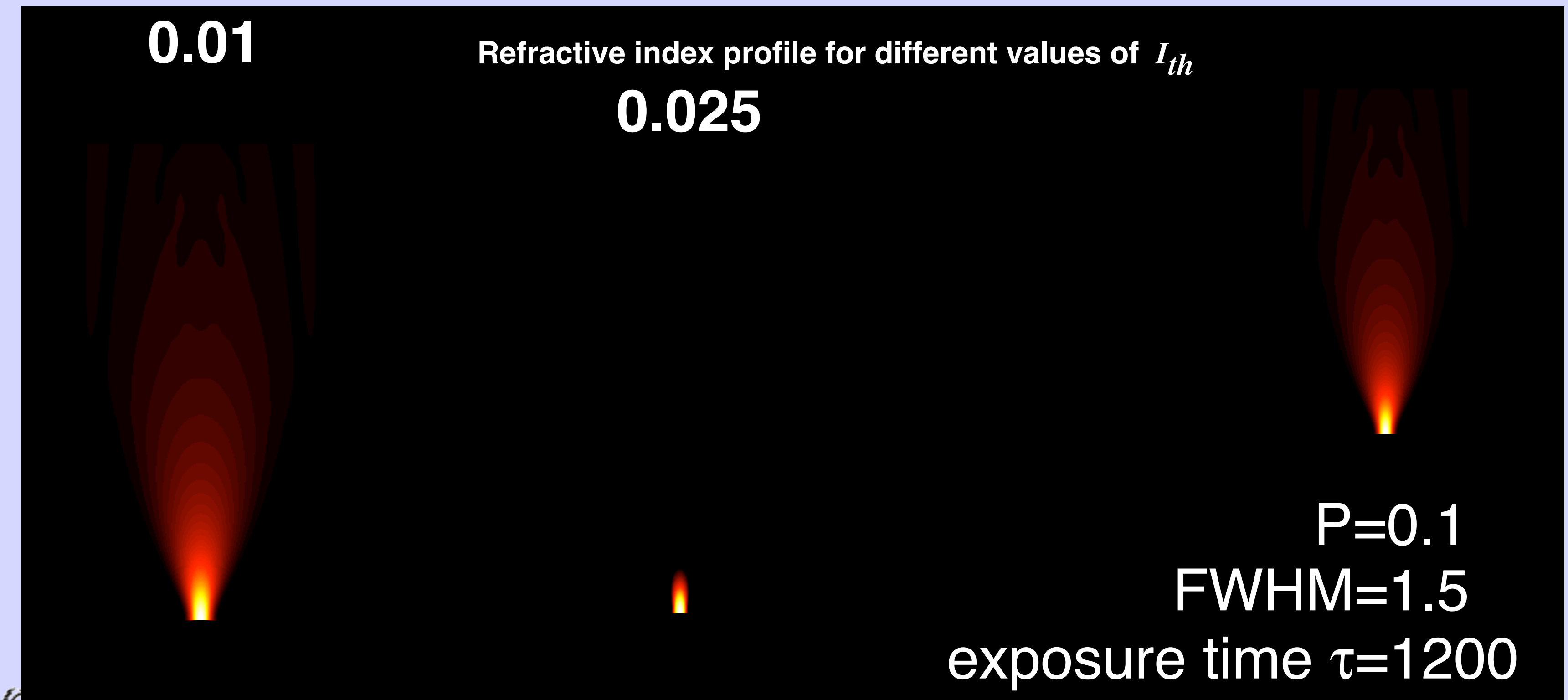
N.A. : 0.23
Power : 0.1mW
exposure time : 2s

(S. Shoji and S. Kawata, Appl. Phys. Lett. 75, 737 (1999))

Self-Guiding in Photo-polymerising resin:

SELF-WRITTEN WAVEGUIDES IN PHOTOSENSITIVE MATERIALS
ANDREY A. SUKHORUKOV, SATORU SHOJI and YURI S. KIVSHAR
Nonlinear Physics Group, Research School of Physical Sciences and Engineering, Australian National University, Canberra ACT 0200, Australia

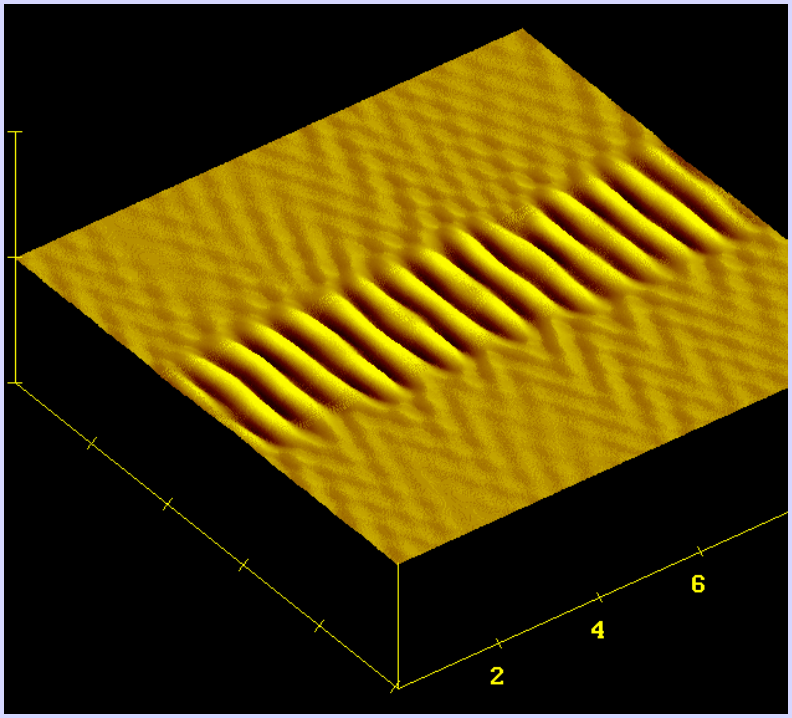
SATOSHI KAWATA
Department of Applied Physics, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan
Nanophotonics Laboratory, RIKEN, Wako, 351-0198, Japan

