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

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Laser Patterning of Crystals in Glass

T. Komatsu,
Nagaoka University of Technology, Japan

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

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Materials design based on glass crystallization

Crystallization of Glass
Glass
Nanocrystals
Oriented ceramics
Single crystals

Glass/Crystal Hybrid Materials
Devices
Transparent nanocrystallized glass

15KzO.15Nb2O5.7TeO2
Nanocrystals (~20nm)
K[Na1/3Te2/3]2O4.8
Distorted fluoride-type
Light wave conversion

15KzO.15Nb2O5.7TeO2
Nanocrystals (~20nm)
K[Na1/3Te2/3]2O4.8
Distorted fluoride-type
Light wave conversion

Highly oriented crystallized glass

BaO-TiO2-GeO2 glasses
BzTiGeO3 crystal
\( \alpha \sim 20 \text{ pm/V} \)

Distorted fluorite-type

Transparent nanocrystallized glass

SH intensity (arb. units)

Light wave conversion

SHG

Ferroelectrics: Electro-optic effect

High speed
Huge capacity

Slow switching rate

Network (glass)

Link

Node

Amplification

O/E/O

O/I/O

WDM

Tunable Optical Switch

E.O. O/E/O

Huge capacity

WDM

Telecommunication network system

New Tunable Optical Switch using Glass

Electrode

Glass fiber

On, OFF

Crystal line

Glass

We need a technique available for spatially selected crystallization of glass

Laser-induced micro-fabrication in glass

1) Hill et al. (1978): Ge-dope SiO2 fiber + \( \lambda = 488 \text{nm} \)
Refractive index change
2) Osterberg et al. (1986): Ge-dope SiO2 fiber + \( \lambda = 1064 \text{nm} \)
Second harmonic generation (SHG)

New challenge in glass science and technology
Glass: SiO2, 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

amorphous

A.V. Kolobov et al., Nature Mater. 3 (2004) 703

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


<table>
<thead>
<tr>
<th>Material</th>
<th>$U_{\text{max}}$ (μm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li2O.2SiO2</td>
<td>70</td>
</tr>
<tr>
<td>Na2O.2SiO2</td>
<td>1</td>
</tr>
<tr>
<td>CaO.MgO.2SiO2 (Diopside)</td>
<td>230</td>
</tr>
<tr>
<td>2MgO.2AlO3.5SiO2 (Cordierite)</td>
<td>9</td>
</tr>
<tr>
<td>2BaO.TiO2.2SiO2 (Fresnoite)</td>
<td>430</td>
</tr>
</tbody>
</table>

~1 μs for ~1nm growth

CW YAG laser → crystallization

laser irradiated spot

Crystallization temp.

Glass transition temp.

Heat dissipation

Temp.

Distance

Nanopulse YAG laser → no crystallization

Lattice vibration (~10^{13}/s) : femtosecond

Heat dissipation


BaO-Sm2O3-TeO2 Glass

cw Nd:YAG $\lambda=1064$ nm

Sm2TeO15 crystals

K.F. excimer laser: $\lambda=248$ nm

Femtosecond pulsed laser: $\lambda=800$ nm

Refractive index change, Abrasion, Crack,
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)

- Glass plate
- YAG laser
- Laser power: $P=0.6 \sim 1.0$ W
- Scanning speed: $S=1 \sim 10 \mu$m/s

CW Nd:YAG laser irradiation

Sm$_{2}$O$_{3}$-Bi$_{2}$O$_{3}$-B$_{2}$O$_{3}$ glass

Sm$_{2}$+Bi$_{2}$O$_{3}$ Crystal

SHG

Transition metal atom heat processing

NiO 1 mol% doped
33.3BaO-16.7TiO$_{2}$-50GeO$_{2}$ glass
$T_e=670^\circ$C $T_T=780^\circ$C

Laser
Power: 0.85 W
Scanning: 5 μm/s

High orientation

BaTiGeO$_{2}$ 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$_3$-Bo$_2$O$_3$ → Sm$_{1-x}$B$_{1-x}$BO$_x$
- Sm$_2$O$_3$-BaO-B$_2$O$_3$ → β-BaB$_2$O$_4$
- 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-Nb$_2$O$_5$-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>

