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

Laser Patterning of Crystals in Glass

T. Komatsu,
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Materials design based on glass crystallization

Crystallization of Glass

Glass
Nanocrystals
Oriented ceramics
Single crystals

Control

Glass/Crystal Hybrid Materials

Devices
transparent nanocrystallized glass

- 15K2O.15Nb2O5.70TeO2
- nanocrystals (~20nm)
- K[Nb1/3Te2/3]2O4.8
- distorted fluorite-type

light wave conversion

- SHG

- BaTiO3-GeO2 glasses
- Ba2TiGeO8 crystal
- $\Delta \sim 20$ pm/V

- 1064 nm
- 532 nm

- electrode

- Ti:LiNbO3 single crystal
- nonlinear optical crystals: SHG
- ferroelectrics: electro-optic effect

- tunable optical switch
- highly oriented crystallized glass

- transparent nanocrystallized glass
- kiln
- light wave conversion

- telecommunication network system

- new tunable optical switch using glass

- laser-induced micro-fabrication in glass

1. Hill et al. (1978): Ge-dope SiO2 fiber + $\lambda = 488$ nm
   - refractive index change
2. Osterberg et al. (1986): Ge-dope SiO2 fiber + $\lambda = 1064$ 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?

we need a technique available for spatially selected crystallization of glass

- high speed
- huge capacity
- slow switching rate
- wdm
- amplification
- o/e/o => o/i/o
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

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>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·2Al2O3·5SiO2 (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

Distance

Temperature

Nano-pulse YAG laser → no crystallization

Lattice vibration (~10¹⁵/s) : ~femtosecond

→ Heat dissipation


BaO-Sm2O3-Te2O5 Glass

cw Nd:YAG $\lambda$=1064 nm

Sm2Te2O15 crystals

Rare-earth Atom Heat Processing

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

Absorption of 1064 nm (Absorption of 1064 nm (Nd:YAG Laser))

Non-radiative relaxation:

10SmO3-35BiO3-58Bo3

Thermal heating: CW Nd:YAG laser irradiation

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

Glass plate
YAG laser

Wavelength (nm)
Absorbance

200°C 7.95 cm$^{-1}$
900°C 7.32 cm$^{-1}$
2500°C 7.32 cm$^{-1}$

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

Sm$_{2}$Bi$_{1-x}$Bo$_{3}$ Crystal

SHG

Transition metal atom heat processing

NiO 1 mol% doped
33.3BaO-16.7TiO$_2$-50GeO$_2$ glass

$\alpha_{\text{1064 nm}} = 6.0 \text{ cm}^{-1}$

$\Delta \rightarrow \pi^*$ (six-fold $N^+$)

Absorption coefficient (cm$^{-1}$)

Wavelength (nm)

300 $\mu$m

NIO 1 mol% doped
33.3BaO-16.7TiO$_2$-50GeO$_2$ glass

$\alpha_{\text{1064 nm}} = 6.0 \text{ cm}^{-1}$

$\Delta \rightarrow \pi^*$ (six-fold $N^+$)

Absorption coefficient (cm$^{-1}$)

Wavelength (nm)

50 $\mu$m

Ba$_2$TiGe$_2$O$_9$ crystal

High orientation
Homogeneous crystal growth

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

Cross-section of crystal line

Sm2O3-MoO3-BaO glasses

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

- Sm2O3-Bi2O3-B2O3 → SmB12-xBO3
- Sm2O3-BaO-B2O3 → β-BaB2O4
- Li2O-Nb2O5-SiO2 → LiNbO3
- SiO2-Al2O3-CaO-NaF-CaF2 → CaF2
- LiO-FeO-Nb2O5-P2O5 → LiFePO4
10Sm₂O₃·35Bi₂O₃·55B₂O₃

Tₐ=474°C, Tₓ=574°C

SmₓBi₁₋ₓBO₃

Crystal

Temp. >> Tₓ

Refractive index change

Wy=474°C, C, Wₓ=574°C

Temp. < Temp. >> Tx

SmₓBi₁₋ₓBO₃

YAG laser

Power: 0.66W

Scanning speed: 10μm/s

Electric Furnace

Surface crystallized glass

Polarization optical microscopy

8Sm₂O₃·37Bi₂O₃·55B₂O₃ glass → SmₓBi₁₋ₓBO₃

P=0.9 W, S=4 μm/s

Critical angle for total reflection

Glass

<table>
<thead>
<tr>
<th>n</th>
<th>1.964</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δn (%)</td>
<td>5.43</td>
</tr>
</tbody>
</table>