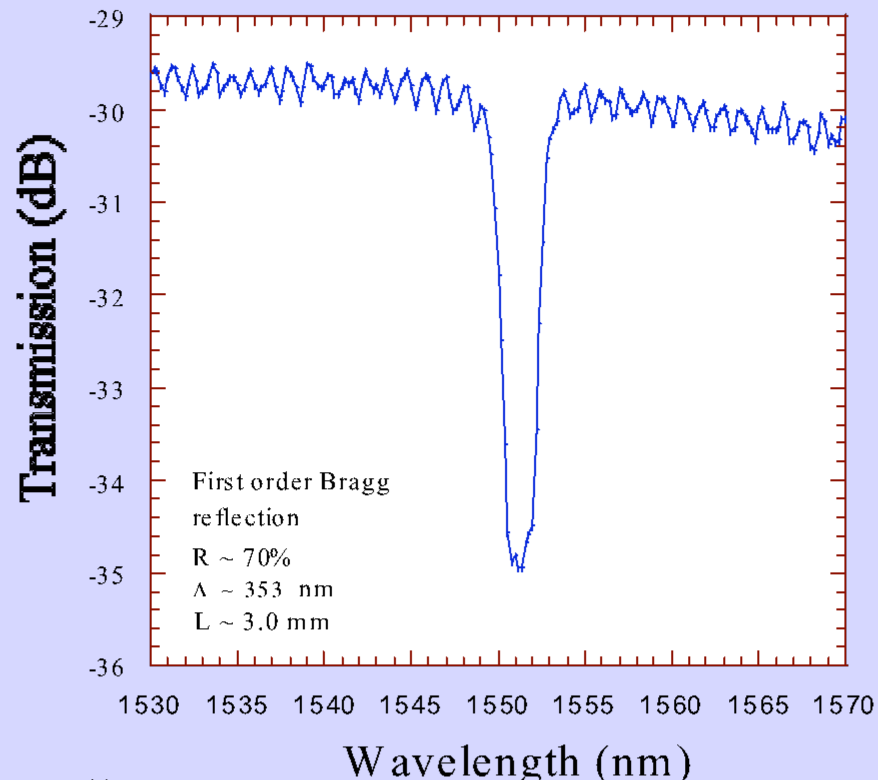


Bragg gratings in amorphous semiconductor waveguides

Integrated IR components (semiconductor glasses As_2S_3)

First order Bragg grating filter (L=353 nm) in waveguides





*Prof. Younes Messaddeq, U Laval

R. VALLÉE, S. FRÉDÉRICK, K. ASATRYAN, M. FISCHER, T.V. GALSTIAN,.
« Real-time Observation of a Bragg grating formation in As2S3 chalcogenide ridge waveguides »,
Optics Communications, **230**, pp. 301-307 (2004).

**Sandor Kokenyesi et al. "In situ surface relief recording in light sensitive chalcogenide glasses, This conf. Poster

League Table of Photosensitive Materials For Photonic Devices

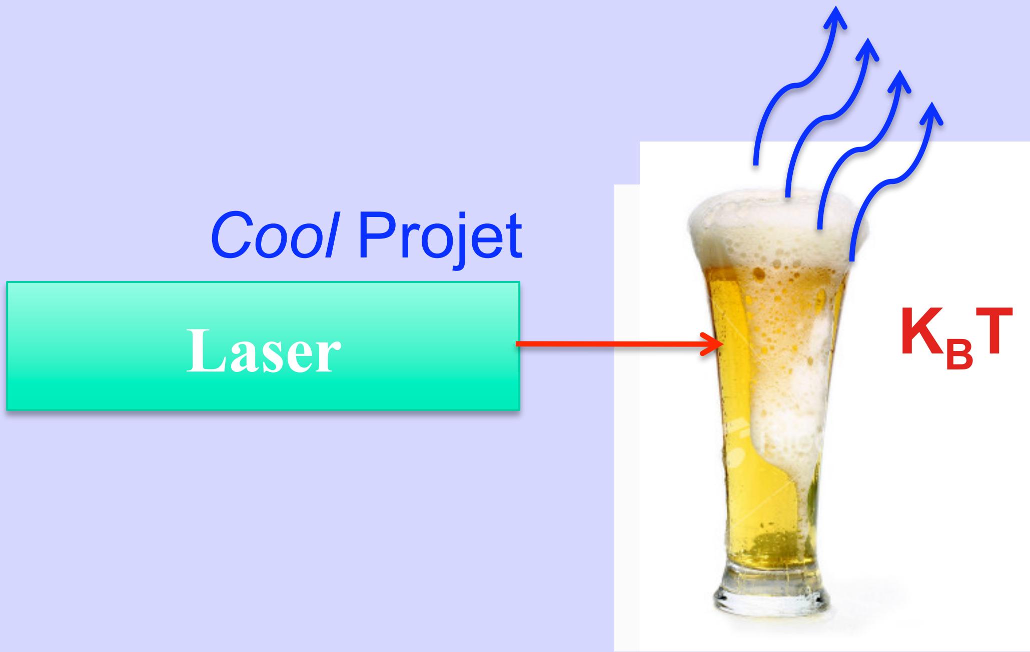
Material	Processing	Refractive index change	Comment	Long term Stability
Ge doped Silica	UV laser	~ +0.02	Waveguide	>500-1000º C
Silica, Borosilicate glass	Femtosecond laser Visible-IR	+/- 0.01-0.001	Bulk and waveguide	>900ºC
Foturan ® Schott	UV 290 – 330nm, Chemical	0.001	Bulk Low resolution	>500ºC
PTR Glasses	UV 300nm, Heat treatment	0.006 + Lossy	Two step process Bulk	>500ºC
Photopolymer LC doped polymer	Self-inducing blue-red radiation	0.001 0.1	Two step process	Poor 150ºC

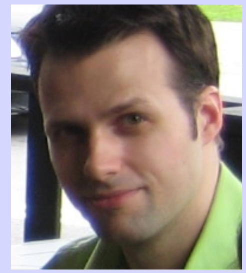
Chalcogenides | Self-inducing red λ | 0.1 | Single step | Poor ~70C

