

# **Modification of Glass by FS Laser for Optical/Memory Applications**

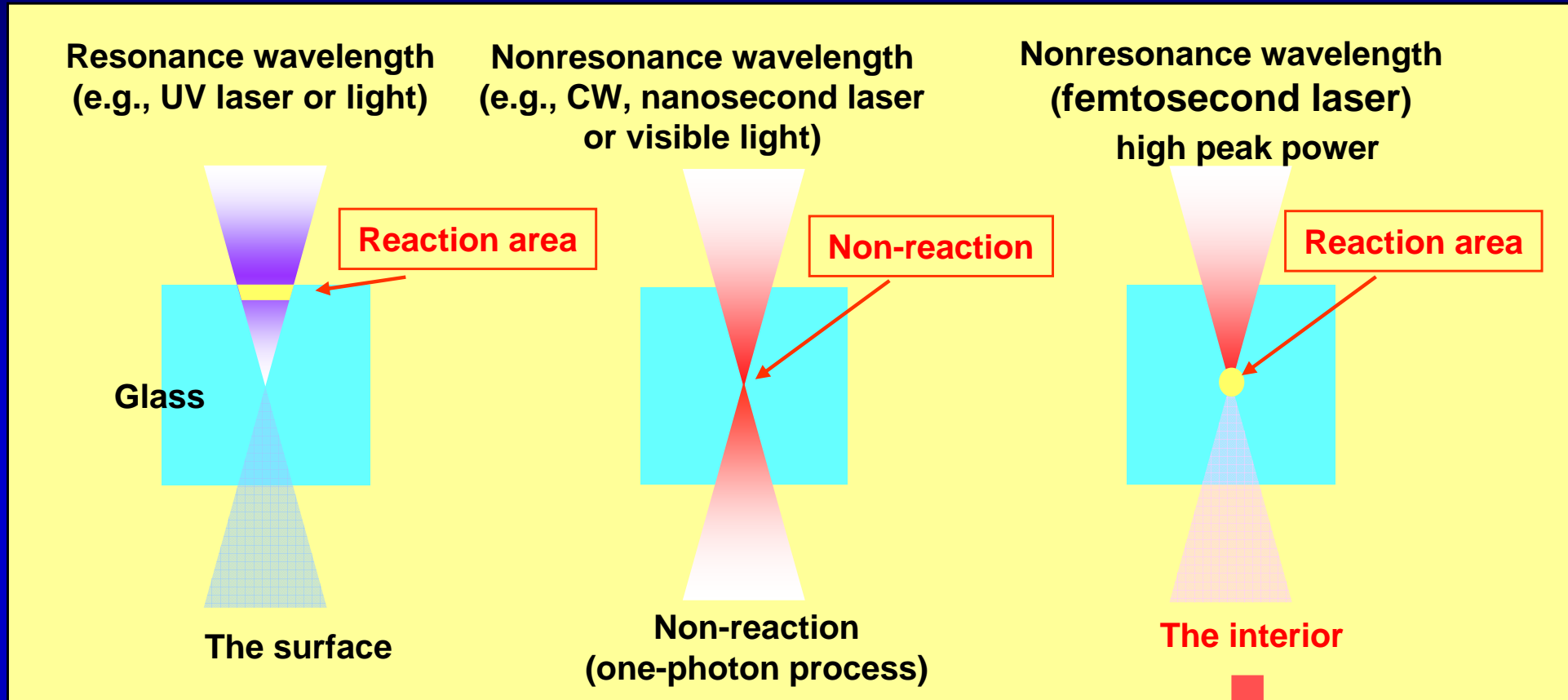
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  - Writing of nano-grating
  - Growth of non-linear optical crystal
- **Precipitation and growth of silicon in the glass**

# Interaction effect between glass and laser

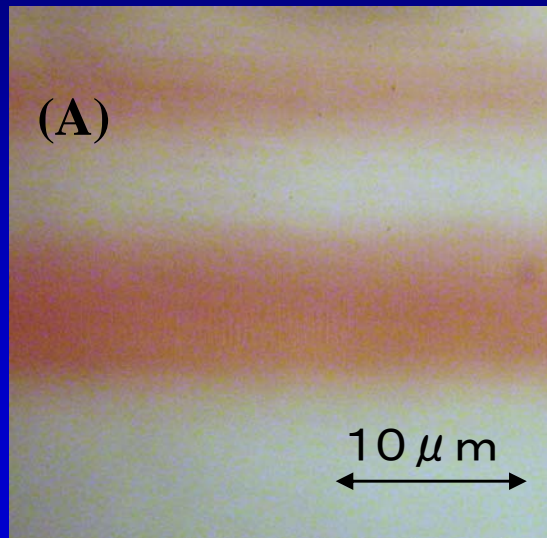


When a transparent material like glass is irradiated by a tightly focused femtosecond laser, photo-induced reactions should occur only near the focused part of the laser beam.

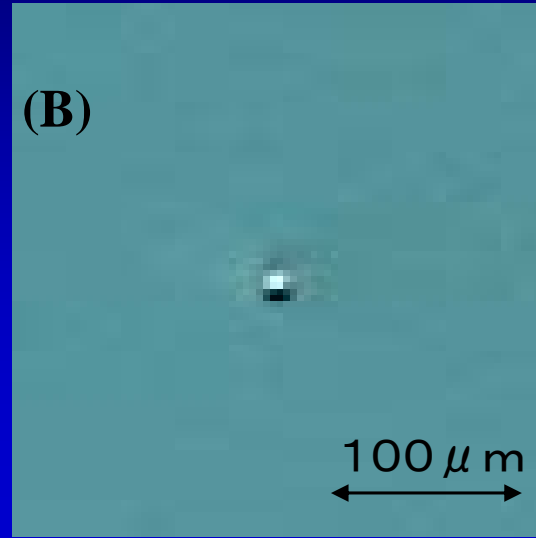
**Femtosecond laser can be used to modify transparent materials like glass microscopically and three-dimensionally.**

# Typical structural changes

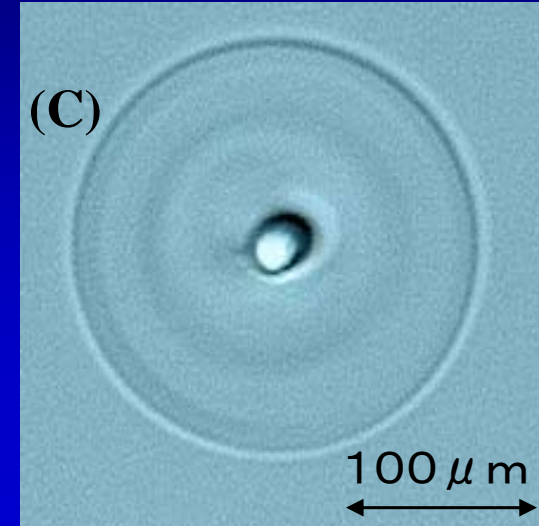
alkali silicate glass



(A) 0.5  $\mu\text{J}$ , f 300, 1 kHz



(B) 1  $\mu\text{J}$ , x 50, single pulse



(C) 3  $\mu\text{J}$ , x 50, 200 kHz

Low

Energy density

High

(A) Coloring line due to defect formation

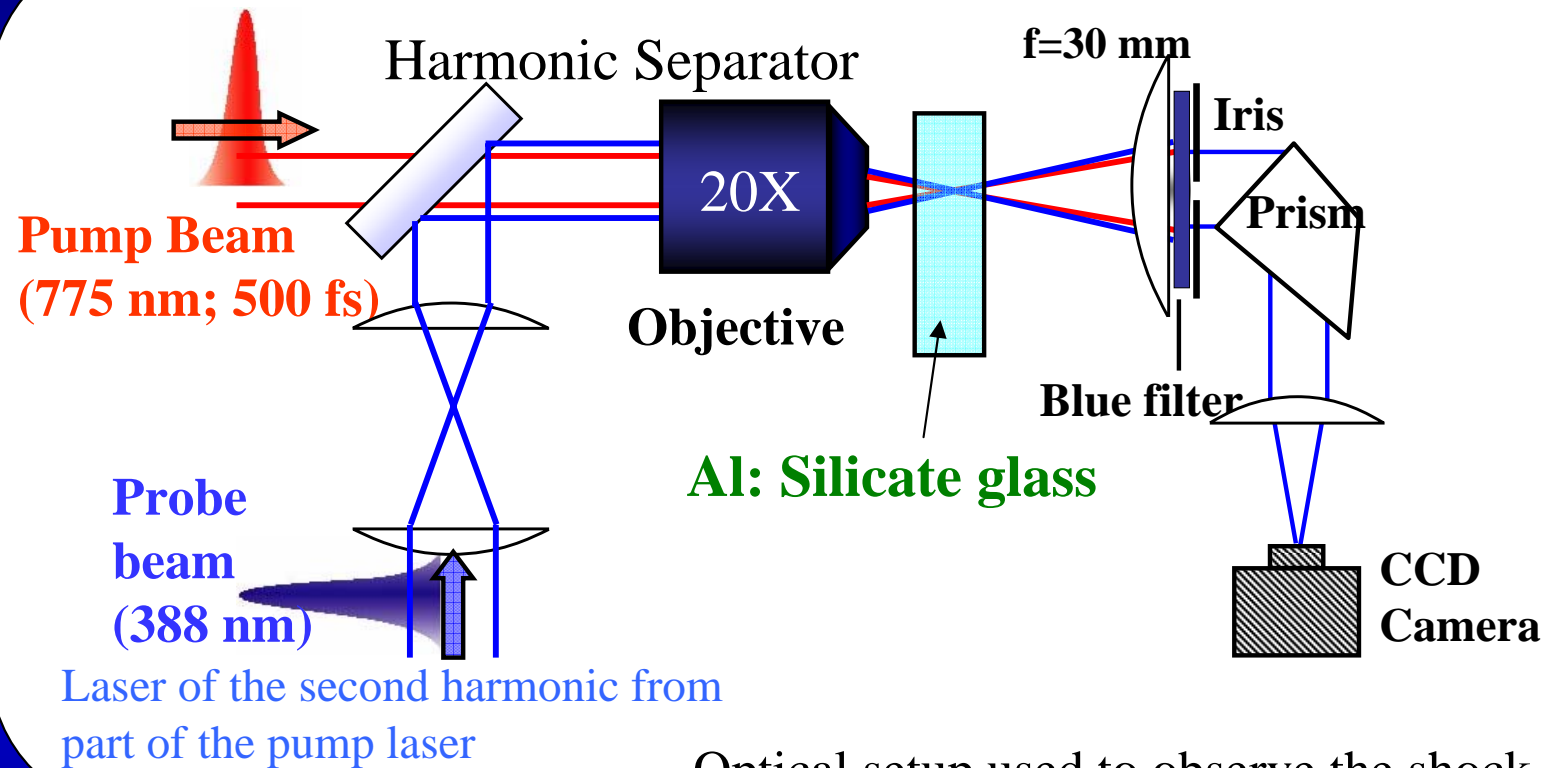
(B) Refractive index changes due to local densification by a single pulse

(C) Melting due to heat accumulation

• The structural changes induced by a femtosecond laser take various forms depending on the condition of laser irradiation.

