An IMI Video Reproduction of Invited Lectures
from the 17th University Glass Conference

Nanofabrication in Transparent Materials with Femtosecond Pulse Laser

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Contents

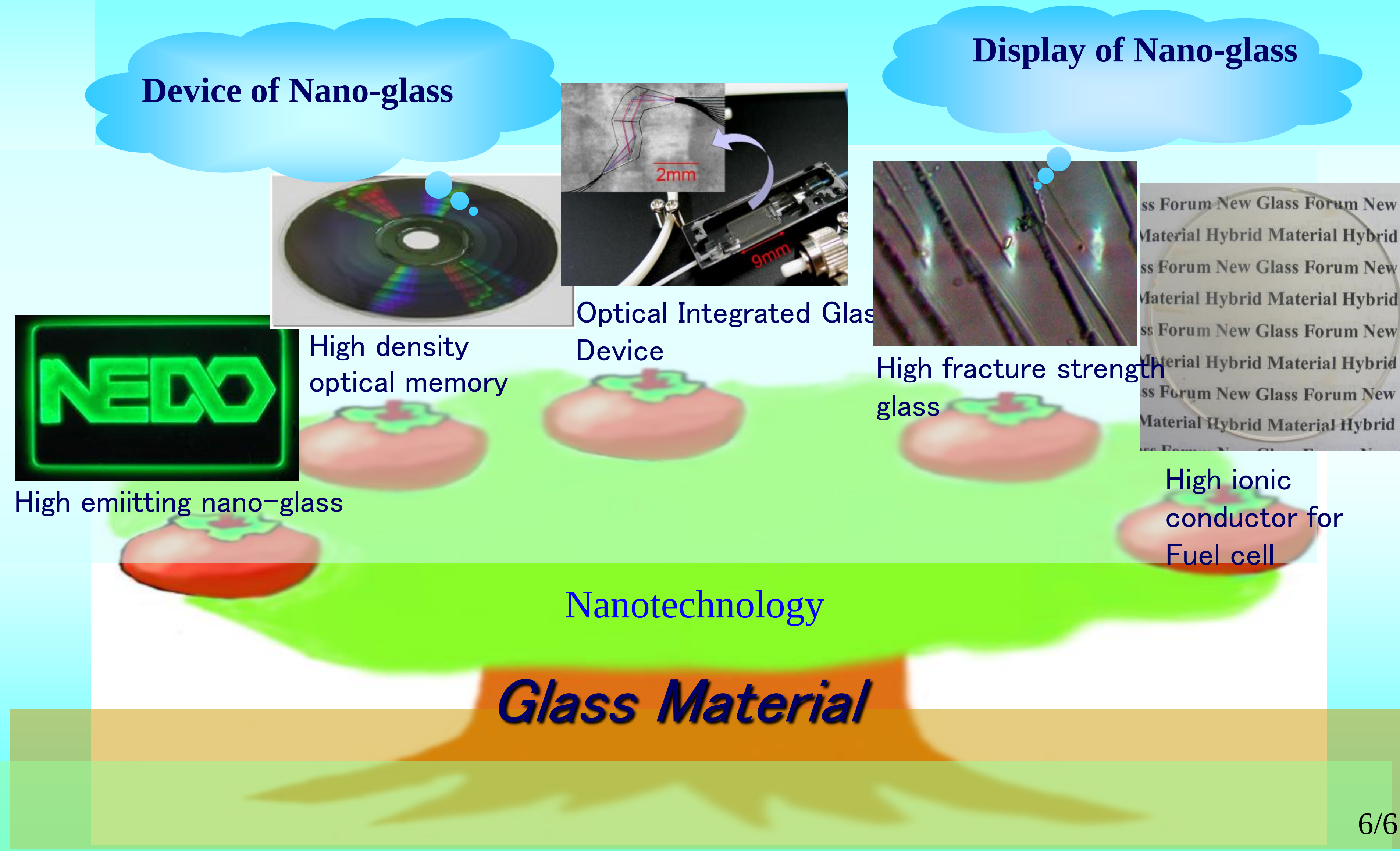
1. Research background

- Transparent
- Easy to form
- Good solvent
- Metastable

Glass is called amorphous because it is a non-crystalline substance (it is neither a solid nor a liquid but exists in a vitreous, or glassy, state). When it cools its atoms remain in the same random arrangement as in the liquid but with sufficient cohesion to produce rigidity. It is sometimes referred to as a super-cooled liquid.

Glass will lead us to a more glorious future

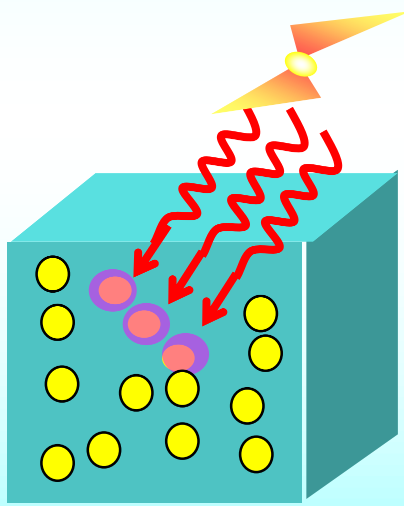
NEDO Nano-glass project 2001-05



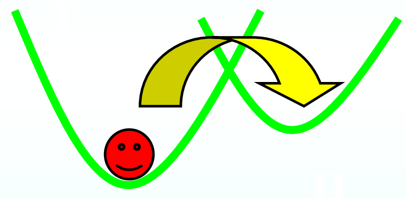
2. Our research idea for
New Functionality glasses

Basic idea of our research

External field



Glass



- induced electronic structure
- e.g. rare-earth

- Electric field
- Magnetic field
- Laser
- Radiation
-
-
-

Ceramics Japan, 30(1995)689.

Some of our positive results in the related scientific research:

1) X-ray induced photostimulated luminescence

***Appl. Phys. Lett.*, 71(1997)43.**

***Appl. Phys. Lett.*, 71(1997)759.**

***J. Non-Cryst. Solids*, 209(1997)200.**

2) UV light induced long-lasting phosphorescence

***Appl. Phys. Lett.*, 73(1998)1763.**

***J. Mat. Res.*, 16(2001)88.**

3) EB induced various nanostructure in glass

***Appl. Phys. Lett.*, 77(2000)3956.**

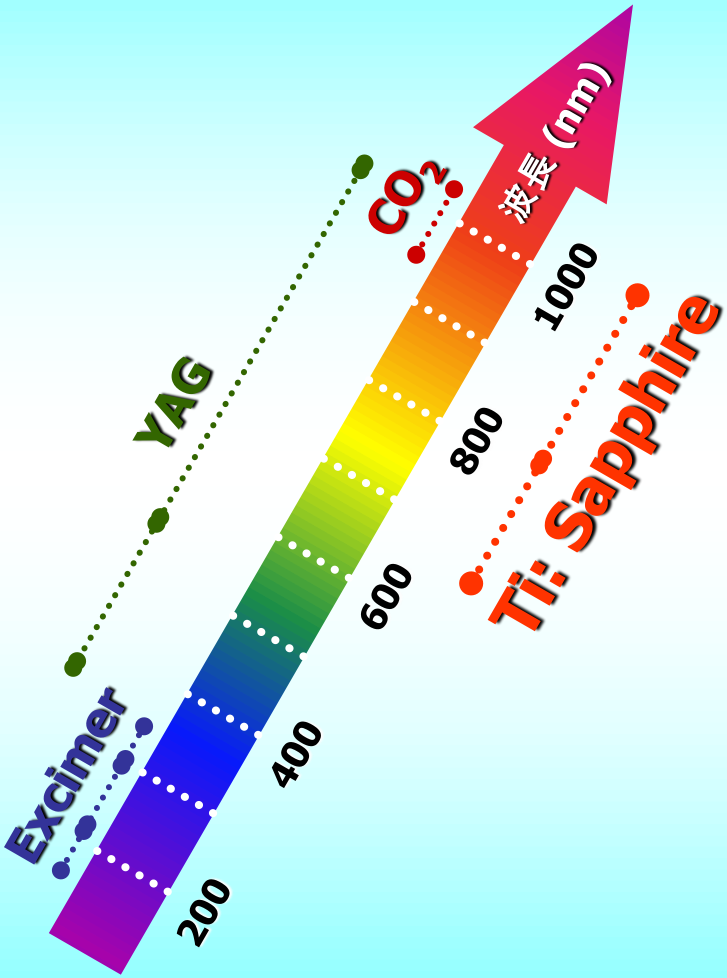
***Phys. Rev. B*, 60(2002)2263.**

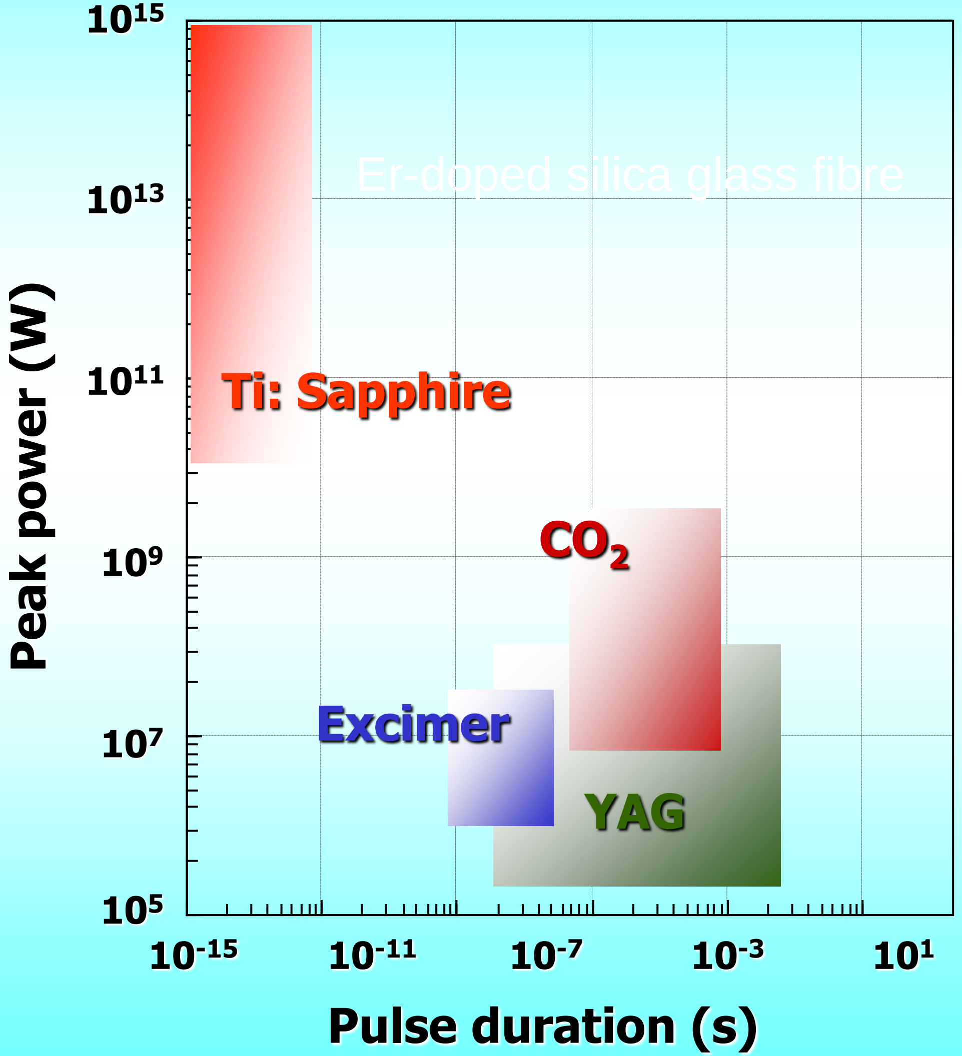
***Appl. Phys. Lett.*, 80(2002)2005.**

***Phys. Rev. B*, 68(2003)64207.**

3. Femtosecond laser-induced nano and micro structures and applications

Ti:Sapphire femtosecond laser

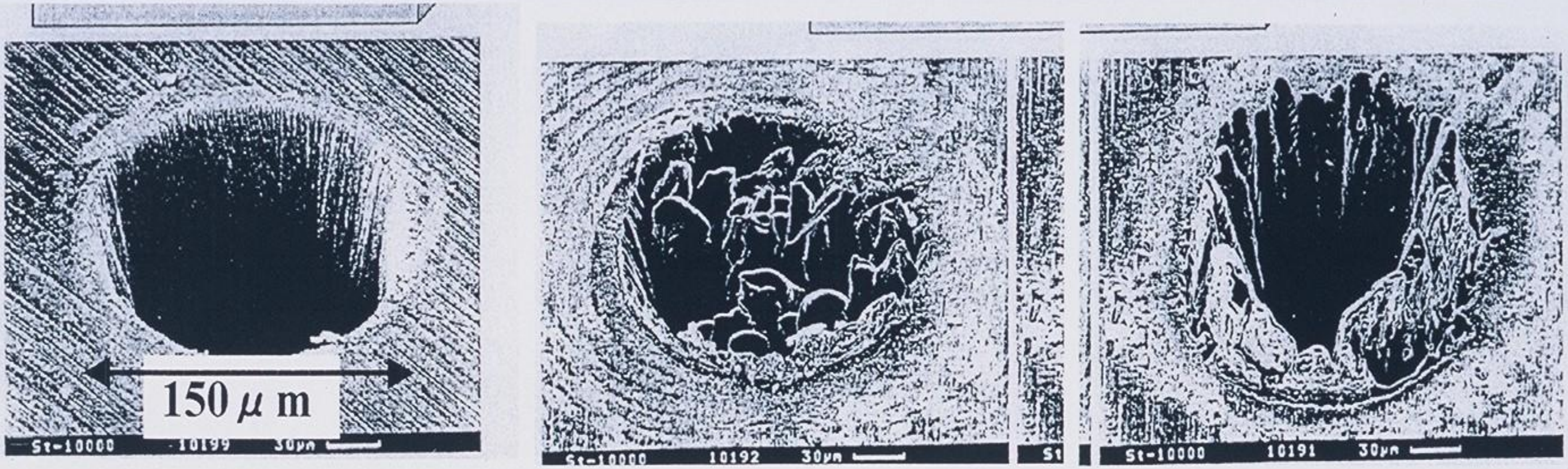




Features of femtosecond laser：

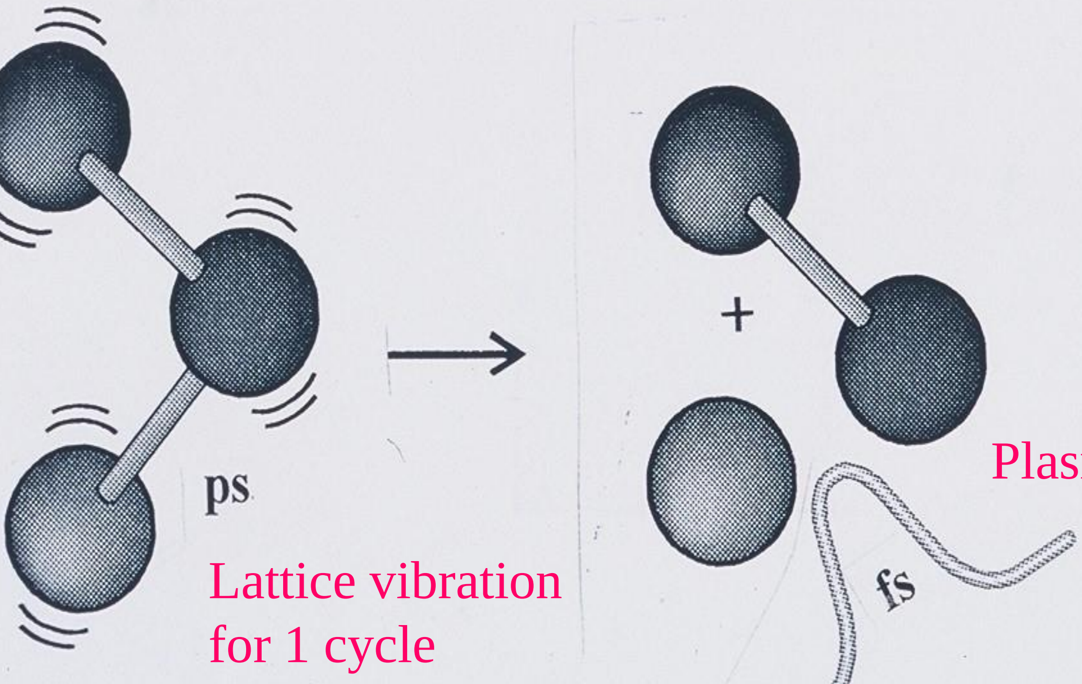
1) Elimination of the thermal effect due to extremely short energy deposition time

2) Participation of various nonlinear processes enabled by high localization of laser photons in both time and spatial domains



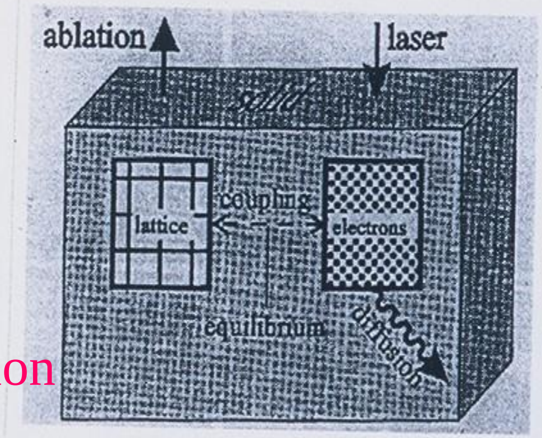
(a) 200fs、120 μ J、0.5J/cm² (b) 80ps、900 μ J、3.7J/cm² (c) 3.3ns、1mJ、4.2J/cm²

Irradiation on stainless steel

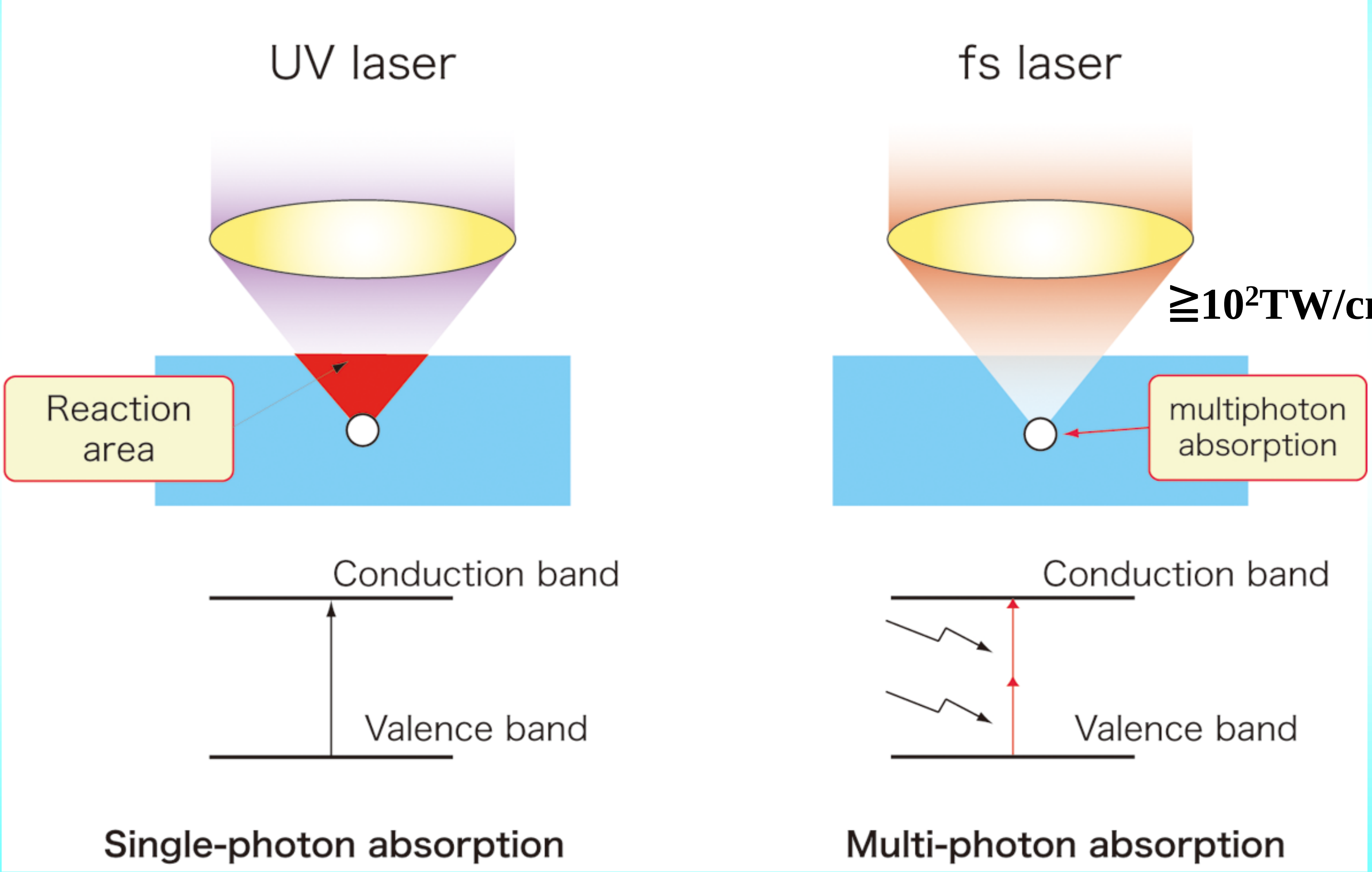


Lattice vibration for 1 cycle

Plasma generation



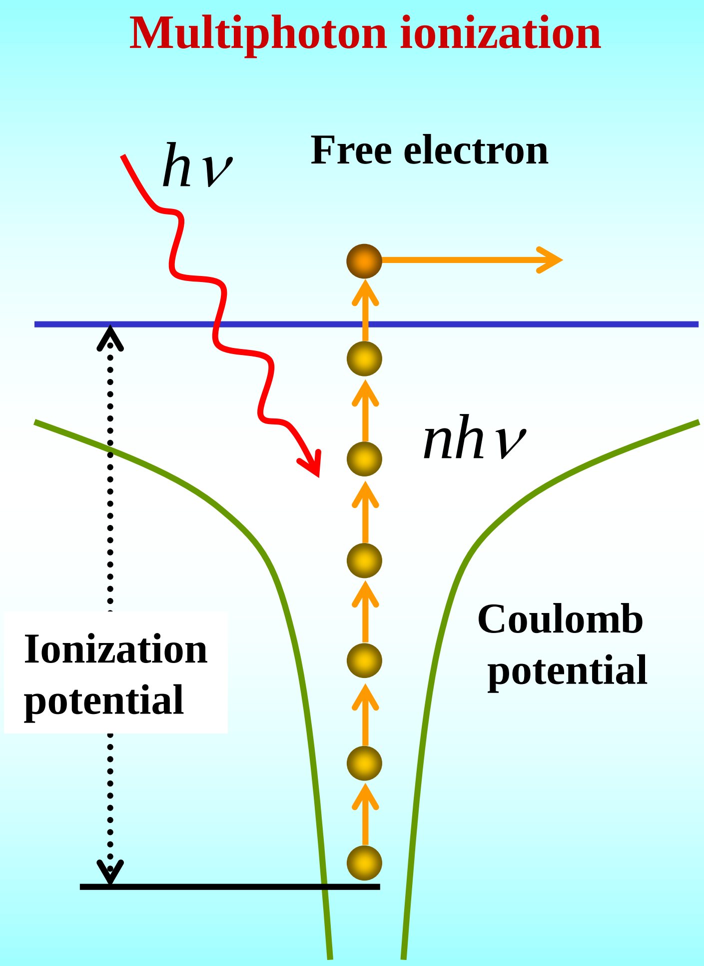
3-dimensional micro-modification

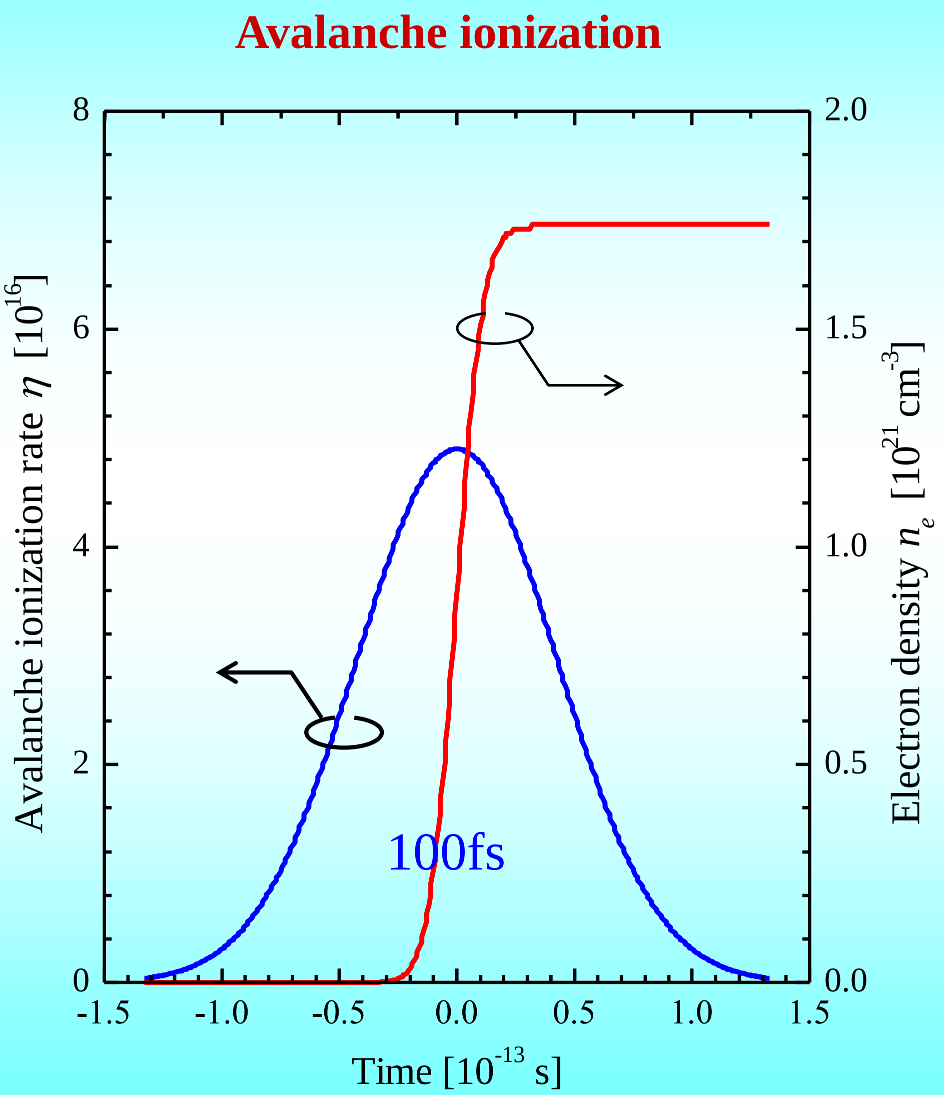


$\geqq 10^2 TW/cm^2$

$\chi = \sigma \ (I/h\nu)^n$

Nonlinear ionization





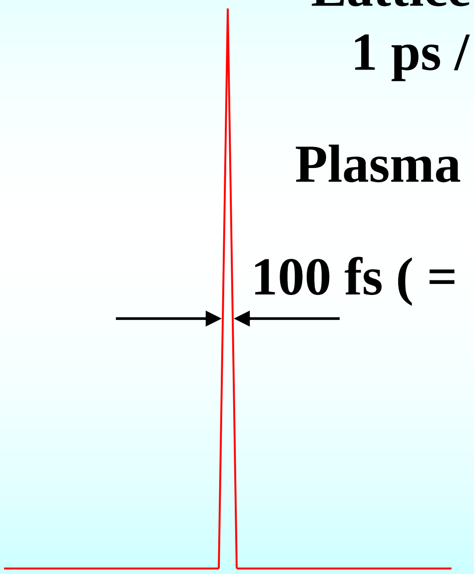
Femtosecond Laser using Er-doped glass fiber