Laser Cooling

Solid and *Liquid* State COOLING WITH LASERS

Cool Projet

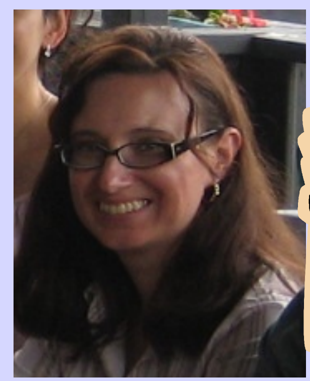




Jerome Poulin: *Cold Atom Guiding*

Elton Soares

Sebastien Loranger

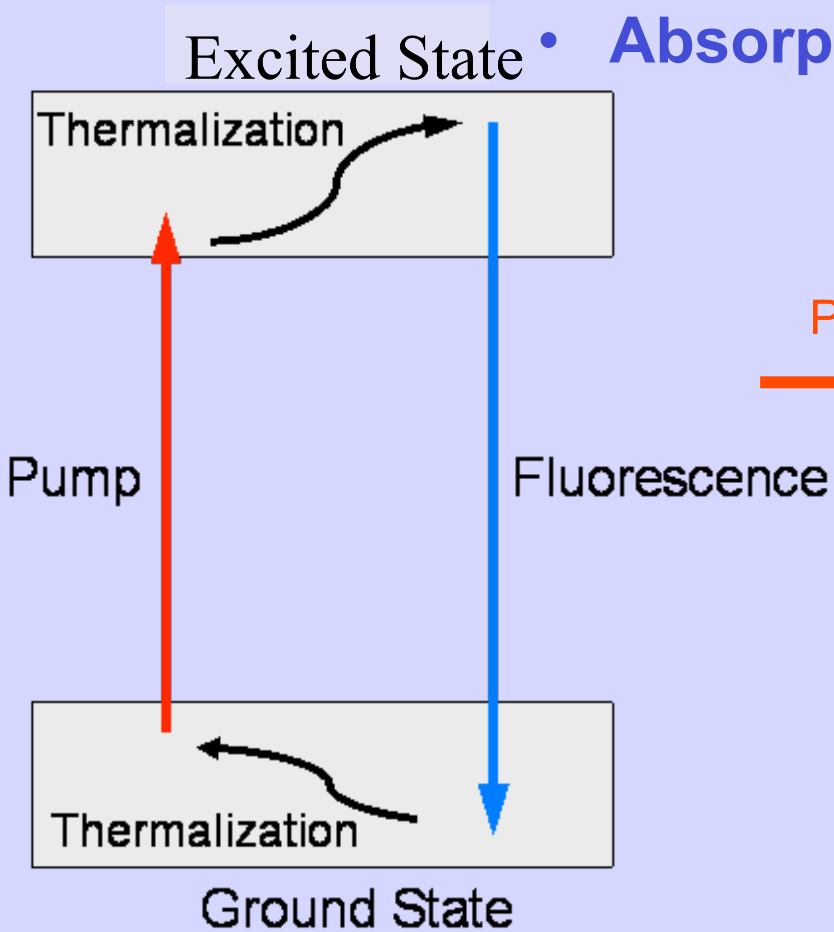


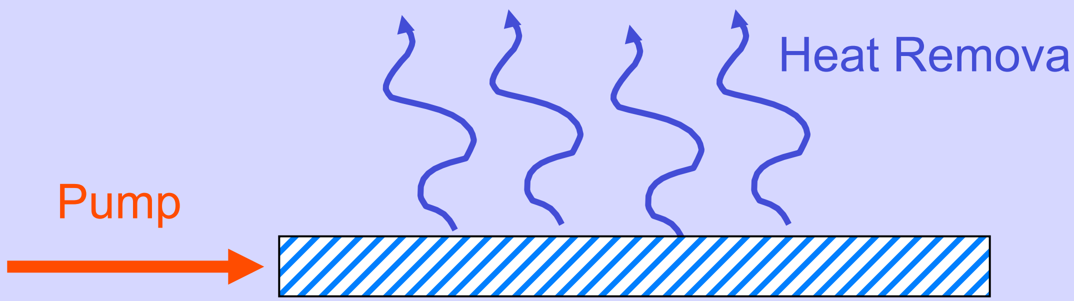
Galina Nemova

More People

Solid State Laser Cooling

- Absorption of energy at long wavelengths





Tilted grating in
Yb3+ doped ZBLAN Fibre

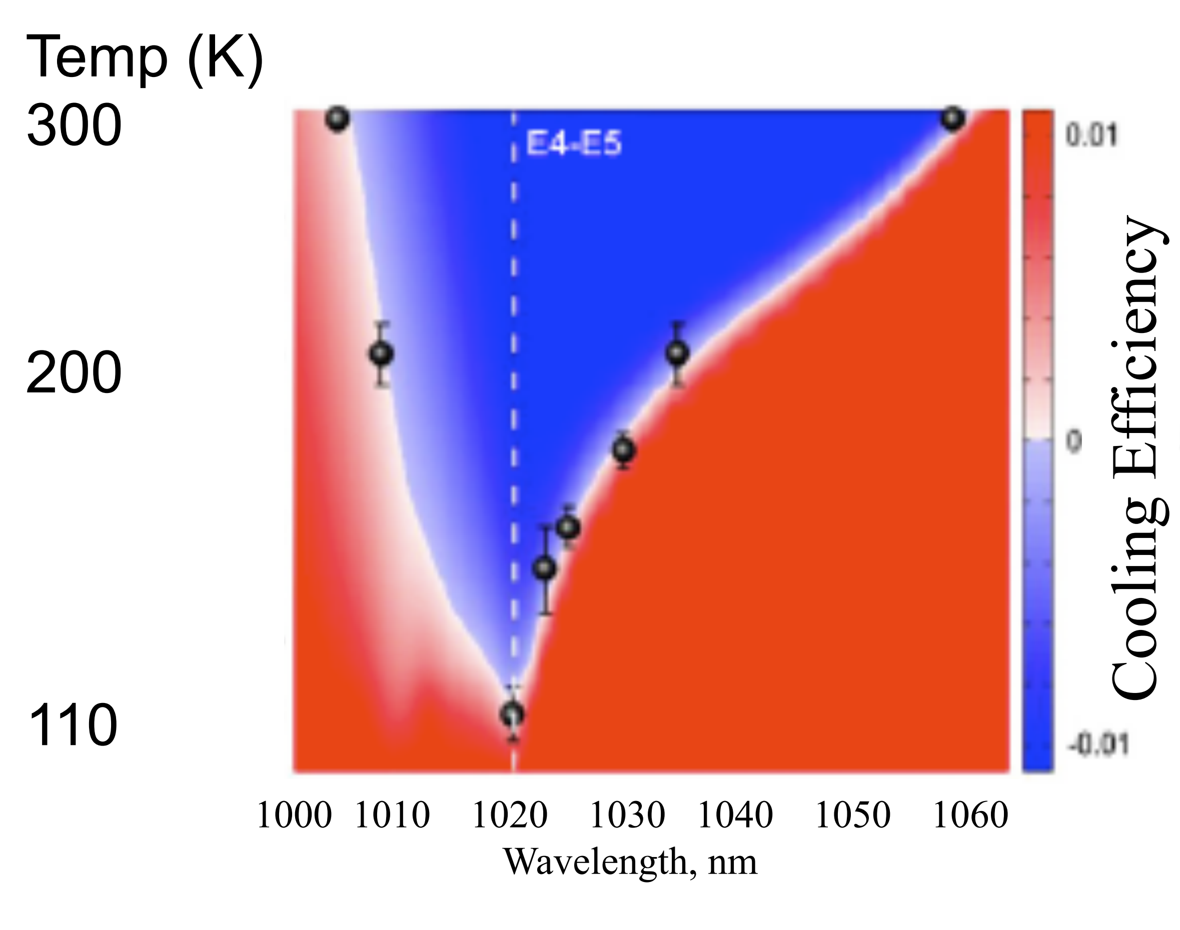
- HEAT Removed by Emission of photon at SHORTER WAVELENGTH

