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Femtosecond laser induced functional microstructures in glass

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Jan. 11th, 2010 Yuquan, Campus



"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 special relativity 狭义相对论 狭義相対論

is a set of scientific principles describing the known behavior of energy and matter that predominate at the atomic scale. 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 雷射(thunder and lightning radiation)



Pumping source



Gain medium

Feature of laser



Monochromatic (10⁻¹⁰m), Narrow beam divergence High brightness (4x10¹³cd/m², 1.7x10⁹cd/m²(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



Energy levels of chromium ions in ruby





LD

Gas laser (CO₂, Ar, Excimer) Liquid laser (dye) Solid State laser (Crystal, glass) Free-electron laser etc. CW laser Pulsed laser

What is femtosecond laser?

1fs(飞秒)=10⁻¹⁵s



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?

CPA (Chirped pulse amplification): *Opt. Commun. 56(1985)219.* D. Strickland and G. Mourou (Univ. Rochester)



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 106 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



is a parametric osillation 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 -BaB₂O₄)

High $\chi^{(2)}$, mechanical strength, high breakdown threshold



Ti:Al₂O₃



- $^{2}E(2)$ 1) Large stimulated emission cross-section
- $^{2}E(1)$ 2) High hardness , thermal conductivity
 - 3) Available pumping source
 - 4) 700nm-1 μ m tunable
 - 5) easy to be mode-locked

Three features of femtosecond laser:

1) ultrashort pulse

2) ultrahigh light intensity (>2x10¹⁶W/cm²)

3) ultrabroad bandwidth (coherent) $(\Delta v = k / \Delta \tau)$

Characteristic time of ultrafast processes



Laser-matter interactions

ns-laser processes



Light intensity (W/cm²)

Applications of femtosecond laser

1 Ultrashort pulse

Nonlinear optics

TeraBit optical communication (soliton transmission etc.)

<u>Ultrafast spectroscopy</u> (Pump-Probe spectroscopy)

Multiphoton Microscope

<u>Nano-Bio</u>

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 <u>Generation of oriented X-ray and γ-ray</u> 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

$$ICN^* \rightarrow [I \cdots CN] * \rightarrow I + CN$$

Intermediate state : life time about 500fs

Femtosecond pump-probe technique



Use two pulses (strong pump and weak probe). A <u>pump</u> pulse excites the sample and triggers the process under investigation. A second delayed pulse, the <u>probe</u>, 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)



T. W. Haensch

J. L. Hall 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



- 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





Fiber grating

Micro-grating

Micro-lenz



Some of the related important research

- 1) H. Misawa, Japanese Patent 1994.
- 2) K. M. Davis et al., Opt. Lett., 21(1996)1729.
- 3) E. N. Glezer et al., Opt. Lett., 21(1996)2023.
- 4) K. Miura et al., Appl. Phys. Lett., 71(1997)3329.
- 5) S. Juodkazis et al., Phys. Rev. Lett., 96(2006)166101.
- 6) P. G. Kazansky et al., Phys. Rev. Lett., 82, 2199 (1999).
- 7) D. Homoelle et al., Opt. Lett., 24(1999)1311.
- 8) K. Kawamura et al., Appl. Phys. Lett., 79(2001)1228.
- 9) A. Marcinkevicius et al., Appl. Phys. Lett., 26(2001)277.
 10) H. Sun et al., Opt. Lett., 20(2001)325.



Laser systems for direct 3D writing

Pulse energy 5µ J



200KHz Ti:Sapphire femtosecond laser system (Coherent Co. Ltd) Pulse energy 1m J



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

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



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

Appl. Phys. Lett., 79(2001)3567.

Fs laser induced valence state change of noble metal ions



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

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

J. Mat. Chem. 19(2009)4603.



Visible and infrared luminescence changes after fs laser irradiation

Fs laser induced valence change of rare earth ions

Appl. Phys. Lett., 74(1999)10. $Sm^{3+} \rightarrow Sm^{2+}$

H (Gauss)

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

ESR spectra of Eu³⁺-doped ZBLAN glass before (a) and after (b) the femtosecond laser irradiation and the spectrum (c) of a Eu²⁺ -doped AlF₃-based glass sample





3D rewriteable memory using valence state change of **Sm ion**





http://www.nature.com/cgi-taf/Gateway.taf?g=3&file=/materials/highlights/articles/m020411-3.html&filetype=& UserReferer

In brief: Writing memories in light



Distributions of photoluminescence intensity, showing selective erasure and rewriting of two neighbouring bits spaced 200 nm apart. a, Both bits in the photoreduced (Sm2+) state. b and c, after 'erasing' bits I and II respectively by photooxidation with a continuouswave laser. d, After 'rewriting' both bits using photoreduction by femtosecond laser irradiation.

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 Sm3+ to Sm2+, 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 Sm²⁺ species that is completely absent in Sm³⁺, 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.

and are distinguished by their different photoluminescence spectra. This

Three-dimensional optical memory with rewriteable and ultrahigh density using the valencestate 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

Femtosecond laser direct writing



XYZ stage



Photo-written lines in a glass formed using 800nm 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 μ m/s and focusing the laser pulses through a 10X or 50X microscope objective, respectively.