High Peak Power

Lattice Vibration
1 ps / 1 cycle

Plasma Generation

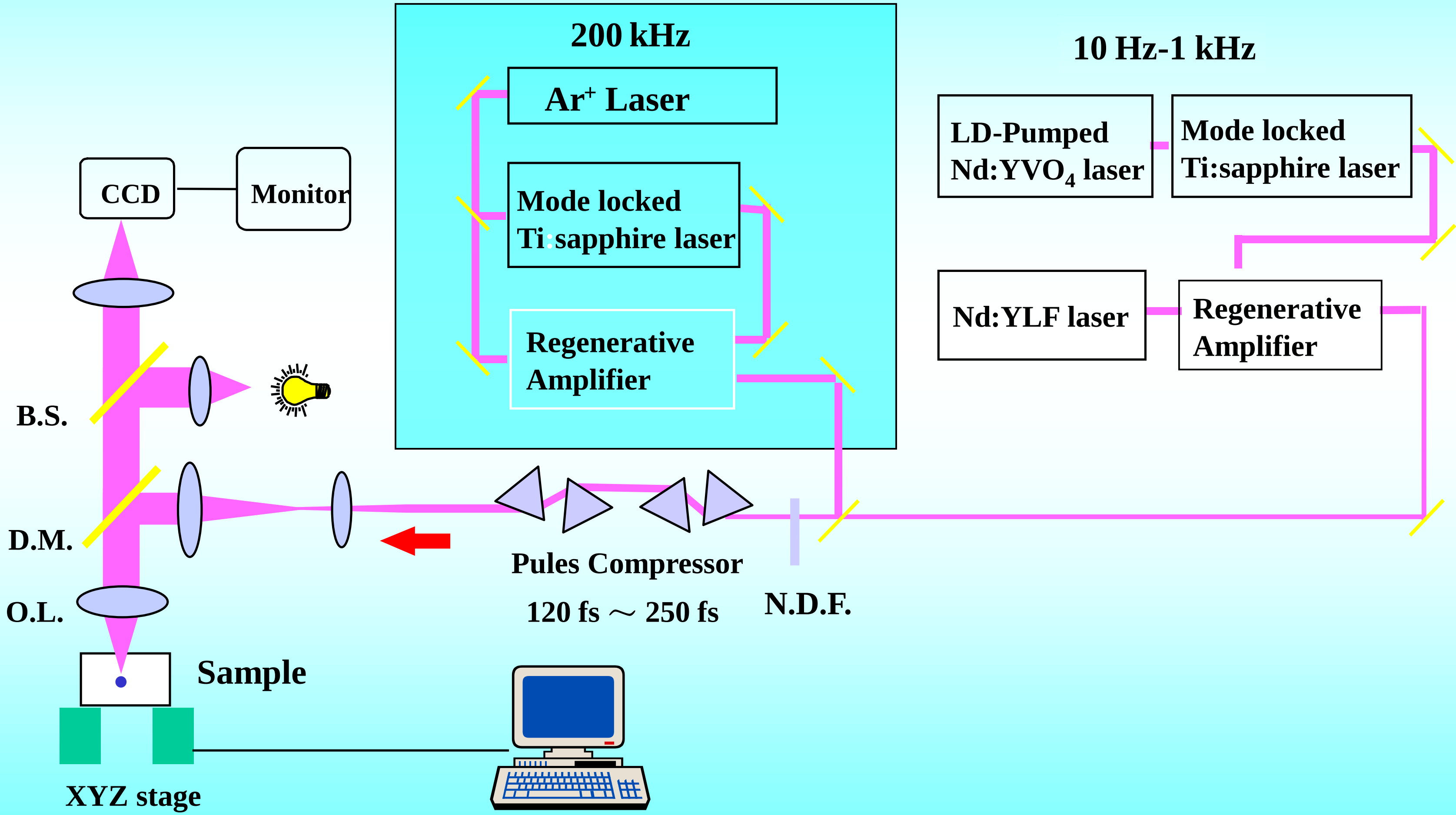
100 fs (= 10^{-13} s)



Femtosecond Pulse Width

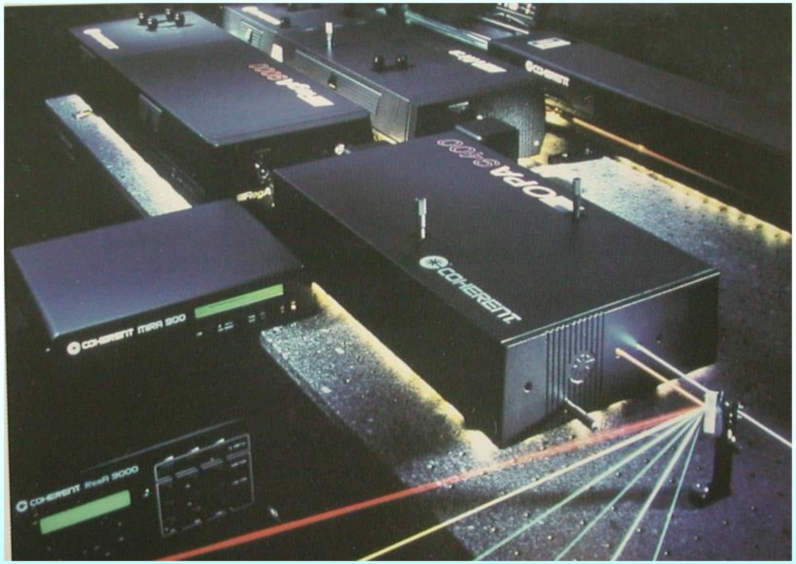
Cyber Laser Ifrit
Reputation 1 KHz
Average Power 1 W

Experimental setup



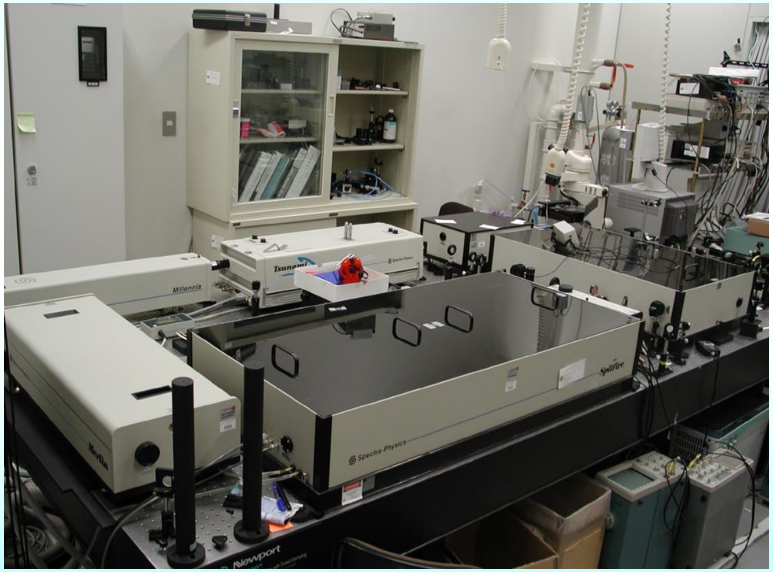
Laser systems for direct 3D writing

Pulse energy
5μJ



200KHz Ti:Sapphire femtosecond laser system (Coherent Co. Ltd)

Pulse energy
1mＪ

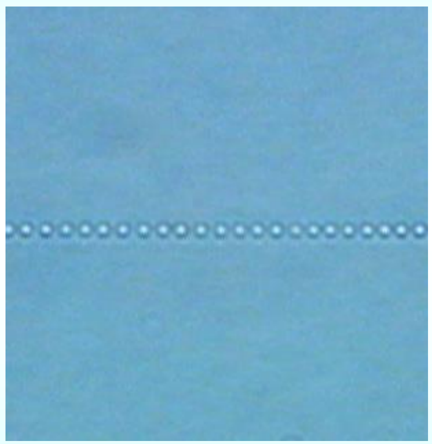


1KHz Ti:Sapphire femtosecond laser system (Spectra-Physics Co. Ltd)

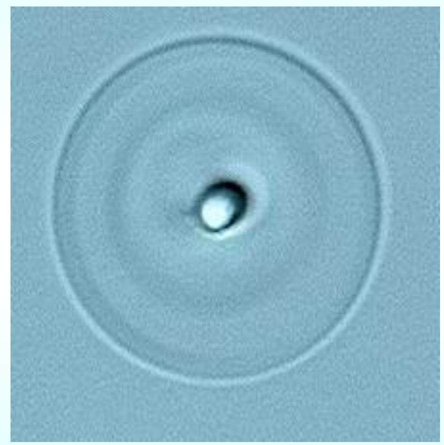
Femtosecond laser induced microstructures

Color center

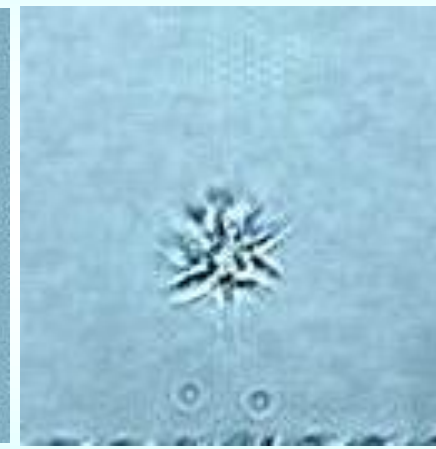
Densification



Thermal effect

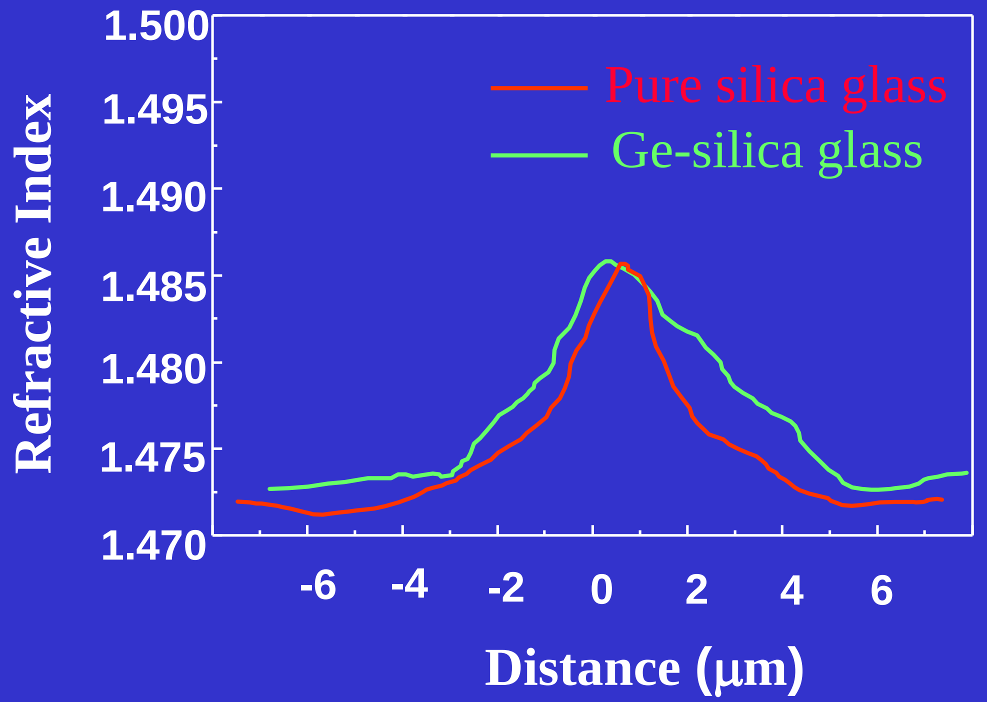


Break down



Various structures induced by fs laser-pulses

Refractive index distribution

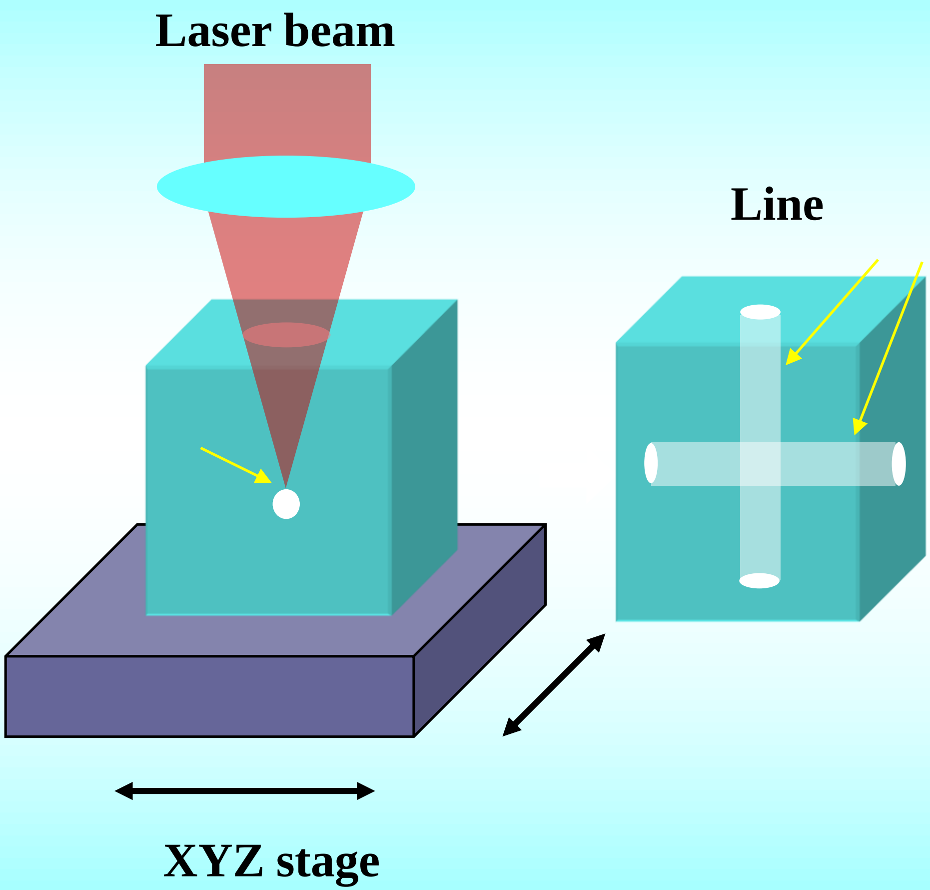


Refractive index profiles of damages formed by the laser beam with a10X lens, 470 mW, 130 fs and 200 kHz.

***Opt. Lett.*, 21(1996)1729**

US, EU, JAPAN Patent（1996）

Femtosecond laser direct writing



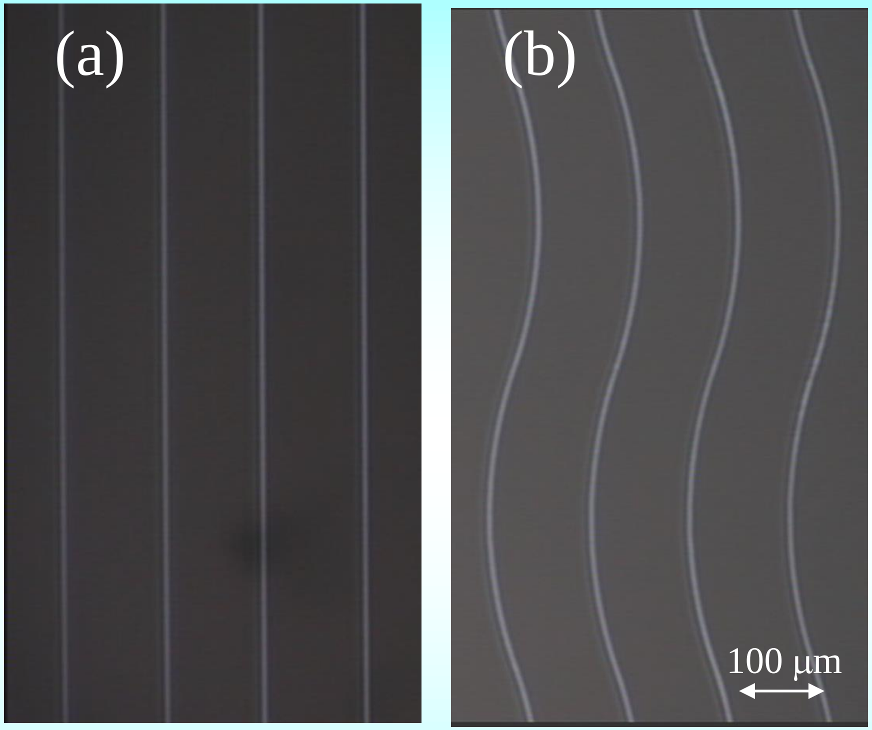


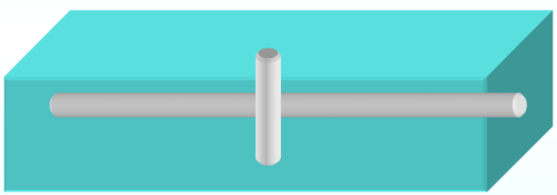
Photo-written lines in a glass formed using 800-nm 200-kHz mode-locked pulses. The lines were written by translating the sample (a) parallel or (b) perpendicular to the axis of the laser beam at a rate of 20 μm/s and focusing the laser pulses through a 10X or 50X microscope objective, respectively.

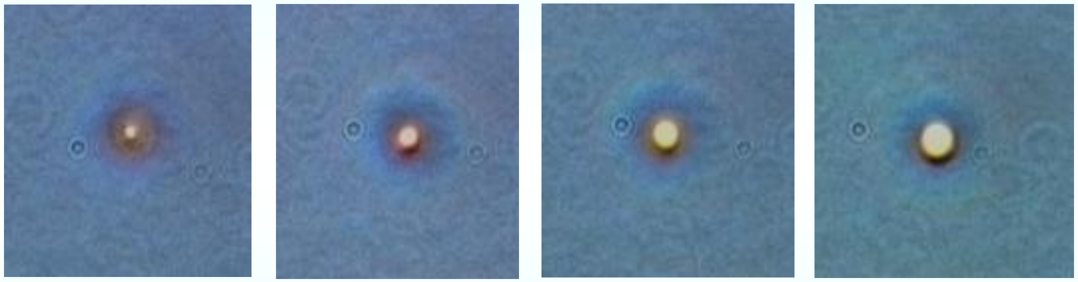
***J. Non-Cryst. Solid*, 257(1999)212.**

Laser-induced waveguide－cross section

Parallel to the laser beam

Laser beam





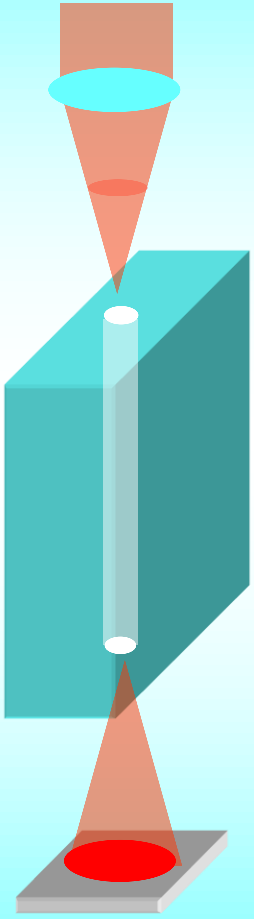
110 mW   190 mW   250 mW   305 mW

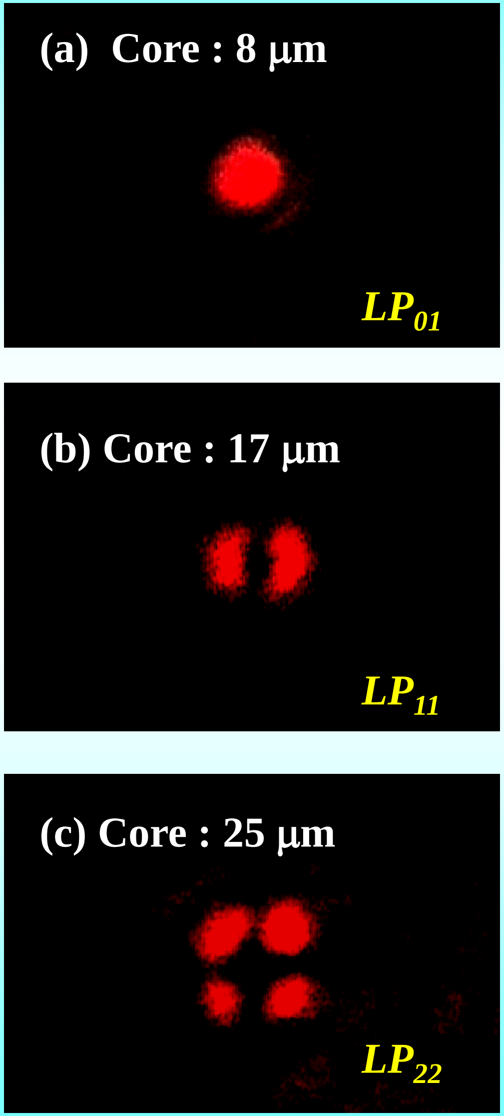
J. Non-Cryst. Solid,

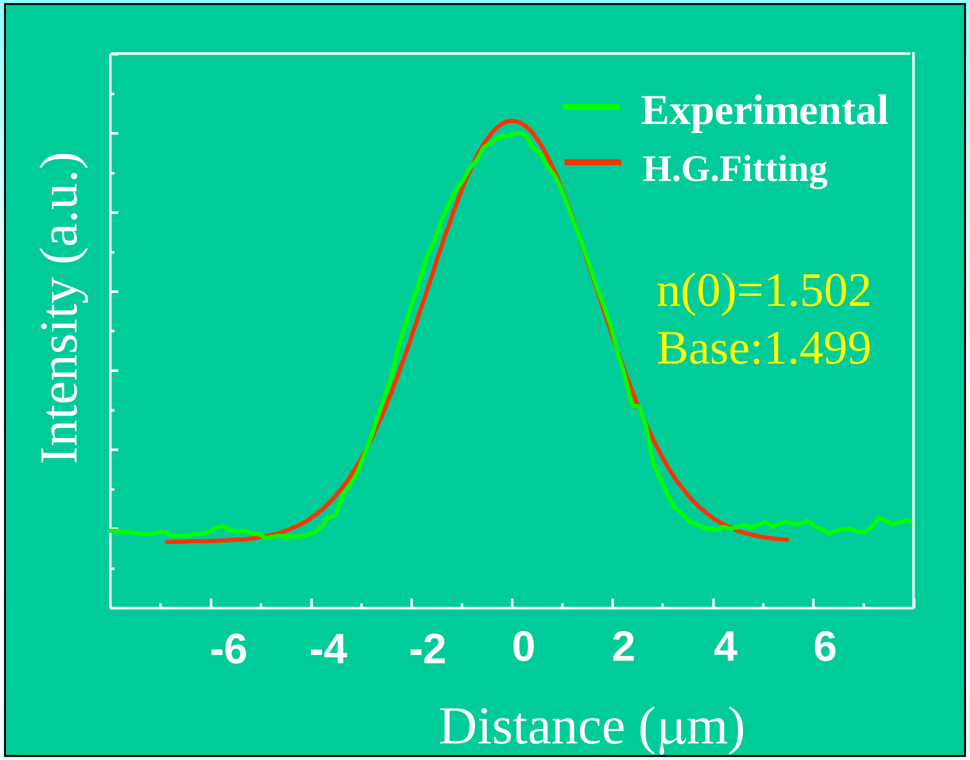
257(1999)212.

Cross sections of waveguides written by translating the sample parallel to the axis of the laser beam.