Maximum Cooling Efficiency (ANTI-STOKES RADIATION)

$$\eta = \frac{\Delta\lambda}{\lambda_f}\left(1 - \frac{k_B T}{h\nu_f}\right)$$

$\Delta\lambda = \lambda_{fluorescence} - \lambda_{pump}$

Cooling in Yb: YLF to110 K



$$CE = P_{cool}/P_{absorbed}$$

PROBLEMS:

Need very pure sample

Non-radiative rate must be LOW

Low phonon energy material

Need laser to match absorption

No tunability

CANNOT USE SIMPLE DOPED GLASSES!

D.V. Seletskiy, et al., J. Lumin. (2011), doi:10.1016/j.jlumin.2011.09.045

Laser Cooling: The Challenges

- MATERIAL REQUIREMENTS:
  - Low Phonon Energy glasses: E_g > 8 phonons
  - Very high purity of materials
  - High quantum efficiency of fluorescence
  - Low background absorption
  - Low NON-RADIATIVE decay rates
  - Low Auger recombination rates
  - Pump wavelength selection
  - Reabsorption of Fluorescence

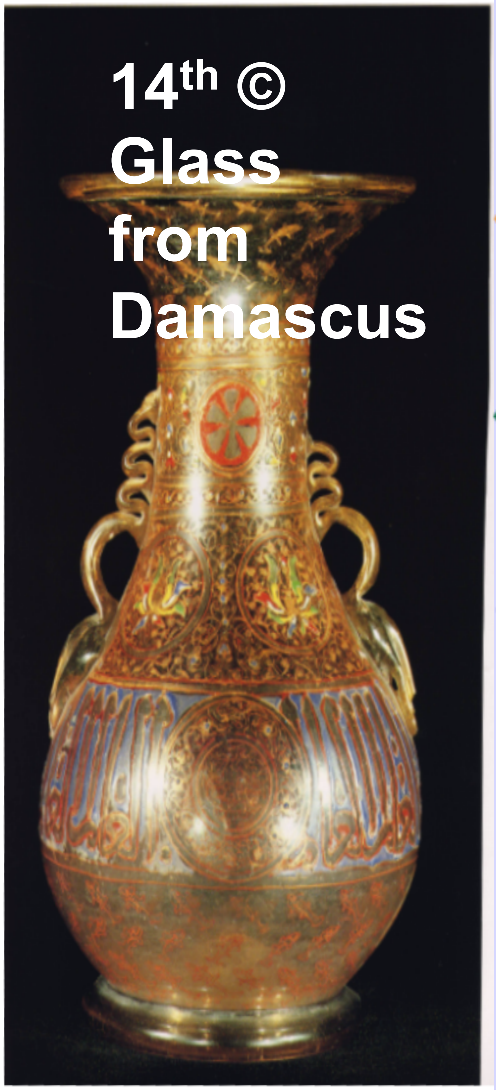
Cooling with QDs

- How can we improve cooling efficiency?
  - Through reduced radiative lifetime of the excited level
- How to improve the figure of merit?
  - By increasing the absorption cross section
- How can we use new materials with higher phonon energy as hosts?
  - When we reduce the radiative lifetime
- How to tune the absorption properties of material?

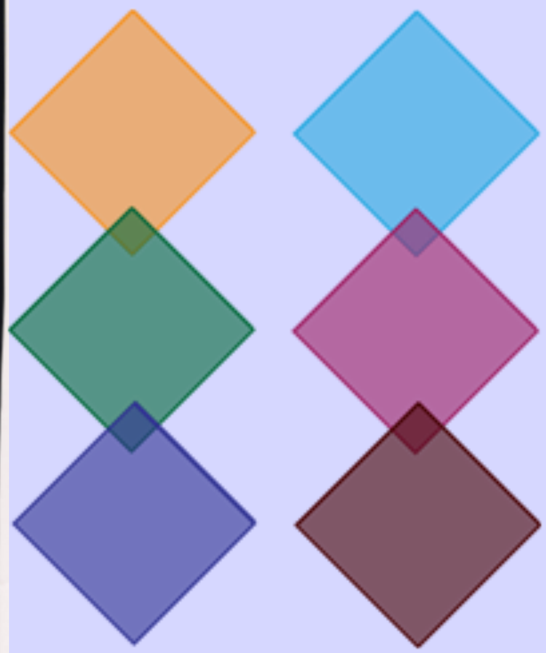
➢ Solution: quantum dots (artificial atoms)

G. Nemova and R. Kashyap, "Laser cooling with PbSe colloidal quantum dots," *Journal of the Optical Society of America B: Optical Physics,* vol. 29(4), pp. 676-682 (2012).