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

8SmO$_3$·3.7Bi$_2$O$_3$·55B$_2$O$_3$ glass → Sm$_{x}$Bi$_{1-x}$BO$_3$

$P=0.9$ W, $S=4 \mu$m/s

8Sm$_2$O$_3$·3.7Bi$_2$O$_3$·55B$_2$O$_3$ glass

Sm$_2$O$_3$·Bi$_2$O$_3$·B$_2$O$_3$ glass → Sm$_{x}$Bi$_{1-x}$BO$_3$

CW Nd:YAG laser with $\lambda=1064$nm

$P=0.9$ W, $S=5 \mu$m/s

Electric Furnace

Surface crystallized glass

Polarization optical microscopy

Bending / Quality of crystal lines

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

$\lambda=632.8$ nm

$\Delta n$ (%) = 5.43

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

$\lambda=632.8$ nm

First scan

Second scan

200 μm

40°

200 μm

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

$\lambda=632.8$ nm

$\Delta n$ (%) = 5.43

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

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$\theta_{\text{MAX}} \approx 36^\circ$
Polarized micro-Raman scattering spectra

### SmₓBi₁₋ₓBO₃

Same crystal orientation

Gradual change in the crystal structure

Laser scanning direction

---

10Sm₂O₃·40BaO·50B₂O₃ → β-BaB₂O₄

Micro-Raman spectra: β-BaB₂O₄

---

Surface: (110) orientation

β-BaB₂O₄ crystal line

Single crystal line

Polycrystal line

※ y-cut β-BaB₂O₄
Azimuthal dependence of SHG

β-BaB$_2$O$_4$

Trigonal system R3c (a=1.2519 nm, c=1.2723 nm)
Stacking of Planar B$_3$O$_5$ rings in c-axis
Origin of optical nonlinearity: polarizability in B$_3$O$_5$

SHG microscope observations

β-BaB$_2$O$_4$ crystal lines

$\theta$: angle between $E$ and B$_3$O$_5$ plane

Strong SHG at $\theta$=0, 180°
no SHG at $\theta$=90, 270°

Electric field in incident light

SH intensity: 532 nm
Linearly polarized YAG laser: YAG laser: 1064 nm
Sample
IR cut filter
Stage

Azimuthal dependence of SHG

β-BaB$_2$O$_4$

γ-Sm$_2$O$_3$-BaO-B$_2$O$_3$ → β-BaB$_2$O$_4$

Single crystal line: strong $\theta$ dependence

B$_3$O$_5$ unit

Surface: (110) orientation

Single crystal line !!
**LiNbO₃**
- Glass
- 0.3wt%CuO-Li₂O-Nb₂O₅-SiO₂
- Laser irradiation
- Yb: Fiber laser (λ = 1080 nm)

**0.5CuO-40Li₂O-32Nb₂O₅-28SiO₂**
- P = 1.3 W
- S = 7 μm/s⁻¹

**Polarized micro-Raman spectra**

**SHG from crystal line**

**Oxyfluoride glass: fluoride crystal**

**Glass D(CaF₂)**

15 nm
Glass part
Line part
520 540 560 580
Wavelength (nm)

Intensity (arb. units)

\( \lambda_{\text{ex}} = 488 \text{ nm} \)

\( 2H_{11/2} \rightarrow 4I_{15/2} \)

\( 4S_{3/2} \rightarrow 4I_{15/2} \)

Glass E(CaF\(_2\))

\[ +0.5\text{ErF}_3 \]

Crystallization of oxyfluoride glass

Laser-induced crystallization

Oxyfluoride base glass

Temperature

U (fluoride)

I (oxide)

U (oxide)

Laser irradiated region

Fluoride nanocrystal

Li\(_2\)O-FeO-Nb\(_2\)O\(_5\)-P\(_2\)O\(_5\) glass

Nd:YAG laser: \( P=0.07 \text{ W}, \ S=10 \text{ \( \mu \)m/s} \)

Highly oriented LiFePO\(_4\) crystals

Cathode materials for Li-ion battery

Combination of Laser irradiation and simple chemical etching

CuO-dope BaO-TiO\(_2\)-GeO\(_2\) glass

Refractive index change

More open structure

Laser irradiation with low powers
1N HNO₃

U-shape groove

Patterning: $P=0.85$ W, $S=10 \mu\text{m/s}$
Etching: 1N HNO₃, 35 min

U-groove depth: 3.5 μm

Etching → Crystallization

Etching rate
Refractive index $>$ glass $>$ crystal

NiO-doped BaO-TiO₂-GeO₂ glass

Original

Etching of crystal dots $P=0.95$ W, $t=60$ s

Crystal line

Glass

Etching rate
Refractive index $>$ glass $>$ crystal

Summary

Crystallization of glass
Laser-induced crystallization
Design of Glass/Crystal Hybrid Materials
New micro-devices !!
Laser-induced crystallization

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

Patterning of crystals by laser irradiation

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