Lecture 8, Part 3: Vacuum-ultraviolet transparency of silica glass and its relation to processes involving mobile interstitial species, continued

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Jan. 10, 2008
Winter School on New Functionalities in Glass

Vacuum-ultraviolet transparency of silica glass and its relation to processes involving mobile interstitial species

Tokyo Metropolitan University
Koichi Kajihara
Overview

1. Introduction

2. Structure and optical properties of defects
   - Strained Si-O-Si bonds
   - Network modifiers (≡SiX)
   - Interstitial hydrogen molecules (H₂)

3. Improvement of UV-VUV transparency of silica glasses
   (a) Effects of structural disorder (strained Si-O-Si bonds) on VUV transparency
   (b) Removal of strained Si-O-Si bonds by doping with network modifiers
   (c) Role of mobile interstitial H₂ molecules

4. Silica glasses for UV-VUV spectral region
   - Silica glasses for excimer laser photolithography
   - Deep-UV optical fibers

5. Interstitial oxygen in silica glass
1. Introduction

Why silica glass?

- One of the simplest light metal amorphous oxides
- Large-size crystalline polymorph (α-quartz) is available
- Good mechanical properties and chemical stability
- High purity products are commercially available
- Various practical applications
  - Optical components
  - Gate dielectric films
  - Catalysts and catalyst supports
1. Introduction

Silica glass (amorphous SiO$_2$) – A promising UV optical material

1. Largest bandgap among glasses commercially available (absorption edge $\sim$8eV)
2. Good shape workability
3. Good physical and chemical properties

<table>
<thead>
<tr>
<th>Transparency region of various optical materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
</tr>
<tr>
<td>Photon energy (eV)</td>
</tr>
<tr>
<td>$\text{Hg}$ i line</td>
</tr>
<tr>
<td>VIS</td>
</tr>
<tr>
<td>$\text{O}_2$ Schumann–Runge band</td>
</tr>
</tbody>
</table>

- $\text{CaF}_2$
- $\text{Al}_2\text{O}_3$
- $\alpha$–quartz (c–SiO$_2$)
- SiO$_2$ glass
- Pyrex glass

Mercury UV lamp

Luminescent glass
Fused silica... Prepared from natural quartz
Good thermal stability; for crucibles and reactor chambers.

- **Type I** Electric melting in crucibles. Contain metallic impurities (e.g. Al, Na), low (<5ppm) OH concentration.
- **Type II** Crucible-free H₂-O₂ flame fusion. Concentrations of metallic impurities are lower than Type I. Medium (~100ppm) OH concentration.

From product catalog, Covalent Materials Co.
1. Introduction  Characteristic types of silica glasses [after Brückner(1998)]

**Synthetic silica** . . . Prepared by vapor-phase decomposition of silane compounds
High purity, various doping techniques; for optical components

- **Type III** Directly deposited by H$_2$-O$_2$ hydrolysis.
  High ($\sim$1,000 ppm) OH concentration.

- **Type IIIa,b** Prepared by “soot”-remelting.
  Suitable for dehydration and doping.

- **Type IV** Prepared by O$_2$-Ar plasma CVD method.
  Nearly OH-free but contains O$_2$ molecules.

There are various types of silica glasses!
1. Introduction

Effect of point defects (color centers)

- Different types of silica glasses
  - different optical properties . . . different concentrations of point defects

  Control of point defects is important!


Absorption spectra

Induced absorption spectra

![Absorption spectra graph](image)

![Induced absorption spectra graph](image)
1. Introduction

Optical properties of silica glass is often influenced by trace amounts of defects!

<table>
<thead>
<tr>
<th>log[Conc. (cm(^{-3}))]</th>
<th>Defect concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>Lattice atom (O: (4.4 \times 10^{22}) cm(^{-3}))</td>
</tr>
<tr>
<td>21</td>
<td>Solubility limit of fluorine (SiF) (several wt%)</td>
</tr>
<tr>
<td>20</td>
<td>SiOH in “wet” silica glass ((~1000) wtppm, (~10^{20}) cm(^{-3}))</td>
</tr>
<tr>
<td>19</td>
<td>Detection limit by X-ray fluorescence spectroscopy</td>
</tr>
<tr>
<td>18</td>
<td>H(_2) in H(_2)-loaded silica, chlorine (SiCl) in dry silica</td>
</tr>
<tr>
<td>17-16</td>
<td>Detection limit by IR and Raman spectroscopy (bulk glasses)</td>
</tr>
<tr>
<td>17-15</td>
<td>Metallic impurities (e.g. Al) in fused silica</td>
</tr>
<tr>
<td>15-14</td>
<td>Common radiation-induced defects</td>
</tr>
<tr>
<td>13</td>
<td>Problematic defect concentration for DUV optical fibers</td>
</tr>
<tr>
<td>12-16</td>
<td>Detection limit by PL and EPR spectroscopy (bulk glasses)</td>
</tr>
<tr>
<td>12-15</td>
<td>SiOH in optical telecom fibers</td>
</tr>
</tbody>
</table>