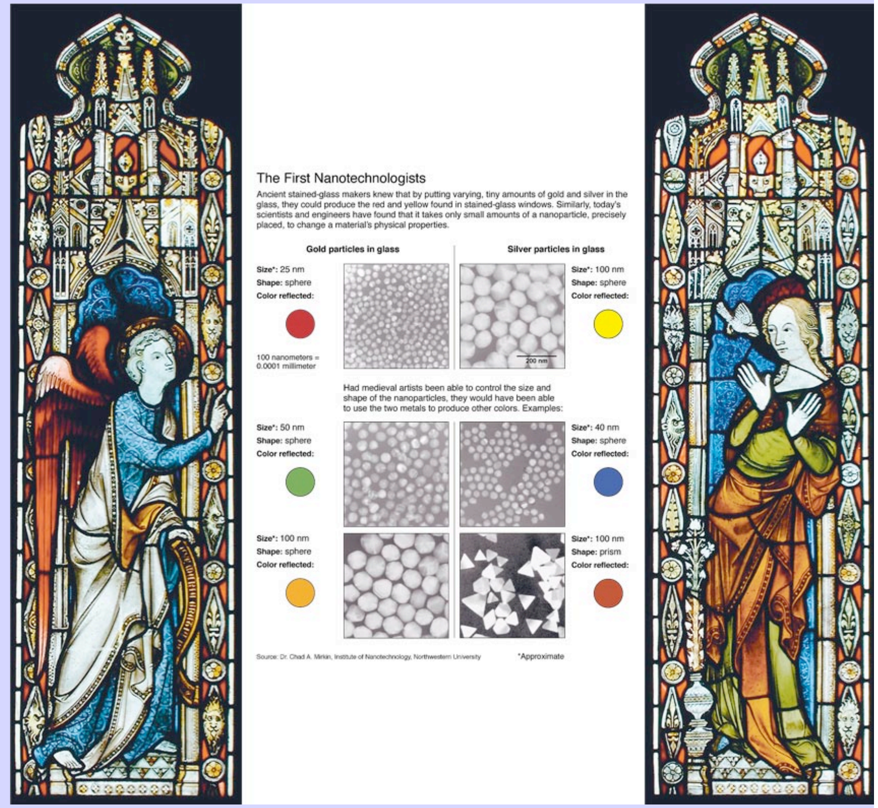
Quantum Dots and Size Dependent Effects



QD Doped Filter

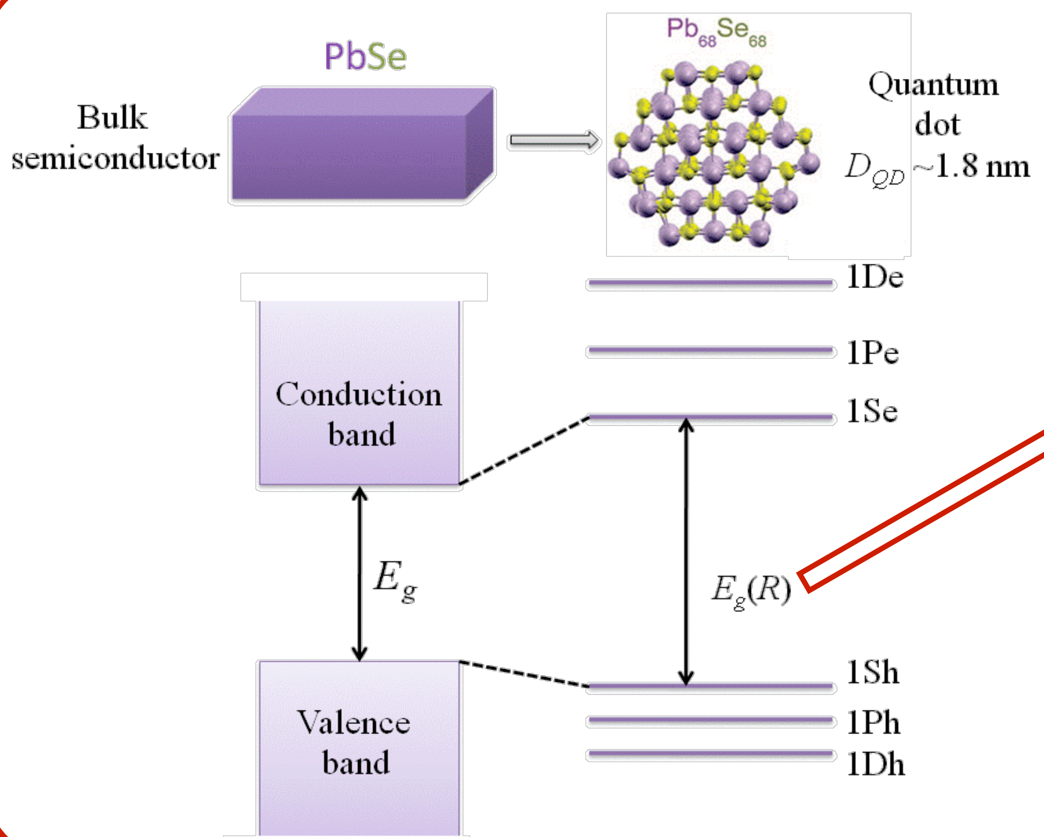


15th © QD Stained Glass Windows



Quantum dots (*artificial atoms*)

- Small size semiconductor (of order exciton Bohr radius) becomes a quantum dot (QD)
- States become quantized



- Bulk semiconductors have fixed band-gaps – material structure dependent.

- QD band gap becomes a function of the size of the QD.

