IV. Nanofabrication in transparent materials with a femtosecond pulse laser

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Nanofabrication in Transparent Materials with Femtosecond Pulse Laser

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1. Research background
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

Device of Nano-glass

High density optical memory

Optical Integrated Glass Device

Display of Nano-glass

High fracture strength glass

High emitting nano-glass

High ionic conductor for Fuel cell

Nanotechnology

Glass Material
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
   

2) UV light induced long-lasting phosphorescence
   

3) EB induced various nanostructure in glass
   
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
Irradiation on stainless steel

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

Irradiation on stainless steel

Lattice vibration for 1 cycle

Plasma generation

(a) 200fs, 120 μJ, 0.5J/cm²
(b) 80ps, 900 μJ, 3.7J/cm²
(c) 3.3ns, 1mJ, 4.2J/cm²
3-dimensional micro-modification

\[ \chi = \sigma \left( \frac{I}{h\nu} \right)^n \]

\( \geq 10^2 \text{TW/cm}^2 \)
Nonlinear ionization

Multiphoton ionization

Avalanche ionization

Ionization potential

Coulomb potential

Free electron

\( n h \nu \)

\( h \nu \)

Avalanche ionization rate

Electron density \( n_e \) [\( 10^{21} \text{ cm}^{-3} \)]

Time [\( 10^{-13} \text{ s} \)]

100fs

\( [10^{16}] \)
Femtosecond Laser using Er-doped glass fiber

**High Peak Power**

- Lattice Vibration
  - 1 ps / 1 cycle
- Plasma Generation
  - 100 fs \( ( = 10^{-13} \text{ s} ) \)

**Femtosecond Pulse Width**

**Cyber Laser  Ifrit**
- Reputation  1 KHz
- Average Power  1 W
Experimental setup

200 kHz

Ar\(^+\) Laser

Mode locked Ti sapphire laser

Regenerative Amplifier

10 Hz-1 kHz

LD-Pumped Nd:YVO\(_4\) laser

Mode locked Ti:sapphire laser

Nd:YLF laser

Regenerative Amplifier

Pules Compressor

120 fs ~ 250 fs

N.D.F.

Sample

CCD

Monitor

B.S.

D.M.

O.L.

XYZ stage

X

Y

Z

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 a 10X lens, 470 mW, 130 fs and 200 kHz.

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.

Laser-induced waveguide—cross section

Parallel to the laser beam

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.

Internal loss of waveguides

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

Average power: 150 mW  Scanning rate: 0.5 mm/s  Pulse width: 130 fs

Average power: 150 mW  Scanning rate: 0.5 mm/s  Pulse width: 400 fs
Common Writing Condition
Wavelength: 800 nm
Repetition rate: 250 kHz
Pulse width: 270 fs
Scanning rate: 50 mm/s

<table>
<thead>
<tr>
<th>Objective</th>
<th>power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.25</td>
</tr>
<tr>
<td>II</td>
<td>0.13</td>
</tr>
<tr>
<td>III</td>
<td>0.13</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Refractive index reference[%]</th>
<th>Change distance[mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.32</td>
<td>20</td>
</tr>
<tr>
<td>II</td>
<td>0.53</td>
<td>18</td>
</tr>
<tr>
<td>III</td>
<td>0.27</td>
<td>11</td>
</tr>
</tbody>
</table>
Laser-induced waveguide—various glasses

- **Silica glass**
  - Threshold (average power): 70 mW

- **Borosilicate glass**
  - Threshold (average power): 30 mW

- **Fluoride glass**
  - Threshold (average power): 100 mW

- **Chalcogenide glass**
  - Threshold (average power): 1 mW

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%.


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.

-40 ps  0 ps  720 ps

60 µm
30 mm
Detection plane

(i) Circular symmetric intensity distribution.
(ii) Dramatic change after irradiation.
What the results suggest?

- Due to the high amplitude of the acoustic wave
  Estimated $\Delta\rho \sim 0.4\%$.
  Simulated $\Delta\rho$ with $\Delta T=500\ K$: $0.04\%$
  It means that
  - $\Delta T > 1000\ K$ (above the glass transition temperature)
  - **Sudden temperature elevation** (<10ps; faster than elastic relaxation) is clearly shown.
  - The high temperature region has a diameter of $\sim 1\ \mu m$.

- The significance of the laser pulse duration

  **Density at the center of the irradiated region.**
  - 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

$R = 30, 32, 34, 36, 38, 40 \text{mm}$

He-Ne laser $\times 10$

Waveguide

Transmission light of the end face of bending waveguides

Beam coupler
Dammann grating and micro-lens

One example of fs laser written waveguide

Beam profile and NFP of the optical-path redirected waveguide
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

Back plain transmission system
One shot of single femtosecond laser induced nanograting

Optical microphotograph

BEI image of SEM

100× (0.95)  
120fs  
200kHz  
200mW  
1s

10nm

200nm

Nanograting in SiO2 glass using polarization light of femtosecond laser

**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

**Microscope image**

**Fabrication system**
- Lens
- Aperture
- Mirror
- ND
- λ/2
- ES
- Focal point
- Sample
- Piezo stage
- Polarizing plate

**Laser**

*Fabrication system* and *Microscope image* show the setup and the resulting pattern, respectively.
Laser Irradiation (>100TW/cm²)

Photon Energy
1.6 eV (800 nm)

