Micro-modification of glass by femtosecond laser—fundamentals and applications

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Acknowledgements
1 $\varepsilon = h\nu$

2 $\varepsilon = mc^2$

3 $P = h/\nu$

4 $\rho = dN/d\tau$

"Imagination is more important than knowledge"

Albert Einstein
Outline

1. Fundamentals of light-matter interaction
2. Femtosecond laser induced phenomena in glass
3. Femtosecond laser induced microstructures in glass
4. Conclusions
Ti:Sapphire femtosecond laser system
(Coherent Co. Ltd)

(>2x10^{16} W/cm^2)
Features of laser

Monochromatic (10^-8 nm), Narrow beam divergence (38000 km/1 km)

High brightness (4x10^{13} cd/m^2, 1.7x10^9 cd/m^2 (sun))

Coherent
Features of femtosecond laser

$1 \text{fs} = 10^{-15} \text{s}$

1) ultrashort pulse
2) ultrahigh electric field ($>2 \times 10^{16} \text{W/cm}^2$)
3) ultrabroad bandwidth (coherent) ($\Delta \nu = \frac{k}{\Delta \tau}$)
Characteristic time of ultrafast processes

- Rotation relaxation of molecules
- Lifetime of excited electronic states
- Coulomb explosion of molecules
- Photodissociation of molecules
- Electron-phonon relaxation
- Molecular vibration period
- Dissociation lifetime of clusters
- Vibration period of phonons
- Electron-electron collision

Characteristic time (sec):
- $10^{-15}$
- $10^{-14}$
- $10^{-13}$
- $10^{-12}$
- $10^{-11}$
- $10^{-10}$

Thermal relaxation
Multiphoton excitation, ionization

Multiply-charged ions ……

Laser intensity (W/cm²)

ns-laser processes

- Tunneling ionization
- Inner shell excitation
- High-pressure generation
- Multiphoton excitation, ionization
- Multiply-charged ions ……

Perturbative nonlinear processes

- ns ablation

Relative effect of ns-laser processes
Characteristics of fs laser with matter:

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

3) Broadband spectrum \( ((\Delta \nu = k / \Delta \tau) \)

Pulse modulation
3-dimensional micro-modification

UV laser

fs laser

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

\( \geq 10^2 \text{TW/cm}^2 \)
Optical setup for manipulating glass structure

- Monitor
- CCD
- O.L.
- Sample
- XYZ stage
- Femtosecond laser system
- Shutter
- N.D.
- Shutter controller
- XYZ stage controller
- PC
Controlling parameters:

1) Fs laser
   Pulse energy, Pulse width, Pulse repetition rate,
   Polarization, Pulse Phase, Pulse front tilt, Pulse train…

2) Focusing system
   NA of lens, immersion oil

3) Controlling system
   Irradiation time, Scanning direction, Scanning speed, Scanning time
Properties of glass:

- Amorphous structure、glass transition
- Isotropic, Designable composition and micro-structure
- Transparent and homogenous
- Metastable
- Solid solvent
- Composition controllable
- Easy fabrication
- Easy processing
- Multi-processing PS, Cryst. Ion Change.
Fs laser induced phenomena

Transient phenomena  Permanent phenomena
Various emissions during fs laser irradiation

Typical emission spectra of fluoride glass and Ge-doped silica glass during irradiation of an ultrashort-pulse laser. Wavelength, average power and pulse width of the laser were 800 nm, 200 mW and 120 fs at 200 kHz, respectively.
F$s$ laser induced long lasting phosphorescence

Emission states of phosphorescence in rare-earth-doped fluorozirconate glasses induced by femtosecond laser

Decay curve of the phosphorescence at 543nm in the femtosecond laser irradiated $\text{Tb}^{3+}$-doped fluorozirconate glass


欠陥があるゆえに発光する

Emitting only with defects
FS laser-induced polarization-dependent emission

Ge-SiO$_2$

Memorized polarization-dependent emission


10X(NA=0.30), 200mW, 150fs, 200kHz, 4mm

Eu-doped AlF₃-based glass

a: 0min  b: 5min  c: 10min  d: 20min
Single fs laser beam-induced polarization-dependent nanograting

Optical microphotograph

BEI image of SEM

100× (0.95)
120fs
200kHz
200mW
1s

SiO₂

Single fs laser beam-induced polarization-dependent nanograting

(a) O and Si concentration AES mapping

(b) Mechanism of the nanograting

Electron movement

Laser (wave vector \( k_w \))

Hot plasma

\[ k_d = k_p - k_w \]

\[ k_d = \frac{2\pi}{\Lambda} \]

