Femtosecond laser induced functional microstructures in glass

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"Imagination is more important than knowledge"

Albert Einstein
Outline

1、Fs laser and its features

2、Mechanisms about fs laser interaction with matter

3、Fs laser induced micro-structures in glass and their applications, and fs laser induced phenomena

4、Conclusion
Two greatest theories in the last century (in the field of science and technology)

quantum mechanics
量子力学
量子力学

is a set of scientific principles describing the known behavior of energy and matter that predominate at the atomic scale.

special relativity
狭义相对论
狭義相対論

is a physical theory of measurement in inertial frame of reference.
Four greatest inventions in the last century

Atomic energy  Semiconductor  Computer  Laser
What is laser?

Light amplification by stimulated emission of radiation

激光 レーザー (thunder and lightning radiation)

Pumping source

Optical cavity

Gain medium
Feature of laser

- Monochromatic \( (10^{-10} \text{m}) \), Narrow beam divergence
- High brightness \( (4 \times 10^{13} \text{cd/m}^2, \ 1.7 \times 10^9 \text{cd/m}^2 \text{(sun)}) \)
- Coherent
Nobel prize winners for laser

Towens, Prokhorov and Basov
for their works in the field of the maser and the laser
(1964)
First Laser

Maiman (1960)

Ruby Laser
LD

Gas laser (CO$_2$, Ar, Excimer)

Liquid laser (dye)

Solid State laser (Crystal, glass)

Free-electron laser

etc.

CW laser      Pulsed laser
What is femtosecond laser?

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

$100 \text{ fs} = 10^{-13} \text{s}$
Femtosecond laser system

Spectral-physics Co. Ltd
How to realize a femtosecond pulse?

**Mode-locking:** *Appl. Phys. Lett. 38*(1981)*671.*

R. L. Fork, B. I. Green and C. V. Shank (Bell Lab.)
CPM (Collision pulse mode-locking)  90fs pulse train

The basis of the technique is to induce a fixed phase relationship between the modes of the laser's resonant cavity. The laser is then said to be *phase-locked* or *mode-locked*. Interference between these modes causes the laser light to be produced as a train of pulses. Depending on the properties of the laser, these pulses may be of extremely brief duration, as short as a few femtoseconds.
How to realize a femtosecond laser pulse with high energy?


An ultrashort laser pulse is stretched out in time prior to introducing it to the gain medium using a pair of grating that are arranged so that the low-frequency component of the laser pulse travels a shorter path than the high-frequency component does. After going through the grating pair, the laser pulse becomes positively chirped, that is, the high-frequency component lags behind the low-frequency component, and has longer pulse duration than the original by a factor of 103 to 105.
Then the stretched pulse, whose intensity is sufficiently low compared with the intensity limit of gigawatts per square centimeter, is safely introduced to the gain medium and amplified by a factor 10^6 or more. Finally, the amplified laser pulse is recompressed back to the original pulse width through the reversal process of stretching, achieving orders of magnitude higher peak power than laser systems could generate before the invention of CPA.
How to get a fs laser pulse with various frequency?

**Optical parametric oscillation**

\[ \omega_3 = \omega_s + \omega_i \]

is a parametric oscillation which oscillates at optical frequencies. It converts an input laser wave (called "pump") into two output waves of lower frequency \((\omega_s, \omega_i)\) by means of nonlinear optical interaction. The sum of the output waves frequencies is equal to the input wave frequency: \(\omega_s + \omega_i = \omega_p\). For historic reasons, the two output waves are called "signal" and "idler".

**β-BBO(β–BaB\textsubscript{2}O\textsubscript{4})**

High \(\chi^{(2)}\), mechanical strength, high breakdown threshold
Ti:Al$_2$O$_3$

$^2E(2)$ 1) Large stimulated emission cross-section

$^2E(1)$ 2) High hardness, thermal conductivity

3) Available pumping source

4) 700nm-1μm tunable

5) easy to be mode-locked
Three features of femtosecond laser:

1) ultrashort pulse

2) ultrahigh light intensity (>2x10^{16} W/cm^2)

3) ultrabroad bandwidth (coherent) \( \Delta \nu = k / \Delta \tau \)
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 times range from $10^{-15}$ to $10^{-10}$ seconds.
Multiphoton excitation, ionization

Multiply-charged ions

ns-laser processes

Light intensity (W/cm²)

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

Laser-matter interactions

Perturbative nonlinear processes

ns ablation

Relative effect
Applications of femtosecond laser

1  **Ultrashort pulse**
   Nonlinear optics
   TeraBit optical communication (soliton transmission etc.)
   Ultrashort pulse
   Ultrafast spectroscopy (Pump-Probe spectroscopy)
   Multiphoton Microscope
   Nano-Bio
   Nano-surgery

2  **High coherent pulse-train**
   Multi-photon excitation spectroscopy
   Precise measurement of light frequency

3  **High electric field**
   Laser-induced plasma and X-ray
   Monochromatic electron beam
   Generation of oriented X-ray and γ-ray
   CIF
   Laser-triggered lightning