Mode-field patterns



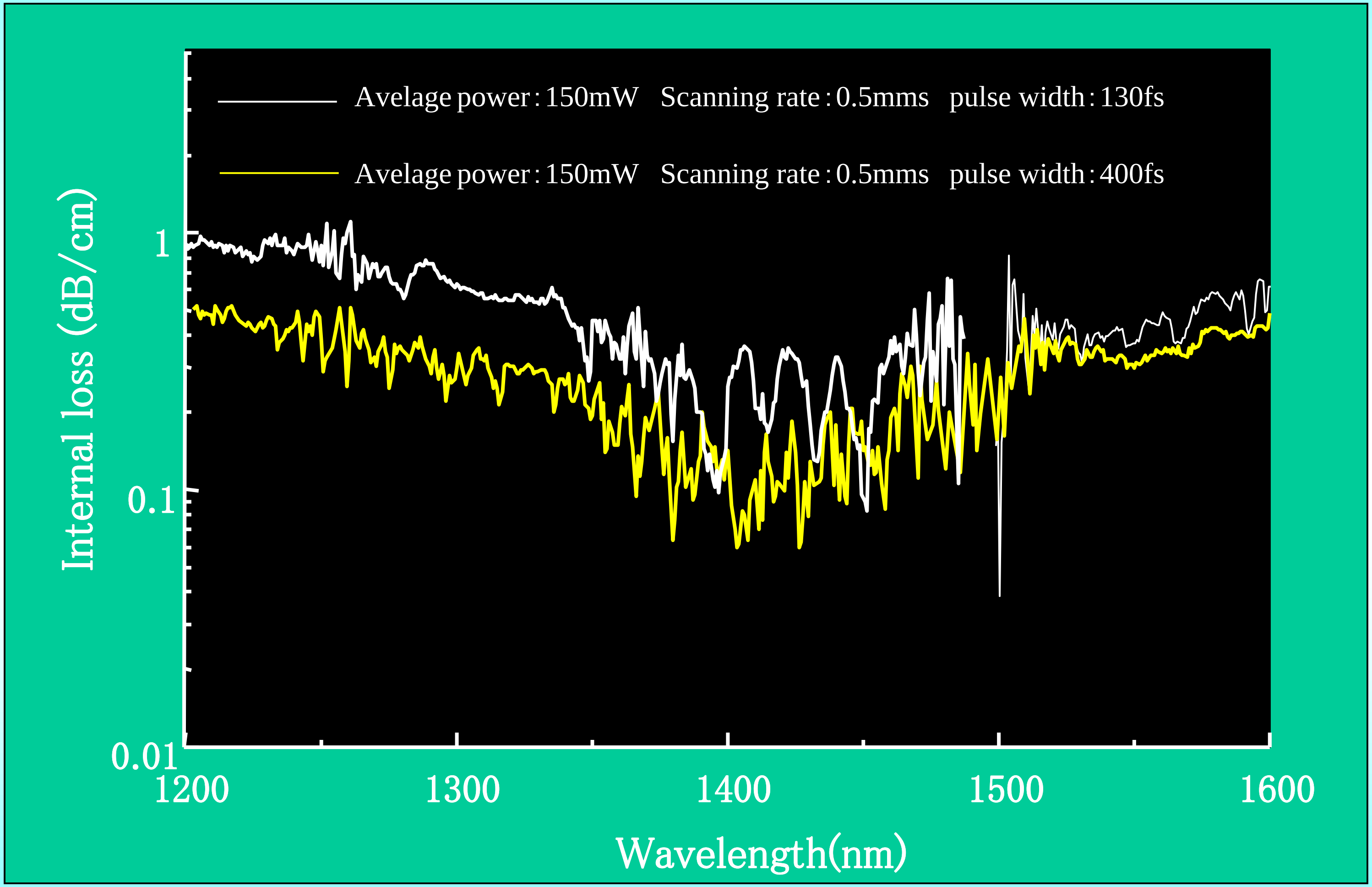




Result of Hermite-Gaussian fitting for the intensity distributions of the near field. The sample was the same as that observed in (a).The calculated result is almost in agreement with the experimental data, indicating that this waveguide is a graded-index type with a quadratic refractive-index distribution.

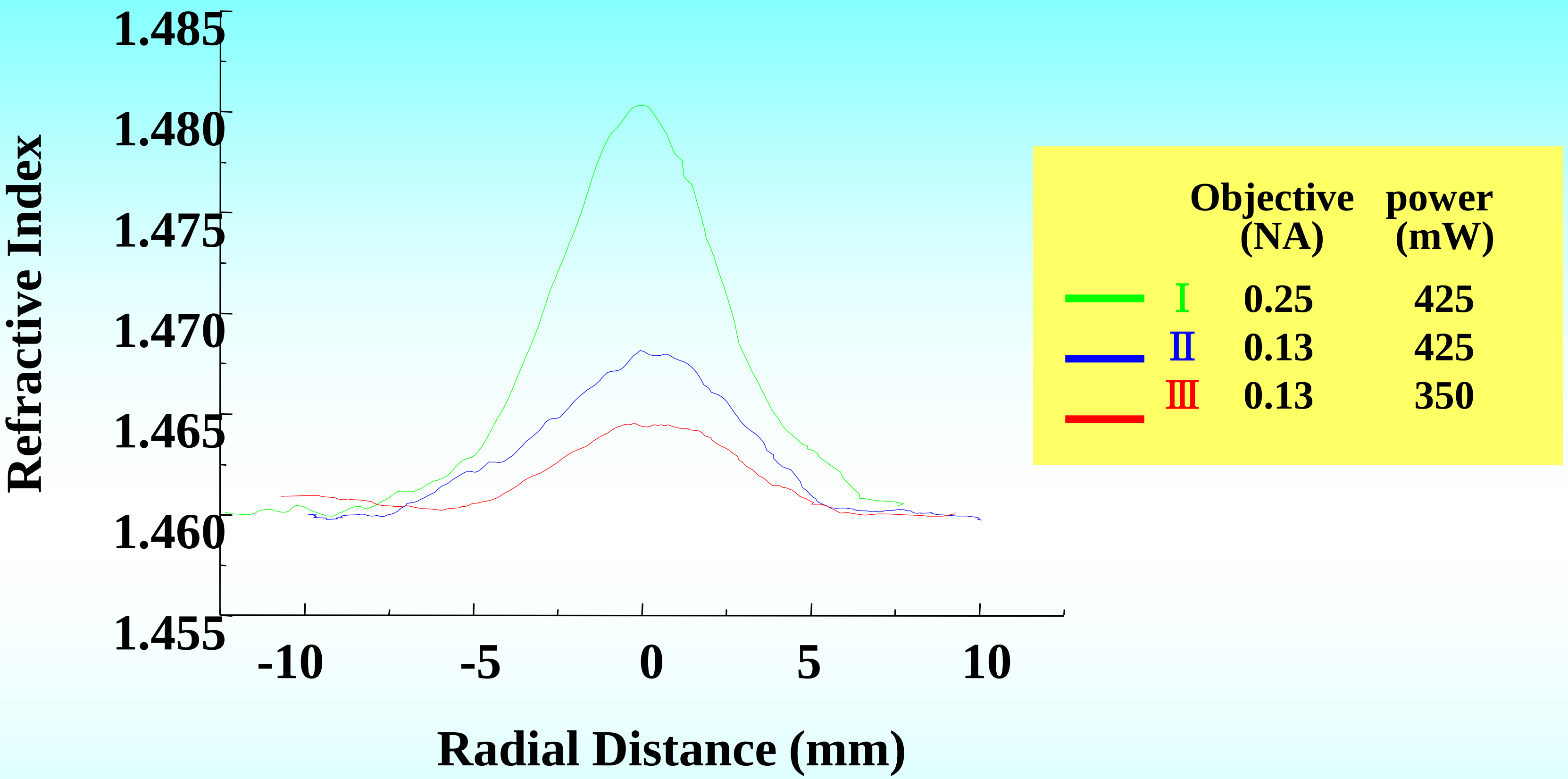
Appl. Phys. Lett., 71(1997)3329.

Internal loss of waveguides



Internal loss of waveguides drawn by translating the silica glass perpendicular to the axis of the laser beam

Measured refractive-index profile



<u>Common Writing Condition</u>

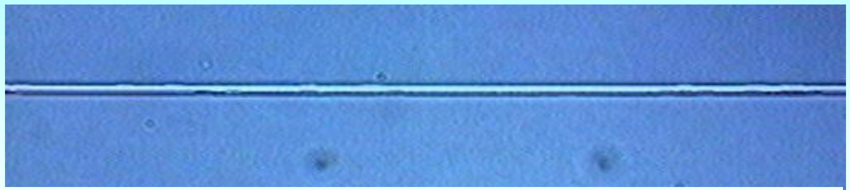
Wavelength:800 nm
Repetition rate:250 kHz
Pulse width: 270 fs
Scanning rate:50 mm/s

	Refractive index reference[%]	Change distance[mm]
I	1.32	20
II	0.53	18
III	0.27	11

Laser-induced waveguide－various glasses

Threshold (average power)

Silica glass

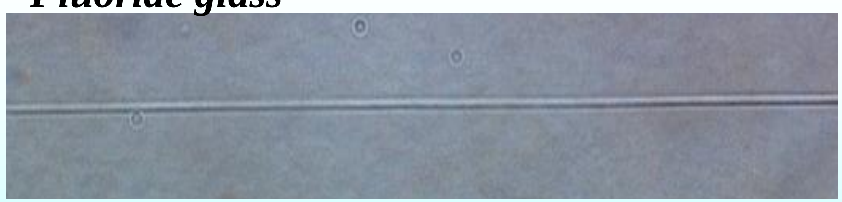


70 mW

Borosilicate glass

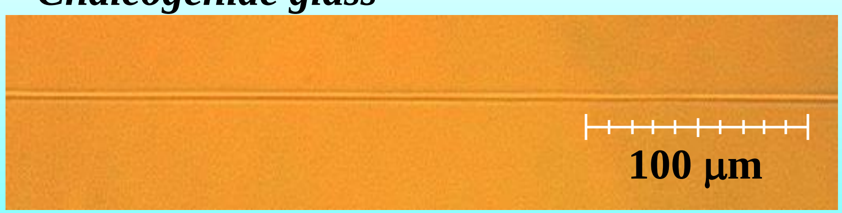
30 mW

Fluoride glass



100 mW

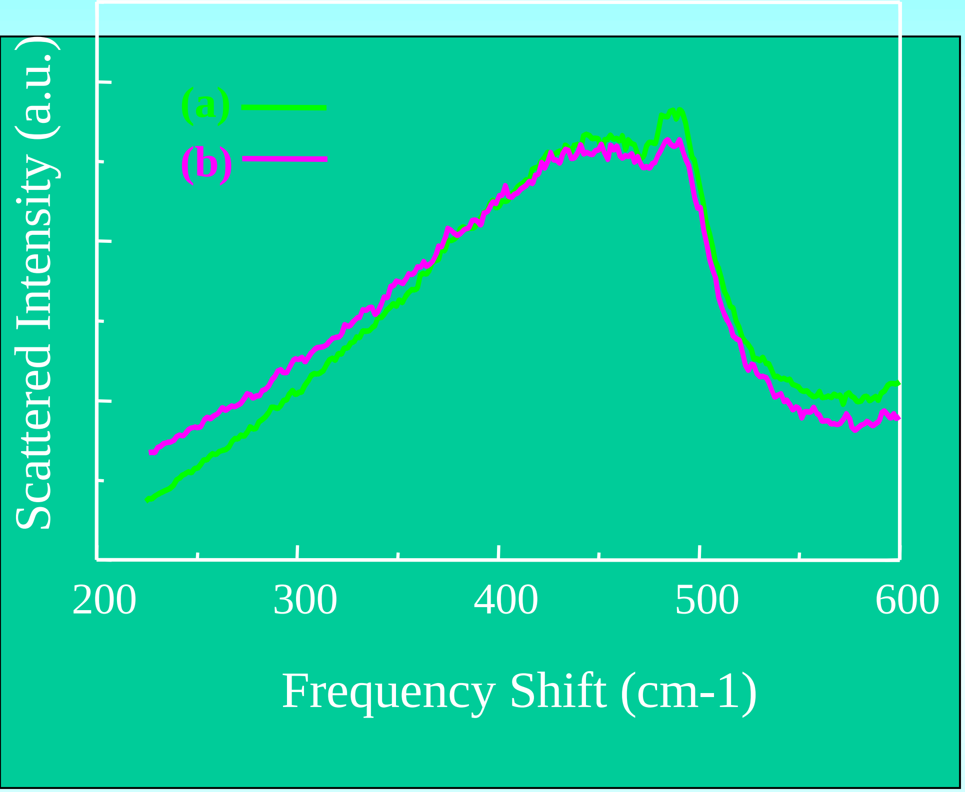
Chalcogenide glass



1 mW

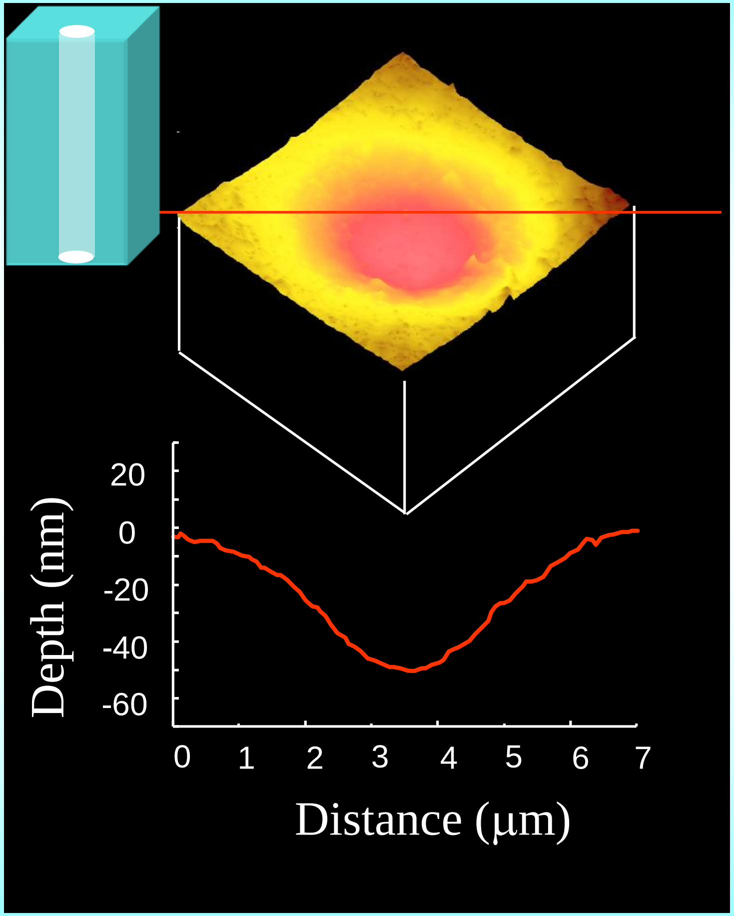
***Appl. Phys. Lett.*, 71(1997)3329.**

Raman spectra and AFM observation



Raman spectra of a silica glass before (b) and after (a) the laser irradiation. The amount of band shift in this figure is 3-5 cm^{-1} corresponding to an increase in density of about 1%.

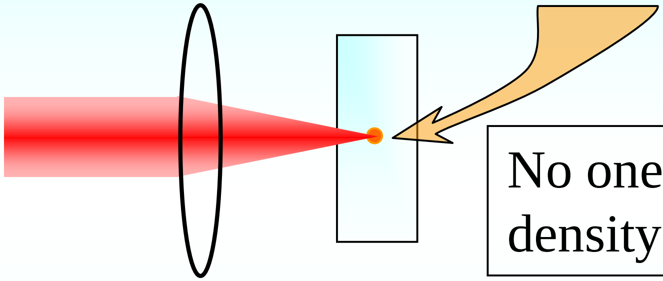
***Appl. Phys. Lett.*, 71(1997)3329.**



AFM (atomic force microscope) observation of the surface of a damage line end on silica glass.

The mechanism of the phenomenon?

HIGH TEMPERATURE and HIGH PRESSURE localized to the focal region play important roles.

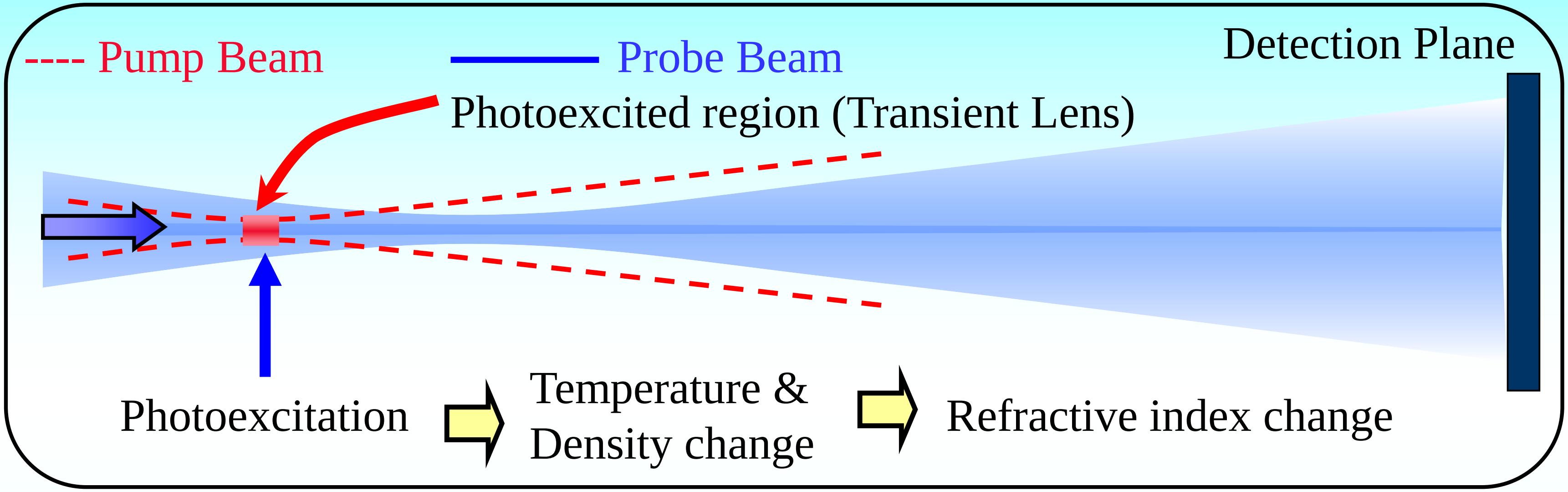


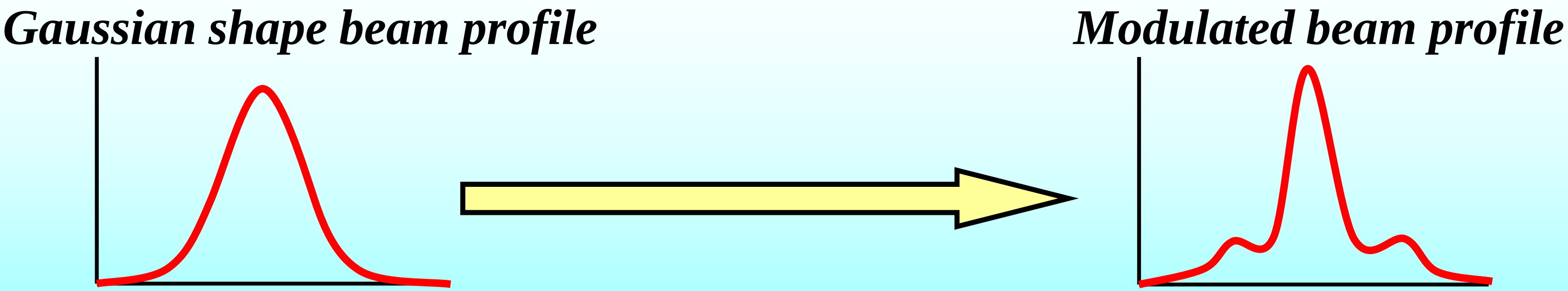
No one has ever observed the dynamics process of density increase.

- We would like to know the **DYNAMIC PROCESS** of the femtosecond laser induced density increase inside a glass.
- To **OBSERVE** the **DYNAMICS** of the **REFRACTIVE INDEX CHANGE** with picosecond time resolution using ***Transient Lens Method.***

How to observe the refractive index change

Transient Lens (TrL) Method

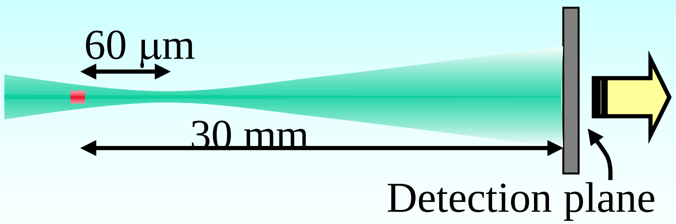


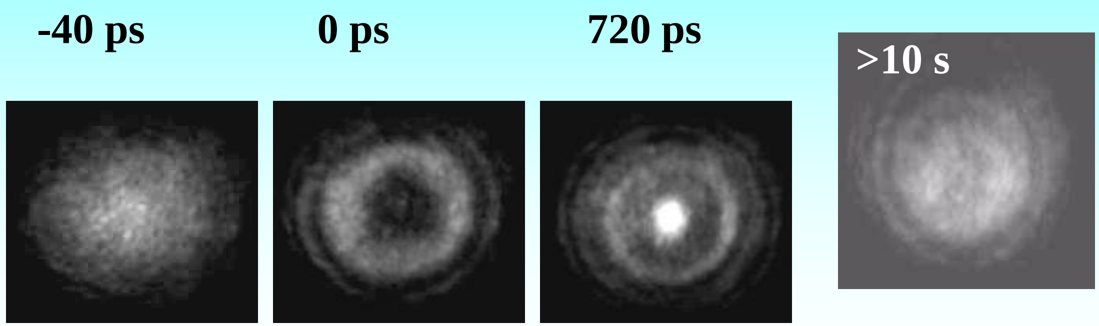


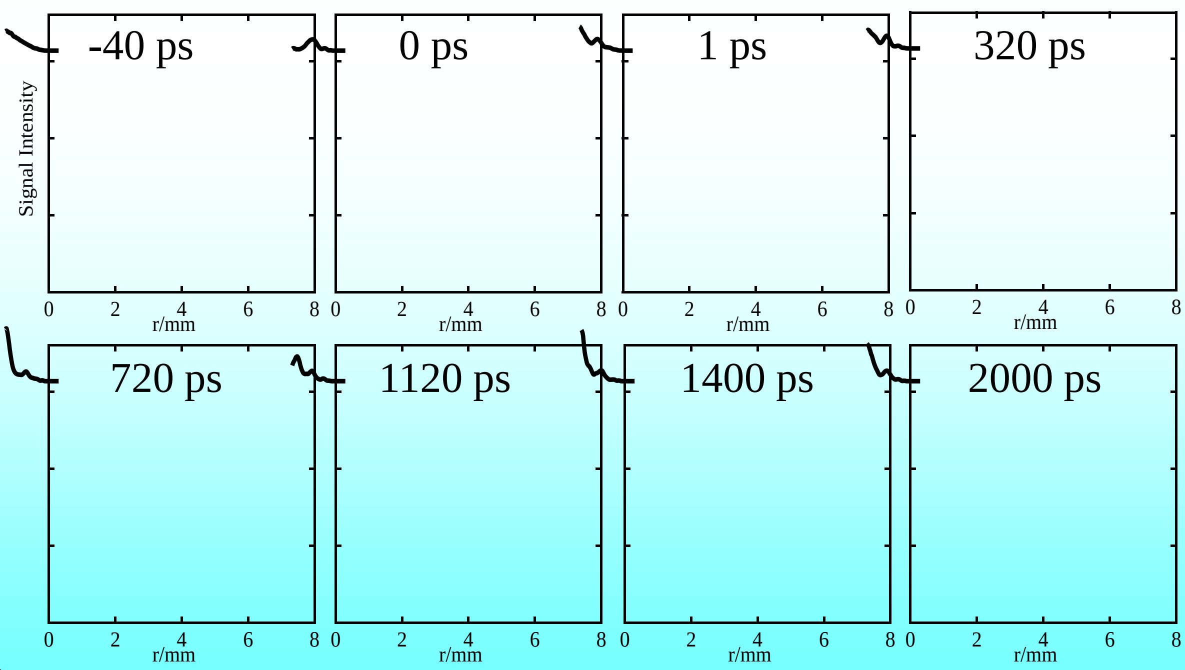
The probe beam profile is modulated at the far field due to the refractive index distribution. (Lens Effect)

Result 1 *Beam profile of the probe beam*

Images of the probe beam detected by the CCD camera at various time delays.







(i) Circular symmetric intensity distribution.

(ii) Dramatic change after irradiation.

What the results suggest?

- **Due to the high amplitude of the acoustic wave** ◇
  Estimated $\Delta\rho$ ~ 0.4%. ◇ Simulated $\Delta\rho$ with <u>ΔT=500 K</u>: 0.04%

It means that

C **ΔT > 1000 K** (above the glass transition temperature)

➤ **Sudden temperature elevation** (<10ps; faster than elastic relaxation) is clearly shown.

➤ The high temperature region has a diameter of **~1 µm.**

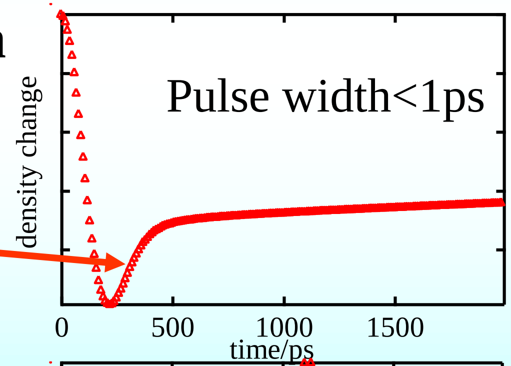
- **The significance of the laser pulse duration**

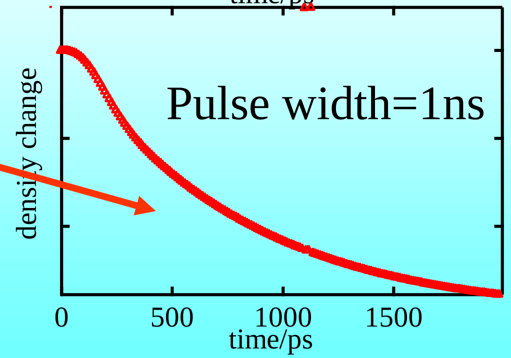
<u>Density at the center of the irradiated region.</u>

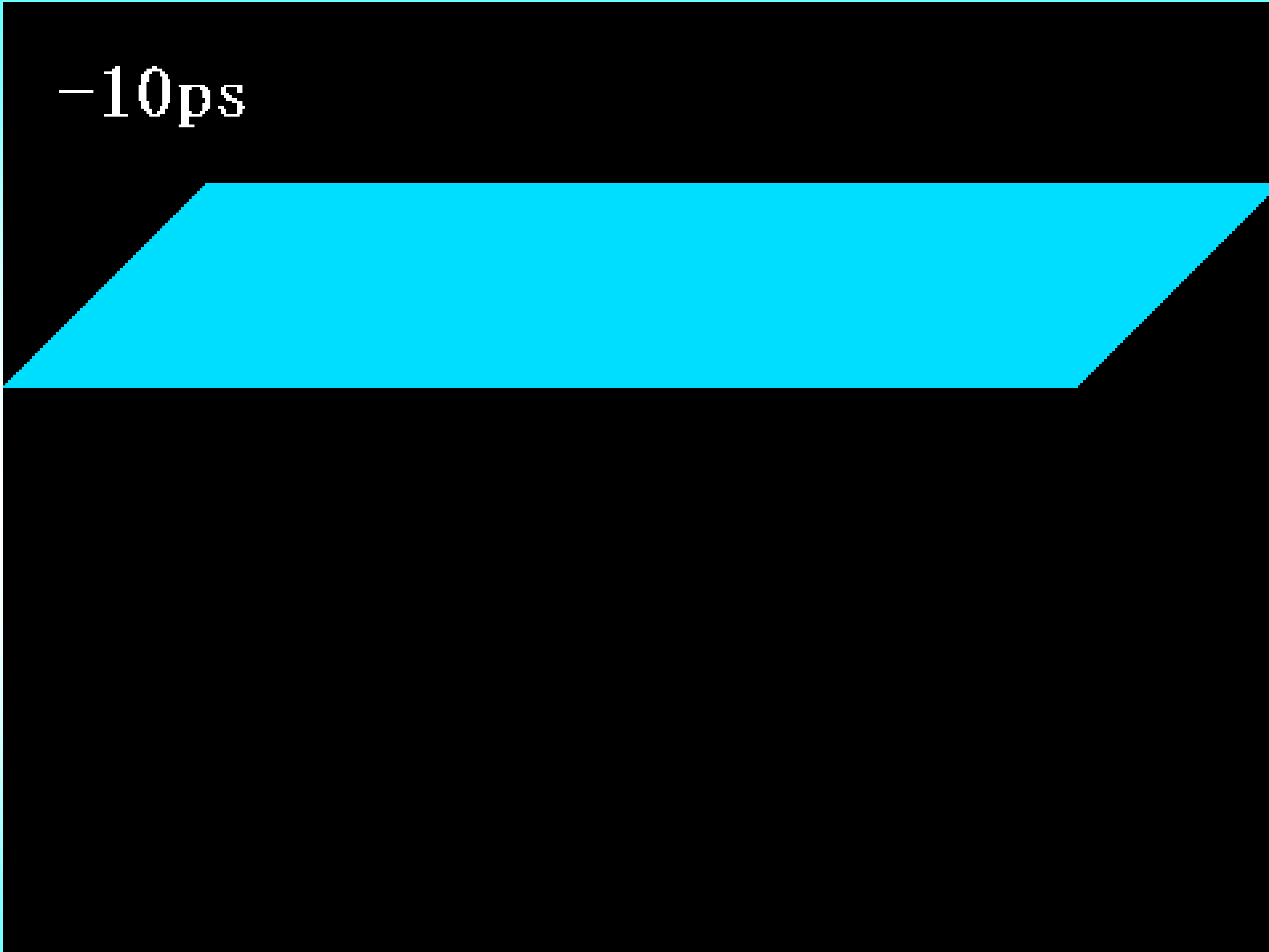
➤ Fast irradiation (<1ps)
 The density recovered
 due to the propagation of the acoustic wave.

