Lecture 6, Part 1: Laser patterning of crystals in glass

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Plan of my talk

1. Basic concept of crystallization in glass
2. What is laser-induced crystallization (LIC)?
3. Patterning and Mechanism of LIC.

Glass

Key materials in information technology

Glass Structure: Inversion Symmetry
No second-order optical nonlinearity
No ferroelectric properties
Not active in light control

Glass/Crystal Hybrid Materials

Glass

Super-cooled liquid

Glass transition
Structural relaxation
Phase separation
Crystallization

Materials design based on glass crystallization

Crystal

Liquid

RT

Tg

Tm

Temperature

I

or

U

Glass

Super-cooled liquid

Melt

Free energy

Temperature

Tg

Tm

Control

Microstructure design

I : Nucleation rate
U : Crystal growth rate

Crystallization of Glass

Glass

Nanocrystals

Oriented ceramics

Single crystals

Glass/Crystal Hybrid Materials

Devices
**Transparent nanocrystallized glass**

- $15K_2O\cdot 15Nb_2O_5\cdot 70TeO_2$
- Nanocrystals (~20nm)
- $K[Nb_{1/3}Te_{2/3}]_2O_4$
- Distorted fluorite-type
- Light wave conversion SHG

**Highly oriented crystallized glass**

- $BaO-TiO_2-GeO_2$ glasses
- $Ba_2TiGeO_3$ crystal
- $\alpha \sim 20$ pm/V

**Telecommunication network system**

- Network (glass)
- Link
- Node
- High speed
- Huge capacity
- Slow switching rate
- WDM Amplification
- O/E/O $\rightarrow$ O/I/O

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**Tunable Optical Switch**

- Electrode
- Glass fiber
- Ti:LiNbO$_3$ Single crystal
- Nonlinear optical crystals: SHG
- Ferroelectrics: Electro-optic effect

**Laser-induced micro-fabrication in glass**

1) Hill et al. (1978): Ge-dope SiO$_2$ fiber + $\lambda$=488nm
   - Refractive index change
2) Osterberg et al. (1986): Ge-dope SiO$_2$ fiber + $\lambda$=1064nm
   - Second harmonic generation (SHG)

**New Tunable Optical Switch using Glass**

- Crystal line
- Glass fiber
- We need a technique available for spatially selected crystallization of glass

**New challenge in glass science and technology**

- Glass: SiO$_2$, Photosensitive glass
- Laser: Excimer, Femtosecond
- Phenomenon: Refractive index change, hole
- Local anisotropy

**Patterning and Designing of Crystallization**
**Laser crystallization (LC)**

In a-Si Engineering

High-quality poly-Si TFT

UV excimer laser

LC technique

Poly-crystalline Si


**Chalcogenide glasses: DVD Ge₂Sb₂Te₅**

LD laser: amorphous-crystal transformation (nano-pulse)

amorphous

crystal


**Laser Irradiation in Glass**

KrF excimer laser: λ=248 nm

Femtosecond pulsed laser: λ=800 nm

Refractive index change, Abrasion, Crack,

**Crystal growth rate $U_{\text{max}}$ in oxide glasses**


<table>
<thead>
<tr>
<th>Glass</th>
<th>Crystal growth rate $U_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O·2SiO₂</td>
<td>70 μm/s</td>
</tr>
<tr>
<td>Na₂O·2SiO₂</td>
<td>1 μm/s</td>
</tr>
<tr>
<td>CaO·MgO·2SiO₂ (Diopside)</td>
<td>230 μm/s</td>
</tr>
<tr>
<td>2MgO·2Al₂O₃·5SiO₂ (Cordierite)</td>
<td>9 μm/s</td>
</tr>
<tr>
<td>2BaO·TiO₂·2SiO₂ (Fresnoite)</td>
<td>430 μm/s</td>
</tr>
</tbody>
</table>

~1 μs for ~ 1nm growth

**CW YAG laser → crystallization**

Laser irradiated spot

Crystallization temp.

Glass transition temp.

Distance

Heat dissipation

Nano-pulse YAG laser → no crystallization

Lattice vibration (~10¹⁵/s) : femtosecond

Heat dissipation


BaO-Sm₂O₃-TeO₂ Glass

cw Nd:YAG λ=1064 nm

Sm₂Te₃O₁₅ crystals

100 μm
Rare-earth Atom Heat Processing

1. Absorption of 1064 nm (Nd:YAG Laser)
2. Non-radiative relaxation: Thermal heating

Absorption of 1064 nm (Nd:YAG Laser)

Non-radiative relaxation: Thermal heating

Laser power: P=0.6 ~ 1.0 W
Scanning speed: S=1 ~ 10 μm/s

Transition metal atom heat processing

SHG

Absorption coefficient (cm⁻¹)

Wavelength (nm)

300 μm

High orientation

Laser
Power: 0.85 W
Scanning: 5 μm/s

BaxTiGeO3 crystal
Homogeneous crystal growth
1. Nucleation should be avoided.
2. Matching of crystal growth rate and laser scanning speeds would be necessary

New challenge in nucleation and crystal growth science

Cross-section of crystal line

Patterning of crystals in glass
1. Rare-earth/transition metal atom heat processing
2. Bending crystal lines
3. Quality of crystal lines and light transmission

- Sm$_2$O$_3$-Bi$_2$O$_3$-B$_2$O$_3$ → Sm$_{3+}$B$_{12+}$BO$_3$
- Sm$_2$O$_3$-BaO-B$_2$O$_3$ → Ba$_{8}$B$_{3}$O$_{14}$
- Li$_2$O-Nb$_2$O$_5$-SiO$_2$ → LiNbO$_3$
- SiO$_2$-Al$_2$O$_3$-CaO-NaF-CaF$_2$ → CaF$_2$
- Li$_2$O-FeO-NbO$_5$-P$_2$O$_5$ → LiFePO$_4$
**Critical angle for total reflection**