- 10: Metallic impurities (e.g. Al) in fused silica
1. Introduction

- Excellent transparency from infrared to vacuum-ultraviolet
- “Blue shift” of the main research field

2. Structure and optical properties of defects

Ideal structure... Corner-shared SiO$_4$ tetrahedra, built only from Si-O bonds

- Chemical defects... Local nonstoichiometry (vacancy, interstitial, dangling bonds, impurity atoms)

- Physical defects... Topological disorder (strained Si-O-Si bonds)
2. Structure and optical properties of defects

Optical absorption bands

Improvement of transparency and radiation hardness . . .

Control of point defects

After Skuja et al., Proc. SPIE 4347, 155 (2001)
3a. Strained Si-O-Si bonds

A comparison among SiO$_2$ polymorphs

- **α-quartz** (ordered SiO$_4$ units)
- **Silica glass** (disordered SiO$_4$ units)

- Larger bandgap than silica glass
- $F_2$ laser irradiation does not form persistent defects

<table>
<thead>
<tr>
<th>Materials</th>
<th>Band gap</th>
<th>Bandgap excitation causes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous silicon</td>
<td>$\sim1.7$eV</td>
<td>Staebler-Wronski effect</td>
</tr>
<tr>
<td>Chalcogenide glasses</td>
<td>$\sim2$eV</td>
<td>Photo darkening</td>
</tr>
<tr>
<td>Silica glass</td>
<td>$\sim9$eV</td>
<td>?</td>
</tr>
</tbody>
</table>
3a. Strained Si-O-Si bonds

Physical disorder in silica glass

Short-range physical disorder... Distribution in Si-O-Si angle
c.f. \(\alpha\)-quartz... No distribution in Si-O-Si and O-Si-O angles, Si-O length

Si-O-Si angle

O-Si-O angle

Si-O length

*Calculated from a periodic silica structure reported in Mukhopadhyay et al., PRB70,195203 (2004)
3a. Strained Si-O-Si bonds

Typical strained Si-O-Si bonds
... 3- and 4-membered rings


- Do not exist in \(\alpha\)-quartz
- The concentration depends on thermal annealing (fictive) temperature

\[
\begin{align*}
\text{D}_2 \text{ band (606cm}^{-1}\text{)} & & \text{D}_1 \text{ band (495cm}^{-1}\text{)} \\
\text{3-membered ring} & & \text{4-membered ring}
\end{align*}
\]

\[\begin{array}{c}
\text{Hosono et al., PRL87, 175501(2001)}
\end{array}\]
3a. Strained Si-O-Si bonds

- $<10 \text{mJ cm}^{-2}$ ... One-photon processes
  \[ \equiv \text{Si-O-Si} \equiv \xrightarrow{\hbar \nu (7.9 \text{eV})} \equiv \text{Si}^* (E' \text{ center}) + \cdot \text{O-Si} \equiv (\text{NBOHC}) \]

- $>10 \text{mJ cm}^{-2}$ ... Two-photon processes (Yield ... $F_2 \gg \text{KrF, ArF}$)

Strained Si-O-Si bonds ... Real intermediate states for defect formation via two-step absorption processes

Hosono et al., PRL 87, 175501 (2001)

Kajihara et al., APL 81, 3164 (2002)
3a. Strained Si-O-Si bonds

Elimination of strained Si-O-Si bonds

- Low temperature heating ("physical" annealing) ... time consuming
- Breaking up glass network by network modifiers (SiF, SiCl, SiOH, SiH)
  ("chemical" annealing)... structural relaxation by lowered viscosity