➤ Slow irradiation (~1ns)
 The density decreases continually.

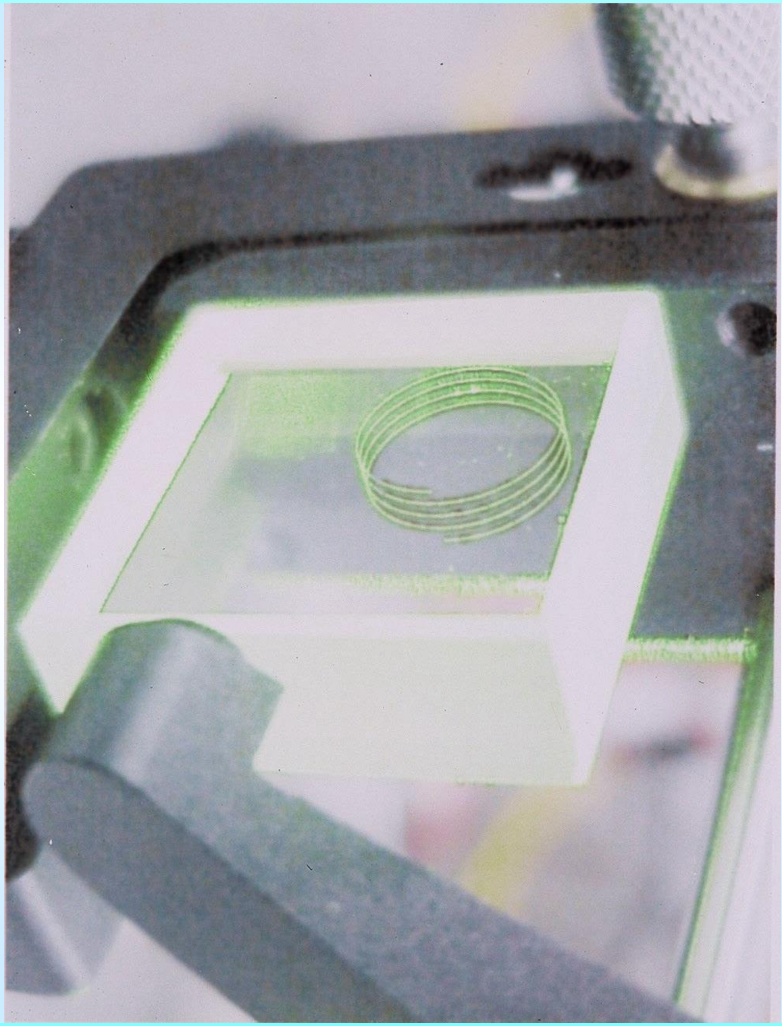
The density increase could play an important role in creating the final structure (dense structure around the irradiated region).



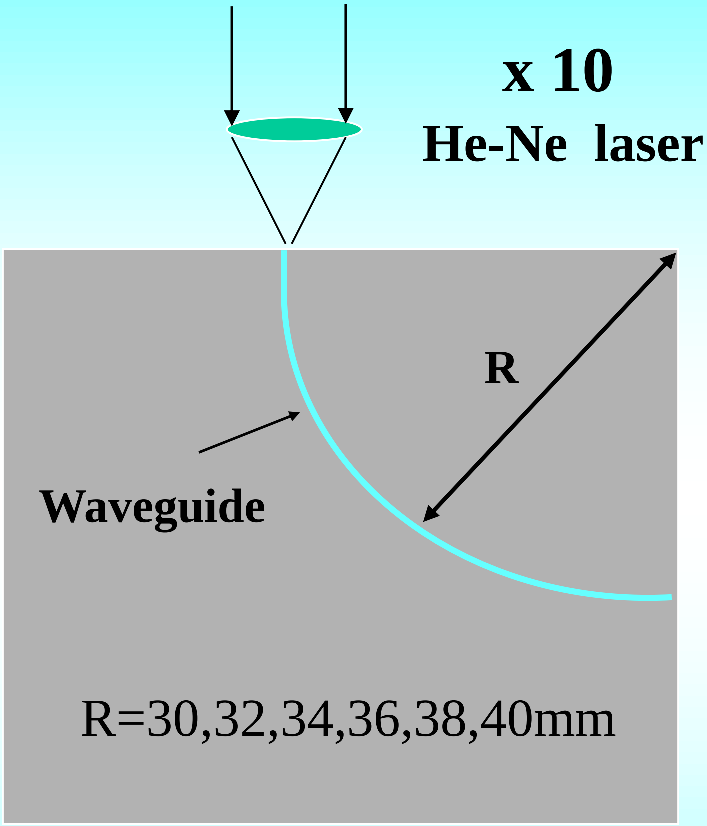


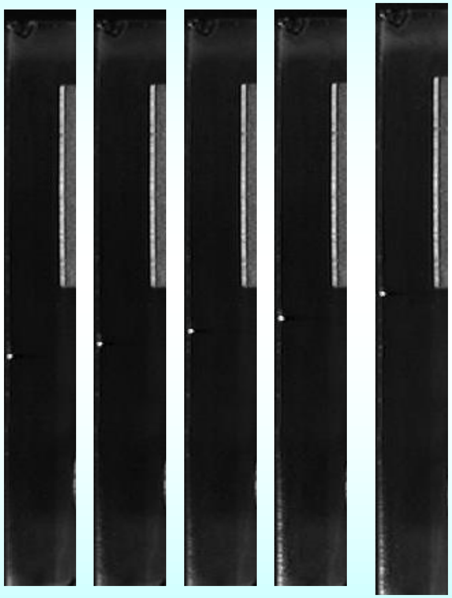

−10ps

3D optical circuit

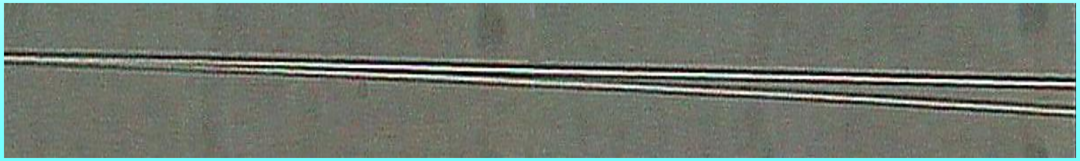


Curved waveguides and coupler

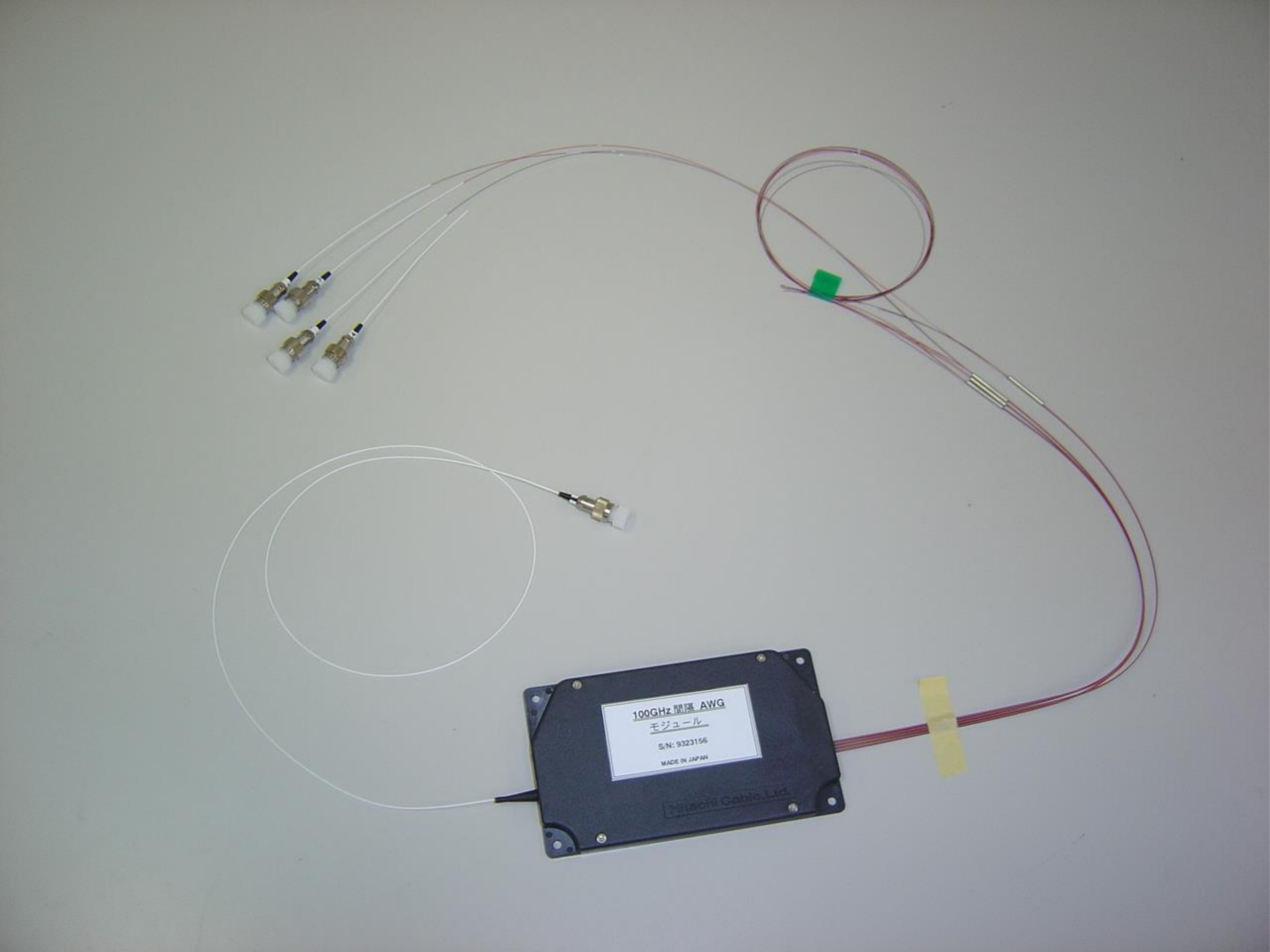




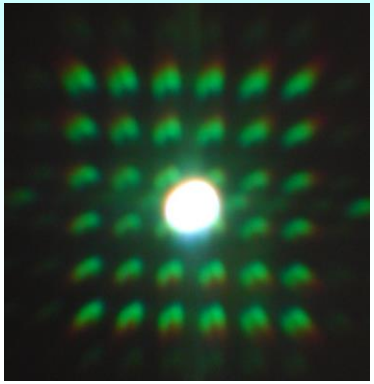
Transmission light of the end face of bending waveguides

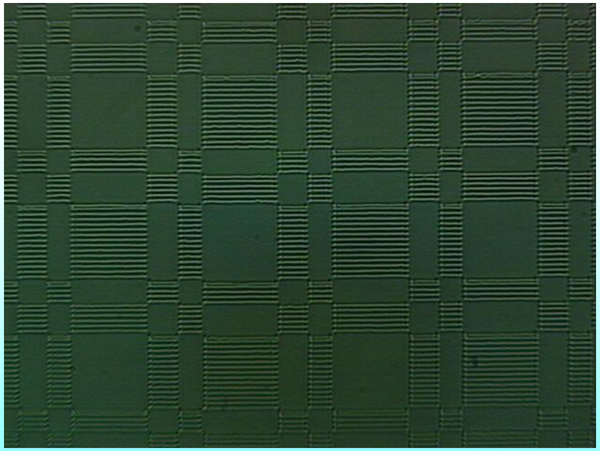


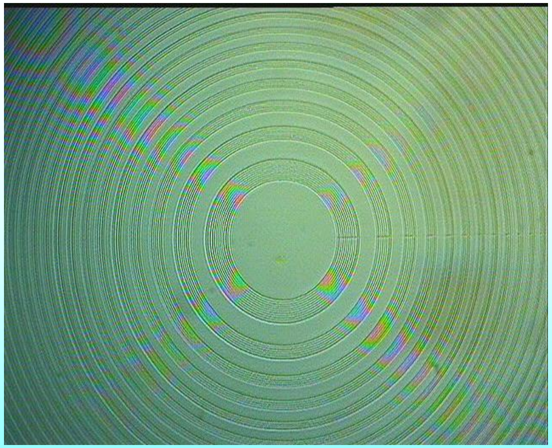
Beam coupler


100GHz 間隔 AWG
モジュール
S/N: 9323156
MADE IN JAPAN
Hitachi Cable, Ltd.

Dammann grating and micro-lens

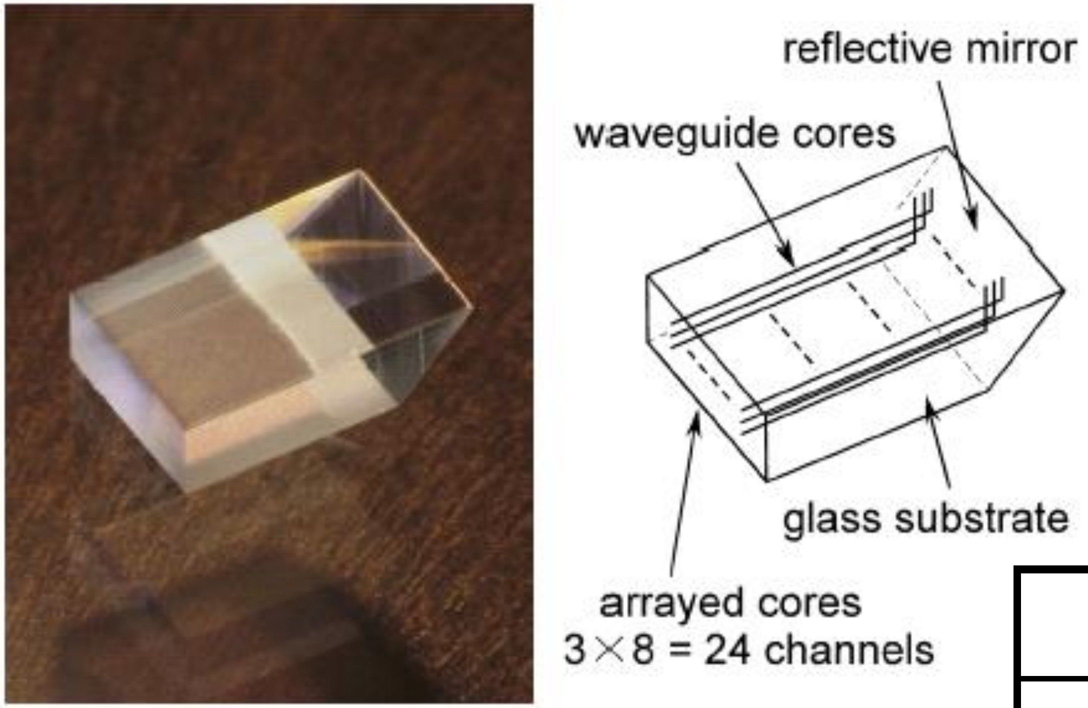






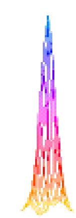
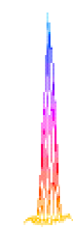
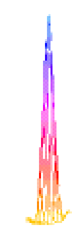
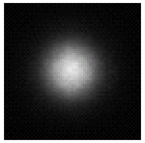
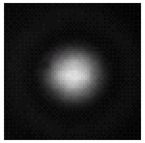
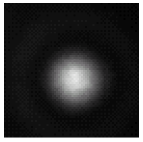
Chin. Phys. Lett., 21(2004)1061.

One example of fs laser written waveguide

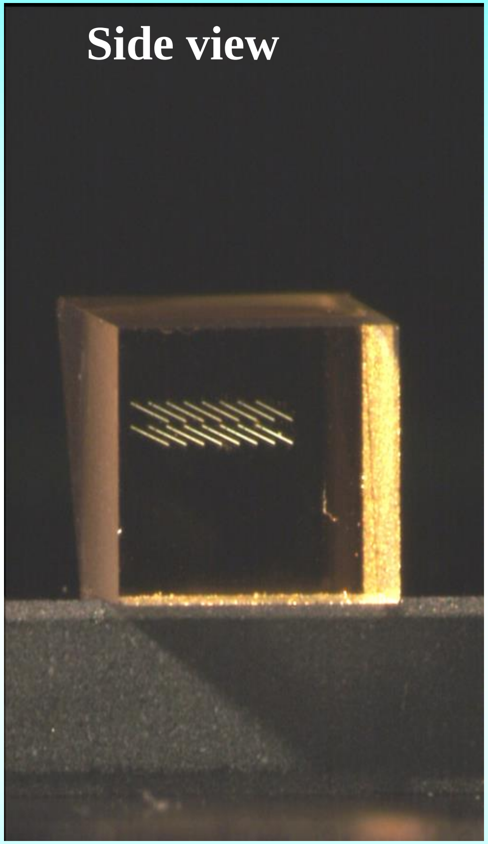


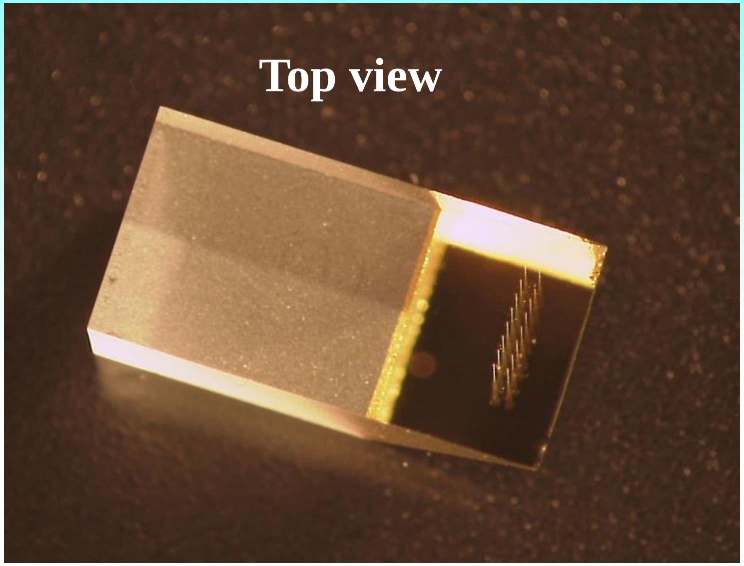
Waveguide

Beam profile and NFP of the optical-path redirected waveguide

	SMF	Laser written optical coupler	
		CH1	CH16
Beam profile			
Near field pattern			

Direction change devices for input light signal

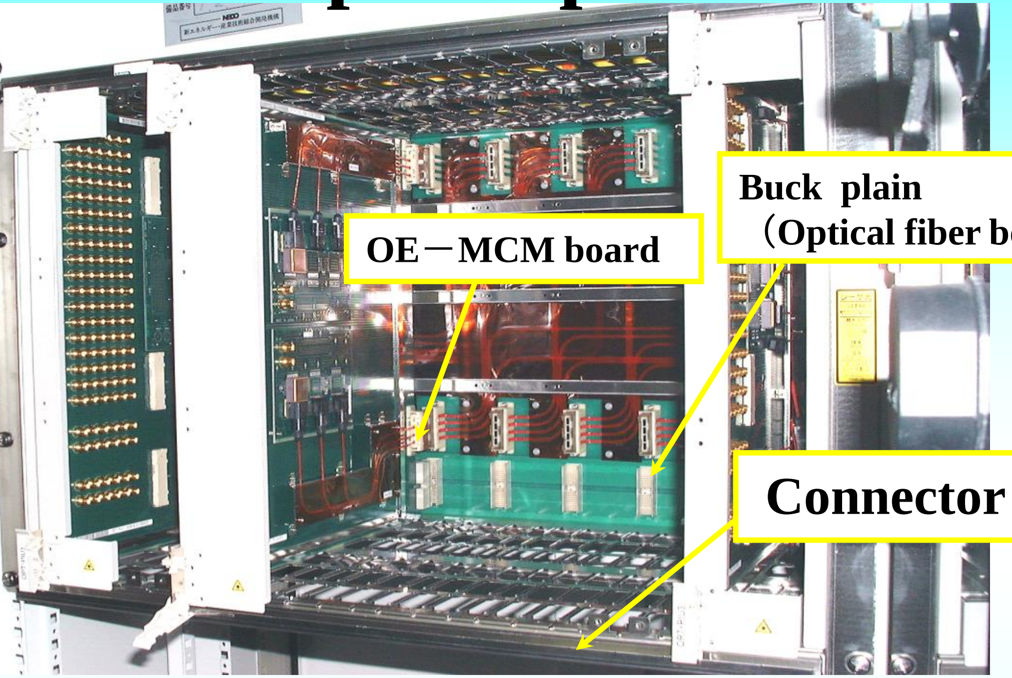


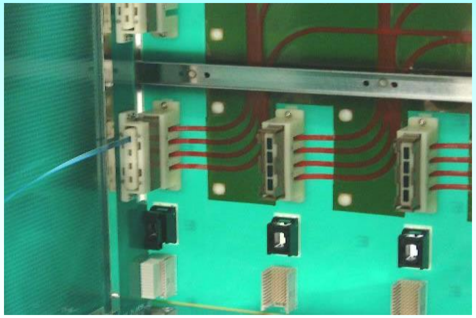


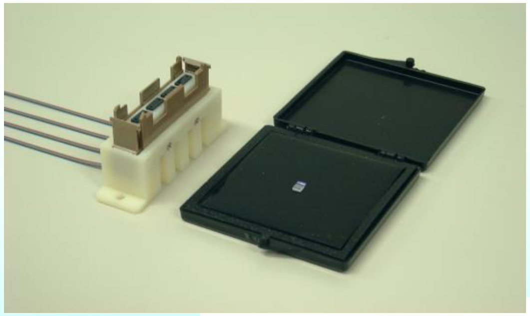
Perpendicular waveguide cannot be taken by camera due to

the 45 mirror plane.