# Characteristics of the femtosecond laser

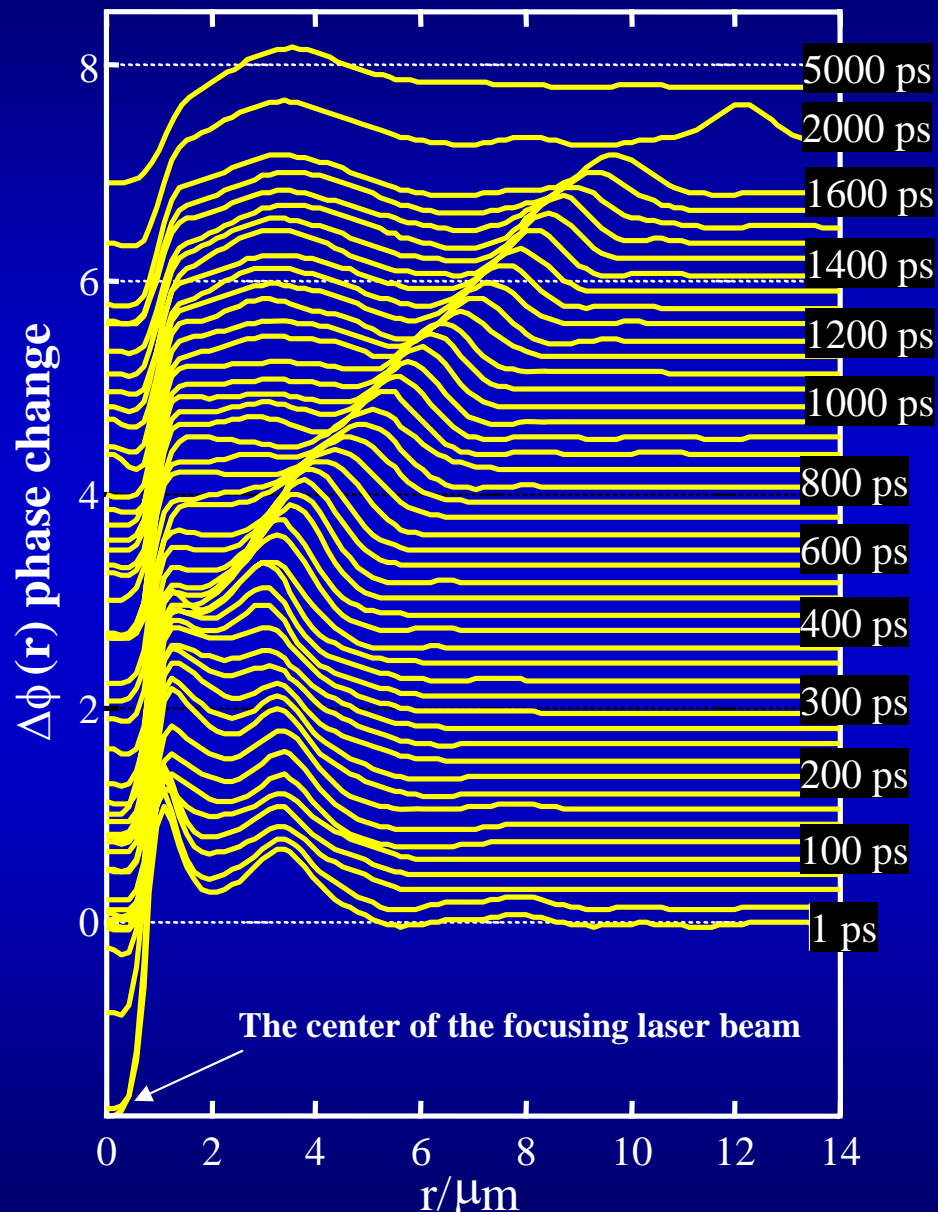
## Transient lens method



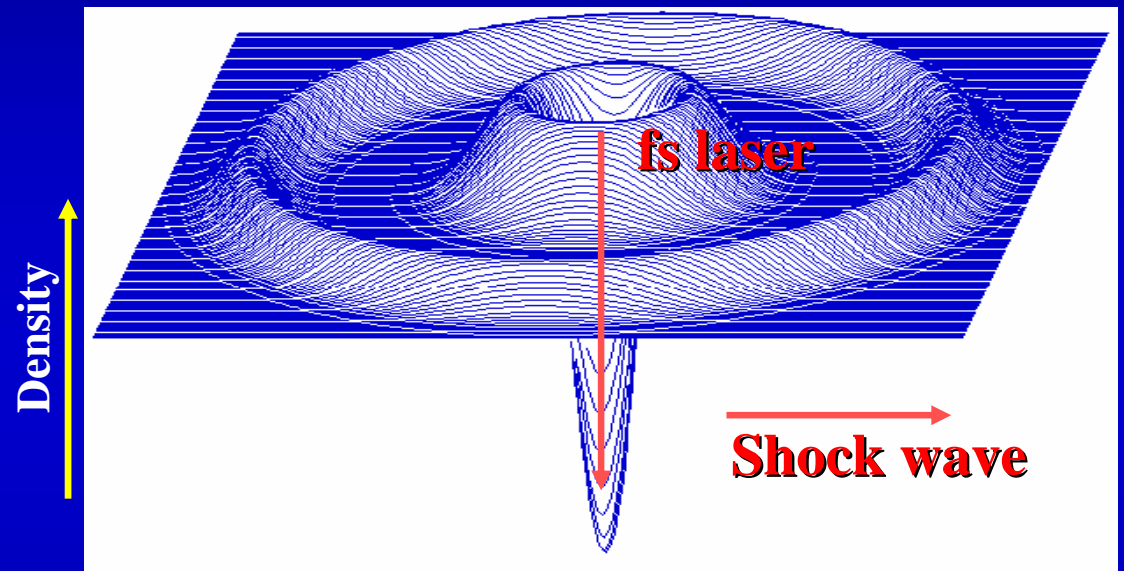
The change in the spatial pattern of the probe beam was monitored to obtain the refractive-index distribution.

**We found that a shock wave forms at the focal point inside the glass of the beam created by a femtosecond laser and propagates to the surrounding area.**

# Generation of shock wave



The density at the center decreases and the high-density area due to pressure-wave generation rapidly expands into the surrounding area.



The positive peak due to the pressure wave propagates outward with a constant velocity.

**$\sim 6.2 \mu\text{m/ns}$**

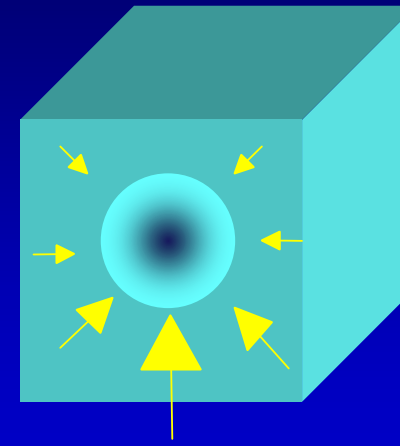
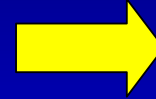
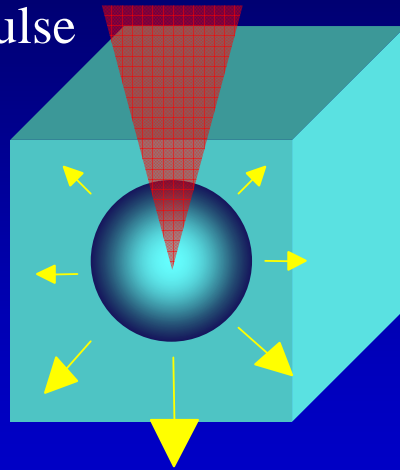
The temperature and pressure of this region rises very rapidly and dramatically.

**$>3000 \text{ K}$ ,  $\sim 1 \text{ GPa}$**

Fig. The phase distribution obtained by a phase retrieval calculation of the spatial pattern.

# Mechanism for the refractive index variation and localized melting

One pulse



## The irradiation of a single pulse

Temperature increase and thermo-elastic stress should be induced in a very limited volume.



The relaxation of the thermo-elastic stress produces the force driving the shock wave.



The shock wave propagates outward.



The structure of the glass is extended outside.

## After pulse irradiation

Compressive stress moves back toward the center.



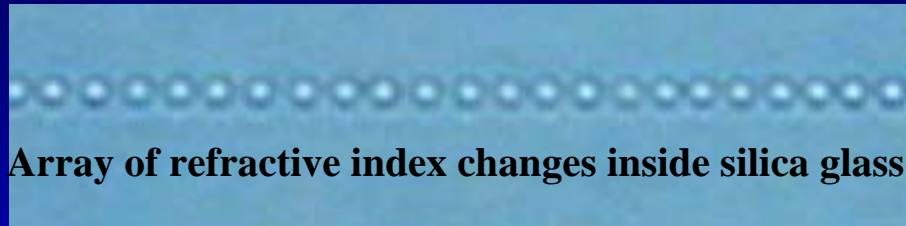
A graduated high-density region is formed in the laser-focusing area.



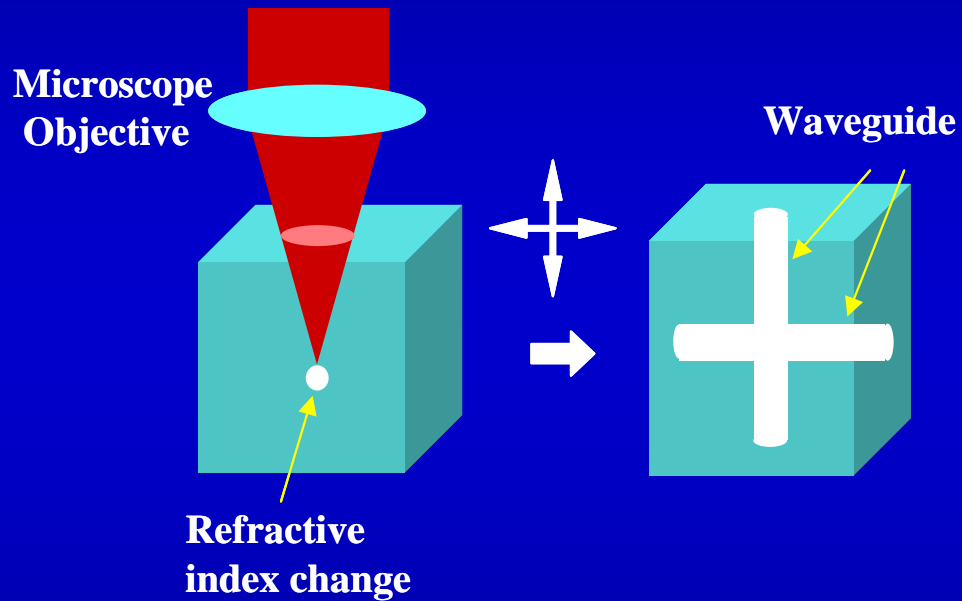
After the thermal diffusion from the irradiated region, the structural change becomes a permanent refractive-index change.

*If laser pulses are repeatedly irradiated, the high-temperature area rapidly expands, and melting regions can be formed at arbitrary sites within the glass.*

# Preparation and characterization of optical waveguides



**250 kHz** Laser Beam



By using a femtosecond laser with a high repetition rate, refractive index changes are continuously induced along a path traversed by the focal point.

↓  
We can write waveguides in glass.