Hosono and Ikuta, NIMB166, 691(2000)
3b. Network modifiers

**Types and the VUV absorption bands**

<table>
<thead>
<tr>
<th>Absorption band</th>
<th>SiOH</th>
<th>SiH</th>
<th>SiF</th>
<th>SiCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gtrsim 7.4 \text{eV}$</td>
<td>Not known ($\gtrsim E_g$)</td>
<td>Not known ($\gtrsim E_g$)</td>
<td>$\gtrsim 7 \text{eV}$</td>
</tr>
</tbody>
</table>

- **SiOH** group
- **SiH** group
- **SiF** group
- **SiCl** group

Kajihara et al. PRB 72, 214112 (2005)

**Absorption cross section, $\sigma$ ($10^{-18} \text{cm}^2$)**

- **Awazu et al. JAP 69, 1849 (1991)**
  - Sintered in He
  - Treated in CCl$_4$, Sintered in He
  - Treated in CCl$_4$, Sintered in Cl$_2$/He=5/10, 3/10, 1/10

**Absorption coefficient ($\text{cm}^{-1}$)**

- **Awazu et al., JAP 69, 1849 (1991)**
3b. Network modifiers

- Increase in SiF concentration
  - Improve VUV transparency
  - Decrease defect concentration
- Most effective at <1% SiF doping
  (Effects do not proportionally with SiF concentration)

**Structural relaxation by SiF doping**

Hosono and Ikuta, NIMB166, 691(2000)

<table>
<thead>
<tr>
<th>SiF</th>
<th>VUV OA</th>
<th>Photolysis</th>
<th>Cost</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOH (Wet)</td>
<td>No</td>
<td>No</td>
<td>High</td>
<td>Excimer laser lithography, DUV fiber</td>
</tr>
<tr>
<td>SiCl (Dry)</td>
<td>$\gtrsim 7.4\text{eV}$</td>
<td>SiO$^\bullet + H^0$</td>
<td>Low-Med.</td>
<td>UV-DUV laser optics</td>
</tr>
<tr>
<td>SiH</td>
<td>No?</td>
<td>Si$^\bullet + Cl^0$</td>
<td>Med</td>
<td>IR optical telecom</td>
</tr>
<tr>
<td>SiF (F-doped)</td>
<td>No</td>
<td>No</td>
<td>High</td>
<td>Excimer laser lithography, DUV fiber</td>
</tr>
</tbody>
</table>
3c. Interstitial H₂ molecules

Silica glass
- Low density as compared with crystalline SiO₂, Al₂O₃... large free volume
- Easy diffusion and reaction of small chemical species
e.g. Doremus, “Diffusion of reactive molecules in solids and melts”, Wiley(2002)
- Neutral interstitial species

- Hydrogen-related... H⁰, H₂
- Oxygen-related ... O⁰, O₂

<table>
<thead>
<tr>
<th></th>
<th>Density (g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica glass</td>
<td>2.21</td>
</tr>
<tr>
<td>Tridymite</td>
<td>2.33</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>2.33</td>
</tr>
<tr>
<td>α-quartz</td>
<td>2.65</td>
</tr>
<tr>
<td>Soda-lime silicate</td>
<td>2.47</td>
</tr>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>3.97</td>
</tr>
</tbody>
</table>
3c. Interstitial H₂ molecules

H₂ in silica glass... fast diffusion (He > H₂ > Ne ≫ Ar, H₂O), high reactivity

- Hydrogen corrosion in telecom fibers (≡Si-O-Si≡ + H₂ → ≡SiOH + ≡SiH)
- Sensitization of photoencoding of Bragg gratings
- Termination of dangling bonds (R* + H₂ → RH + H⁰)
- Improvement of KrF and ArF laser hardness

![Optical loss vs. Wavelength graph](image1)

![Transmittance vs. Wavelength graph](image2)
3c. Interstitial H\textsubscript{2} molecules

In-situ study of diffusion and reactions

F\textsubscript{2}-laser-irradiated “wet” silica glass

- F\textsubscript{2} laser (7.9eV) \( \equiv \text{SiO-H} \rightarrow \equiv \text{SiO}^\bullet + \text{H}^0 \) (quantum yield \( \sim 0.1-0.2 \))
- Nd:YAG 4HG (4.7eV) \( \equiv \text{SiO}^\bullet \rightarrow \equiv \text{SiO}^\bullet \) (1.9eV PL)