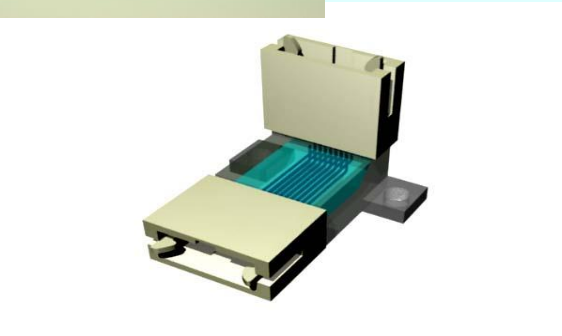
Practical application of the optical-path redirected waveguide





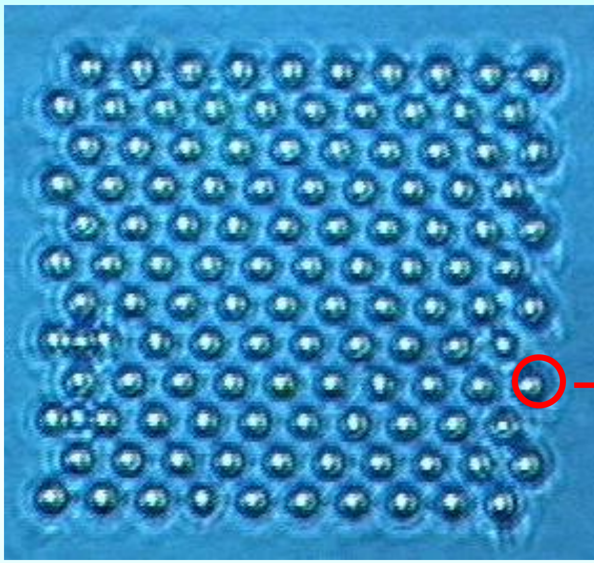


Comparision



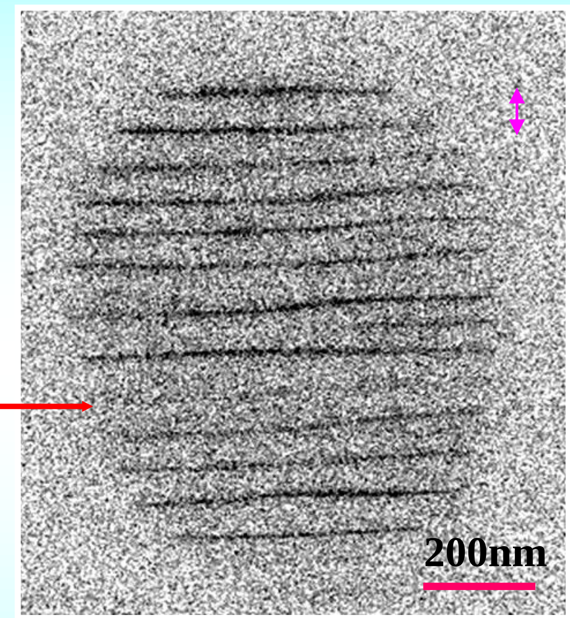
Back plain transmission system

One shot of single femtosecond laser induced nanograting



Optical microphotograph

100× (0.95)
120fs
200kHz
200mW
1s



10nm

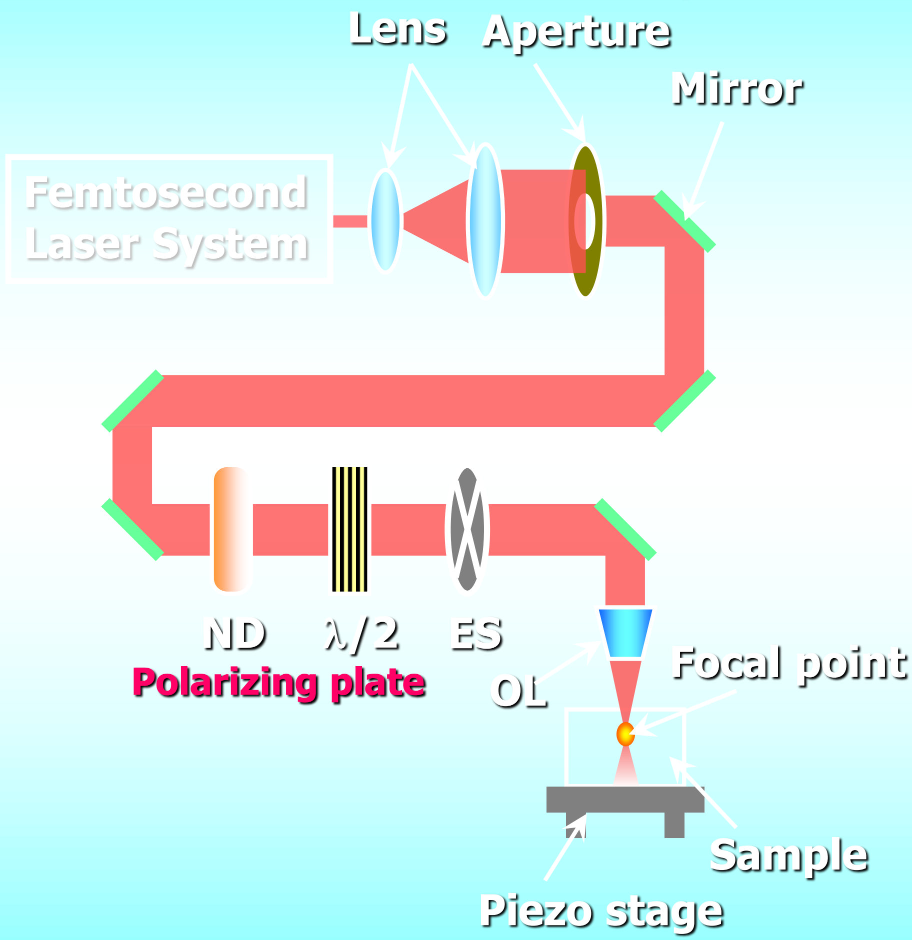
E

BEI image of SEM

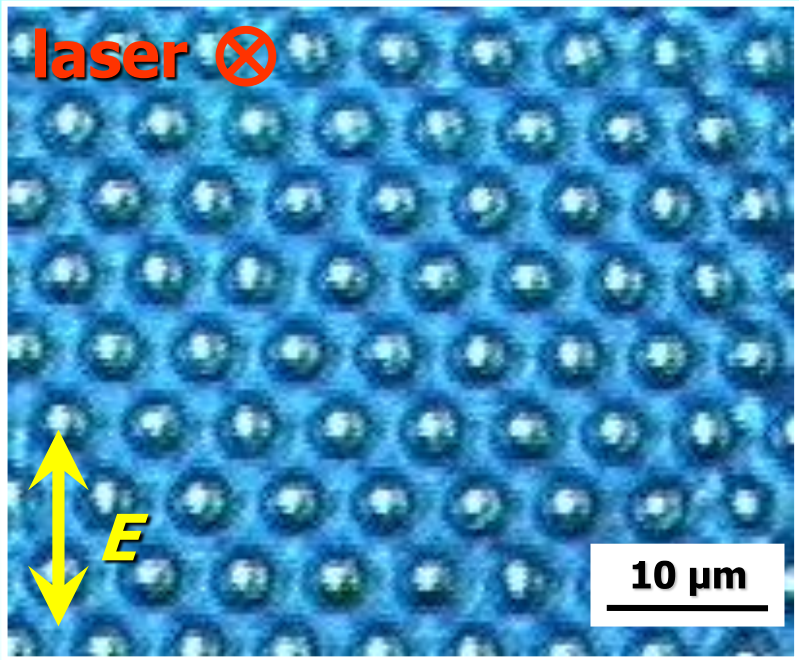
Phys. Rev. Lett., 91(2003)247405.

Nanograting in SiO2 glass using polarization light of femtosecond laser

Fabrication system

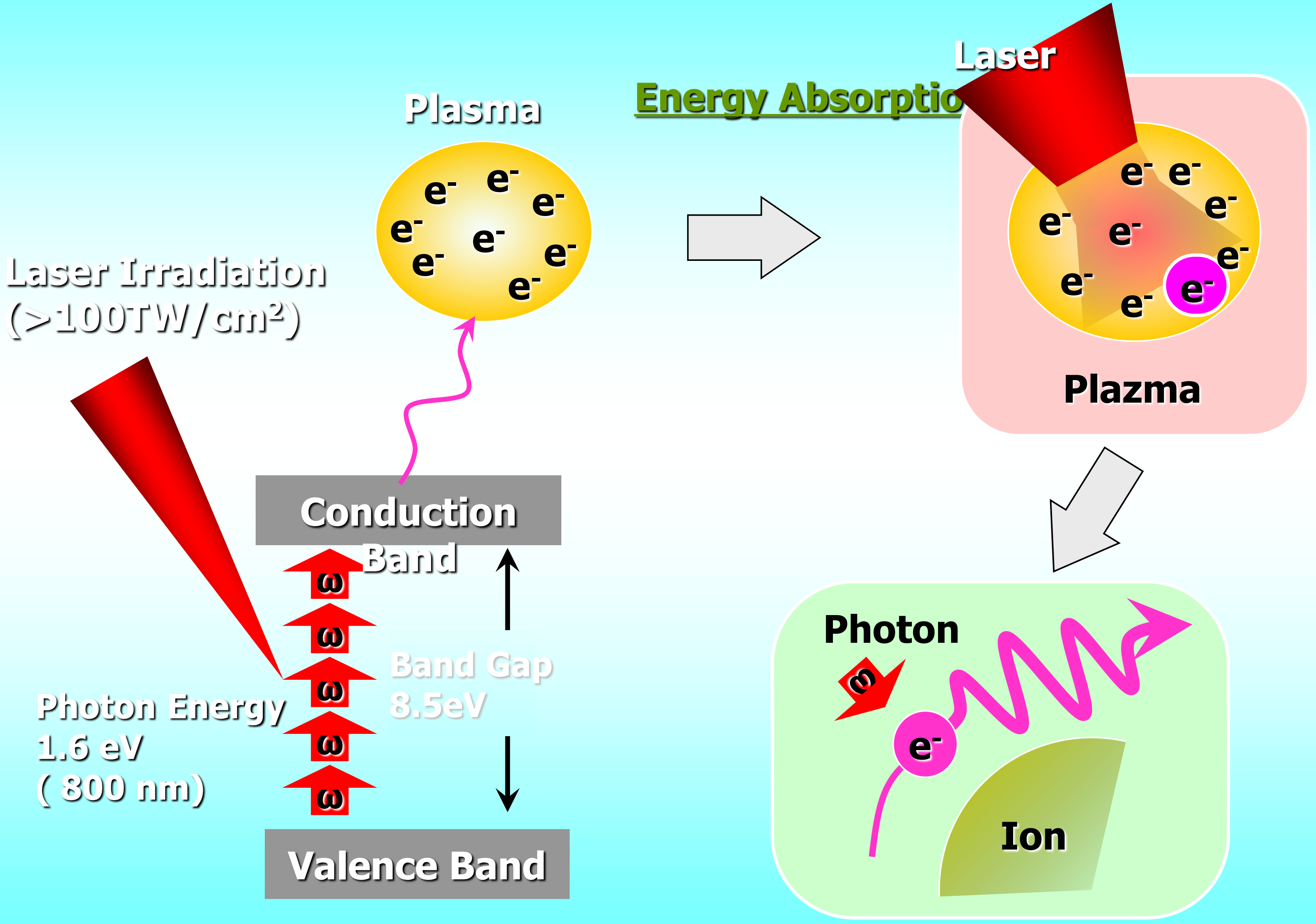


Microscope image



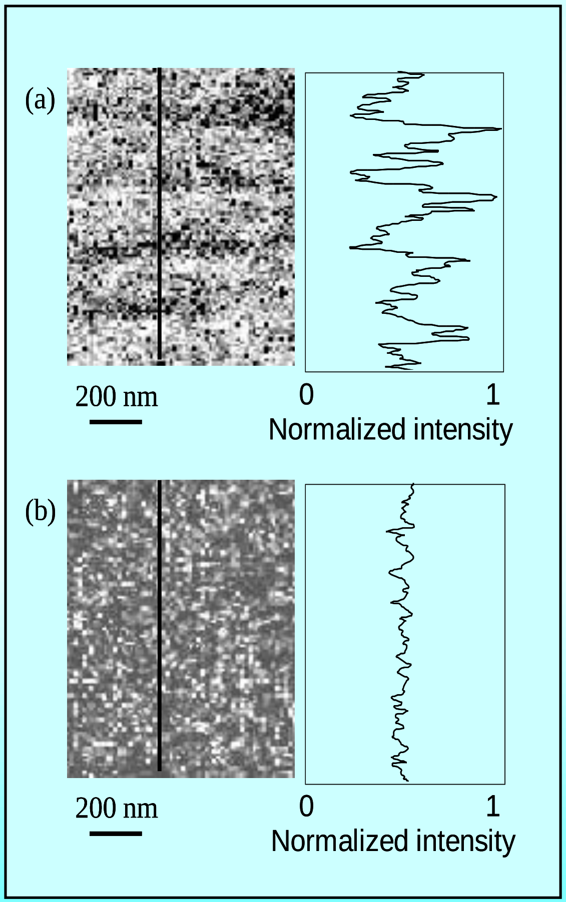
Condition

wavelength	: 800 nm
pulse duration	: 150 fs
repetition rate	: 200 kHz
pulse energy	: ~1.0 μJ
objective	: ×100 (NA=0.95)
polarization	: vertical direction

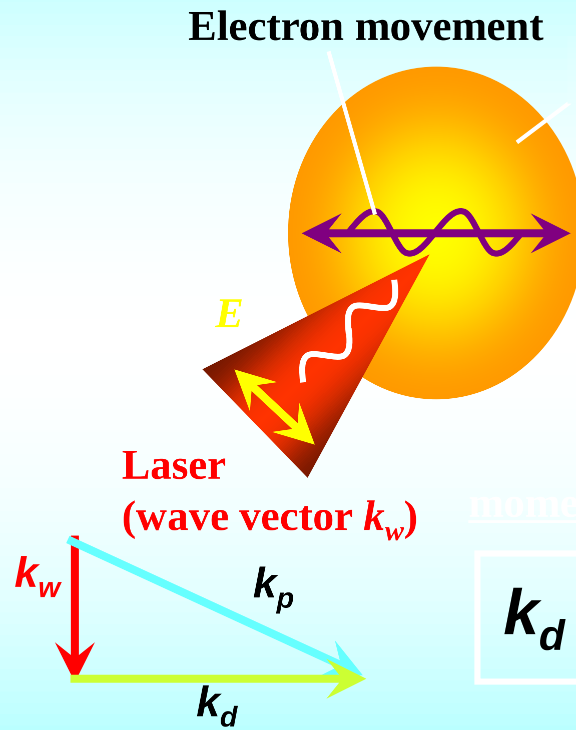

Laser Irradiation
(>100TW/cm²)
Photon Energy
1.6 eV
(800 nm)
ω
Conduction Band
Valence Band
Band Gap
8.5eV
Plasma
e⁻
Energy Absorption
Laser
Plazma
Photon
Ion

Mechanism of the formation of nanograting

Phys. Rev. Lett., 91(2003)247405.



O and Si concentration AES mapping



momentum conservation

$$k_d = k_p - k_w$$

$$k_d = \frac{2\pi}{\Lambda}$$

k_w: laser wave vector

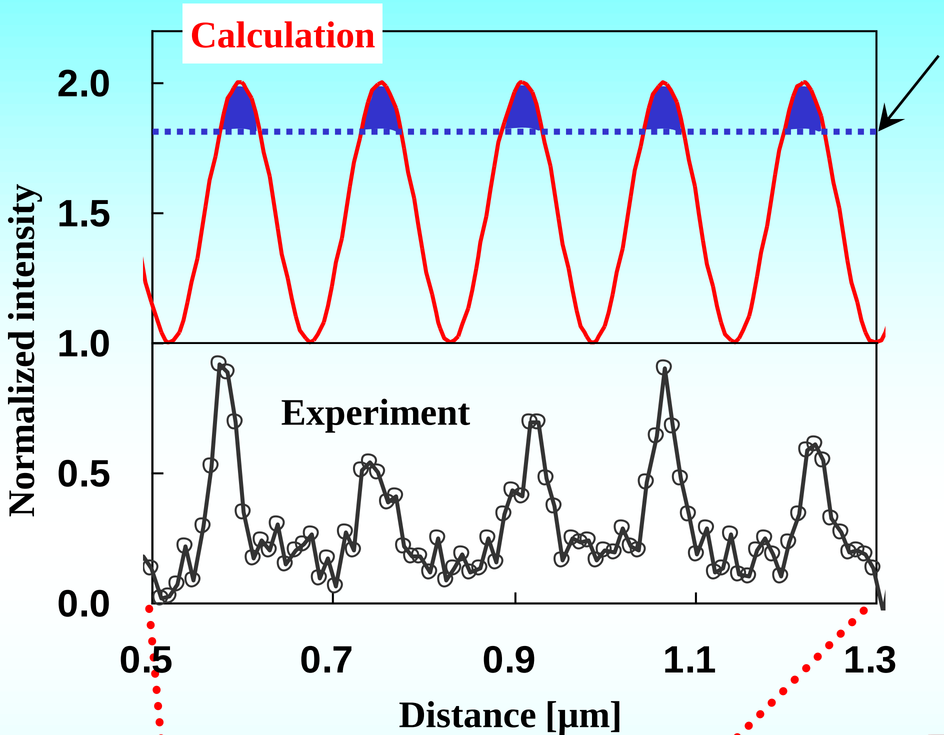
k_p: plasmon wave vector

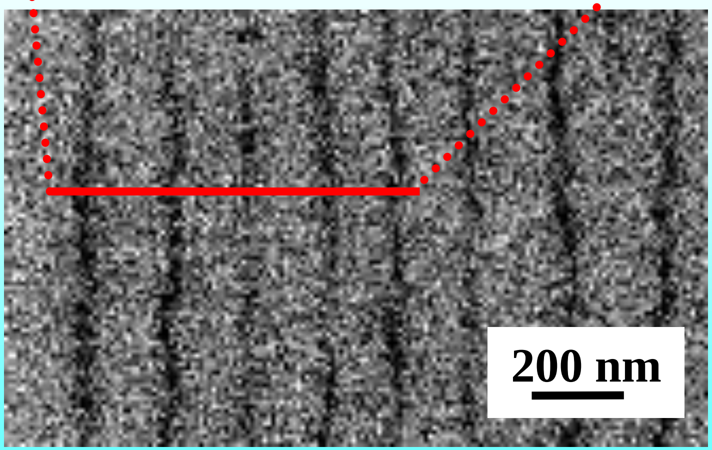
k_d: dielectric constant modulation vector

Λ: period of nanostructure

Mechanism of the nanograting

Electron plasma standing wave





Threshold of oxygen defects formation

Plasma standing wave

$$\vec{E}_w \approx \sin^6(\omega_\mathrm{w} t)$$

$$\vec{E}_{pl} \approx \sin(\omega_\mathrm{pl} t)$$

$\omega_\mathrm{w} = \omega_\mathrm{pl}$ **: Energy conservation**

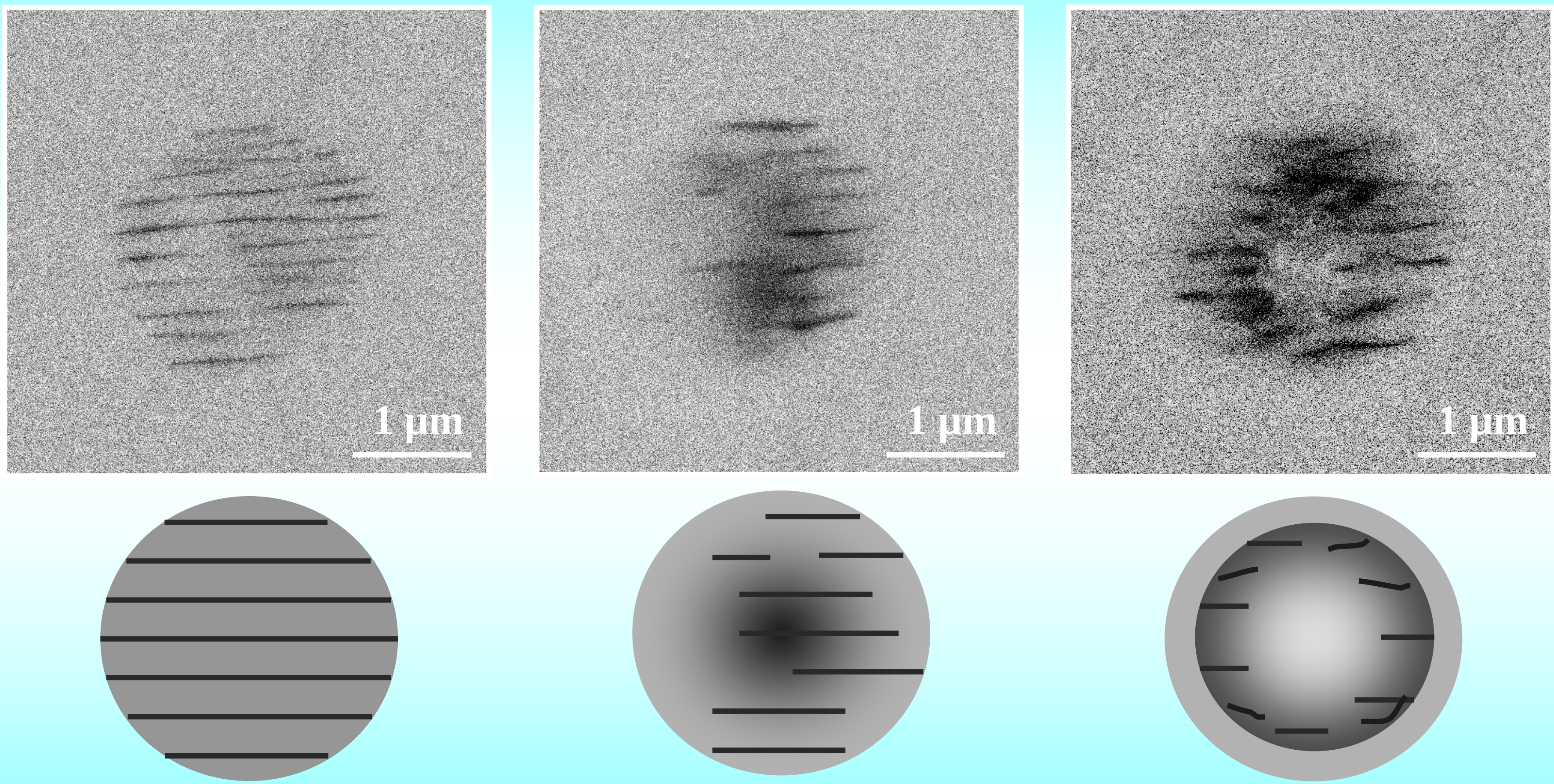
$$\left|\vec{E}_w \cdot \vec{E}_{pl}\right| \approx \left|\sin^7(\omega_\mathrm{w} t)\right|$$

Electron plasma wave behaves as standing wave within the focal spot.

Oxygen defects are formed in the domain beyond the threshold.

Pulse energy threshold

1.0 μJ **2.0 μJ** **2.8 μJ**

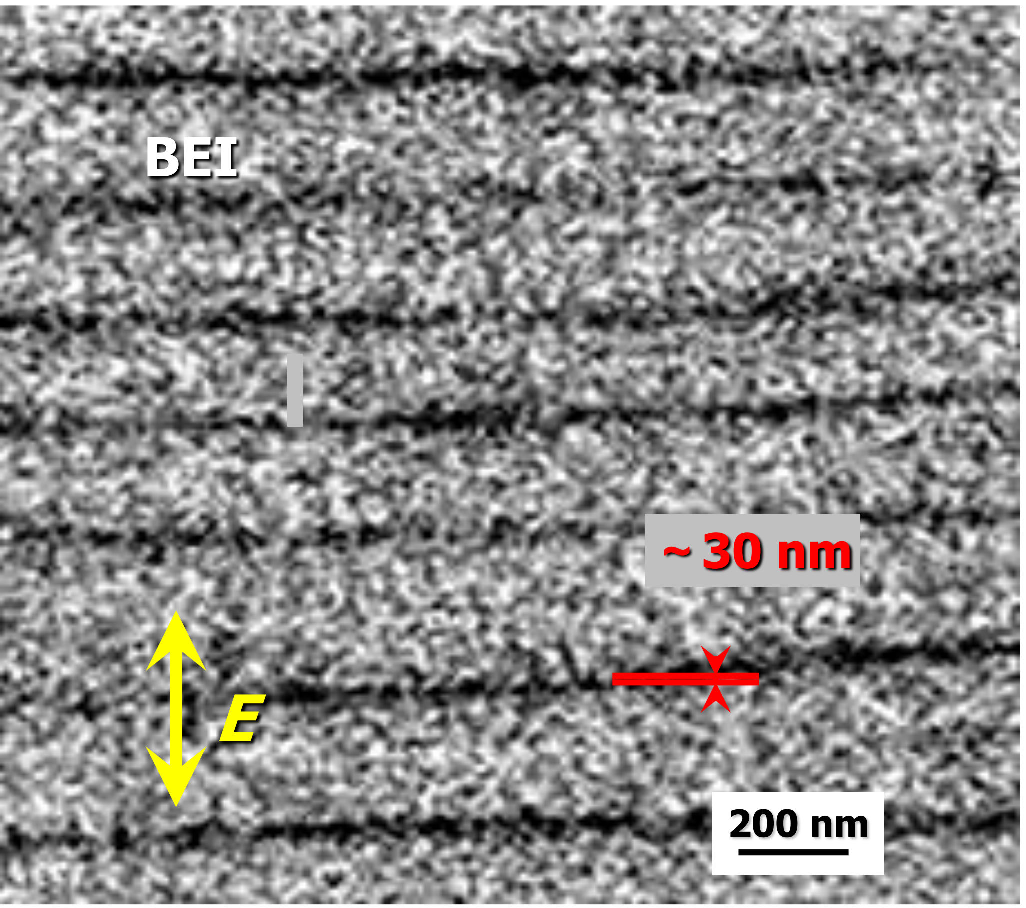


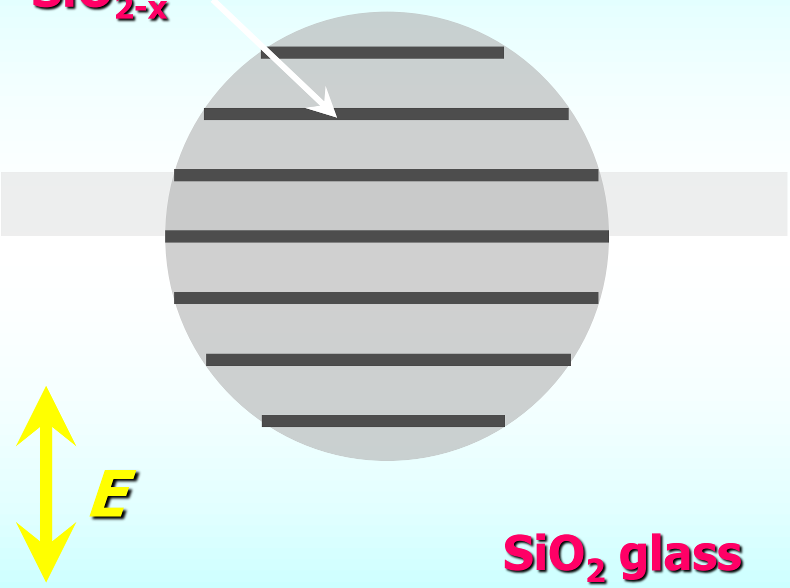
k_w ⊗ E ↕

Oxygen defects concentrate on a center.

Oxygen defects are diffused around.