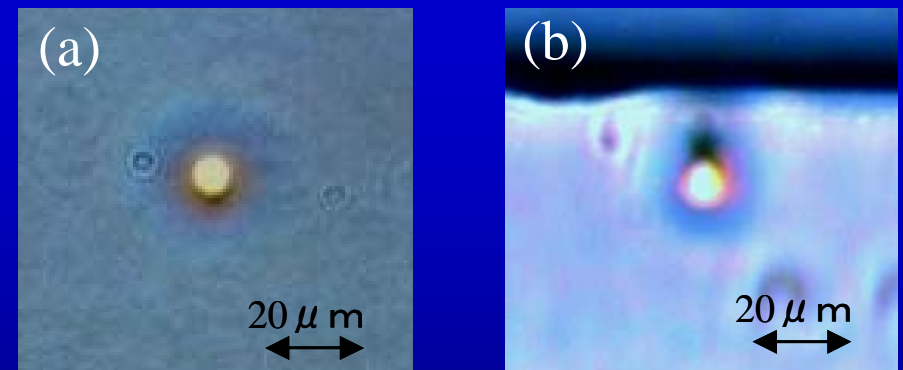
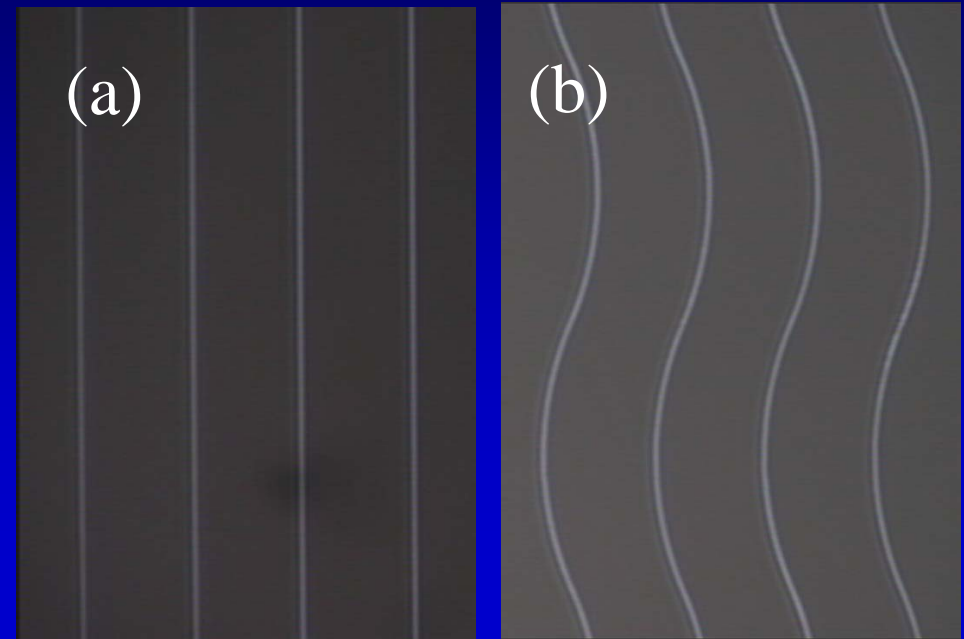
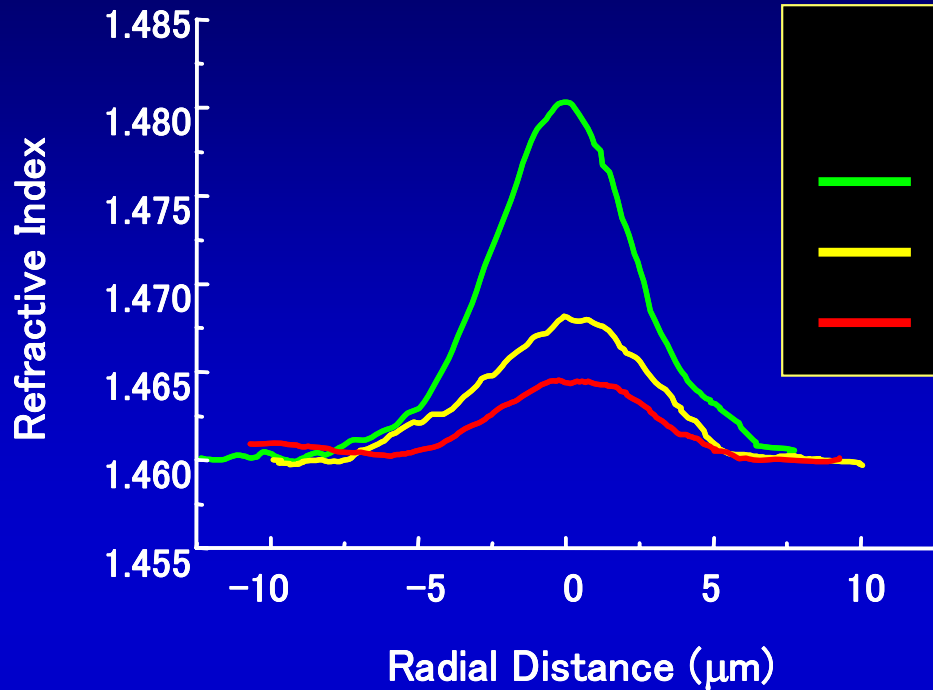


Fig. Photo-written waveguides were written by translating the sample (a) **parallel** or (b) **perpendicular** to the axis of the laser beam

**Similar waveguides can be written inside various types of glass, such as silica, borosilicate, fluoride and chalcogenide glass.**



# Refractive index profiles of the core



	Objective (NA)	power (mW)	Common Writing Condition
— I	0.25	425	Wavelength : 800 nm Repetition rate : 250 kHz Pulse width : 270 fs Scanning rate : 50 μm/s
— II	0.13	425	
— III	0.13	350	

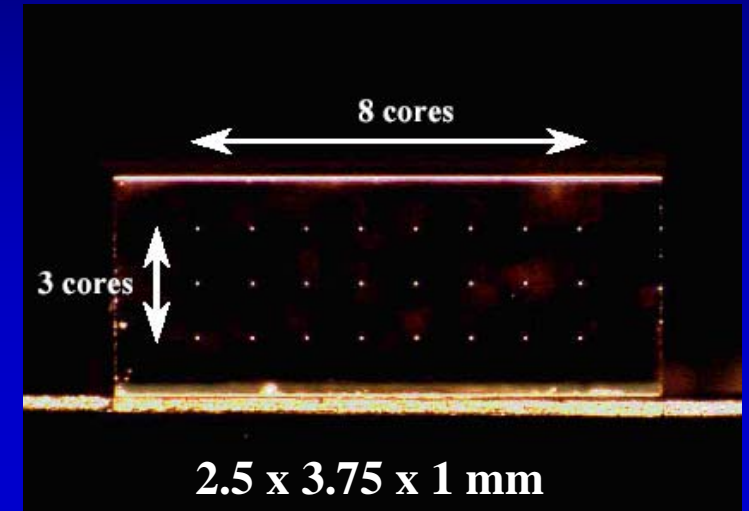
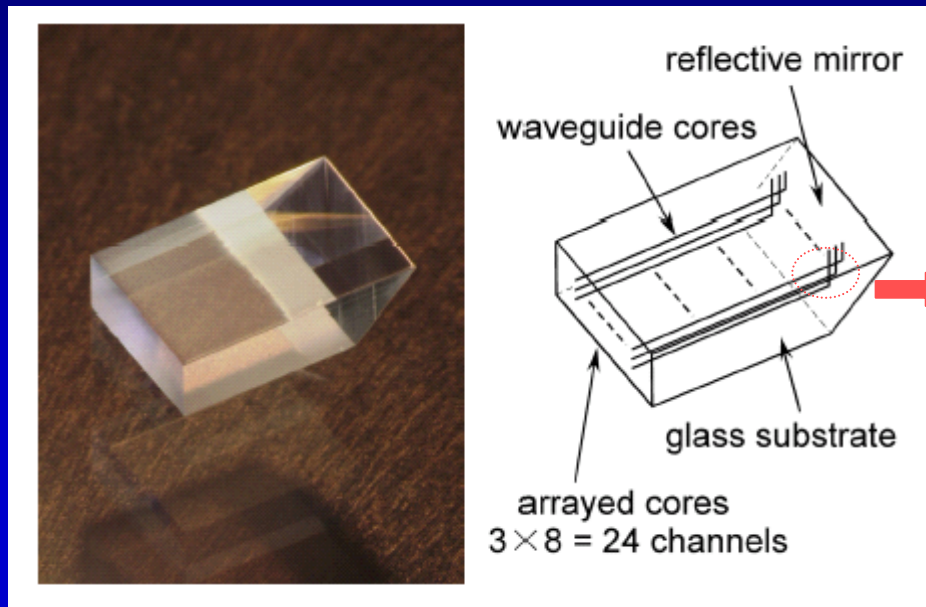
Fig. The refractive index profiles of the core of waveguides written in silica glass at various numerical apertures and average powers.

The characteristics of a writing waveguide can be controlled by adjusting the writing conditions

Table Guide mode and mode field diameter calculated from the refractive-index profile

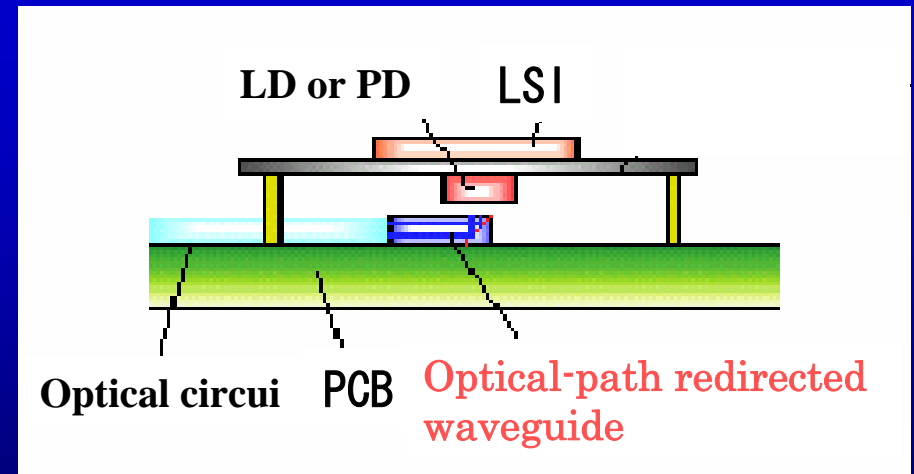
	Refractive index reference[%]	Change diameter[μm]	MFD@1.3 μm	MFD@1.55 μm	Calculated guide mode@1.3μm	Calculated guide mode@1.55μm
I	1.32	20	6.0	6.7	LP <sub>01</sub> , LP <sub>02</sub> , LP <sub>11</sub>	LP <sub>01</sub> , LP <sub>11</sub>
II	0.53	18	9.0	10.3	LP <sub>01</sub> , LP <sub>11</sub>	LP <sub>01</sub> , LP <sub>11</sub>
III	0.27	11	12.0	13.5	LP <sub>01</sub>	LP <sub>01</sub>