4  **High coherent broadband spectrum**
   Terahertz time-resolved spectroscopy
Pictures taken during a bullet shooting a steel plate using ultrafast camera
Time resolution: 5µs
Studying the dynamic process of chemical reaction

ICN* → [I···CN] * → I+CN

Intermediate state: life time about 500fs
Use two pulses (strong pump and weak probe). A **pump** pulse excites the sample and triggers the process under investigation. A second delayed pulse, the **probe**, monitors an optical property. By varying the time delay between the pump and probe pulses, it is possible to assemble measurements as a function of time.
Ultrashort pulse: Femto-spectroscopy
Femtochemistry

Prof. Zewail
(Caltech)

for showing that it is possible with rapid laser technique to see how atoms in a molecule move during a chemical reaction.
Ultrashort pulse train: Femto-spectroscopy
Precise measurement of light frequency
(Optical comb)

J. L. Hall
T. W. Haensch
for their contributions to the development of laser-based precision spectroscopy, including the optical frequency comb technique: a very precise tool for measuring different colors—or frequencies—of light, only made possible by recent advances in ultrafast femtosecond lasers.
Basic idea of our research

Glass

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

External field

- Electric field
- Magnetic field
- Laser
- Radiation
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
3-dimensional micro-modification

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

\[ \geq 10^2 \text{TW/cm}^2 \]
Applications of induced microstructures

Why not nano or pico-second laser?

No intrinsic absorption \( n \hbar \omega \geq E_g \)

Multiphoton absorption rate \( P(I)_{MPI} = \sigma_n I^n \)

Avalanche ionization (via impact ionization)

Exponential growth of the free electrons.

A highly absorptive and dense plasma, induce various phenomena due to nonlinear processes
Some of the related important research

Optical setup

200 kHz

Ar\(^+\) Laser

Mode locked Ti:sapphire laser

Regenerative Amplifier

1 kHz

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

Mode locked Ti:sapphire laser

Nd:YLF laser

Regenerative Amplifier

Pulses Compressor

120 fs ~ 250 fs

N.D.F.

Sample

XYZ stage

CCD

Monitor

B.S.

D.M.

O.L.
Laser systems for direct 3D writing

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

1KHz Ti:Sapphire femtosecond laser system
(Spectra-Physics Co. Ltd)
During and after fs laser irradiation

Emission

Coloration
Femtosecond laser induced microstructures

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

1KHz
10x(NA=0.3)
3mW
120fs

20Na\textsubscript{2}O-10CaO-70SiO\textsubscript{2}-0.1Fe\textsubscript{2}O\textsubscript{3}-0.1MnO (mol%)

Fs laser induced valence state change of noble metal ions

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

Na$_2$O-Al$_2$O$_3$-P$_2$O$_5$-0.1Ag$_2$O (mol%)

Emission and excitation spectra

- a, b: before irradiation
- c, d: after irradiation

ESR spectra

- a: before irradiation
- b: after irradiation

Fs laser induced valence change of heavy metal ions

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

Visible and infrared luminescence changes after fs laser irradiation

Fs laser induced valence change of rare earth ions

**Eu**$^{3+}$ → **Eu**$^{2+}$


**Sm**$^{3+}$ → **Sm**$^{2+}$

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

Potoluminescence spectra of a **Sm**$^{3+}$-doped borate glass before and after the femtosecond laser irradiation
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$^+$
In brief: Writing memories in light

Three-dimensional memories offer the potential for incredibly high data storage densities, but creating a rewritable 3D memory medium has proved tricky. Now a group of Japanese researchers have developed an all-optical rewritable memory material with a capacity of 10 Tbit cm⁻³.

11 April 2002

Jonathan Davids

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 = 10¹² 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, Qi, Fujiwara, Sakaguchi and Hirao demonstrate a high-capacity 3D memory that can be written, read, erased and rewritten using all-optical methods.

The material in question is glass doped with ions of samarium, a rare-earth metal. These can be switched between two stable valence states, Sm⁺³ and Sm⁺⁴, by photoreduction and photo-oxidation respectively, 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⁺³ species that is completely absent in Sm⁺², 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 memory with rewriteable and ultrahigh density using the valence-state change of samarium ions

We report the recording, readout, and erasure of a three-dimensional optical memory using the valence-state change of samarium ions to represent a bit. A photoreduction bit of 200 nm diam can be recorded with a femtosecond laser and readout clearly by detecting the fluorescence as a signal.
Femtosecond laser induced microstructures

Various structures induced by 800 nm, 120fs laser-pulses
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.
Mode-field patterns

(a) Core : 8 μm

(b) Core : 17 μm

(c) Core : 25 μm

Experimental
H.G.Fitting
n(0)=1.502
Base:1.499

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 drawn by translating the silica glass perpendicular to the axis of the laser beam.

Direct writing of grating and lens


Precipitation of functional crystal

Fs laser with high repetition rate = Local heat source

XRD pattern

Variation of emission spectra obtained from moving the laser focal point that accompanies growth of frequency conversion crystals.
Effect of Ag\(^+\) on fs laser induced precipitation of crystals

Micrographs of side-view of the focal regions illuminated by natural light after femtosecond laser irradiation (laser power: 900 mW, irradiation time: 0.1-30 s).