Periodic nanostructure



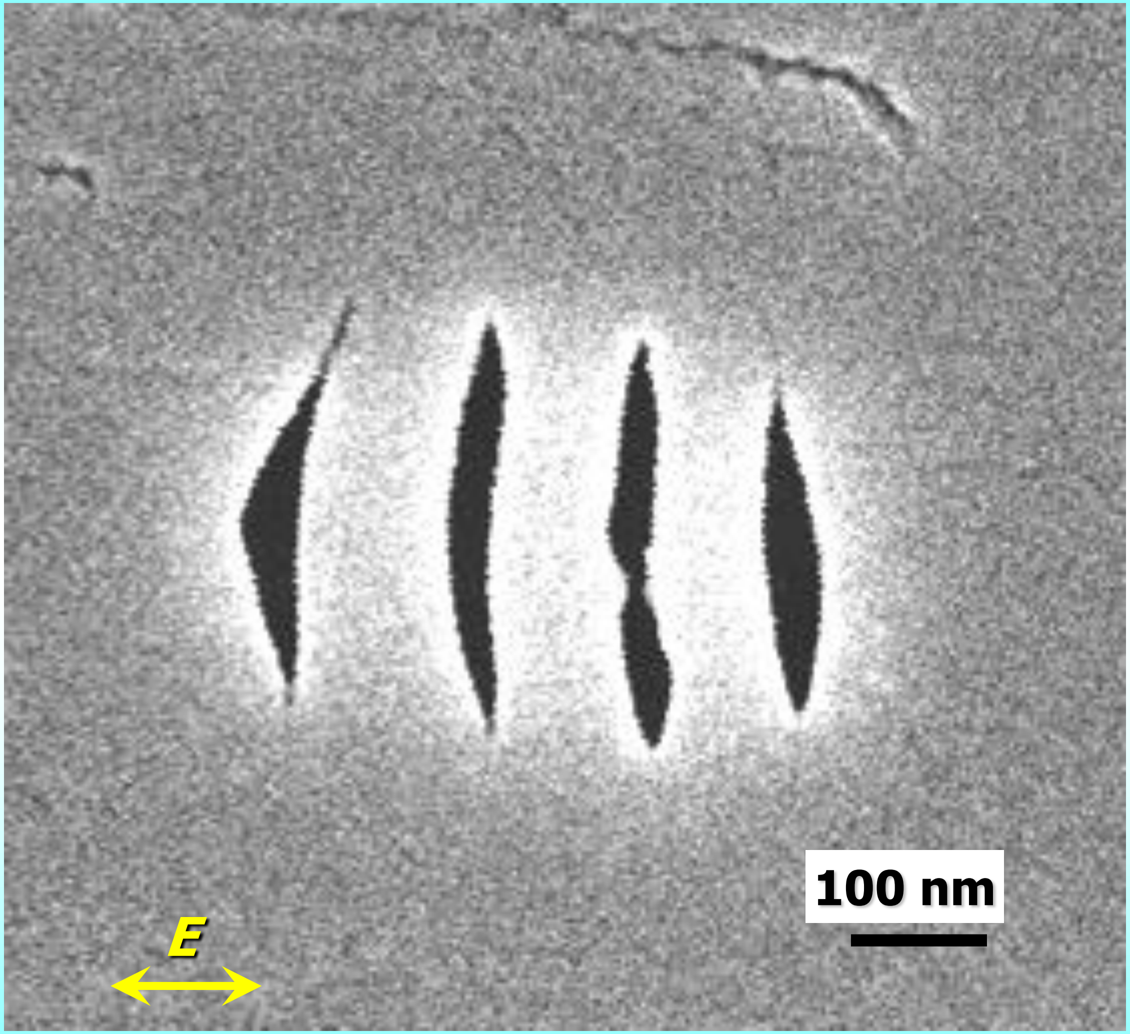


Dark region

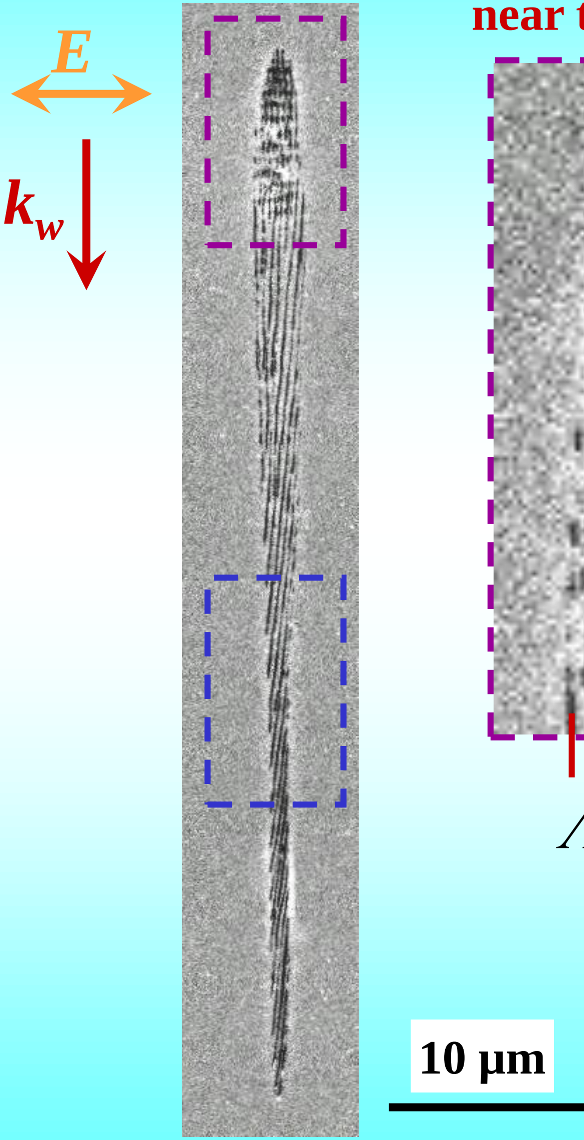
- **Light elements**
  - ► **generation of oxygen defect**
- **Low-density**
  - ► **recombination of Si-O bonds**

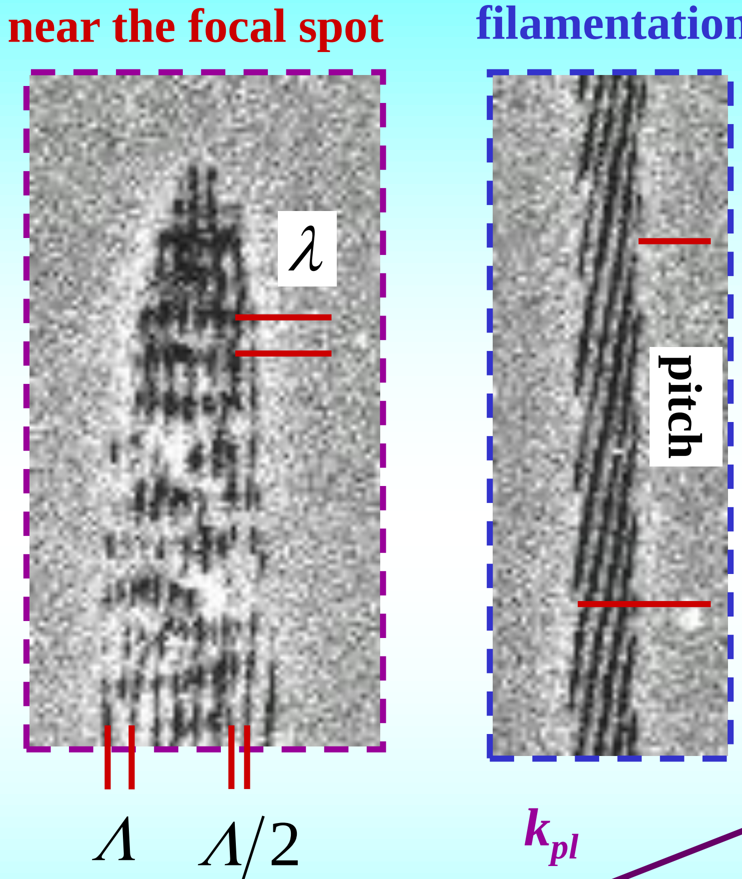
Periodic modulation of refractive constant

Tellurite glass



Cross section of nanograting





Λ	~ 330 nm
$\Lambda/2$	~ 165 nm
λ	~ 600 nm (= λ_0/n)
pitch	~ 10 μm

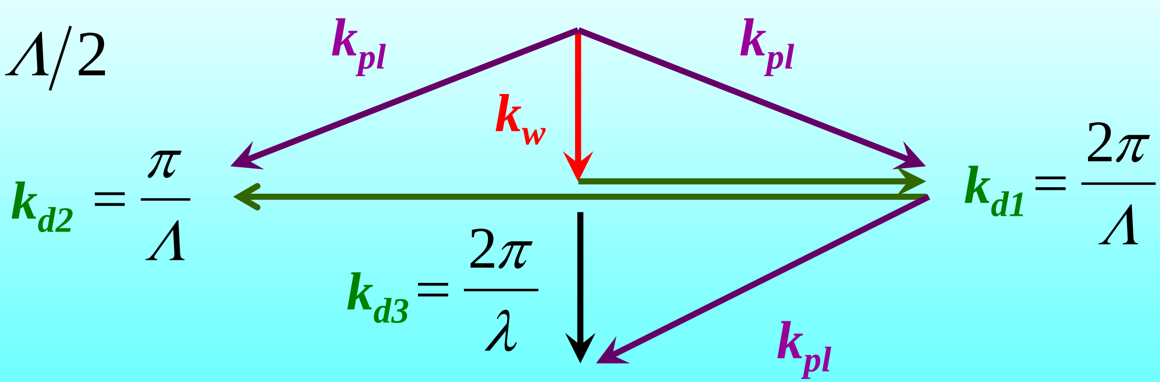


Photo-oxidation of transition metal ion

Mn^{2+}, Fe^{3+} co-doped silicate glass

Electron trapping center

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

Hole trapping center

$$Mn^{2+} + h^+ \rightarrow Mn^{3+}$$

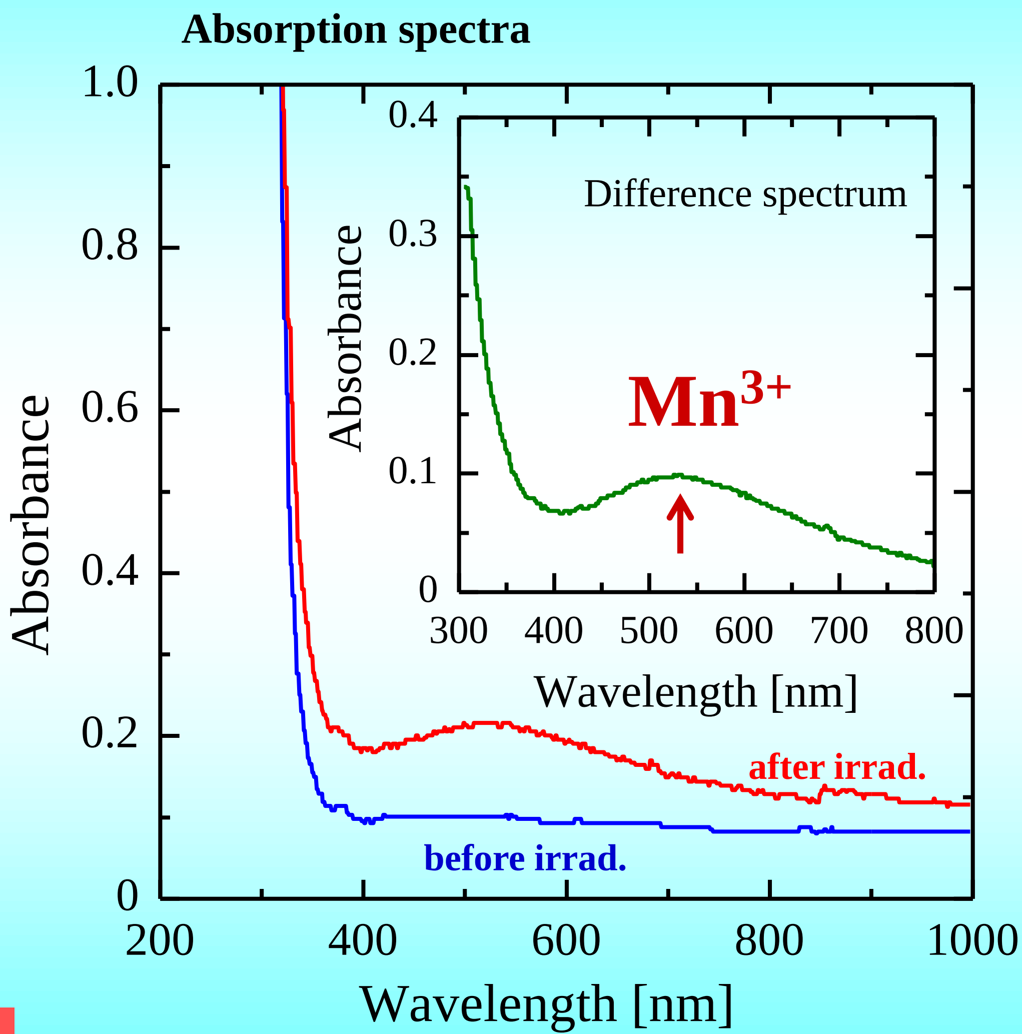


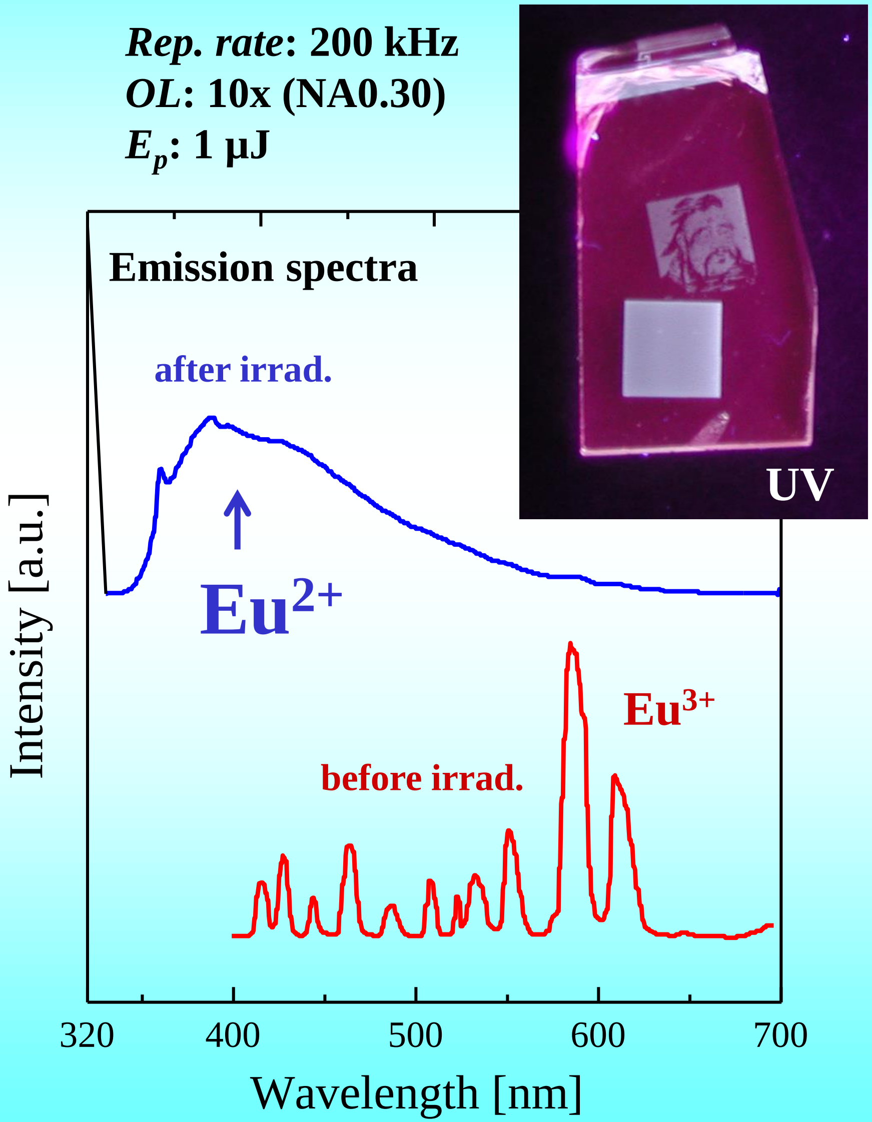
Photo-reduction of Eu^{3+} ion

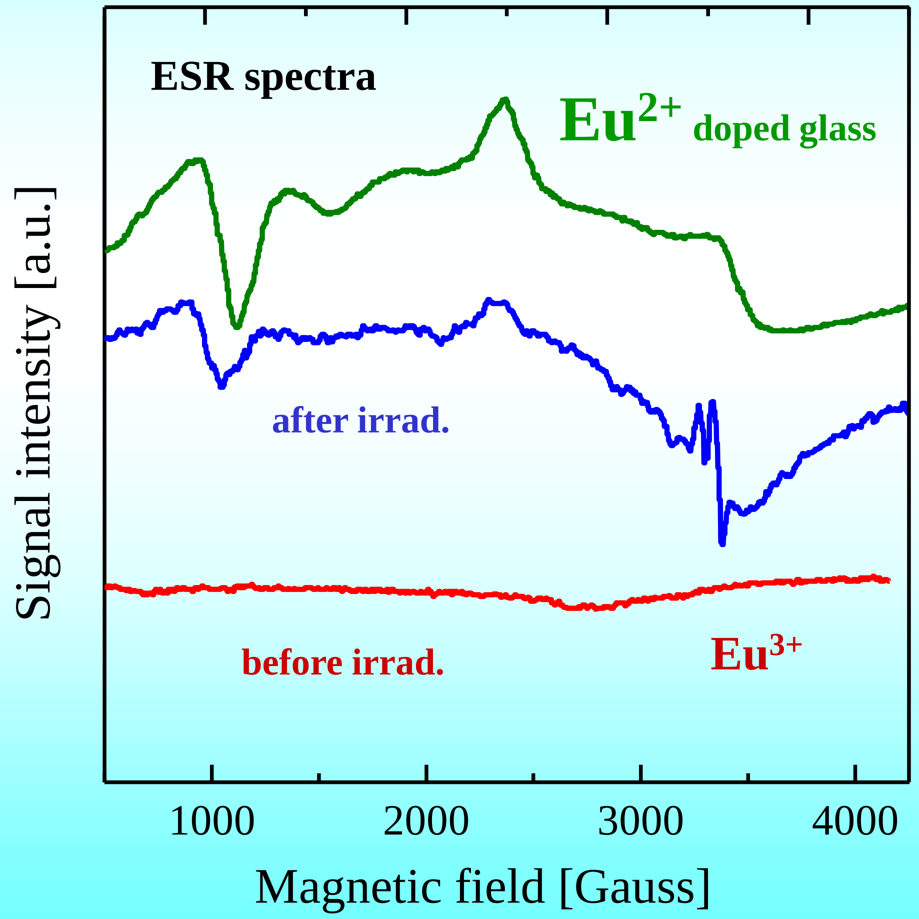
Eu^{3+} doped fluorozirconate glass

***Rep. rate*: 200 kHz**
***OL*: 10x (NA0.30)**
E_p: 1 μJ

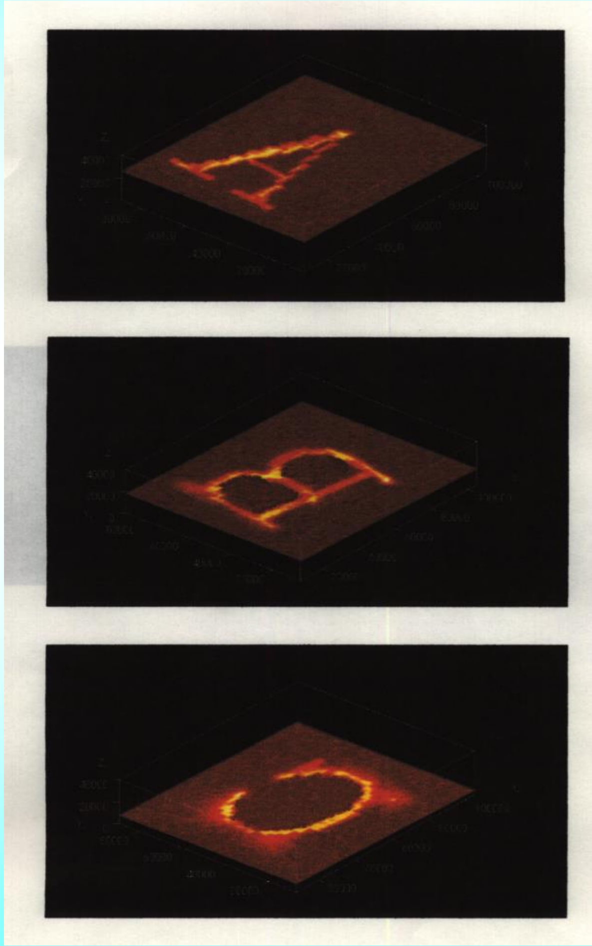
Eu^{3+} → Eu^{2+}

Red emission **Blue emission**

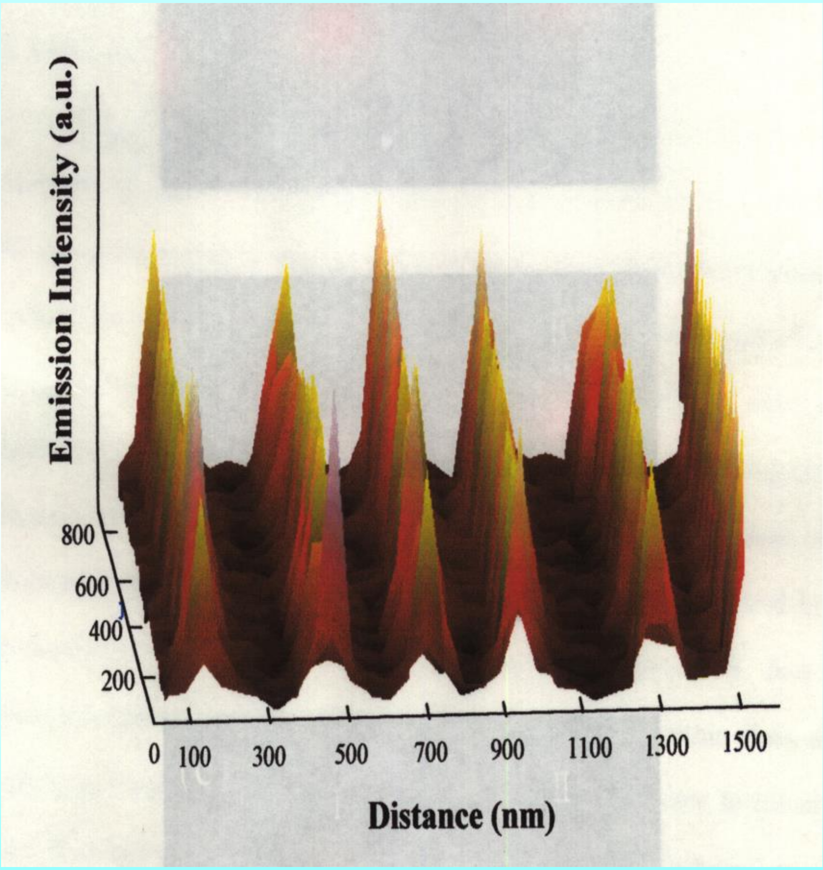




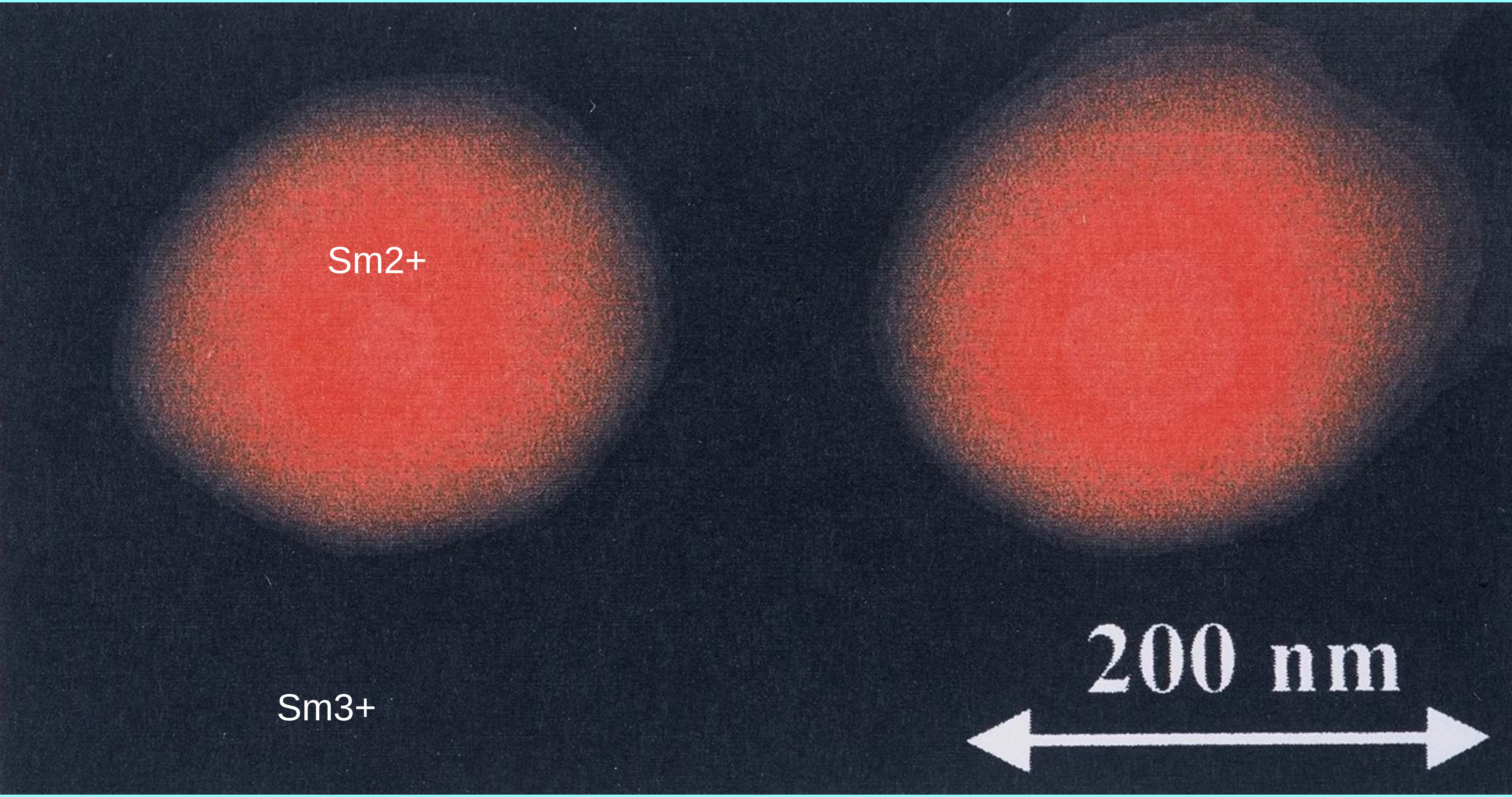
3D memory using valence state change of Sm ion