$$E_g(R) = E_g + \frac{2\hbar^2\pi^2}{m_{eh} D_{QD}^2},$$

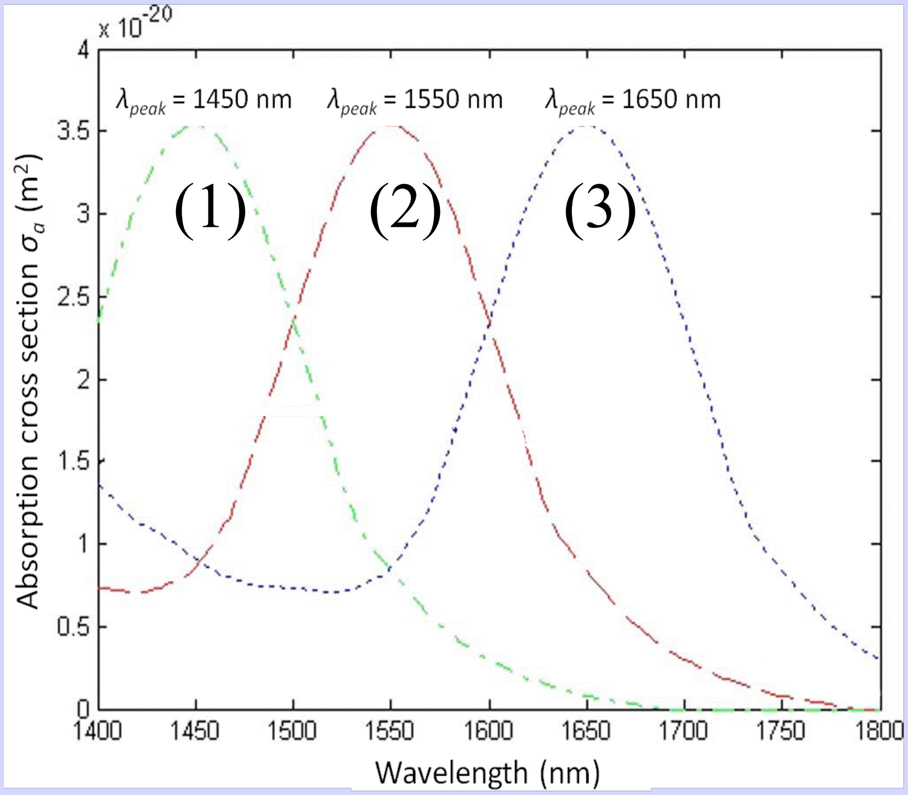
where $m_{eh}=m_e m_h/(m_e+m_{h-})$**,**

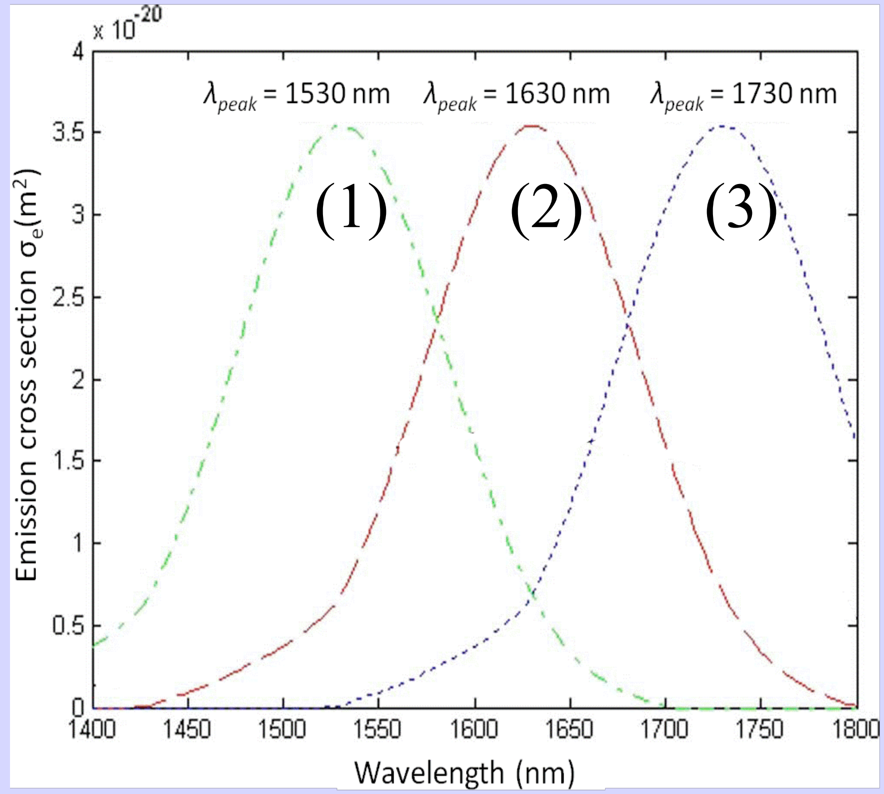
m_e **= effective mass of** electron
m_h = **effective mass** of hole
D_{QD} **= diameter of QD**

Advantages of PbSe QDs for cooling

- Lead-salt QDs (e.g. PbS, PbSe, and PbTe) have strong quantum confinement
- Exciton Bohr radius of a PbSe QD is huge: a_{exc}= 46nm
- Due to high permittivity (ε = 23) + small effective masses (< 0.1*m*) of electron/hole, where *m* = rest mass of the electron
- Radiative lifetime of 1Sh level of the PbSe QDs doped glass is microseconds
- Radiative lifetime of rare-earth (RE) ions is miliseconds (1000x)
- Size of QDs, as artificial atoms, changes distance between the 1Se and 1Sh levels to match any available pump sources
- Large absorption cross section makes QDs very attractive for laser cooling

Cooling with quantum dots (spectra)