Dependence between the required time for crystallization and the laser power in Ag+-doped BTS glass and BTS glass.

3D microdrilling of photosensitive glasses
(developed by Dr. Stookey)

\[ \text{Ag}^+ \rightarrow \text{Ag} \]
\[ n\text{Ag} \rightarrow \text{Ag}_n \]

\[ \text{V}_c \succ \text{V}_g \]
in diluted HF solution

Straight hole


Y-branch holes
Space-selective precipitation of nanoparticles


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

Au³⁺-doped glass
Size control of precipitated Au nanoparticles


Absorption spectra

a: $6.5 \times 10^{13}$ W/cm²
b: $2.3 \times 10^{14}$
c: $5.0 \times 10^{16}$
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
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.

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.
Three-dimensional engrave in glass
Novel femtosecond laser-induced phenomena

Polarization-dependent light scattering

Memorized polarization-dependent light scattering in doped glasses and crystals

**a)**

**b)**

**c)**

**d)**

100 µm

Single femtosecond laser beam-induced nanograting

Polarization-dependent femtosecond laser-induced nano-structure

O and Si concentration AES mapping

Mechanism of the nanograting
Femtosecond laser induced long lasting phosphorescence

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

Fs laser-induced nano-void array

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

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

\[
\frac{\partial^2 E}{\partial z^2} + i 2k \frac{\partial E}{\partial z} + \nabla_z E = \left( \frac{\partial^2 E}{\partial \xi^2} - i k \sigma (1 + i \omega \tau_r) \rho \right) E - i k \beta^{(K)} \left| E \right|^{2K} E - 2 kk_n \left| E \right|^2 E
\]

Electron density

\[
\frac{\partial \rho}{\partial \xi} = \frac{1}{n^2} \frac{\sigma}{E_{\rho}} \rho \left| E \right|^2 + \frac{\beta^{(K)} \left| E \right|^{2K}}{K \hbar \omega} - \frac{\rho}{\tau_r}
\]

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

\[
I^{(e)}_{0} = \int_{-\infty}^{\infty} (\cos \phi_1)^{1/2} (\sin \phi_1) \exp \left[ ik_{\rho} \psi (\phi_1, \phi_2, -d) \right] \times \left( \tau_1 + \tau_2 \cos \phi_2 \right) J_0 \left( k_{\rho} \frac{\sin \phi_1 \sin \phi_1}{\tau_2} \right) \times \exp \left( ik_{\rho} \frac{\cos \phi_1 \cos \phi_2}{\tau_2} \right) d \phi_1
\]
Fs laser-induced nano-void array

Self-aligned voids structure

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


electromagnetic diffraction theory

On-axis electric strength distribution along the direction of the laser propagation (spherical aberration)
Coordination state change due to fs laser induced migration of ions

Different positions A–G inside or outside the laser modified zone shown in microscope images and their corresponding micro-Raman spectra a–g.

Coordination state change due to fs laser induced migration of ions

The relative integrated intensity Ar vs the distance from the central laser focal volume.

EDX line scanning spectra showing element distribution from the laser focal point to the edge of the laser modified zone.

\[
[\text{BO}_3^+] + \text{NBO}^+ \text{Na}^+ \rightarrow [\text{BO}_4^-]\text{Na}^+
\]
EDX line scanning spectra 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.

65SiO$_2$-10CaO-20Na$_2$O-5Eu$_2$O$_3$

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

\[(\omega + \omega)\]

\[\eta > 90\%\]

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

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

θ = 7°
\(d = 4 \, \mu m\)

θ = 15°
\(d = 2 \, \mu m\)

θ = 45°
\(d = 0.7 \, \mu m\)
All-optical poling ($\omega + 2\omega$)

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

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

Micro structures looks like bear-paw induced by fs laser beam

Famous Chinese Dish
Bear-paw
(熊掌)
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.
This is a mysterious land

You will harvest (in Autumn) if you sow seeds (in Spring)

Ask and it will be given to you; seek and you will find; knock and the door will be opened to you
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Thanks!
Compact femtosecond laser
Ultrashort-pulse laser machining of dielectric materials

FIG. 10. Cuts in explosive pellet (LX-16-95% PETN) by a Ti:sapphire laser operating at 120 fs (a) and 600 ps (b). Thermal deposition in the long-pulse case caused the pellet to ignite and burn (b).
Space-selective emission in rare-earth-doped glasses excited by an 800nm femtosecond laser
Emission spectra of rare-earth doped glass

Excitation power-dependence of the photoluminescence spectra of a Tb$^{3+}$-doped ZBLAN glass

Energy levels of Tb$^{3+}$
Precise surface processing


\[ L_D = (D \tau)^{1/2} \]
\[ D = \frac{k_T}{\rho C_p} \]

(1ps, 10nm)

a hole drilled in steel with 200fs laser pulses at 780nm

holes drilled in steel with 80ps(left) and 3.3ns(right) laser pulses at 780nm
\[ \gamma = \frac{\omega}{e} \left[ \frac{m c n \varepsilon_0 E_g}{I} \right]^{1/2} \]