# 3-D optical waveguide / Optical-path redirected waveguide



## Characterization

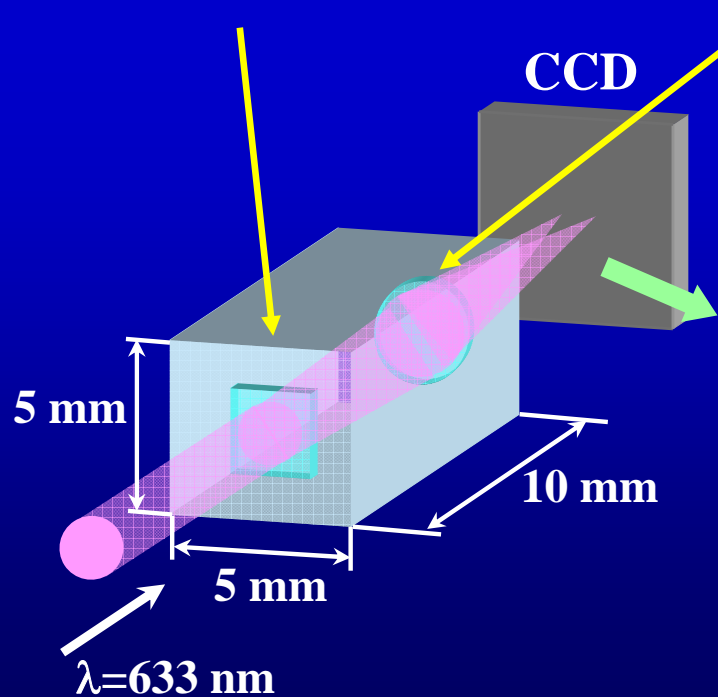
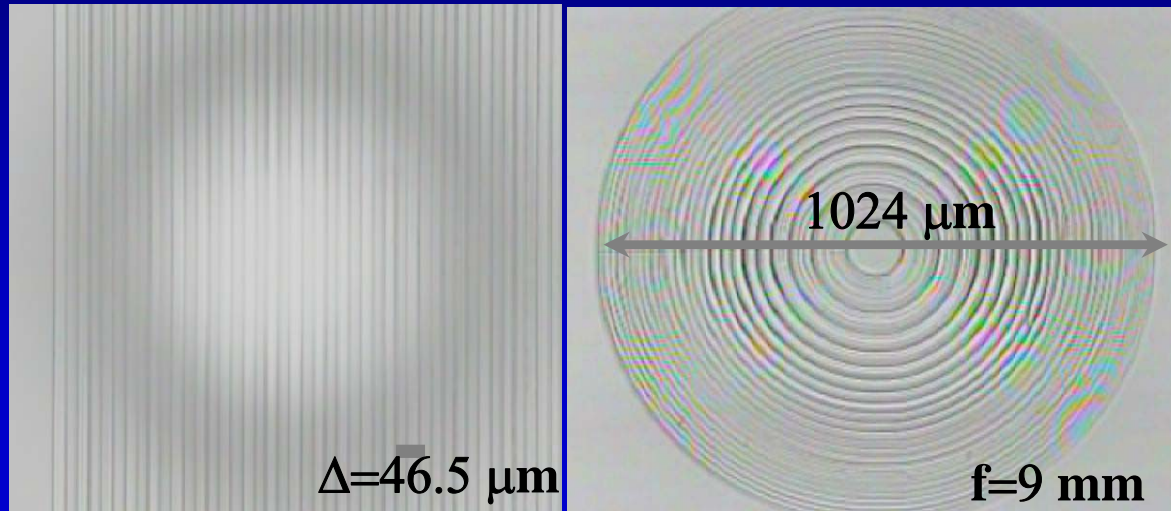
- This device has matrix-arrayed multichannel optical I/Os.
- The optical path are redirected by 90 degrees.
- This structure and size enable optical interconnects to be integrated in a board-to-board or board-to-backplane communication structure more densely.



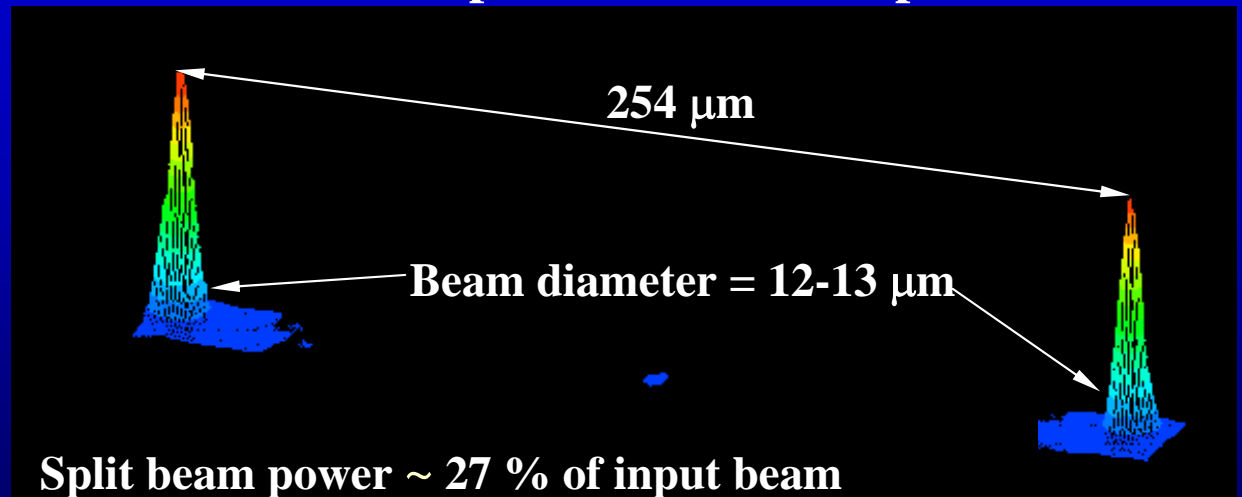
**It's not easy to fabricate an optical-path redirected waveguide using the conventional method, so this is an example where the laser writing technique has a clear advantage.**

# Diffraction optical elements

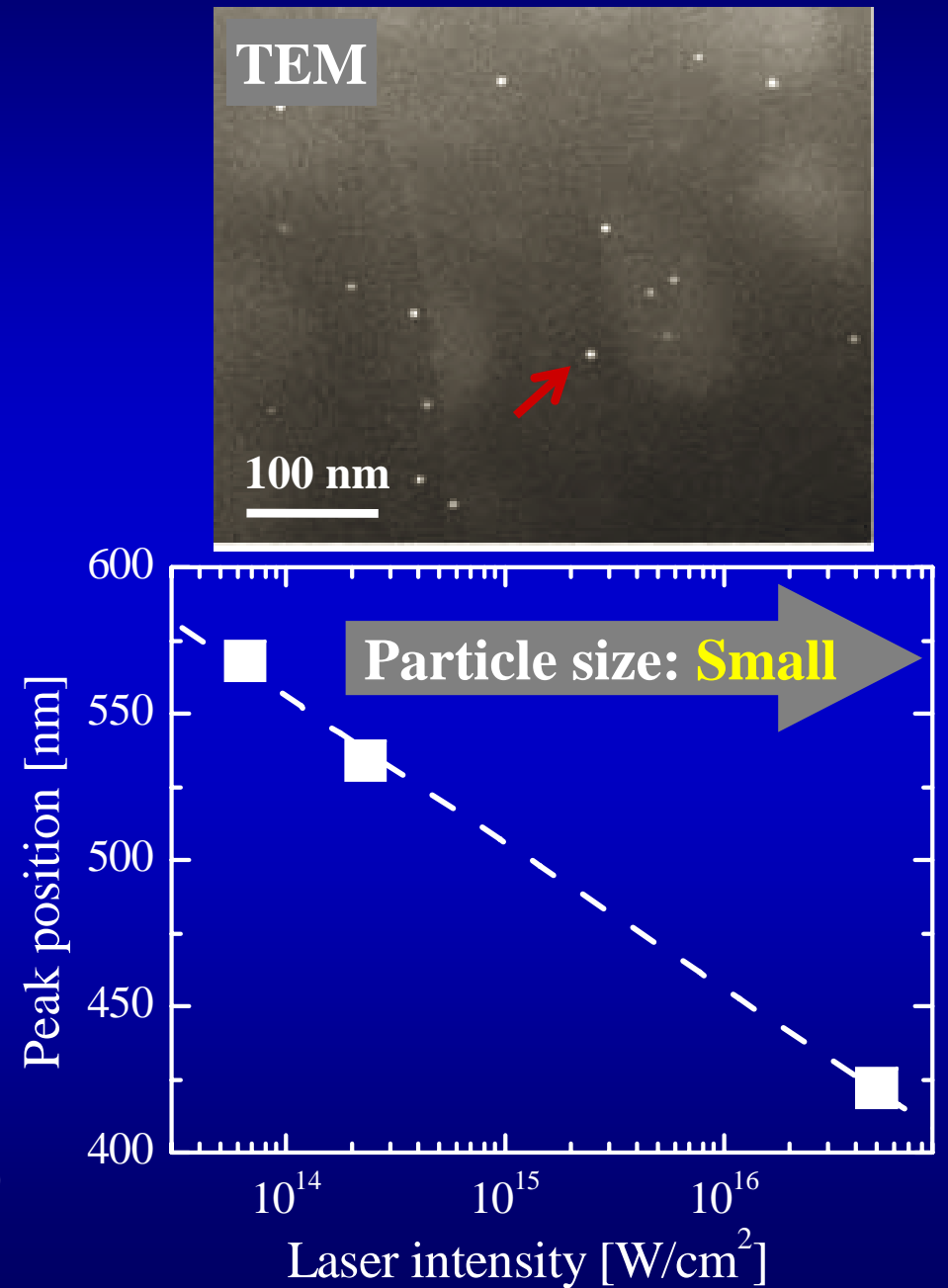
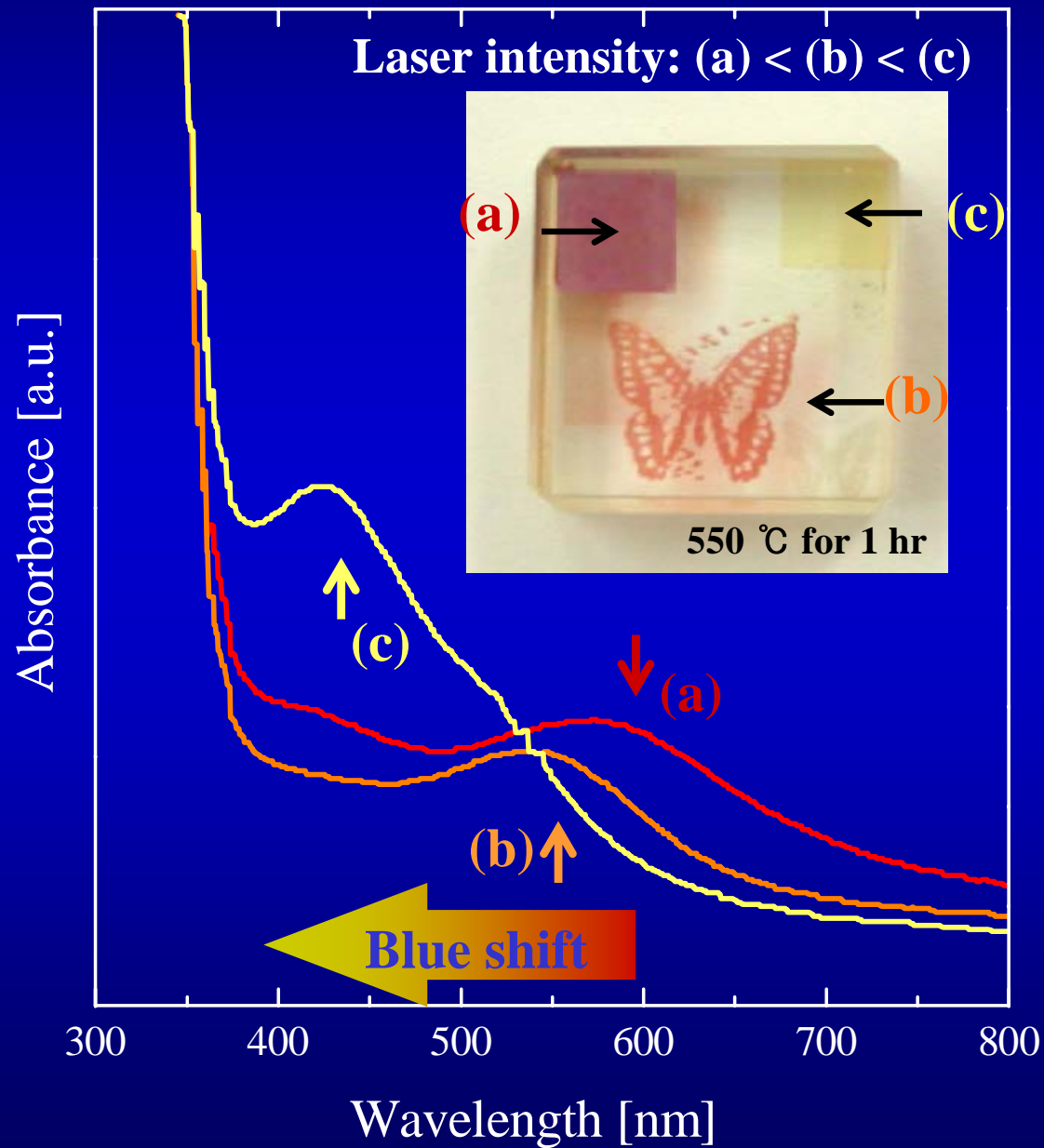
## Grating & Binary lens (microscopic view)