<table>
<thead>
<tr>
<th></th>
<th>Glass</th>
<th>Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>1.964</td>
<td>2.070</td>
</tr>
<tr>
<td>$\Delta n$ (%)</td>
<td>5.43</td>
<td></td>
</tr>
</tbody>
</table>

$\theta_{\text{MAX}} \approx 36^\circ$

**Power: 0.66 W**

**Scanning speed: 10 μm/s**

**8Sm2O3:37Bi2O3:55B2O3 glass**

- CW Nd:YAG laser with $\lambda=1064\text{nm}$
- $P=0.9\text{W}$, $S=5\mu\text{m/s}$

- Bending / Quality of crystal lines
- Surface crystallized glass
- Random orientation

**Electric Furnace**

- YAG laser
- Power: 0.66 W
- Scanning speed: 10 μm/s

**Power: 0.9 W**

**Scanning speed: 5 μm/s**

**6Sm2O3:35Bi2O3:55B2O3 glass**

- CW Nd:YAG laser with $\lambda=1064\text{nm}$
- $P=0.9\text{W}$, $S=5\mu\text{m/s}$

**Electric Furnace**

- YAG laser
- Power: 0.66 W
- Scanning speed: 10 μm/s

**Crystal Reagent**

- Random orientation
Polarized micro-Raman scattering spectra

Sm$_{2-x}$Bi$_x$BO$_3$

Same crystal orientation

Gradual change in the crystal structure

Polarization direction of incident laser

Laser scanning direction

10Sm$_{0.4}$.BaO$_{0.6}$.BO$_3$ → β-BaB$_2$O$_4$

Micro-Raman spectra: β-BaB$_2$O$_4$

Surface: (110) orientation

β-BaB$_2$O$_4$ crystal line

Single crystal line

Polycrystal line

※ y-cut β-BaB$_2$O$_4$
**Azimuthal dependence of SHG**

- Linearly polarized YAG laser: 1064 nm
- Sample
- IR cut filter
- SH intensity: 532 nm as a function of θ

**β-BaB₂O₄**

- Trigonal system R3c (a=1.2519 nm, c=1.2723 nm)
- Stacking of Planar B₃O₆ rings in c-axis
- Origin of optical nonlinearity: polarizability in B₃O₆

- Strong SHG at θ=0, 180°
- No SHG at θ=90, 270°
- θ: angle between E and B₃O₆ plane

**SHG microscope observations**

- Single crystal line: strong θ dependence

**Azimuthal dependence of SHG**

- β-BaB₂O₄ crystal lines
- Y-cut β-BaB₂O₄ single crystal

**Sm₂O₃-BaO-B₂O₃ → β-BaB₂O₄**

- B₃O₆ unit
- Single crystal line!!
LiNbO$_3$
- Glass
- 0.3wt%CuO-Li$_2$O-Nb$_2$O$_5$-SiO$_2$
- Laser irradiation
  - Yb: Fiber laser ($\lambda = 1080$ nm)

0.5CuO-40Li$_2$O-32Nb$_2$O$_5$-28SiO$_2$

$P = 1.3$ W
$S = 7$ $\mu$m$s^{-1}$

Scanning direction
Width: 5$\mu$m

Polarized micro-Raman spectra

High orientation: c-axis growth

SHG from crystal line

Intensity (arb.units)

Oxyfluoride glass: fluoride crystal

$43$SiO$_2$-$22$Al$_2$O$_3$-$5$CaO-$13$NaF-$17$CaF$_2$-$3$NiO

$T_g=573$°C, $T_p=617$°C

Intensity (arb.units)
Glass E(CaF$_2$) + 0.5ErF$_3$

Crystallization of oxyfluoride glass

Laser-induced crystallization

Laser irradiation with low powers

More open structure

Cathode materials for Li-ion battery

Highly oriented LiFePO$_4$ crystals

Combination of Laser irradiation and simple chemical etching

CuO-dope BaO-TiO$_2$-GeO$_2$ glass

Refractive index change

Temperature

Molar volume

Laser irradiated

P=0.8 W

P=0.7 W

Base glass

Bump height: 2.5 μm

P=0.8 W

Laser irradiated

Cooling

Heating
**Patterning:** $P=0.85 \text{ W}, \ S=10 \ \mu\text{m/s}$

**Etching:** 1N HNO$_3$, 35 min

U-groove depth: 3.5 $\mu$m

Etching $\rightarrow$ Crystallization

**NiO-doped BaO-TiO$_2$-GeO$_2$ glass**

Etching of crystal dots $P=0.95 \text{ W}, \ t=60 \text{ s}$

Summary

- Crystallization of glass $+$ Laser-induced crystallization
- Design of Glass/Crystal Hybrid Materials
- New micro-devices !!
Progress in laser technology
High power laser
Ultra short pulse (femtosecond) laser
Short wavelength laser
※ Conventional technique: everybody can use!

High potential in micro-fabrication
Spatially selected
Direct and non-contact process
Fast and easily automated

Laser-induced crystallization

1. Factors
Glass system
glass compositions
Laser irradiation conditions
Laser power
Laser scanning speed

2. Mechanism
Laser-induced nucleation
Very rapid crystal growth: 1 ~ 10 μm/s
→ Large temperature gradient in laser irradiated spot (region): large diffusions

Patterning of crystals by laser irradiation