\( k_w \): laser wave vector

\( k_p \): plasmon wave vector

\( k_d \): dielectric constant modulation vector

\( \Lambda \): period of nanostructure
Images of the “Small World Map” taken with optical (a) and polarization (b – azimuth angle, c – retardance) microscopes. The structure was printed in silica glass using femtosecond laser beam modulated with LCOS-SLM. Actual size of the structure is 3.4 mm × 1.8 mm. The highly magnified images of the marked area are shown on the right.
Single femtosecond laser beam-induced rotated nanograting
Single femtosecond laser beam-induced rotated nanograting
Fs laser-induced nano-void array

**Condition:**
- Repetition rate: 1 kHz
- Pulse number: 250 pulses
- Pulse energy: 10 µJ
- Objective lens: 100× (NA = 0.9)

**Dimensions:**
- Diameter: 1.6 µm
- Period: 7.3 µm
- Diameter: 380 nm
- Period: 1.7 µm

Non-paraxial nonlinear Schrödinger equation to exactly describe the pulse propagation:

\[
\frac{\partial^2 E}{\partial z^2} + i 2k \frac{\partial E}{\partial z} + \nabla E = kk' \frac{\partial^2 E}{\partial \xi^2} - ik \sigma(1 + i \omega \tau_c) \rho E - ik \beta^{(K)} |E|^{2K-2} E - 2kk_0 n_2 |E|^2 E
\]

Electron density

\[
\frac{\partial \rho}{\partial \xi} = \frac{1}{n^2 E_s} \rho |E|^2 + \frac{\beta^{(K)} |E|^{(2K)}}{K h \omega} - \frac{\rho}{\tau_c}
\]

Analysis of interface spherical aberration by P. Török et al (electromagnetic diffraction theory)

\[
I_0^{(c)} = \int \left( \cos \phi \right)^{1/2} \left( \sin \phi \right) \exp \left[ ik_0 \psi \left( \phi, \phi_2, -d \right) \right] \times \left( \tau_c + \tau_\rho \cos \phi_2 \right) J_0 \left( k_1 r_\rho \sin \phi_1 \sin \phi_2 \right) \times \exp \left( ik_2 r_\rho \cos \phi_1 \cos \phi_2 \right) d\phi_1
\]
Fs laser-induced nano-void array

Self-aligned voids structure

On-axis electric strength distribution along the direction of the laser propagation (spherical aberration)

Fs laser-induced nano-void array

Condition:
Repetition rate: 1 kHz
Pulse number: 250 pulses
Pulse energy: 10 uJ
Objective lens: 100× (NA = 0.9)

Fs laser-induced tilted grating

Fs laser induced migration of ions

$65\text{SiO}_2-10\text{CaO}-20\text{Na}_2\text{O}-5\text{Eu}_2\text{O}_3$


EPMA mapping showing element distribution from the laser focal point to the edge of the laser modified zone.

Confocal fluorescence spectra from different positions (A-C) of a laser modified zone.
Fs laser induced migration of ions

(Color online) EPMA mapping showing the distribution of Ca$^{2+}$ ions in the glass with different pulse energies. (a) 2μJ, (b) 2.72μJ, (c) 3.12μJ, (d) 3.52μJ
Micro structures looks like bear-paw induced by fs laser beam


Na$_2$O-CaO-SiO$_2$ glass

Famous Chinese Dish Bear-paw (熊掌)
Fs laser induced mysterious structure

*Opt. Express, 2012*

Aluminosilicate glass
250KHz
120fs
Femtosecond laser induced microstructures

Various structures induced by 800 nm, 120fs laser-pulses

*The Chemical Record,*
**Fs laser induced valence state change of transition metal ions**

\[
\text{Mn}^{2+} + \text{Fe}^{3+} \rightarrow \text{Mn}^{3+} + \text{Fe}^{2+}
\]

Absorption spectra

- **a**: before irradiation
- **b**: after irradiation (iron and manganese)

**Materials:**
- 20Na\(_2\)O-10CaO-70SiO\(_2\)-0.1Fe\(_2\)O\(_3\)-0.1MnO (mol%)

**Conditions:**
- 1KHz
- 10x(NA=0.3)
- 3mW
- 120fs

**References:**
Fs laser induced valence state change of noble metal ions

\[
\text{Ag}^+ \rightarrow \text{Ag}^{2+} + \text{Ag}
\]

Na\textsubscript{2}O-Al\textsubscript{2}O\textsubscript{3}-P\textsubscript{2}O\textsubscript{5}-0.1Ag\textsubscript{2}O (mol%)
Fs laser induced valence change of heavy metal ions

$\text{Bi}^{3+} \rightarrow \text{Bi}^{2+} \rightarrow \text{Bi}^+(\text{Bi})$

Visible and infrared luminescence changes after fs laser irradiation

$\text{J. Mat. Chem. 19(2009)4603.}$
Fs laser induced valence change of rare earth ions

\[ \text{Eu}^{3+} \rightarrow \text{Eu}^{2+} \]