Three layers spaced 2μm

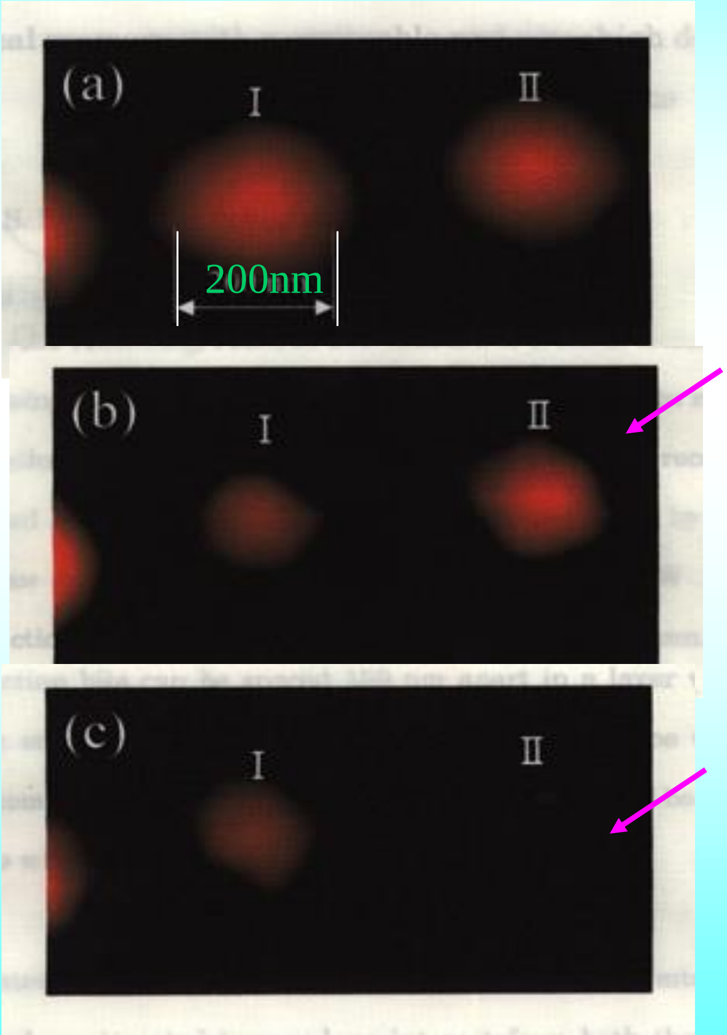


Recorded by fs laser read out by
488 nm Ar^+ laser ff transition of Sm^{2+} at 682nm



at the focal point

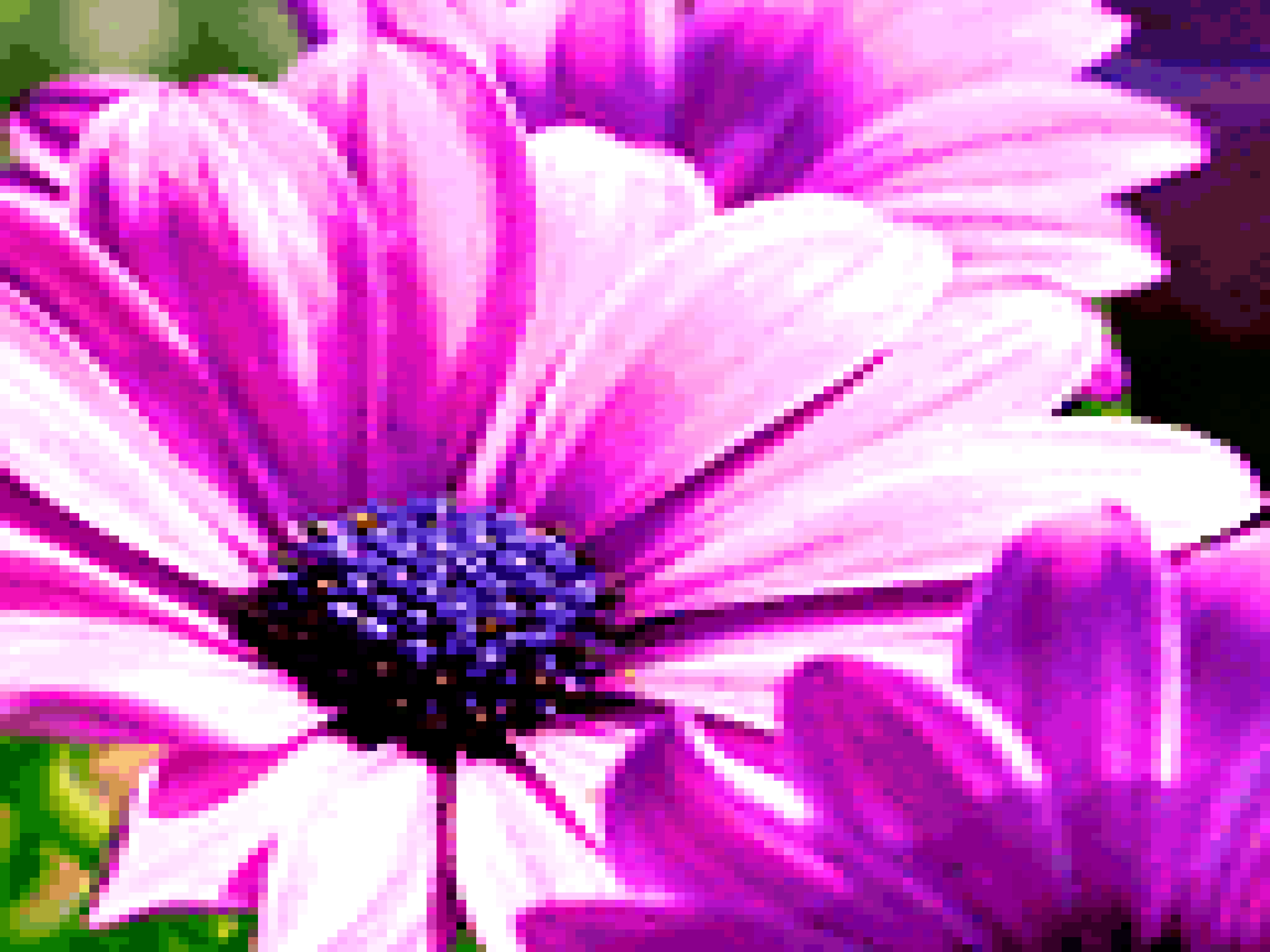
Rewritable 3D optical memory



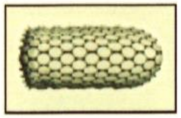
Appl. Phys. Lett., 80(2002)2263.

fs
488nm Ar^{+}

fs + 514nmAr^{+}
488nm Ar^{+}



materials update

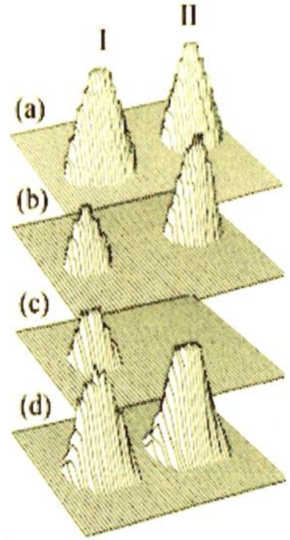


In brief: Writing memories

Three-dimensional memories offer t but creating a rewritable 3D memor researchers have developed an all-o Tbit cm^{-3}.

11 April 2002

Jonathan Dawid



Distributions of photoluminescence intensity, showing selective erasure and rewriting of two neighbouring bits spaced

and are distinguished by their different photoluminescence spectra. This combination of properties allowed the authors to develop an all-optical memory device in which bits are represented by the ionic valence state. Femtosecond laser pulses are used to 'write' bits by photoreducing Sm^{3+} to Sm^{2+}, whereas to 'erase' the bit, the ions are photo-oxidized back to the 3+ state with a continuous-wave laser. Read-out is achieved using a weaker laser to excite a photoluminescence peak of the Sm^{2+} species that is completely absent in Sm^{3+}, giving excellent signal-to-noise characteristics and allowing bits to be packed very close together. Crucially, the physical independence of neighbouring bits makes it possible to store information in three dimensions, which the authors demonstrate by recording three separate images on planes spaced 2 μm apart. Because each bit can be made with an in-plane diameter of only 150 nm, this corresponds to an information storage density of 10 Tbit cm^{-3}.

Three-dimensional optical memories, which store data on multiple planes in a transparent medium, offer incredibly high storage capacities – as much as several terabits in a block the size of a sugar cube. (1 Tbit = 10^{12} bit, equivalent to 200 CD-ROMs.) But although several suitable materials have been demonstrated that are suitable for read-only purposes, the ability to selectively erase and rewrite information has proved much harder to achieve. Now, writing in *Applied Physics Letters*, Miura, Qiu, Fujiwara, Sakaguchi and Hirao demonstrate a high-capacity 3D memory that can be written, read, erased and rewritten using all-optical methods.

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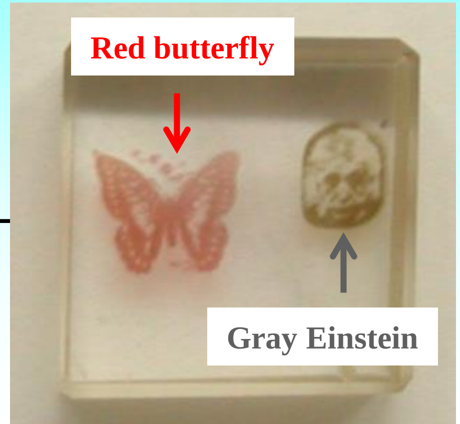
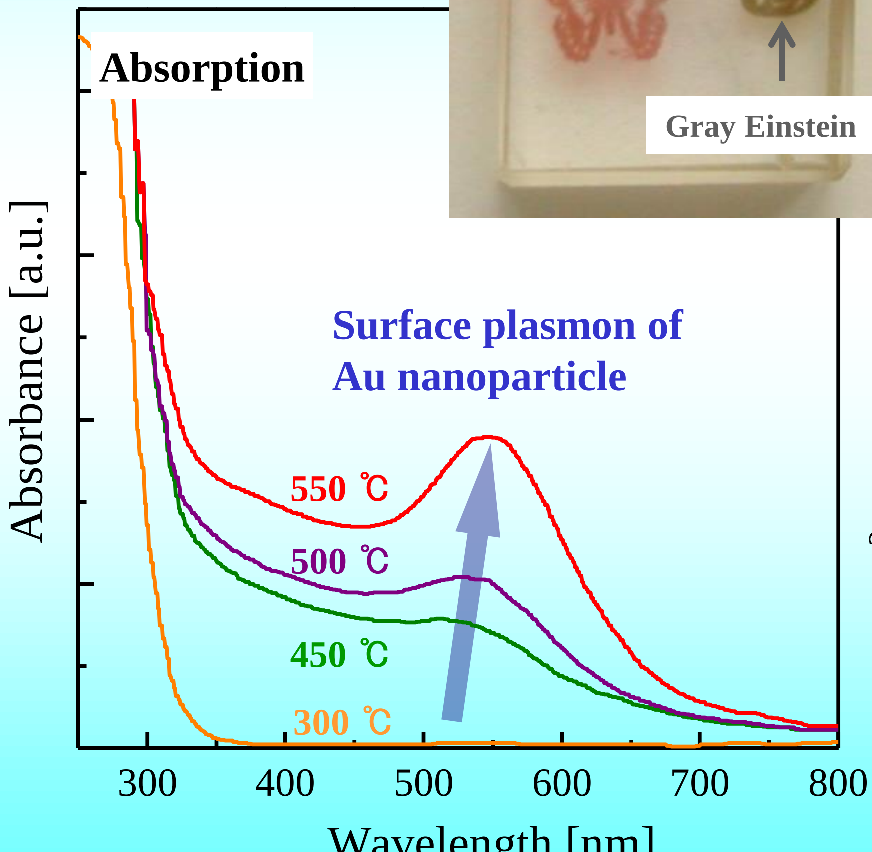
diam can be
ignal

Precipitation of Au nanoparticle

Au^{3+} doped silicate glass

***Rep. rate*: 1 kHz**
***OL*: 10x (NA0.30)**
E_p: 35 μJ



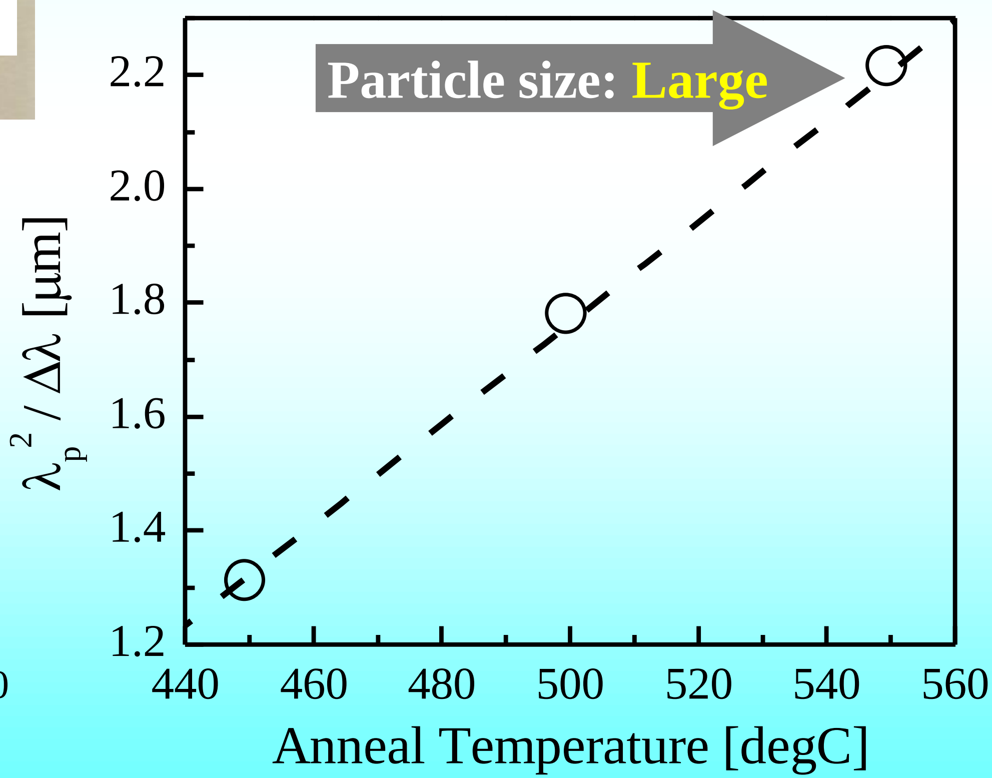


Mie theory

$$R \propto \frac{\lambda_p^2}{\Delta\lambda}$$

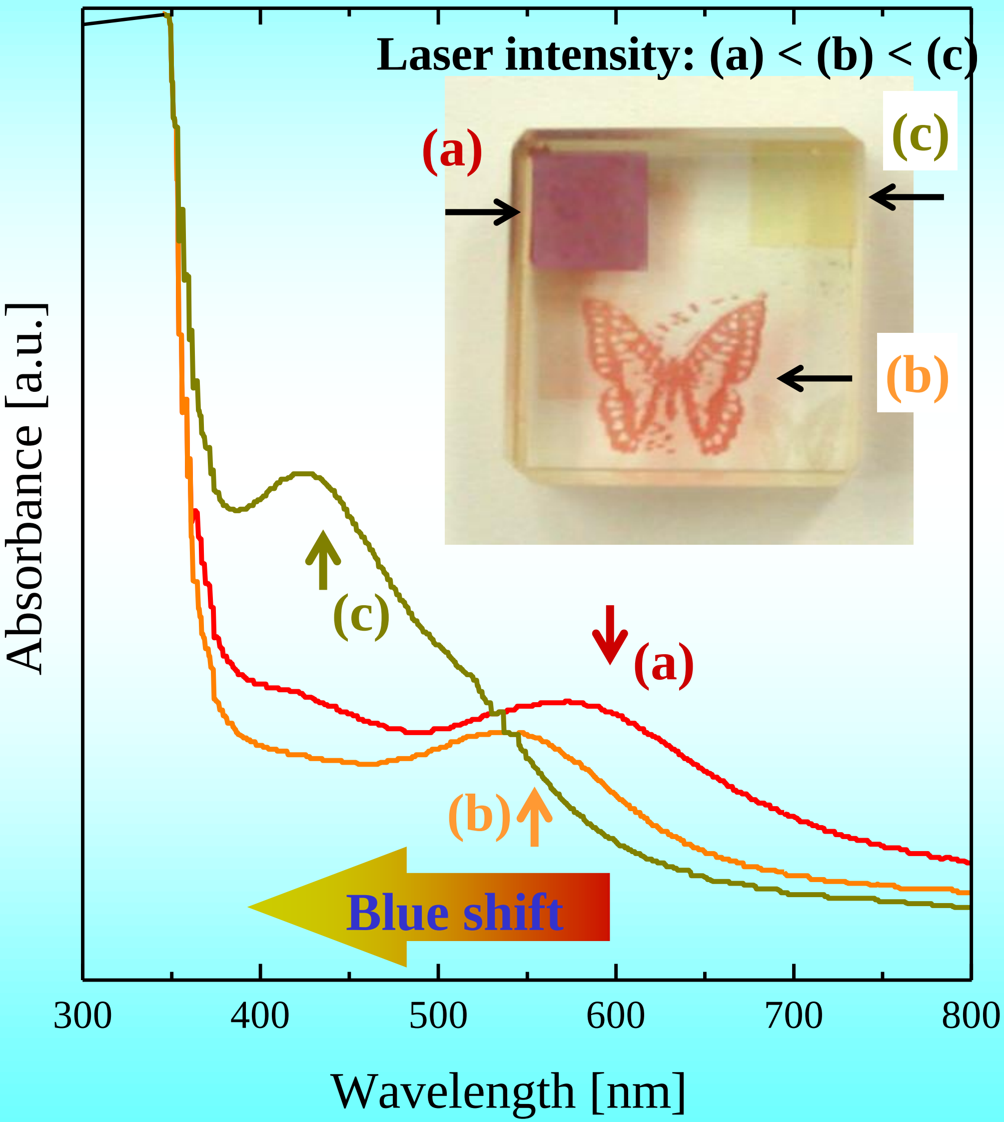
- R **: Particle radius**
- λ_p **: Wavelength of surface plasmon resonant**
- $\Delta\lambda$ **: Absorption band width**

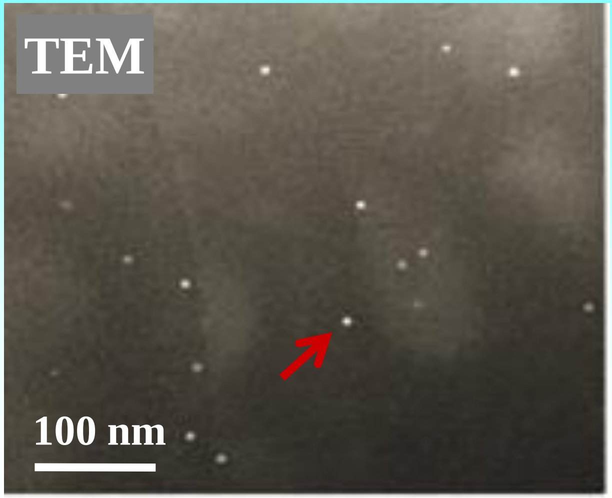
***D. Manikandan, et al.*, Phys. B, 325, 86 (2003).**

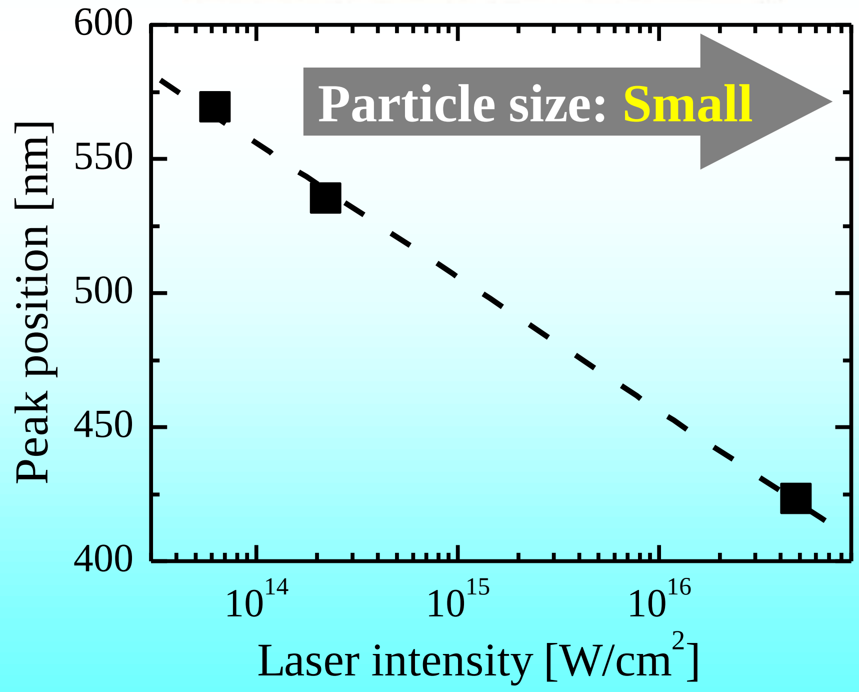


Size control of Au nanoparticle

Au^{3+} doped silicate glass







Faster circuits go for gold: Lasers could build three-dimensional ...

naturejobs graduatechannel

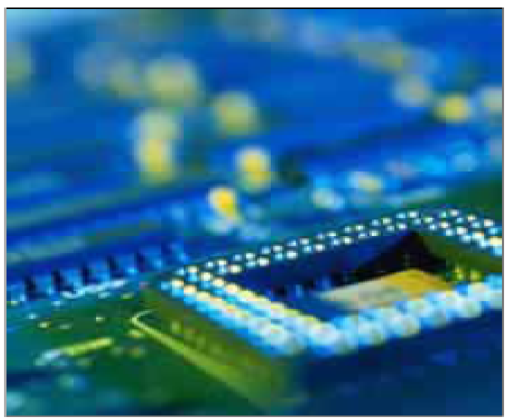
Research Scientist, Laboratory Postdoctoral Fellow...

nature science

Faster circuits go for gold

Mark Peplow

Lasers could build three-dimensional com



Flat circuit boards are running out of room.

© GettyImages

Creating tiny gold blocks of glass mi latest in up-marke design. But the te lead to a new gen electronics.

One route to faste increase the numb between compone But computer chip are fast running o conventional, flat for the next gener only way is up.

"The microelectro two-dimensional at the moment," says Mark M materials scientist from King's College London

naturejobs graduatechannel

Research Scientist, Laboratory Technician, Postdoctoral Fellow...

nature scienceupdate

updated at midnight GMT today is sunday, june 27

Going dotty

Making a three-dimensional circuit is no easy task, however. At the moment, chip designers build them layer by layer, but this is a laborious process and it limits the designs that can be used. Now Jianrong Qiu, a physicist at the Shanghai Institute of Optics and Fine Mechanics, and colleagues from China and Japan have worked out a way to draw the desired circuit directly into a block of glass.

Three dimensions means faster chips and more memory.

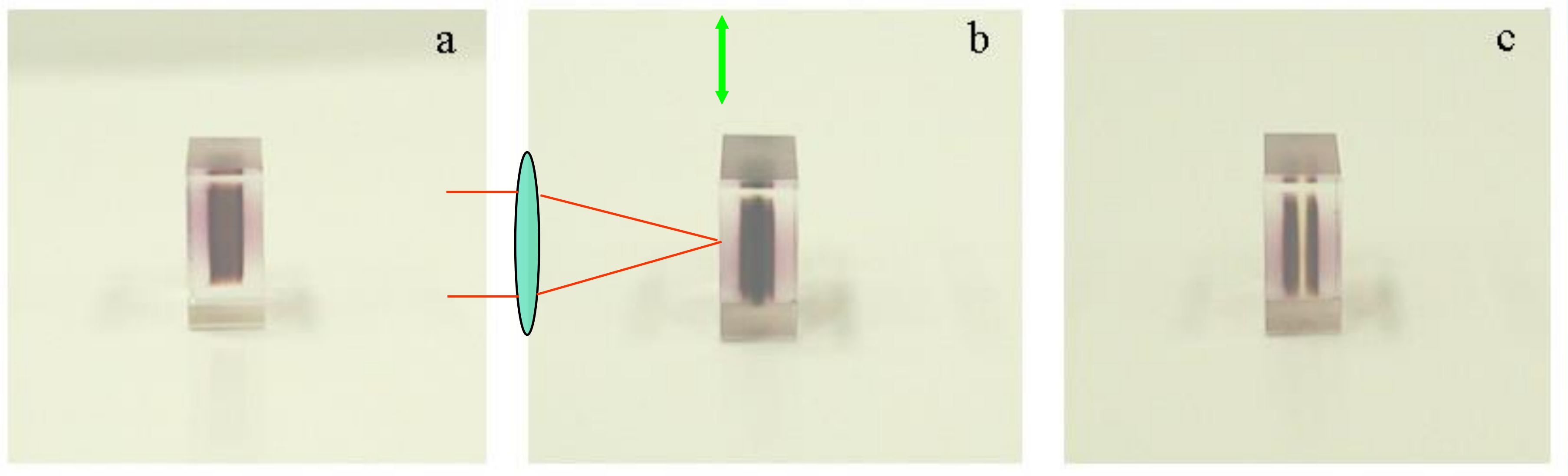
© Angewandte Chemie

Sofar the researchers have used the technique to create three-dimensional images in the glass, such as the butterfly shown here. The 5-millimetre-wide image is made from millions of tiny balls of gold, each about seven nanometres across, which is roughly 10,000 times thinner than a human hair. The researchers report their results in the latest edition of the chemistry journal *Angewandte Chemie*[1].

It is even possible to erase structures after they have been created by using a second set of laser pulses to blast the golden globules apart.