Crystal

| n     | 2.070 |

θ MAX ≒ 36°

※ λ=632.8 nm

 poids central

Bending / Quality of crystal lines

8Sm₂O₃·37Bi₂O₃·55B₂O₃ glass

SmₓBi₁₋ₓBO₃

Glass

Crystal

First scan

Second scan

200 μm

200 μm

SmₓO₃·Bi₂O₃·B₂O₃ glass

SmₓO₃·Bi₂O₃·B₂O₃ glass → SmₓBi₁₋ₓBO₃

CW Nd:YAG laser with λ=1064nm

P=0.9W, S=5μm/s
**Polarized micro-Raman scattering spectra**

- Incident laser
- Raman scattering light

**SmₓBi₁₋ₓBO₃**

- Same crystal orientation

**Gradual change in the crystal structure**

- Laser scanning direction

**Electric furnace: 760°C, 1h**

- Single crystal line
- Polycrystal line

**Surface: (110) orientation**

- β-BaB₂O₄ crystal line

**10Sm₂O₃·40BaO·50B₂O₃ → β-BaB₂O₄**

- Micro-Raman spectra: β-BaB₂O₄

- y-cut β-BaB₂O₄
Azimuthal dependence of SHG

\( \beta-BaB_2O_4 \)

Trigonal system R3c  \((a=1.2519\ nm, c=1.2723\ nm)\)

Stacking of Planar \(B_3O_6\) rings in \(c\)-axis

Origin of optical nonlinearity: polarizability in \(B_3O_6\)

Electric field in incident light

Strong SHG at \(\theta=0, 180^\circ\) \(B_3O_6\) unit

no SHG at \(\theta=90, 270^\circ\)

\(\theta\): angle between \(E\) and \(B_3O_6\) plane

Single crystal line: strong \(\theta\) dependence

SHG microscope observations

\(\beta-BaB_2O_4\) crystal lines

\(Y\)-cut \(\beta-BaB_2O_4\) single crystal

Sm \(\rightarrow\) \(\beta-BaB_2O_4\)
**LiNbO₃**
- Glass
- 0.3wt%CuO-0.3wt%Li₂O-Nb₂O₅-SiO₂
- Laser irradiation
- Yb: Fiber laser (λ = 1080 nm)

**Oxyfluoride glass: fluoride crystal**
- 43SiO₂-22Al₂O₃-5CaO-13NaF-17CaF₂-3NiO
- T_g=573°C, T_p=617°C
- P=1.7 W, S=2 μm/s
- I=1 μm, W=3 μm

**Polarized micro-Raman spectra**
- High orientation: c-axis growth
Glass part

Line part

520 540 560 580

Wavelength (nm)

Intensity (arb. units)

λ_{\text{ex} } = 488 \text{ nm}

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

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

Glass E (CaF}_2

+0.5ErF}_3

Crystallization of oxyfluoride glass

Laser-induced crystallization

Oxyfluoride base glass

Temperature

U (fluoride)

I (oxide)

U (oxide)

Fluoride nanocrystal

Laser irradiated region

Oxyfluoride glass

Combination of Laser irradiation and simple chemical etching

CuO-dope BaO-TiO_2-GeO_2 glass

Cathode materials for Li-ion battery

Laser irradiation with low powers

More open structure

Base glass

Laser irradiated

Cooling

Temperature

P = 0.7 W

Base glass

Temperature

P = 0.8 W

Refractive index change

Combined effects
1N HNO₃ → U-shape groove

1N HNO₃, 35 min

Patterning: \( P=0.85 \text{ W}, S=10 \ \mu\text{m/s} \)

Etching rate
Refractive index > glass > crystal

NiO-doped BaO-TiO₂-GeO₂ glass

NiO-doped BaO-TiO₂-GeO₂ glass

Laser-induced crystallization

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: $1 - 10 \, \mu m/s$
  → Large temperature gradient in laser irradiated spot (region): large diffusions