## Beam profile at the focal plane



# Precipitation of gold nano-particles



# 3-D multicolored industrial art object



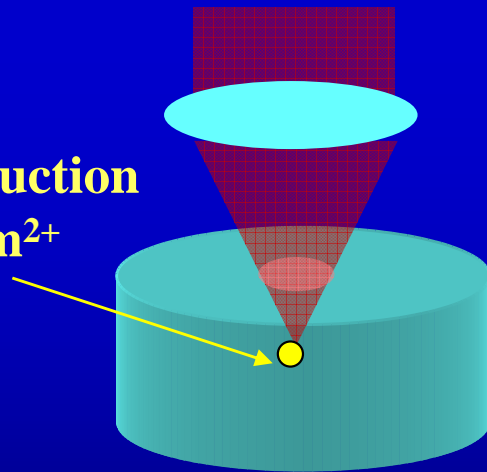
**Applications may also include developments in techniques such as surface plasmon resonance and near-field scanning optical microscopy.**

# Valence state change of samarium ions

## LASER BEAM

Wavelength: 800 nm  
Pulse width: 50 fs  
Repetition rate: 250 kHz  
Average power: 100 mW  
Objective: 50x, NA=0.6

Photo-reduction  
 $\text{Sm}^{3+} \rightarrow \text{Sm}^{2+}$



GLASS

$\text{SmF}_3 : \text{AlF}_3\text{-YF}_3\text{-BaF}_2\text{-SrF}_2\text{-CaF}_2\text{-MgF}_2$

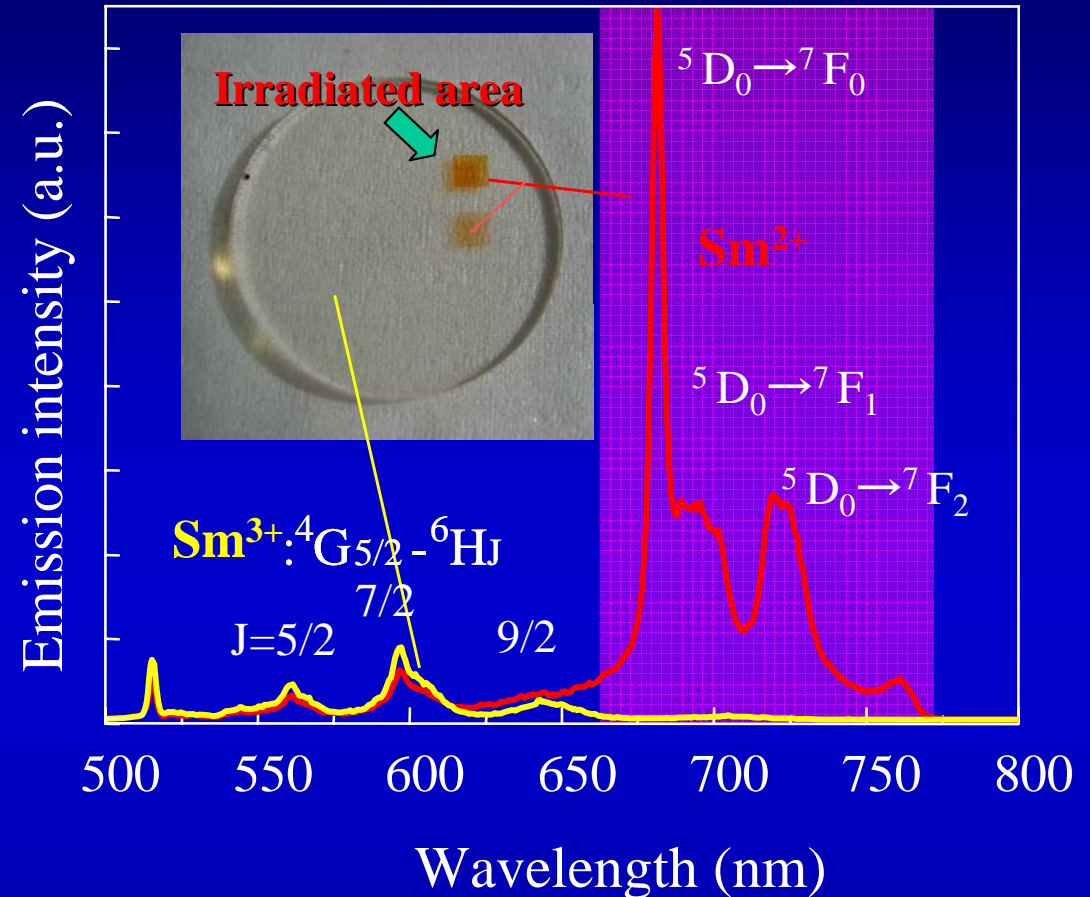
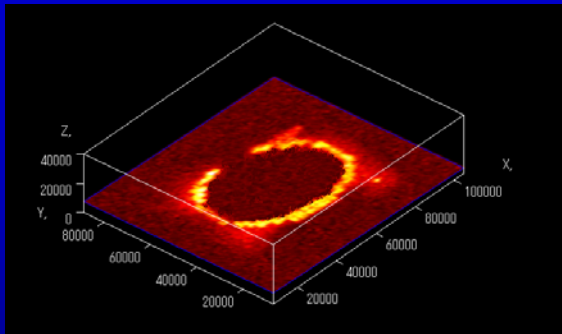
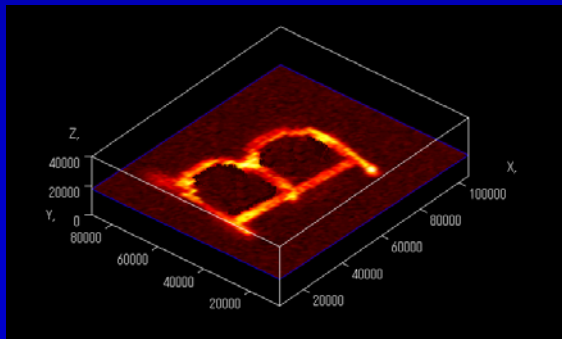
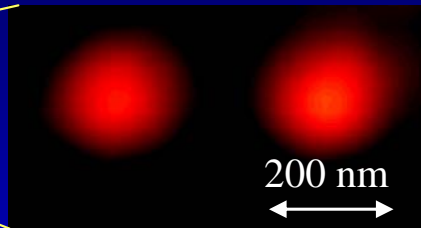
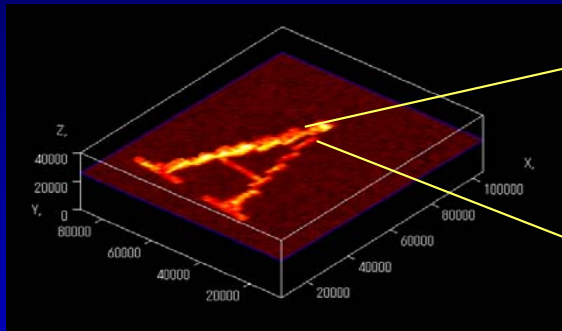


Fig. Photoluminescence spectra for glass excited at 488 nm : red line shows spectrum for laser-irradiated areas; yellow line shows spectrum for non-irradiated area.

Laser-irradiated areas (photo-reduced areas) recorded inside glass can be detected only by emissions at 680, 700 or 725 nm.

# Three-dimensional optical memory



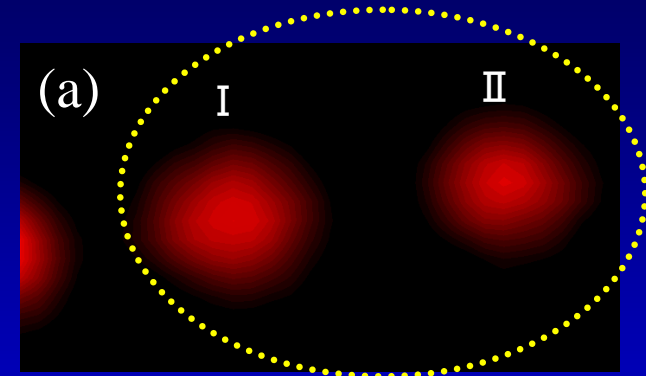
Photoluminescence images of alphabetic characters recorded by using the photo-reduction of samarium ion on different layers.

Alphabetical character comprised 300 to 500 photo-reduction bits. The bits had a diameter of 200 nm. The spacing between each characters was 1  $\mu\text{m}$ .

Recording :  $\text{Sm}^{3+} \rightarrow \text{Sm}^{2+}$   
Femtosecond laser  
100 nJ/pulse at 800nm

Readout :  
Ar<sup>+</sup> laser  
1 mW at 488 nm

Erasure :  $\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$   
Ar<sup>+</sup> laser  
10 mW at 488 nm



Photoluminescence image before the erasure.