3D colored engrave

Space-selective dissolution of Au nanoparticles



a: before second laser irradiation

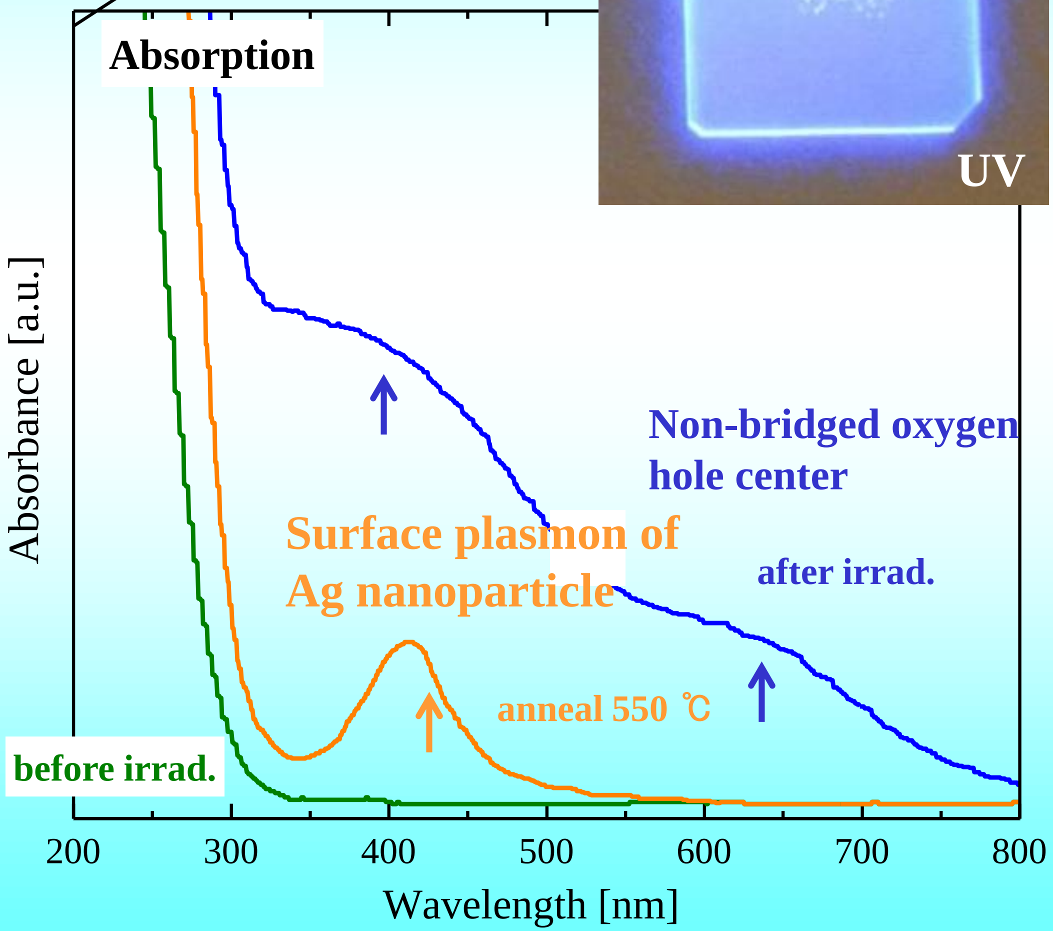
b: after second laser irradiation

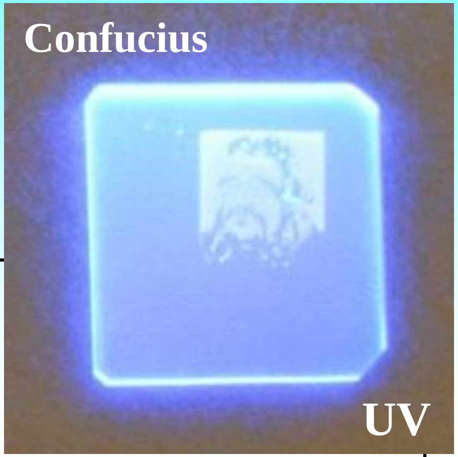
c: after second laser irradiation and annealing at 300℃ for 30min

Precipitation of Ag nanoparticle

Ag^+ doped silicate glass

***Rep. rate*: 1 kHz**
***OL*: 10x (NA0.30)**
E_p: 0.8 μJ

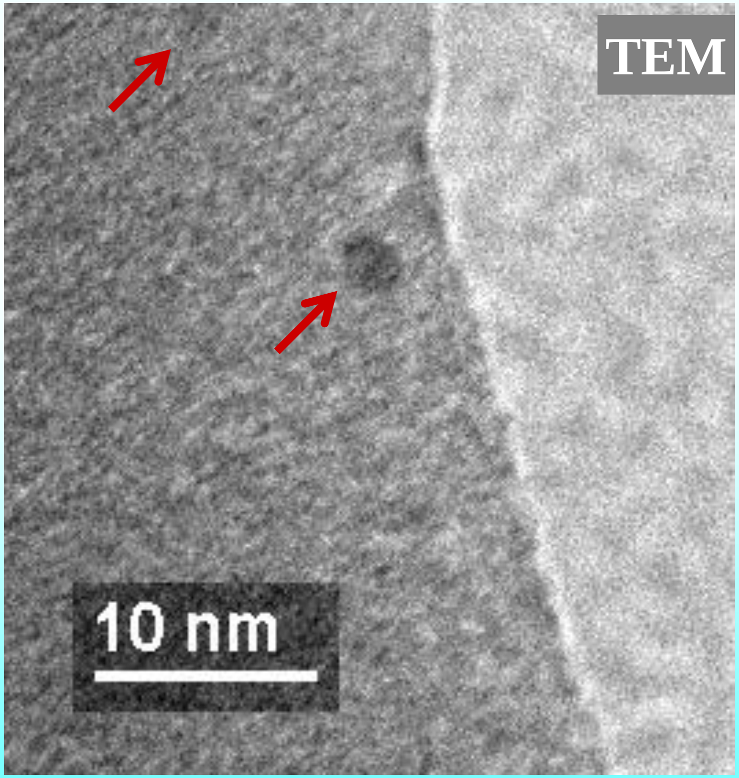




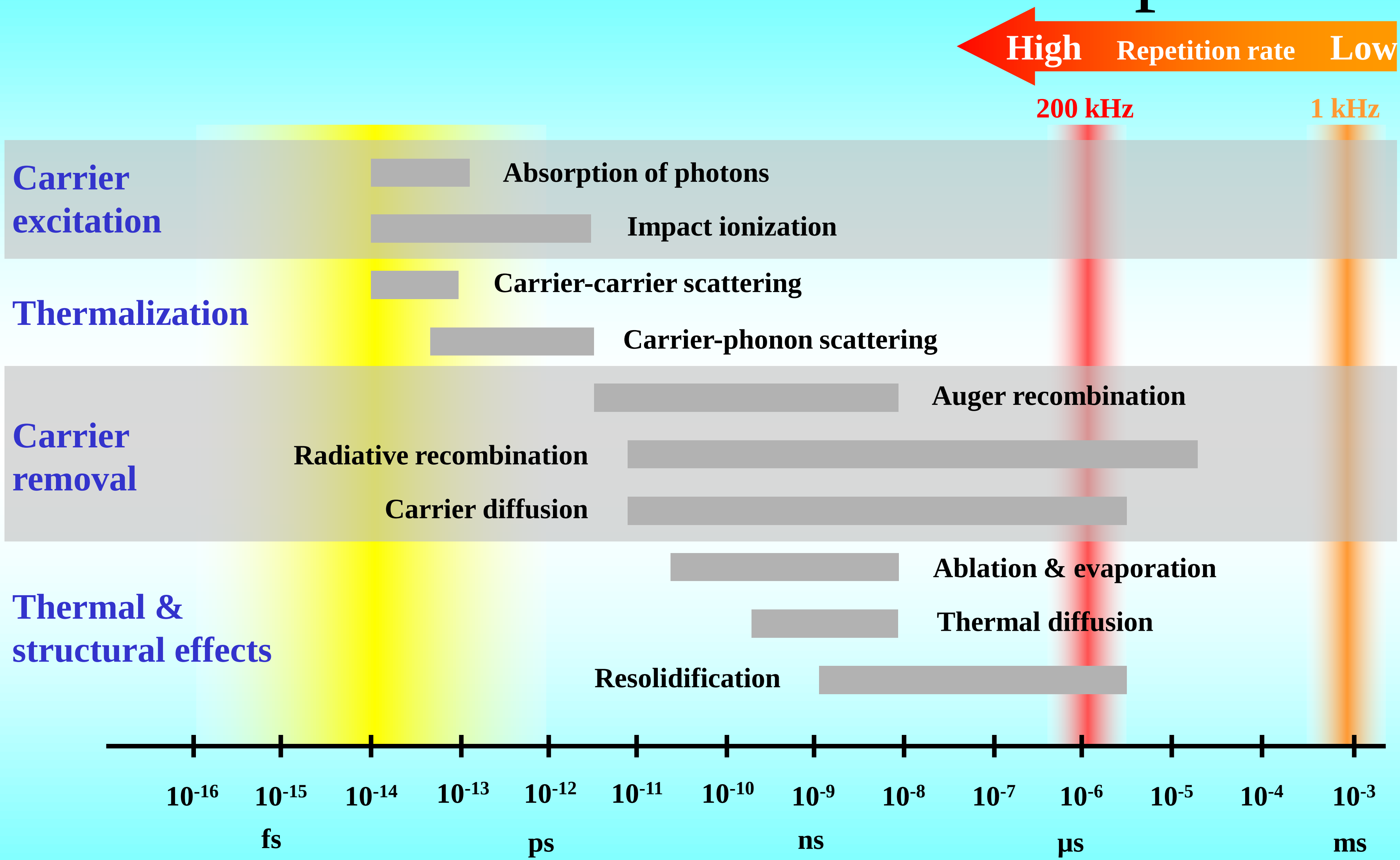
$$\text{matrix} \xrightarrow{nh\nu} h^+ + e^-$$

$$2Ag^+ + e^- \xrightarrow{kT} Ag^0$$

Blue **Orange**



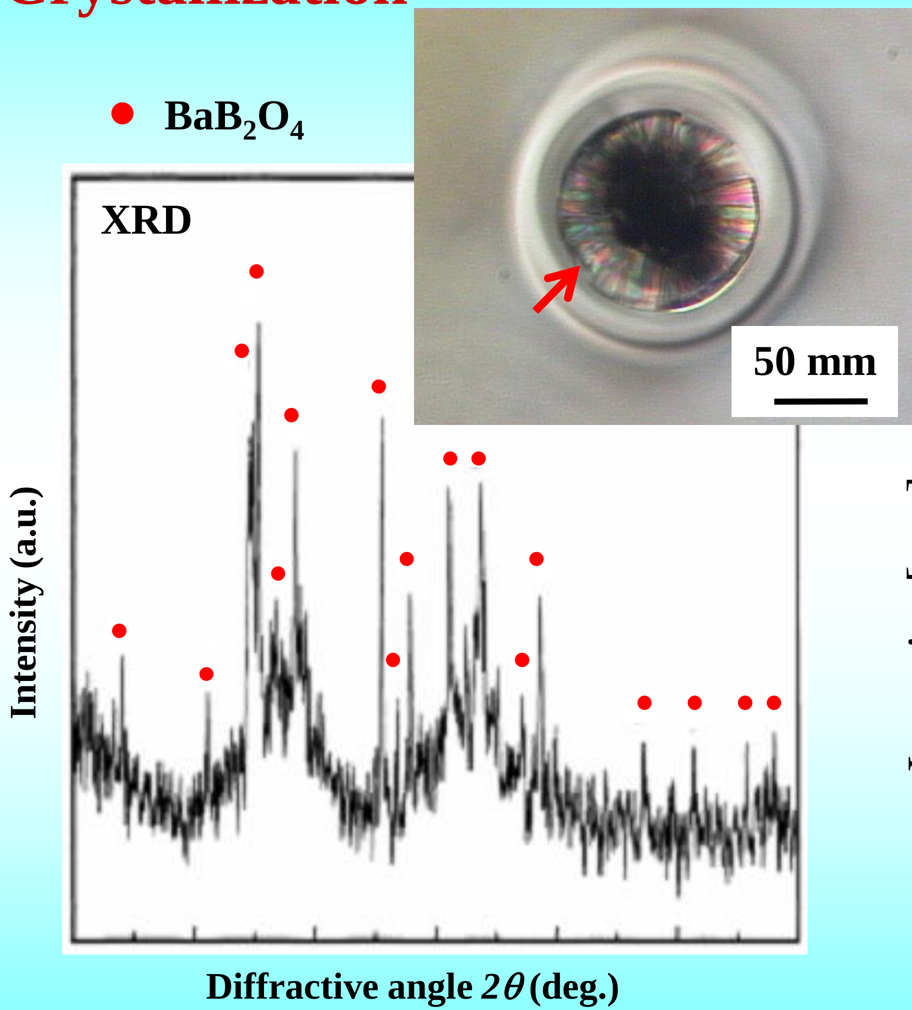
Timescales of electron & lattice process



S. K. Sundaram, et al., Nature materials, 1, 217 (2002).

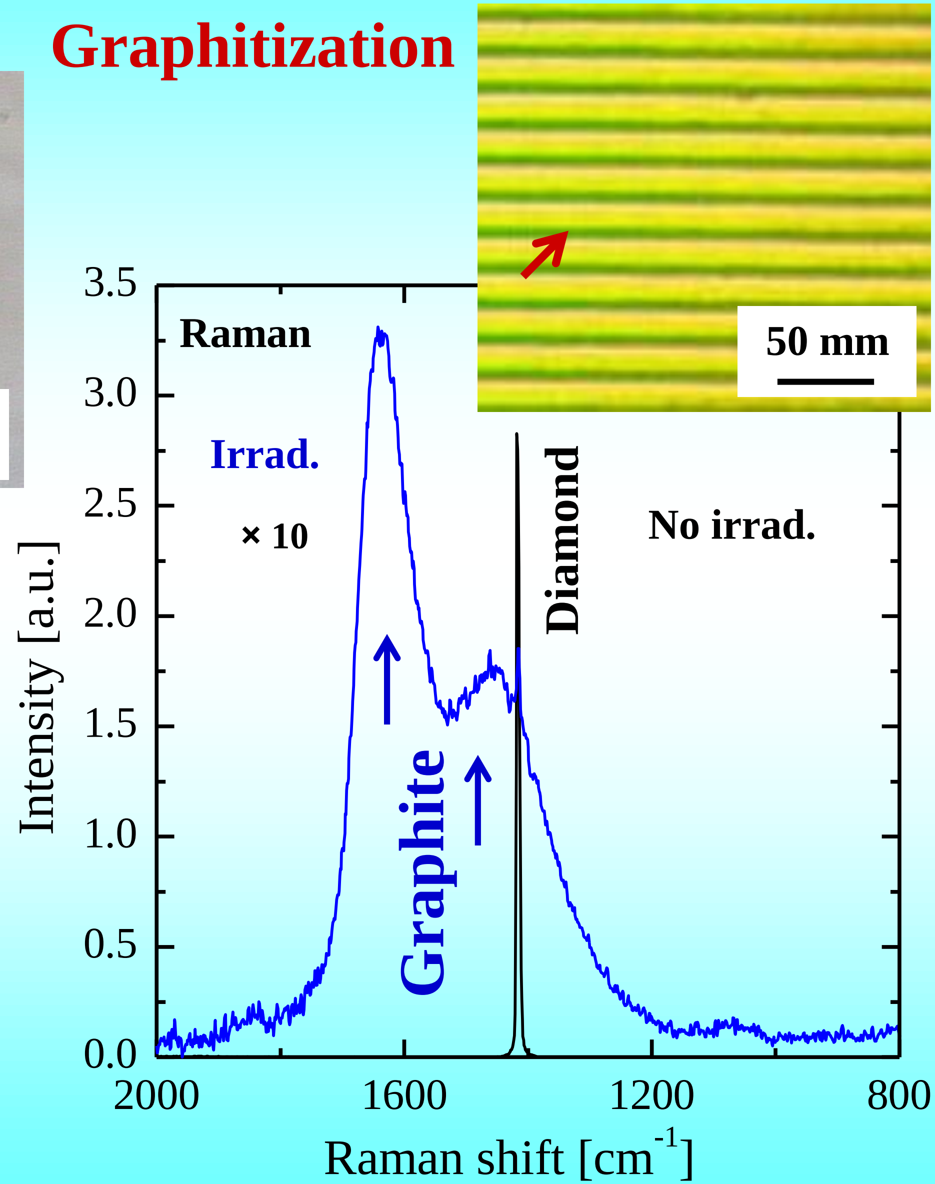
Crystallization & Graphitization

Crystallization



K. Miura et al., OL, 25, 408 (2000).

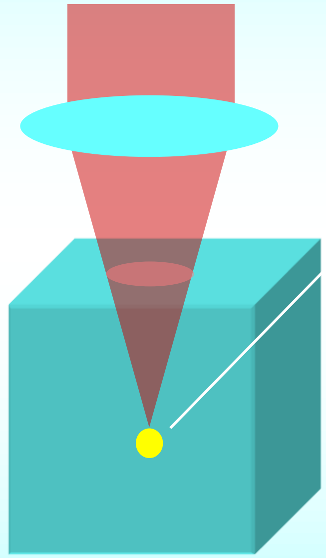
Graphitization



Precipitation of functional crystal

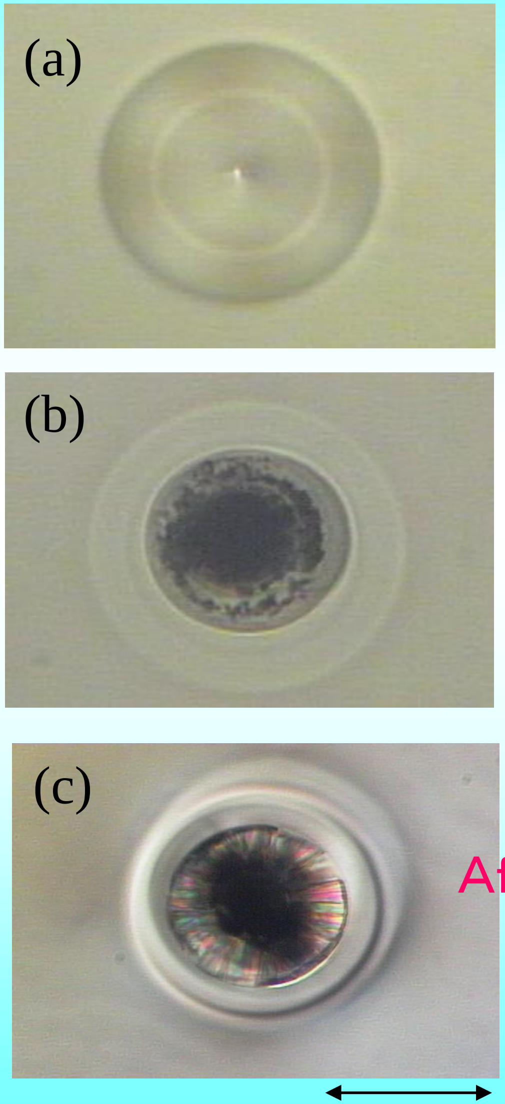
***Opt. Lett.*, 25(2000)408.**

Laser beam



BaO-Al_2O_3-B_2O_3 glass

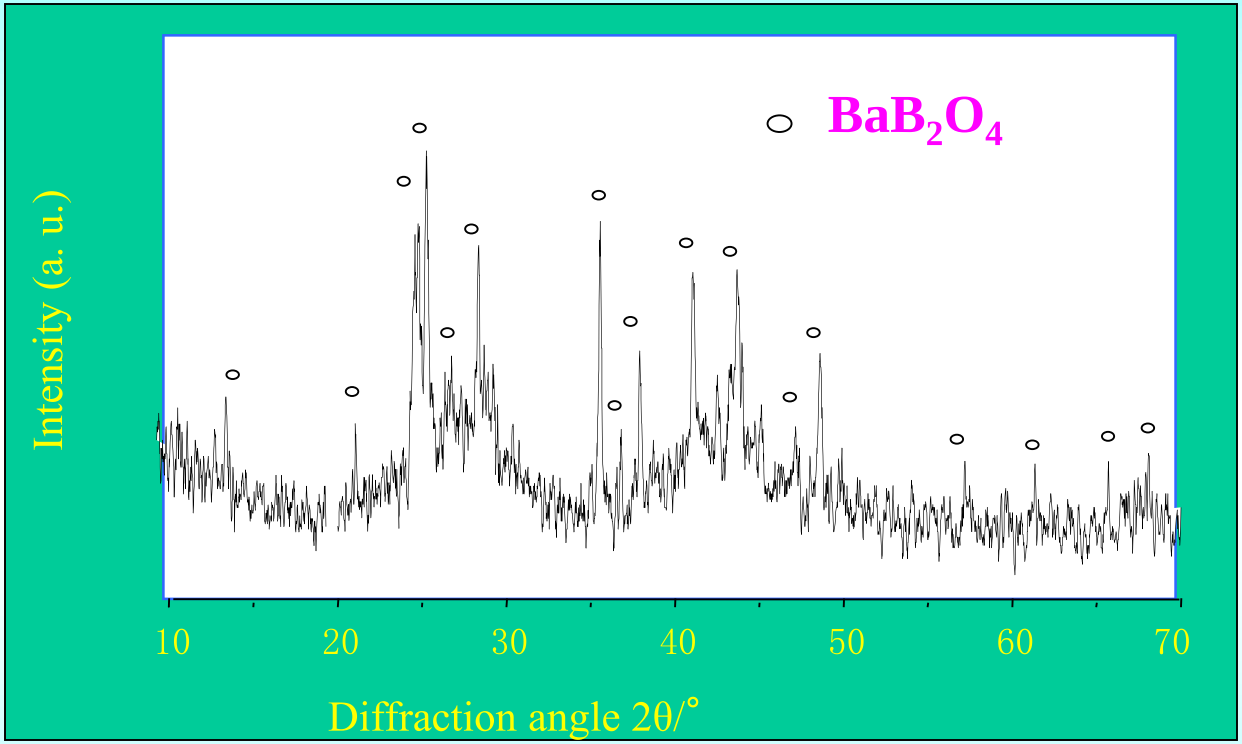
200KHz, 150fs, 800nm
100mW, 50X



After 30min

100μm

Precipitation of functional crystal



XRD pattern

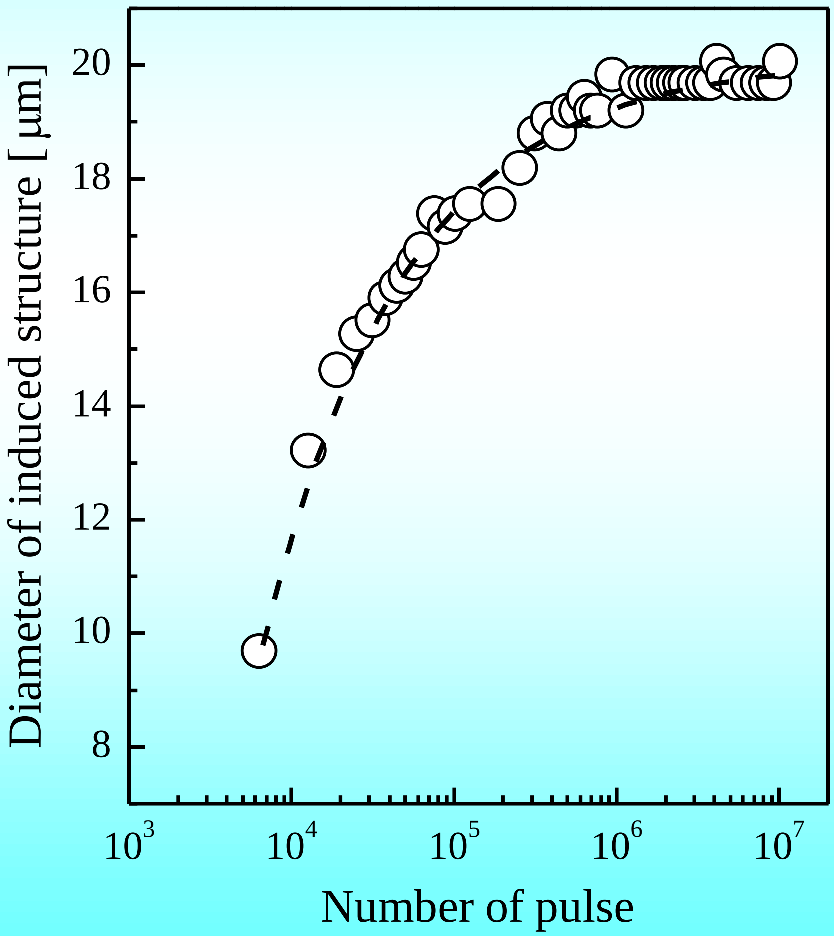
Single BBO4 crystal fiber

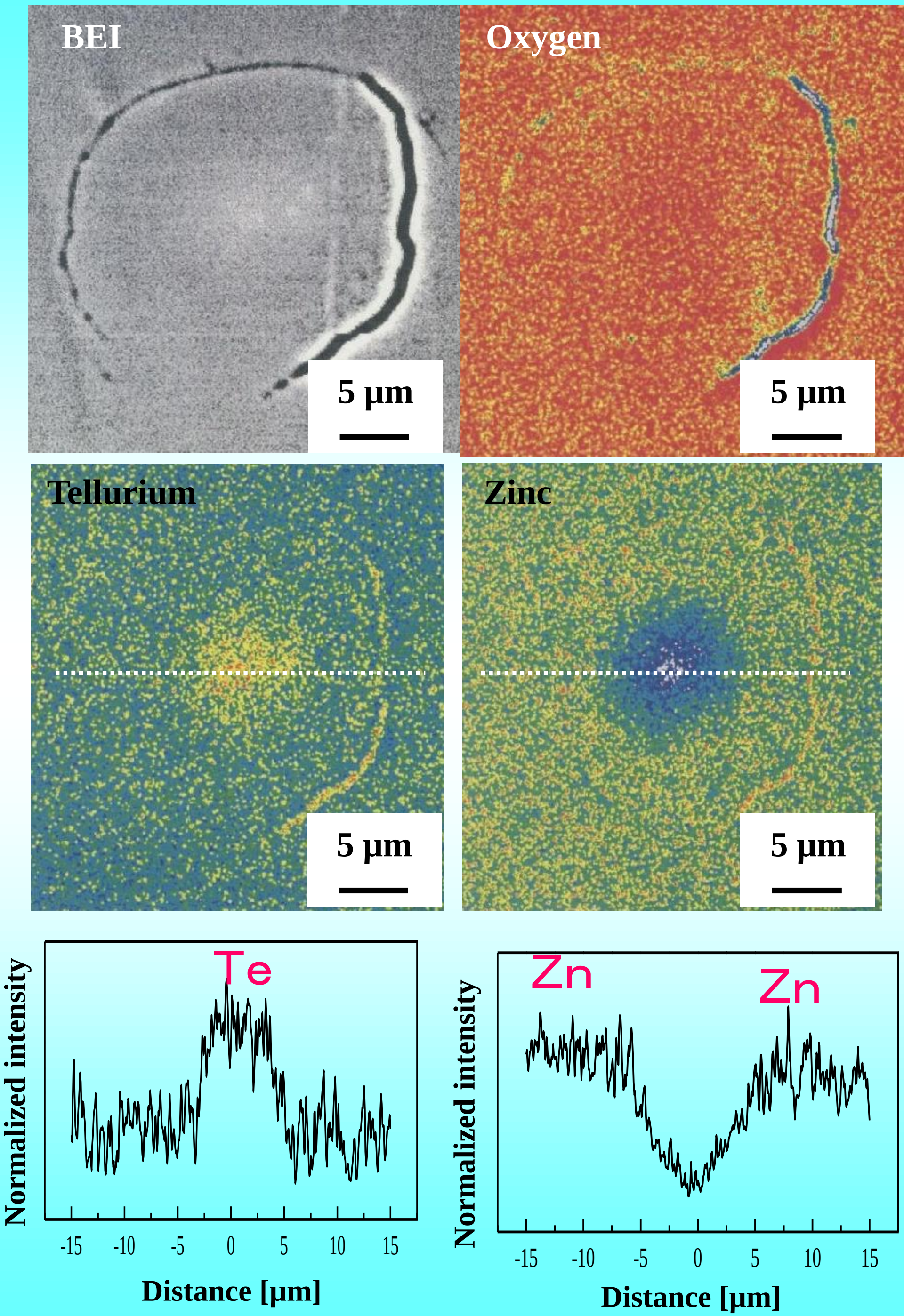
Phase separation of Zinc tellurite Glass

***Rep. rate*: 200 kHz**

***OL*: 100x (NA0.95)**

E_p: 1 μJ





Summary

1. Introduction of a femtosecond pulse laser

2. Various microscopic modifications using femtosecond pulse laser

a) Color-center engineering in glasses

b) Densification and refractive index change in glasses

c) Valence state manipulation of active ions doped glasses

d) Space selective precipitation of crystals inside glasses

e) Coherent field-induced nanosilicon from SiO_2 glasses and nano-grating for optical devices

f) Nanofilter inside glasses

Acknowledgement

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(Active Glass Project and Photon Craft Project, JST, Japan)

Prof. P. Kazansky **(Southampton Univ., UK)**

Dr. N. Jiang **(Arizona State Univ., USA)**

kind cooperation

and helpful discussion