$D^{(1)}_{QD} \approx 5.0$ nm,

$D^{(2)}_{QD} \approx 5.5$ nm,

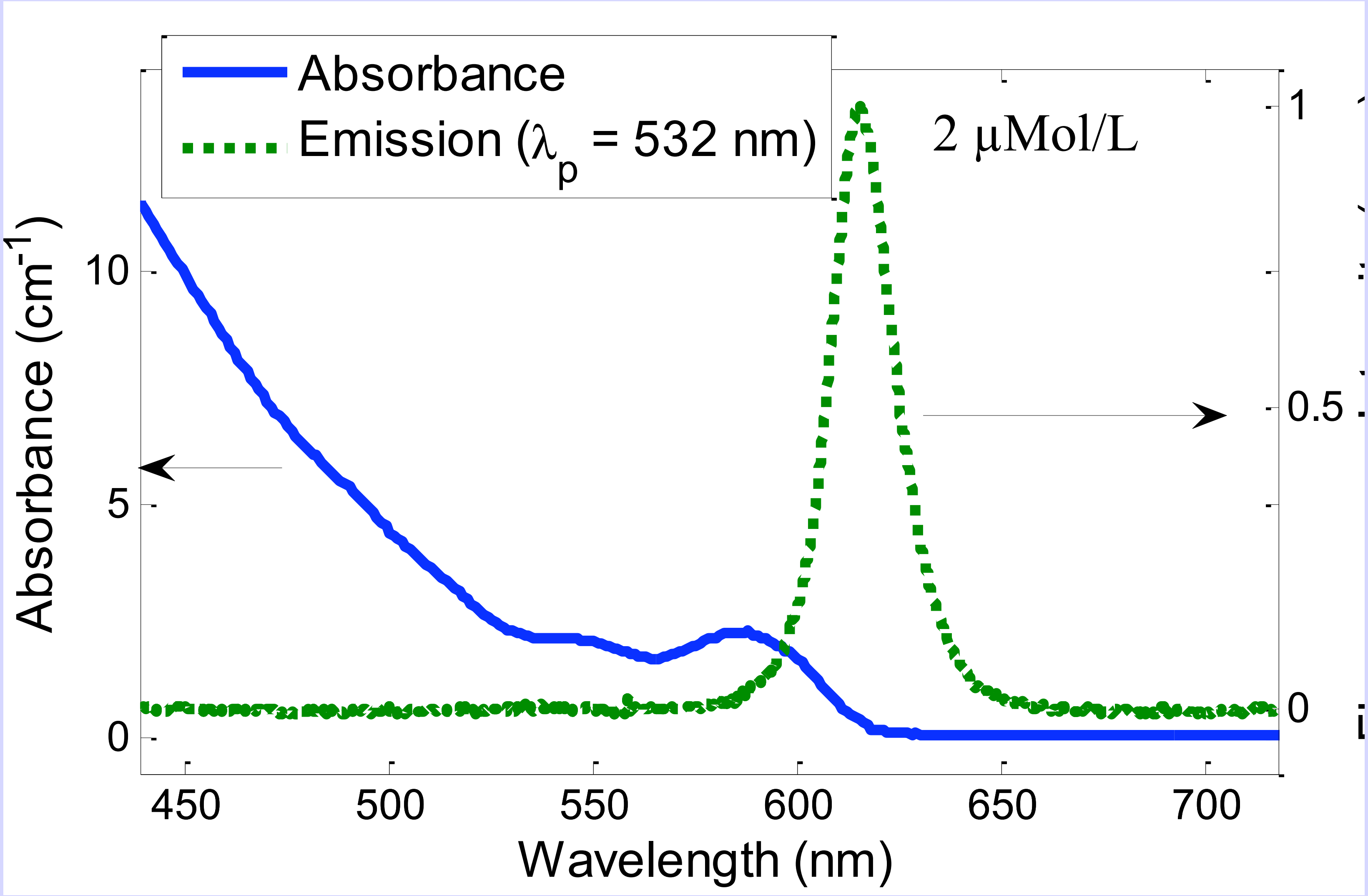
$D^{(3)}_{QD} \approx 6$ nm.

C. Cheng *et al, J. Lightwave. Technol* 26, 1404-1410 (2008)

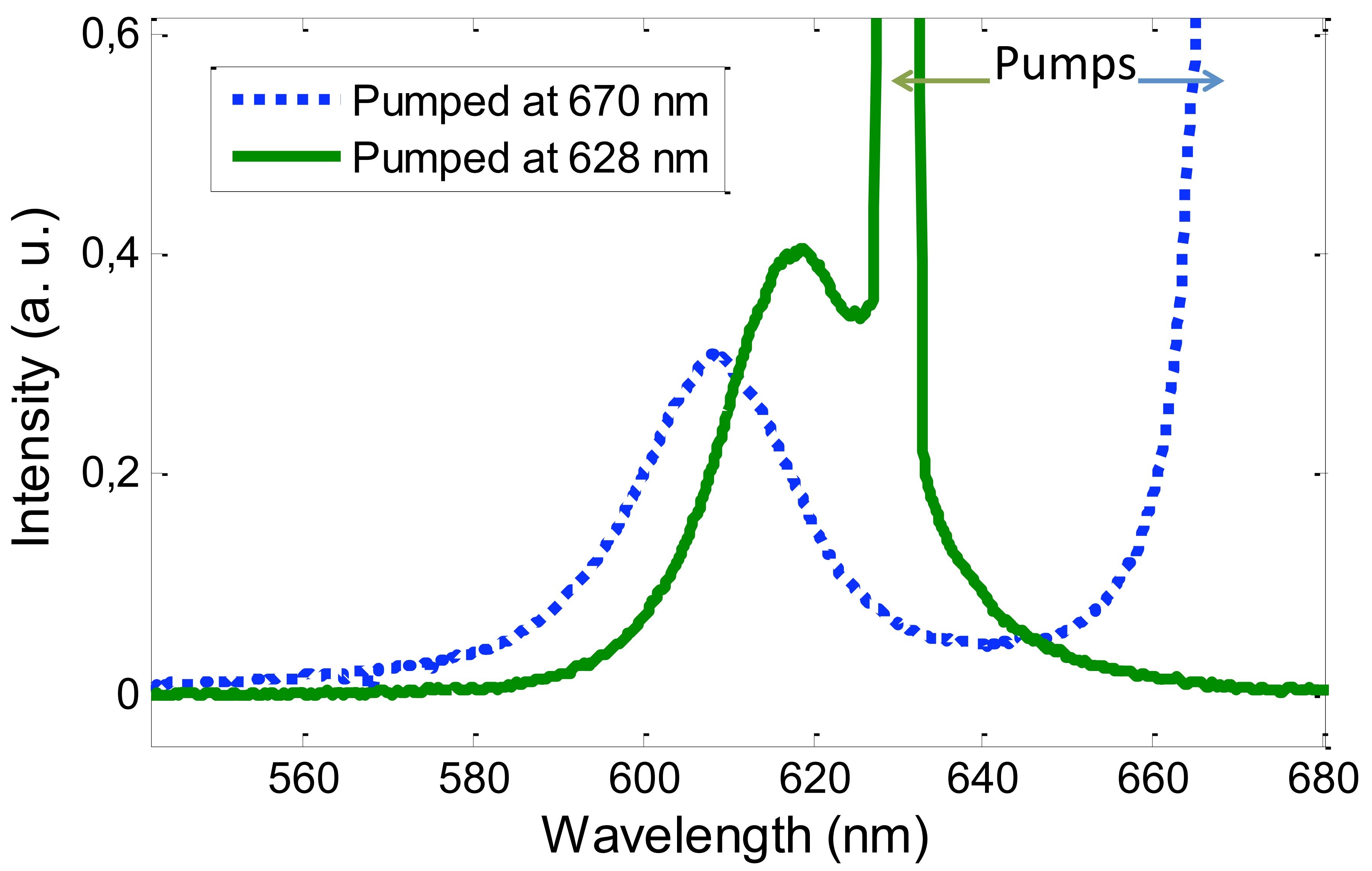
Robodots
CdSe QD
with CdS, CdZnS and ZnS shell