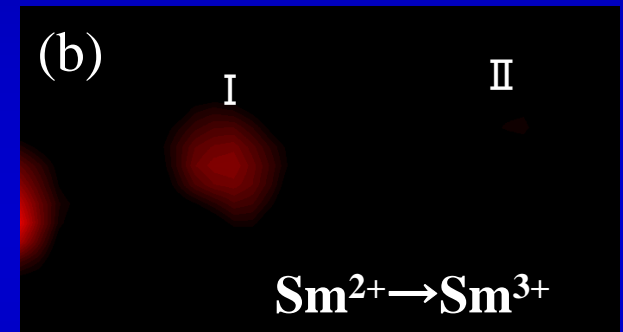


Image after an Ar<sup>+</sup> laser irradiation to photo-reduction bit I and II

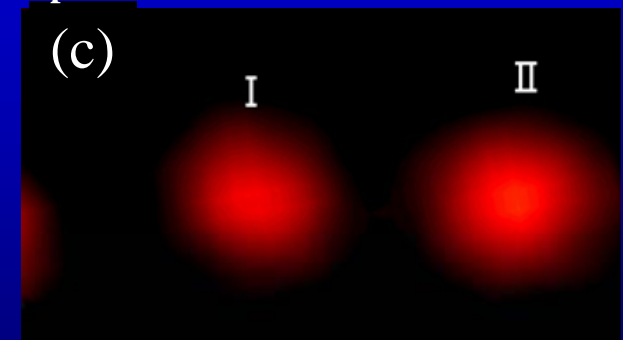
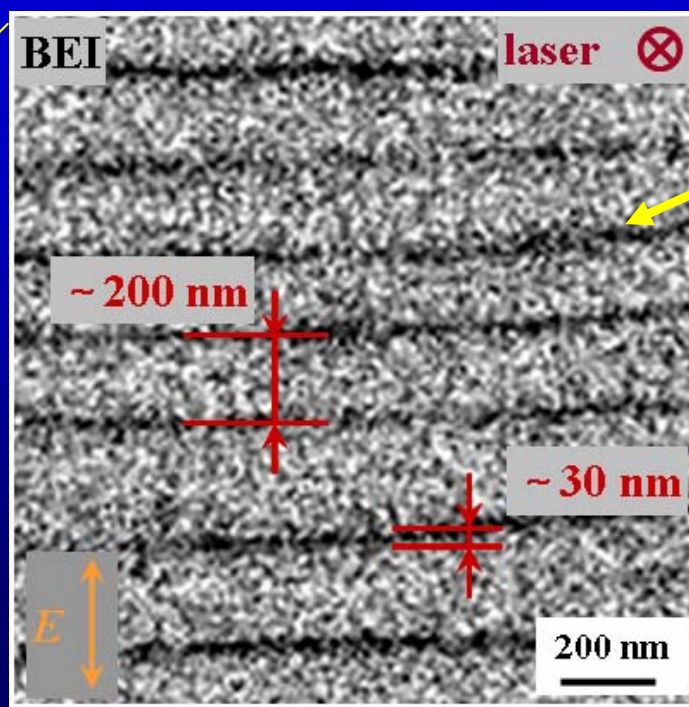
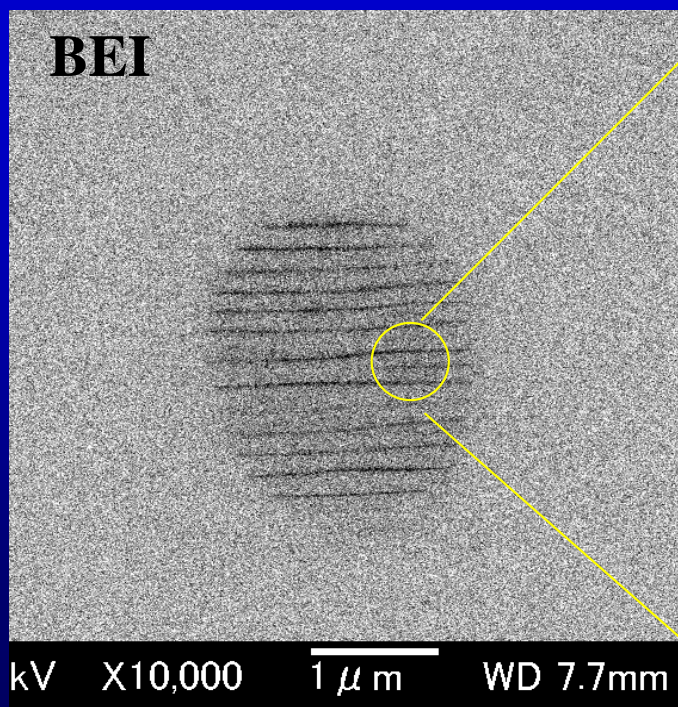
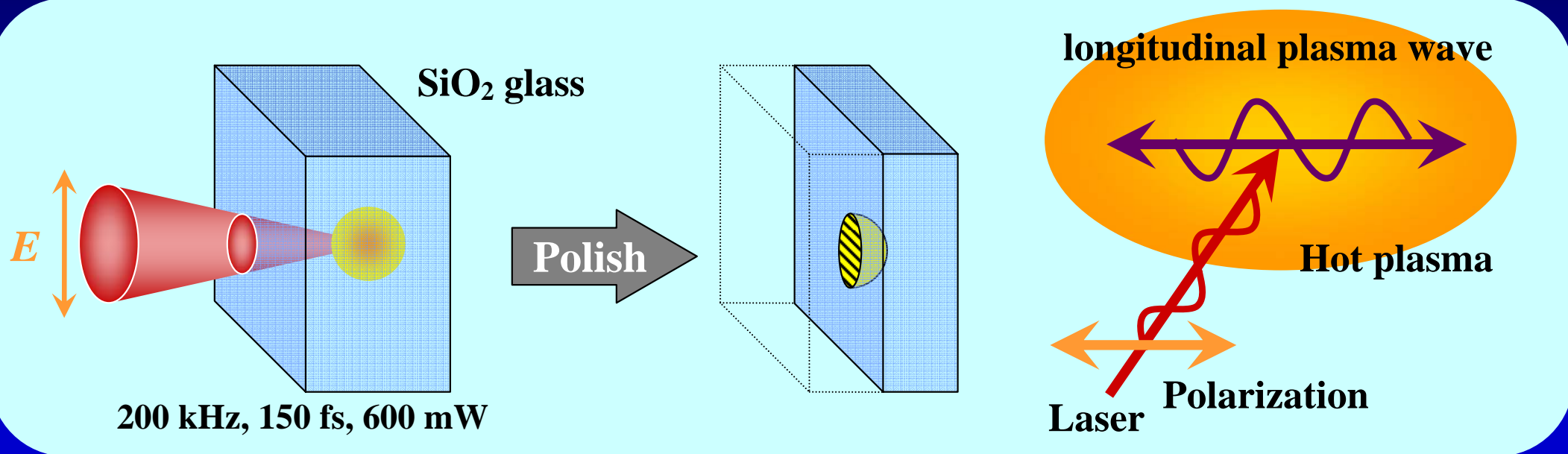


Image after a femtosecond laser irradiation to areas I and II.

Three-dimensional optical memory with rewrite capability is achievable.

# Writing of nano-gratings using one laser beam



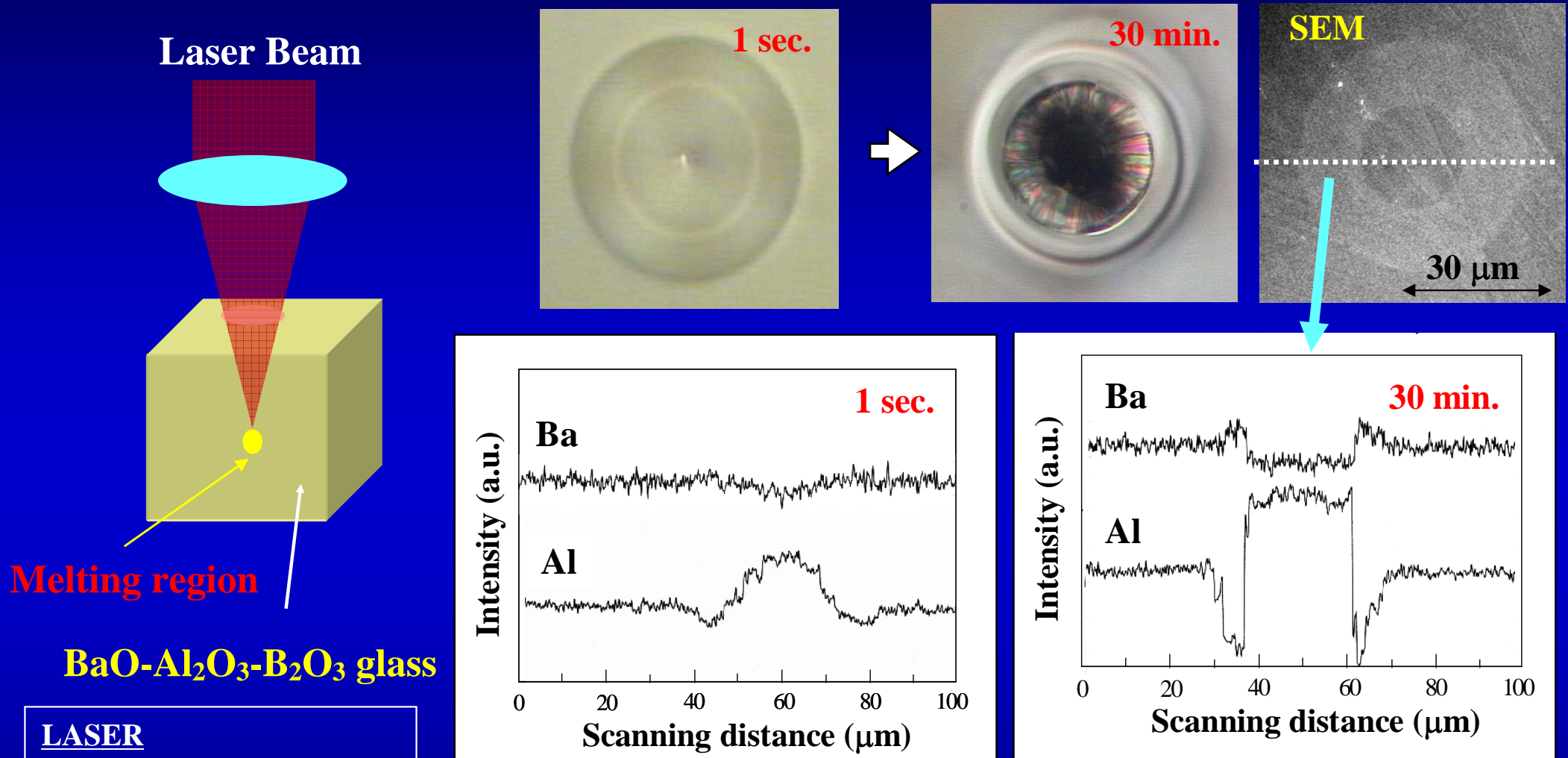
Oxygen defect  
SiO<sub>2-x</sub> (x ~ 0.4)

$$\Delta n \sim -0.1$$

The refractive index of nano lines is lower than that of the circumference, and periodic nano lines function as a grating.



# Growth of non-linear optical crystals (e.g., $\beta$ -BBO)



## LASER

Wavelength: 800 nm  
Pulse width: 50 fs  
Repetition rate: 250 kHz  
Average power: 400 mW  
Objective: 100x, NA=0.9

Elemental distributions of Ba and Al at around the focal point of the laser.

The concentration of Al increased at the center of the irradiated area, and Ba increased outside the center with the passage of time.

**Measurement of the x-ray diffraction patterns confirmed that only beta-BBO crystals grew in the focused area.**

# Silicon deposition in silicate glass

- Metallic clusters or particles can be precipitated.
- Specific ion can be reduced or oxidized.
- Oxygen-deficiency centers ( $\equiv\text{Si-Si}\equiv$ , etc. ) can be formed.
- Specific ions can be diffused at the micrometer order.

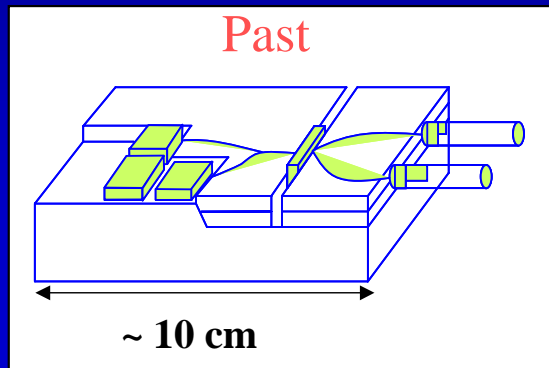
 Silicon cluster or particle can be extracted from silica or silicate glass.