Potoluminescence spectra of a Sm\(^{3+}\)-doped borate glass before and after the femtosecond laser irradiation

ESR spectra of Eu\(^{3+}\)-doped ZBLAN glass before (a) and after (b) the femtosecond laser irradiation and the spectrum (c) of a Eu\(^{2+}\) -doped AlF\(_3\)-based glass sample

\[ \text{Sm}^{3+} \rightarrow \text{Sm}^{2+} \]

3D rewriteable memory using valence state change of Sm ion

Three layers spaced 2μm

4f-4f Sm$^{2+}$ 692nm

fs 488nm Ar$^{+}$

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

Fs laser direct writing of refractive index changed pattern

Laser beam

XYZ stage
Direct writing of optical waveguide

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.

Direct writing of optical waveguide

Internal loss of waveguides

Average power: 150mW  Scanning rate: 0.5mms  pulse width: 130fs

Average power: 150mW  Scanning rate: 0.5mms  pulse width: 400fs

Wavelength (nm)

Intensity (a.u.)

8µm
Direct writing of grating and lens


Direct writing of integrated DOEs

Grating & Binary lens (microscopic view)

Beam diameter = 12~13μm

Split beam power ~ 27% of input beam

Beam profile at the focal plane
Direct writing of optical waveguide

Precipitation of functional crystal

**SHG crystals** \((\text{Ba}_2\text{TiSi}_2\text{O}_8)\)

Photographs around the focal regions during fs laser irradiating for (a) 10s, (b) 30s, (c) 60s, respectively. (d) Time dependence of second-harmonic intensity during fs laser irradiation.

Microphotographs of the focal regions under the glass surface of 200mm illuminated by a) the natural light and b) the cross-polarized light after fs laser irradiating for 10s, 30s, 60s and 120s, respectively.
Space-selective precipitation of crystals

TiO$_2$ crystals

Microphotograph of the fs laser irradiated TiO$_2$-B$_2$O$_3$-SiO$_2$ glass.

XRD pattern of the glass before and after the laser irradiation.
Space-selective precipitation of crystals

Yb$^{3+}$-Er$^{3+}$ co-doped CaF$_2$ nanocrystals
Space-selective precipitation of nanoparticles

Metal: Au, Ag, Cu, Pb, Zn, Ga, Na etc.

a: before irradiation
b: after irradiation
c: after annealing at 550°C for 10 min

Size control of precipitated Au nanoparticles

Absorption spectra

a: 6.5 x 10^{13} W/cm^2
b: 2.3 x 10^{14}
c: 5.0 x 10^{16}

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
Three-dimensional engrave in glass
Space-selective precipitation of nanoparticles

Semiconductor: Si, Ge, PbS, PbSe etc.

a: Optical microscope images
b: Raman spectra
c: XRD patterns
d: Z-scan results

AFM observation of micro-grating in glasses by interference field of ultrashort pulsed lasers

\[ d = \frac{\lambda}{2 \sin(\theta/2)} \]

[Equation]

\[ \eta > 90\% \]

[Caption]

\( (\omega+\omega) \)

[Reference]

Observation of micro-grating in azobenzene polyimide by interference field of ultrashort pulsed lasers

\( (\omega + \omega + \omega) \)

\[
\begin{align*}
\theta &= 7^\circ \\
d &= 4 \ \mu m
\end{align*}
\]

\[
\begin{align*}
\theta &= 15^\circ \\
d &= 2 \ \mu m
\end{align*}
\]

\[
\begin{align*}
\theta &= 45^\circ \\
d &= 0.7 \ \mu m
\end{align*}
\]
Microstructures by interference field of ultrashort lasers

2θ = 46.1°, Λ = 1μm

2θ = 90.7°, Λ = 563nm

ZnO

Polarization Direction
All-optical poling \((\omega + 2\omega)\)

Non-linear interference field induced large and stable second harmonic generation in chalcogenide glasses.

Photoinduced noncentrosymmetry \(\chi^{(2)}\)

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Features of femtosecond laser

1) ultrashort pulse
2) ultrahigh electric field (>2x10^{16} W/cm^2)
3) ultrabroad bandwidth (coherent) \( \Delta v = k / \Delta \tau \)
Pulse-shaping: Spatial Mask

Grating

Liquid crystal spatial modulator

FT

shaping

FT⁻¹
Various mysterious emission patterns
Conclusion

We have observed many interesting phenomena due to the interaction between femtosecond laser and transparent materials e.g. glasses.

We have demonstrated 3D rewritable optical memory, fabrication of 3D optical circuits, 3D micro-hole drilling, and 3D precipitation of functional crystals.

Our findings will pave the way for the fabrication of functional micro-optical elements and integrated optical circuits.
Grazie!
谢谢! Thanks!
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