Valence Band

Conduction Band

Band Gap
8.5 eV

Energy Absorption

Plasma

Laser

Photon

Ion
Mechanism of the formation of nanograting


Mechanism of the nanograting

Electron movement

Hot plasma

Laser

\( k_w \): laser wave vector
\( k_p \): plasmon wave vector
\( k_d \): dielectric constant modulation vector
\( \Lambda \): period of nanostructure

\[ k_d = k_p - k_w \]

\[ k_d = \frac{2\pi}{\Lambda} \]
Electron plasma standing wave

Threshold of oxygen defects formation

Plasma standing wave

\[ \vec{E}_w \approx \sin^6(\omega_w t) \]
\[ \vec{E}_{pl} \approx \sin(\omega_{pl} t) \]

\[ \omega_w = \omega_{pl} : \text{Energy conservation} \]

\[ \left| \vec{E}_w \cdot \vec{E}_{pl} \right| \approx \left| \sin^7(\omega_w t) \right| \]

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

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

Oxygen defect modulation

BEI

~ 30 nm

200 nm

Oxygen defect modulation

X = 1.6

Laser

SiO$_2$ glass

Periodic modulation of refractive constant
Tellurite glass

100 nm
Cross section of nanograting

near the focal spot

filamentation

\[ \Lambda \approx 330 \text{ nm} \]
\[ \Lambda/2 \approx 165 \text{ nm} \]
\[ \lambda \approx 600 \text{ nm} \]
\[ (= \lambda_0/n) \]
\[ \text{pitch} \approx 10 \mu\text{m} \]

E

\[ k_w \]

\[ L \approx \frac{\pi}{\Lambda} \]

\[ 2\pi \]

\[ \lambda \]

\[ \Lambda \]

k_{d2} = \frac{\pi}{\Lambda}

k_{d3} = \frac{2\pi}{\lambda}

k_{d1} = \frac{2\pi}{\Lambda}
Photo-oxidation of transition metal ion

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

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

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

Red emission
Blue emission

Emission spectra

before irradiation
after irradiation

320 400 500 600 700
Wavelength [nm]

Signal intensity [a.u.]

ESR spectra

before irradiation
after irradiation

1000 2000 3000 4000
Magnetic field [Gauss]

Eu$^{3+}$
Eu$^{2+}$

Red emission
Blue emission

Eu$^{3+}$ doped glass
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 Sm²⁺ at 682nm
at the focal point

Sm$_{2+}$

Sm$_{3+}$

200 nm
Rewritable 3D optical memory

\[ \text{fs} + 514\text{nm Ar}^+ \]

\[ 488\text{nm Ar}^+ \]

\[ \text{Appl. Phys. Lett.}, 80(2002)2263. \]
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.
Precipitation of Au nanoparticle

\[ R \propto \frac{\lambda_p^2}{\Delta \lambda} \]

- \( R \) : Particle radius
- \( \lambda_p \) : Wavelength of surface plasmon resonant
- \( \Delta \lambda \) : Absorption band width

\[ l_D \]

\( l_p \): Wavelength of surface plasmon resonant

- Red butterfly: Surface plasmon of Au nanoparticle
- Gray Einstein: Surface plasmon of Au nanoparticle

\[ \text{Rep. rate: } 1 \text{ kHz} \]
\[ \text{OL: } 10x \text{ (NA0.30)} \]
\[ E_p: 35 \text{ µJ} \]

\[ \Delta \text{Mie theory} \]

\[ \lambda_p^2 / \Delta \lambda \text{ [µm]} \]

\[ 440 \text{ to } 560 \text{ degC} \]

Size control of Au nanoparticle

Au$^{3+}$ doped silicate glass

Laser intensity: (a) < (b) < (c)

Blue shift

TEM

Particle size: Small

Absorbance [a.u.]

Wavelength [nm]

Peak position [nm]

Laser intensity [W/cm$^2$]
Faster circuits go for gold

Mark Peplow

Lasers could build three-dimensional computers

Creating tiny gold blocks of glass might be the latest in up-market design. But the technology could lead to a new generation of electronics.

One route to faster circuits is to increase the number of connections between components. But computer chips are fast running out of room. Conventional, flat substrates are reaching their limits, so new ways of thinking become necessary.

Flat circuit boards are running out of room.

Three dimensions means faster chips and more memory. © Angewandte Chemie

"The microelectrode structures are two-dimensional at the moment," says Mark N. Haynes, materials scientist from King's College London. "If we want to increase the number of interconnections on a chip, we hit a limit."

So far 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*

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°C for 30min
Precipitation of Ag nanoparticle

Ag$^+$ doped silicate glass

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

Absorbance [a.u.]
Wavelength [nm]

after irrad.

before irrad.

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

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

Blue
Orange

Surface plasmon of Ag nanoparticle
Non-bridged oxygen hole center

anneal 550 °C

TEM

10 nm

Confucius
Timescales of electron & lattice process

Carrier excitation
- Absorption of photons
- Impact ionization
- Carrier-carrier scattering
- Carrier-phonon scattering

Thermalization

Carrier removal
- Radiative recombination
- Auger recombination
- Radiative recombination
- Carrier diffusion

Thermal & structural effects
- Ablation & evaporation
- Thermal diffusion
- Resolidification

Crystallization & Graphitization

Crystallization

**BaB$_2$O$_4$**

XRD

Diffractive angle $2\theta$ (deg.)


Graphitization

Raman

Intensity [a.u.]

Raman shift [cm$^{-1}$]

Diamond

Graphite

Irrad. × 10

No irrad.
Precipitation of functional crystal

*Laser beam*

**BaO-Al$_2$O$_3$-B$_2$O$_3$ glass**

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


After 30min

100μm
Precipitation of functional crystal

BaB$_2$O$_4$

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
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