*General oxide glasses can not trap superfluous oxygen ions generated by cutting the Si-O bond and growth of the silicon in a closed space like the glass inside it.*

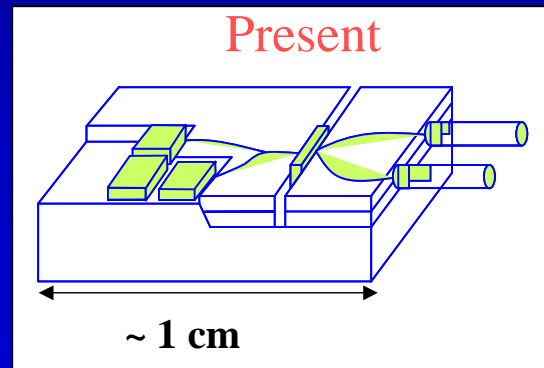
**We tried to deposit silicon from silicate glass prepared using metallic aluminum as the starting material.**

# Motivation

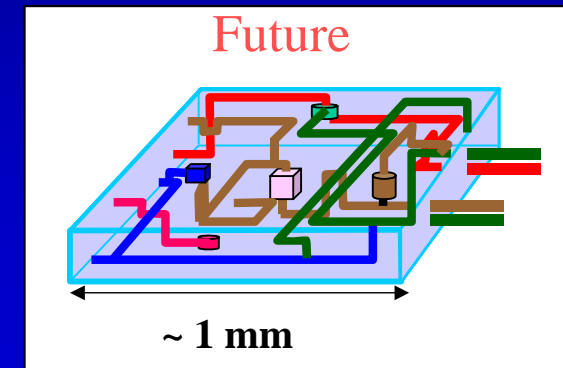
Silicon as a photonic medium has unique advantages for photonic integrated circuits



*Refractive indices of core and cladding layers are approximately 1.50 and 1.45, respectively.*



*Refractive indices of silicon and conventional oxide glass are approximately 3.5 and 1.5, respectively.*



**Three-dimensional integration of different optical components in the glass**

In order to achieve compact and integrated devices, high refractive index difference is required. The high refractive index contrast between the silicon waveguide core and a surrounding glass cladding enables the fabrication of small optical structures.

If silicon can be deposited in the glass at three dimensions, this leads to further compactness and higher integration of optical devices.

# Silicate glass prepared using metallic aluminum

Si - Na - Al - O

Si - Ca - Al - O

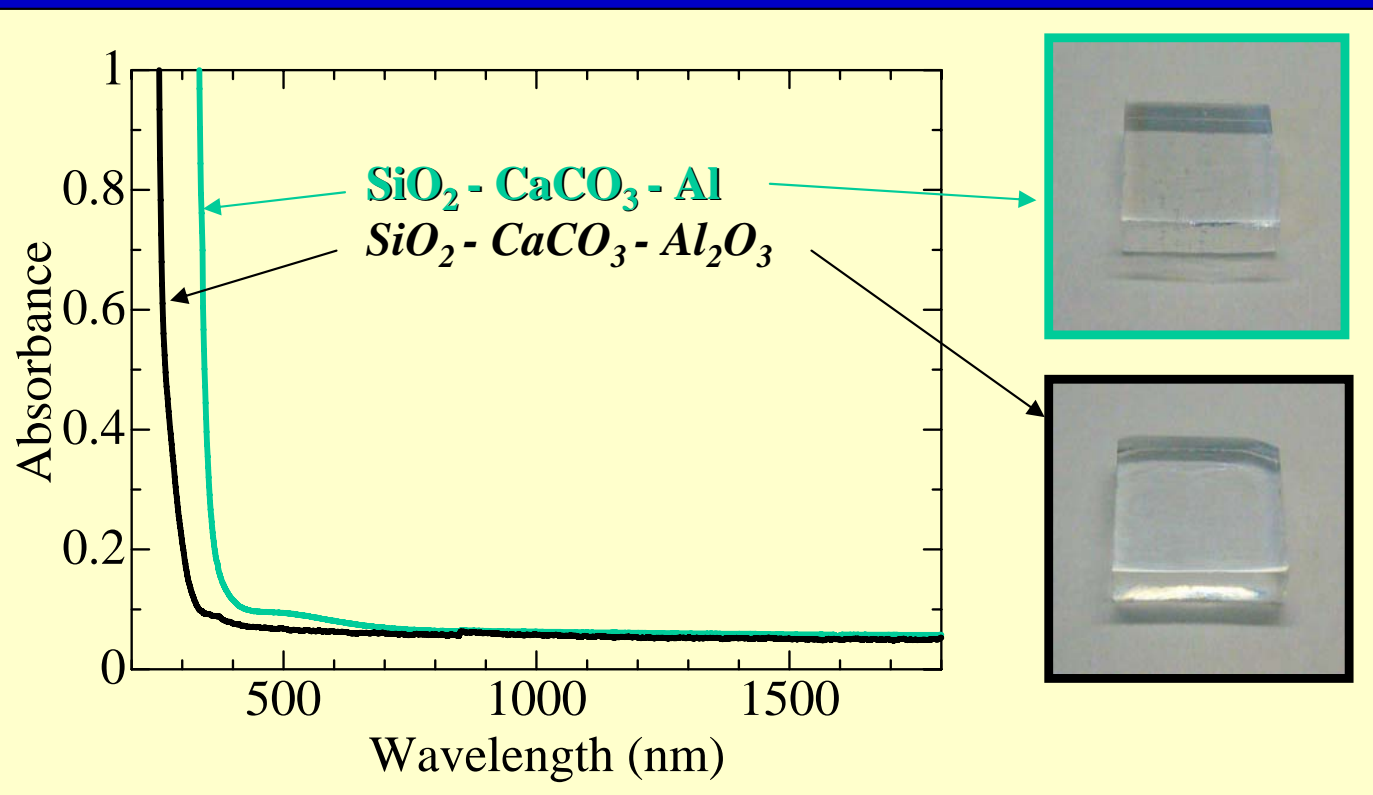
Si - Ca - Na - Al - O

Si - Ca - B - Al - O

Metallic aluminum : ~20 mol% in air

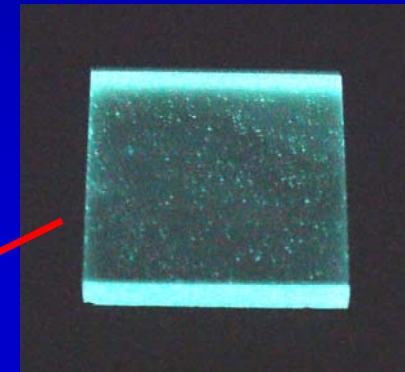
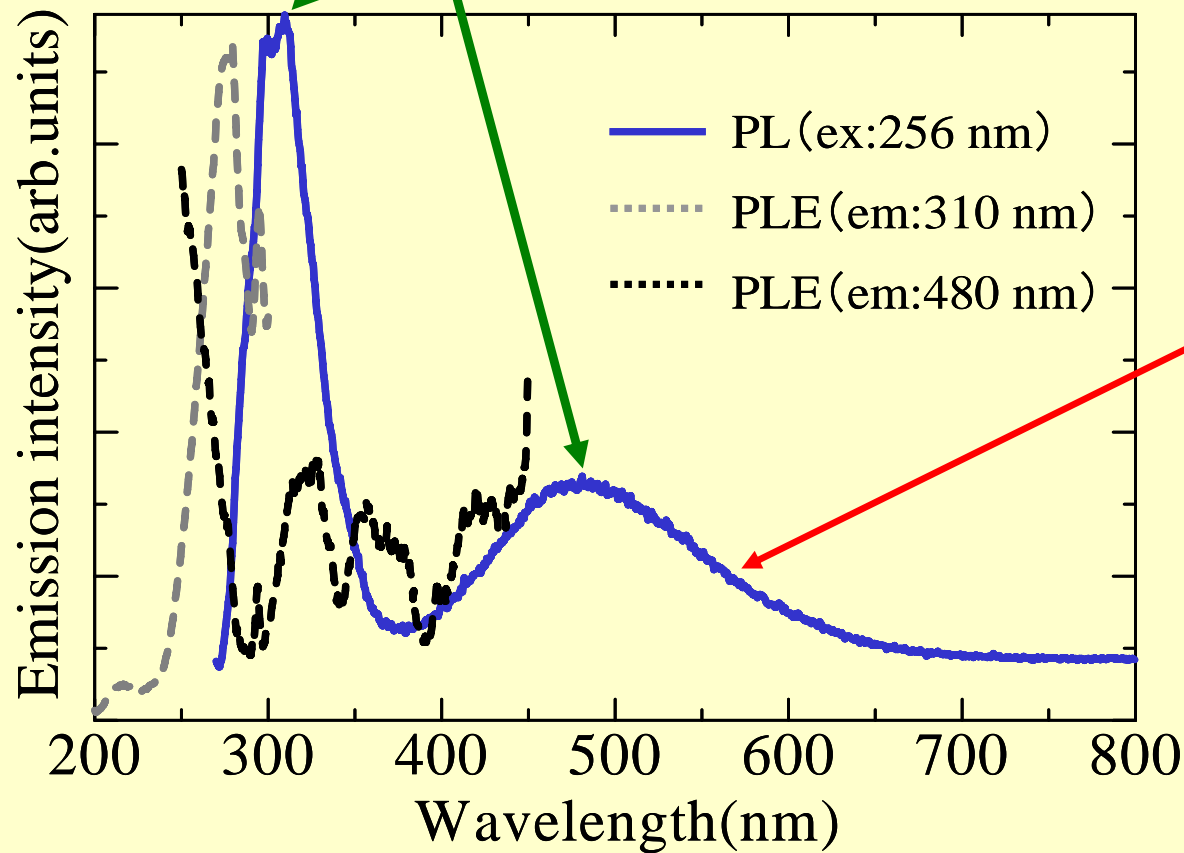
Melting Temp. : 1400 -1500 °C

Crucible :  $\text{Al}_2\text{O}_3$



# Silicate glass prepared using metallic aluminum

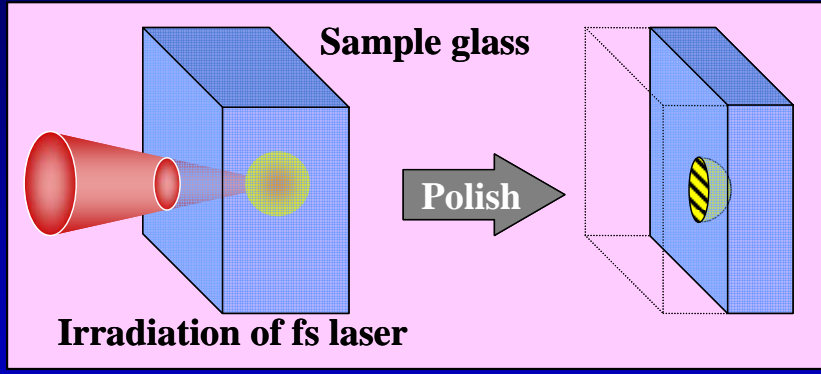
Oxygen deficiency defect :  $O_3 \equiv Si-Si \equiv O_3$



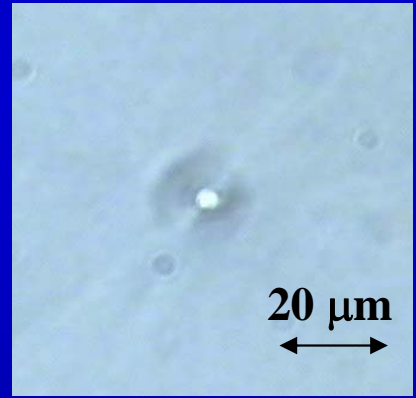
$SiO_2 - CaCO_3 (CaO) - Al (20 \text{ mol}\%)$

# Element distribution formed by pressure wave

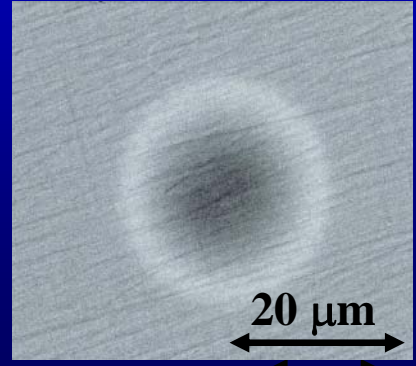
**LASER**  
Pulse width: 130 fs  
Pulse energy: 3  $\mu$ J  
Repetition rate: 200kHz  
Objective: 50x, NA=0.85  
Irradiation Time: 5 sec.