Mode-field patterns



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



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

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

Direct writing of grating and lens



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

Opt. Lett., 29(2004)2728.

Precipitation of functional crystal

Fs laser with high repetition rate=Local heat source



XRD pattern

Opt. Lett., 25(2000)408.



Effect of Ag⁺ on fs laser induced precipitation of crystals



Micrographs of side-view of the focal
regions illuminated by natural light afterDependence between the required
time for crystallization and the laserfemtosecond laser irradiation (laser power: power in Ag+-doped BTS glass and
900 mW, irradiation time: 0.1-30 s).BTS glass.

3D microdrilling of photosensitive glasses

(developed by Dr. Stookey)

$$Ag^{+} \longrightarrow Ag$$

 $nAg \longrightarrow Ag_n$

in diluted HF solution





Y-branch holes

Straight hole

Jpn. J. Appl. Phys., 38(1999)L1146.

Space-selective precipitation of nanoparticles

Angew. Chem. Int. Ed., 43(2004)2230.





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

Size control of precipitated Au nanoparticles

Angew. Chem. Int. Ed., 43(2004)2230.



a: 6.5 x 10¹³W/cm² b: 2.3 x 10¹⁴ c: 5.0 x 10¹⁶

Absorption spectra

Space-selective dissolution of Au nanoparticles

Angew. Chem. Int. Ed., 43(2004)2230.



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.



Three dimensions means faster chips and more memory.

Sofar the researchers have used the technique to create threedimensional 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 Chemie¹.

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It is avon possible to or

Three-dimensional engrave in glass





Novel femtosecond laser-induced phenomena



<u>100 μm</u> Polarization-dependent light scattering *Phys. Rev. Lett.*, 82(1999)2199.

Memorized polarization-dependent light scattering in doped glasses and crystals



100 µm

Appl. Phys. Lett., 77(2000)1940.

Single femtosecond laser beam-induced nanograting



Optical microphotograph

BEI image of SEM

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

Polarization-dependent femtosecond laser -induced nano-structure



O and Si concentration AES mapping



Mechanism of the nanograting

Femtosecond laser induced long lasting phosphorescence



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

Decay curve of the phosphorescence at 543nm in the femtosecond laser irradiated Tb³⁺ -doped fluorozirconate glass

Fs laser-induced nano-void array



Condition :

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



Nano Lett., 5(2005)1591.

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

$$\frac{\partial^{2} E}{\partial z^{2}} + i2k \frac{\partial E}{\partial z} + \nabla_{\perp} E = kk^{*} \frac{\partial^{2} E}{\partial \xi^{2}} - ik\sigma(1 + i\omega\tau_{c})\rho E - ik\beta^{(K)} \left|E\right|^{2K-2} E - 2kk_{0}n_{2}\left|E\right|^{2} E$$
(1)
Nonlinear effects

Electron density

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

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

$$I_{0}^{(e)} = \int_{0}^{\sqrt{a_{axx}}} \left(\cos\phi_{1}\right)^{1/2} \left(\sin\phi_{1}\right) \exp\left[ik_{0}\psi\left(\phi_{1},\phi_{2},-d\right)\right] \times \left(\tau_{s}+\tau_{p}\cos\phi_{2}\right) J_{0}\left(k_{1}r_{p}\sin\phi_{p}\sin\phi_{1}\right) \times \exp\left(ik_{2}r_{p}\cos\phi_{p}\cos\phi_{2}\right) d\phi$$

$$(3)$$
aberration function

Appl. Phys. Lett., 92(2008)121113

Fs laser-induced nano-void array

Self-aligned voids structure





z (µ m)

Appl. Phys. Lett., **92(2008)92904.**



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

Appl. Phys. Lett., 92(2008)121113.





Raman shift (cm⁻¹) 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.

 $[BO_3] + NBO + Na^+ \rightarrow [BO_4]^-Na^+$



Fs laser induced migration of ions

65SiO₂-10CaO-20Na₂O-5Eu₂O₃

Opt. Lett., 92(2009)121113.



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.

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

($\omega + \omega$) Appl. Phys. Lett., 77(2000)3887.





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

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







 $\theta = 7^{\circ}$ d = 4 μ m

 $\theta = 15^{\circ}$ $\mathbf{d} = 2 \ \mu \mathbf{m}$

 $\theta = 45^{\circ}$ d = 0.7 µm



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


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.



Xiaosheng Liang 这是一片神奇的土地 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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(Zhejiang University and SIOM, CAS)

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

Dr. N. Jiang (Arizona State Univ., UK)



Compact femtosecond laser



Ultrashort-pulse laser machining of dielectric materials M. D. Perry et al., J. Appl. Phys., 85(1999)6803.



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



Front view



Side view

Emission spectra of rare-earth doped glass



Excitation power-dependence of the photoluminescence spectra of a Tb³⁺ -doped ZBLAN glass



Energy levels of Tb³⁺

Precise surface processing

B. N. Chichkov et al., Appl. Phys. A63 (1996) 109.



 $L_{\rm D} = (D\tau)^{1/2}$ $D = k_{\rm T} / \rho C_{\rm p}$

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

$$\gamma = \frac{\omega}{e} \left[\frac{m c n \varepsilon_0 E_g}{I} \right]^{\frac{1}{2}}$$