From Laval University

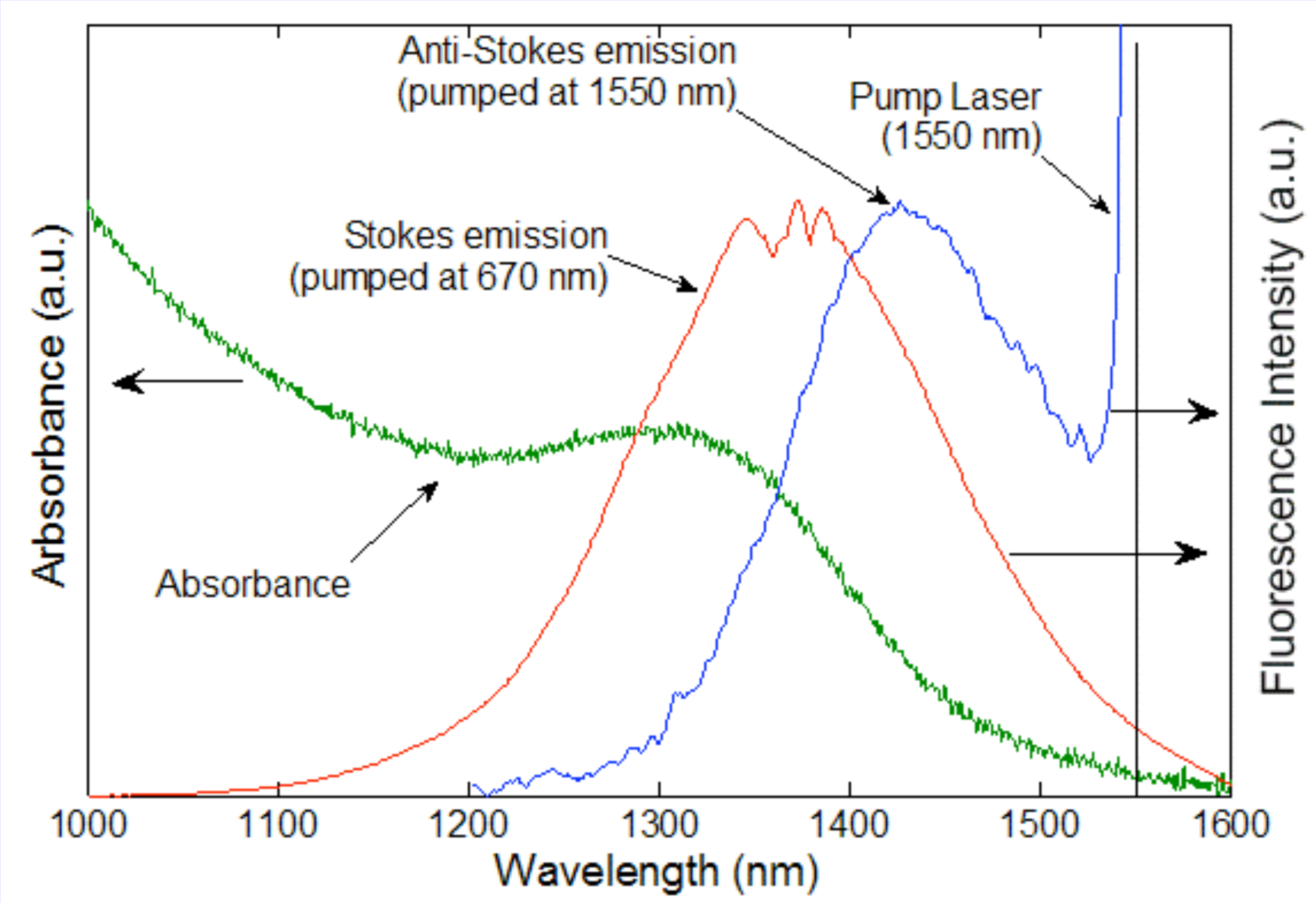
Absorbance and emission spectrum



Anti-Stokes emission in QDs



Anti-Stokes Emission in PbS QDs in SNAB Glass



Sébastien Loranger, Antoine Lesage-Landry, Elton Soares de Lima Filho, Galina Nemova ,Noelio O. Dantas, Paulo C. Morais, Raman Kashyap **"Spectroscopic and life-time measurements of quantum dot doped glass for optical refrigeration: A feasibility study", Photonics West Feb 2013.**

Results

- Despite ~80% efficiency of QDs no Cooling yet!
- Work is progressing to change this with better QDs.

Challenges with Semiconductor QDs

- High QE of passivated QDs in liquids >80%
- Excellent Control of QD size in liquids

- Control sizes to 1% in glass
- Reduce Non-radiative effects in glass
- Increase QE to 95% in glass
- Passivate QDs in glass host: Core-Shell?

CONCLUSIONS AND SOME THOUGHTS FOR THE FUTURE

- Materials must have a *key* advantage over existing solutions
- It is not just necessary to be better in *one* respect
- Applications can be *very* demanding of material properties
- With the correct materials, photosensitivity must lead to:
  - Direct writing of interconnect….point to point/ multipoint
  - 3D-ICs: High density chips
- Bio-compatible photosensitive materials are needed
  - Integrated functionality for micro-fluidics and waveguides
- Need Techniques for Passivation of QDs in solids
- Bubble Formation in Optical Fibres for Nuclear Fusion……???

The Advanced Photonics Concepts Group

Acknowledgements:

- Dr. Kivshar, *Australian National University, Canberra*
- Mr Shoji, *Department of Applied Physics, Osaka University*
- Prof. Tigran Galstian, U Laval, Canada
- Prof. Real Vallee, U Laval, Canada
- Dr Ravi Bhardwaj, NRC, Canada
- Prof. Hirao, Japan
- Prof. Peter Kazansky, U. Southampton

Mille Grazie!