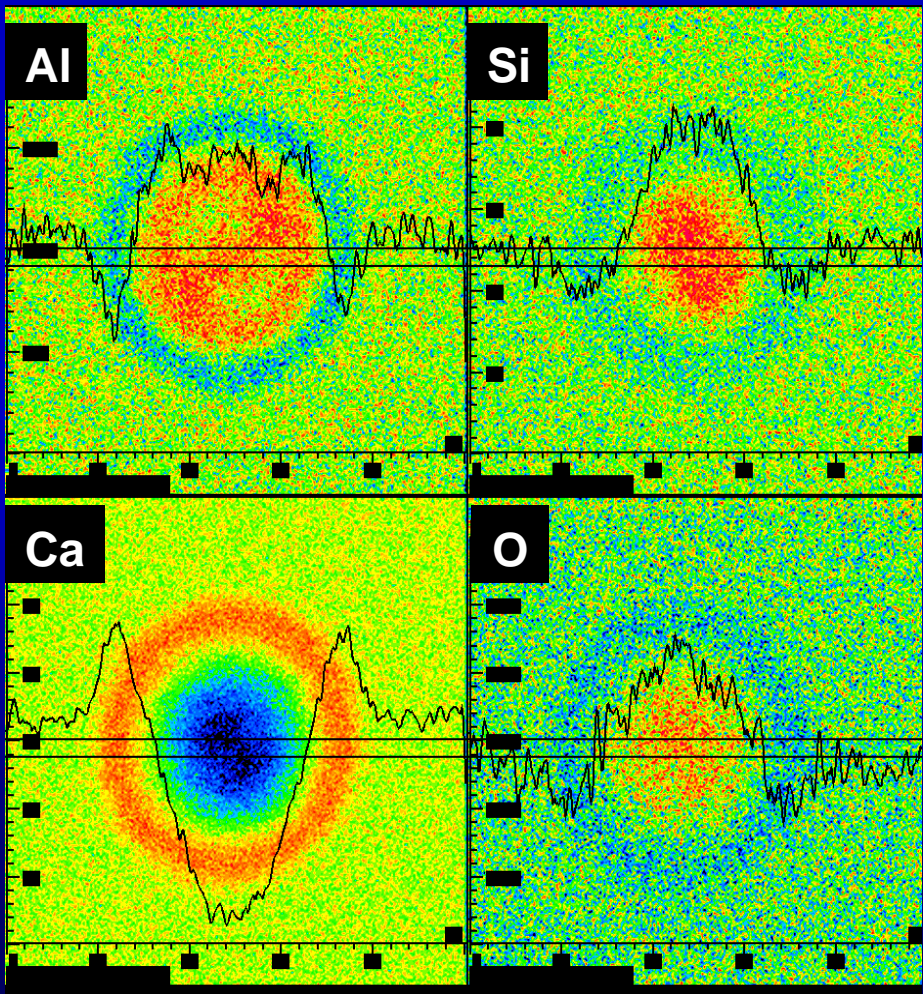
**Si - Ca - Al - O glass**



Microscope

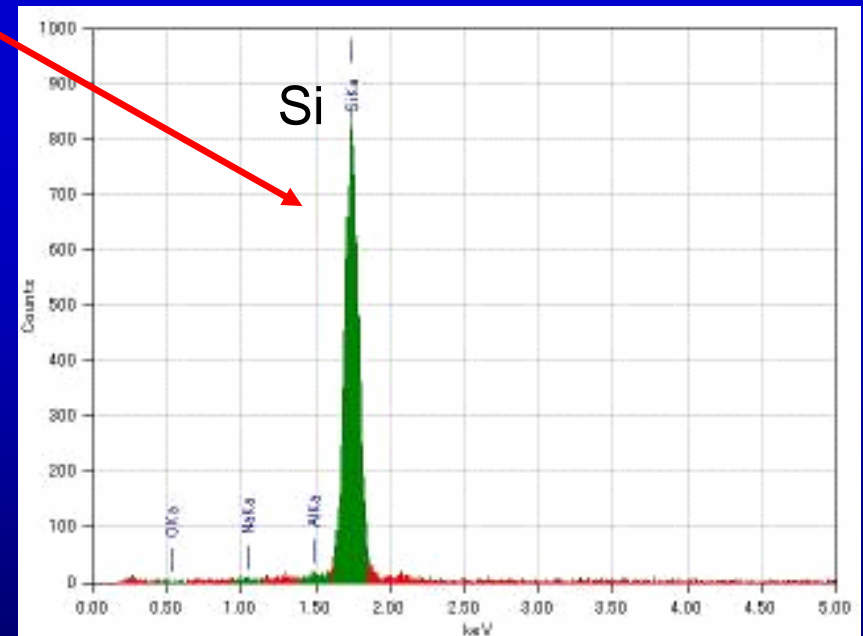
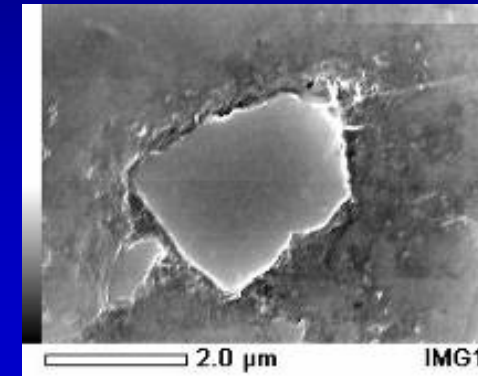
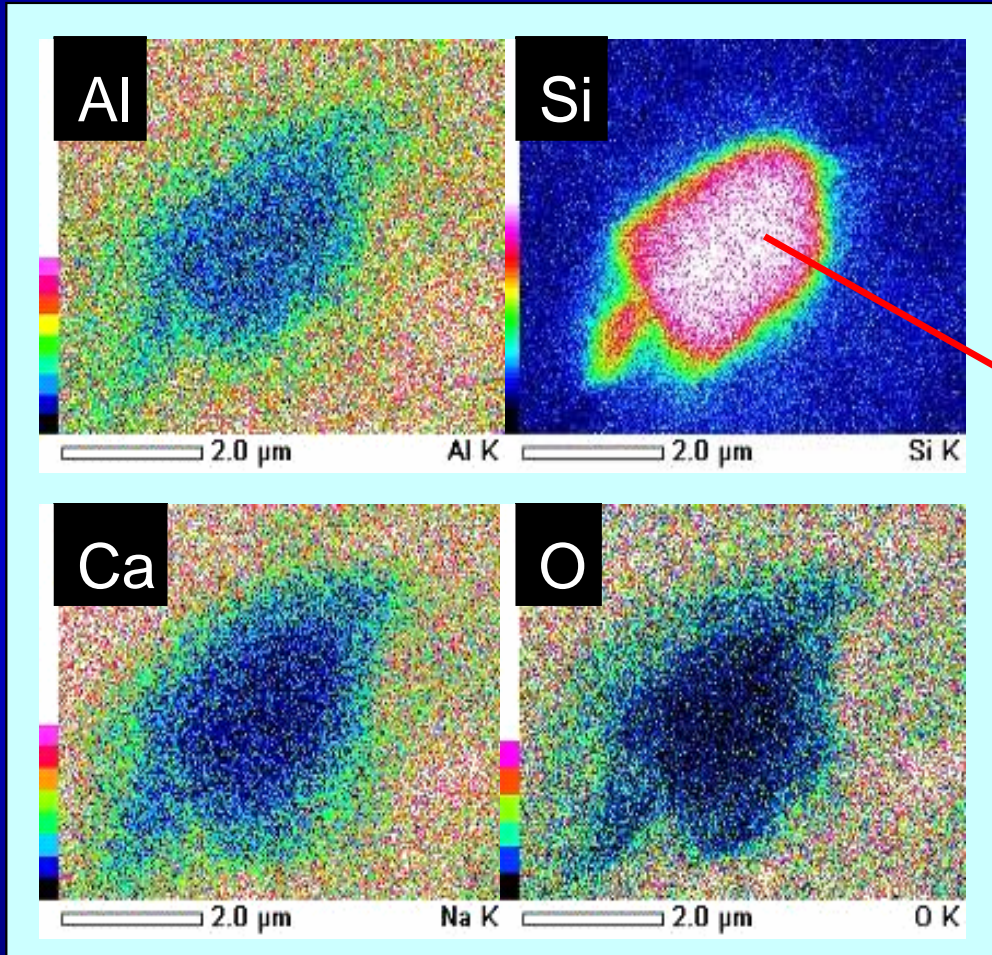


Backscattered electron



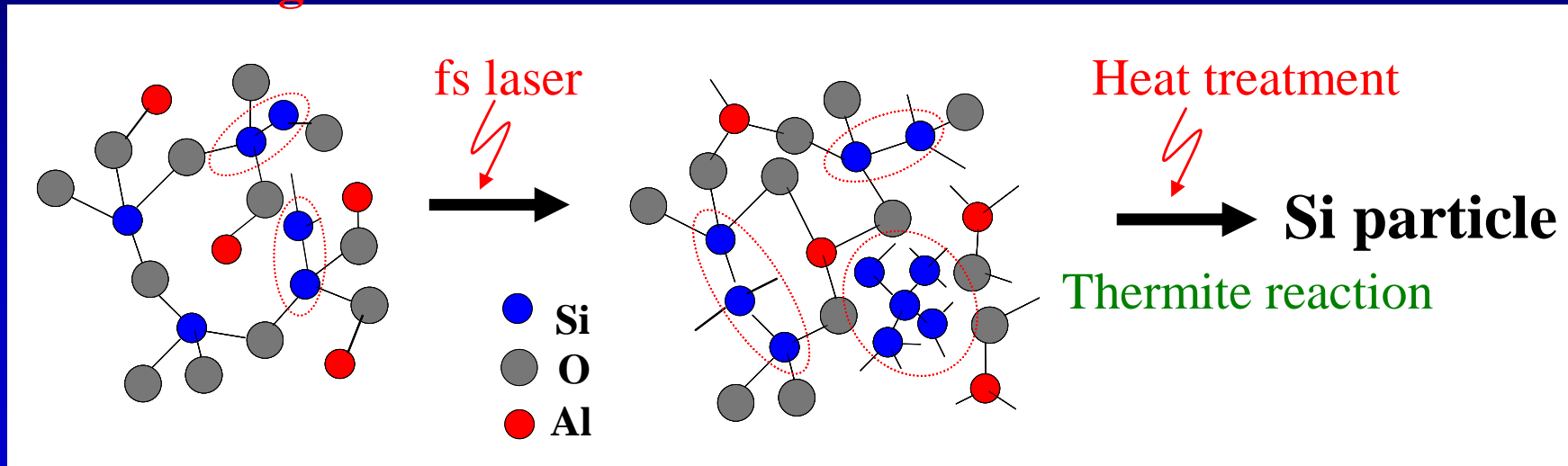
EPMA

# Example of silicon deposition



# Mechanism of silicon deposition

## Al: Silicate glass



**Oxygen deficiency centers**  
 $\equiv\text{Si-Si}\equiv$  etc.

+

**Aluminum rich structures**

**Silicon rich structure**

$\equiv\text{Si-Si}\equiv$

+

$\equiv\text{Si-Si-Si}\equiv$

: more

**Silicon cluster**

**Silicon rich structure grows into a particle because of the thermite reaction promoted by the heat treatment**

- Glass prepared using metallic aluminum as the source material has oxygen deficiency centers
- Si-O bonds are continuously broken and re-formed with numerous unbound atoms
- Si and Al-rich structures are formed at the center of the irradiated area.
- Si rich structure grows into a particle because of the thermite-like reaction.