- Concentration of radiation-induced NBOHC(\( \equiv \text{SiO}^\bullet \)) ... insensitive to H\textsubscript{2} loading
- NBOHC does not accumulate in H\textsubscript{2}-loaded glass

Kajihara et al., APL79, 1575(2001); NIMB33, 323(2004); PRB74, 094202(2006)
3c. Interstitial \( \text{H}_2 \) molecules

Various effects of interstitial \( \text{H}_2 \)

1. Termination of dangling bonds \([\equiv \text{Si}^* (5.8\text{eV}), \equiv \text{SiO}^* (4.8\text{eV}, 6.8\text{eV})]\)
2. Acceleration of oxygen vacancy formation \([\equiv \text{Si-Si} \equiv (7.6\text{eV})]\)
   ... Photoreduction \((\equiv \text{Si-O}^*-\text{Si} \equiv + \text{H}_2 \rightarrow \equiv \text{Si-Si} \equiv + \text{H}_2\text{O})\)
3. Crack formation ... Stress corrosion \((\equiv \text{Si-O-Si} \equiv + \text{H}_2\text{O} \rightarrow 2\equiv \text{SiOH})\)

\( \text{H}_2 \) conc. should be strictly optimized

Ikuta et al., APL80, 3916(2002); Appl. Opt. 43, 2332(2004)

Termination of dangling bonds

Photo-reduction of \( \text{Si-O-Si} \) bond

\[\begin{align*}
\text{Si} & \quad \text{O} & \quad \text{Si} \\
\text{Si} & \quad \text{H} & \quad \text{O} & \quad \text{Si} \\
+ \text{H}_2 & & &
\end{align*}\]

\[\begin{align*}
\text{Si} & \quad \text{O} & \quad \text{Si} \\
\text{Si} & \quad \text{H} & \quad \text{O} & \quad \text{H} \\
+ \text{H}_2 & & &
\end{align*}\]

\[\begin{align*}
\Delta \text{Absorption coefficient (cm}^{-1}\text{)} & \quad \text{Absorption coefficient (cm}^{-1}\text{)} \\
\text{Photon energy (eV)} & \quad \text{Photon energy (eV)}
\end{align*}\]

(a) ArF, OH-doped, \( \text{H}_2 \)-free
(b) \( \text{F}_2 \), OH-free, \( \text{H}_2 \)-free

\( \equiv \text{Si-Si} \equiv \)
4. Silica glasses for UV-VUV spectral region

<table>
<thead>
<tr>
<th>Type</th>
<th>Defect species</th>
<th>Conventional applications</th>
<th>7.9eV Transparency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet</td>
<td>SiOH</td>
<td>UV optics</td>
<td>Poor (OA by SiOH)</td>
</tr>
<tr>
<td>Dry</td>
<td>SiCl, Si-Si</td>
<td>IR telecom. fibers</td>
<td>Poor (OA by Si-Si)</td>
</tr>
<tr>
<td>F-doped</td>
<td>SiF</td>
<td>X- and γ-resistant fibers</td>
<td>Good</td>
</tr>
</tbody>
</table>

Fluorine-doped silica... Suitable for photomask substrates in F_2 laser photolithography

Hosono et al. APL74,2755(1999), Mizuguchi et al. JVSTB17,3280(1999)
4. Silica glasses for UV-VUV spectral region

Conventional fibers (Ge-doped core and pure-silica cladding)

- Not transparent for UV light
- High viscosity – drawing-induced defects
- High radiation sensitivity

⇒ 1. F-doped core and cladding
⇒ 2. Defect annihilation by $H_2$ impregnation

4. Silica glasses for UV-VUV spectral region  

- Processing of fiber ends
  - End sharpening by chemical etching in hydrofluoric acid
    - Possible application to scanning nearfield optical microscopy (SNOM)

HF etching
5. Interstitial oxygen in silica glass

- Oxygen-deficiency related defects...Si-Si, ≡Si•, –Si–, ...
  - Main color centers in DUV fibers
- Oxygen-excess related defects...≡SiOO•, O₂, Si-O-O-Si, ...
  - May be used to oxidize oxygen-deficiency related color centers
  - Chemical and optical properties remain largely unclear
5. Interstitial oxygen in silica glass

Interstitial $\text{O}_2$... The most common form of excess oxygen in silica glass

- Nassau and Shiever (1975) Preparation of low-OH $\alpha$-SiO$_2$ by plasma-CVD method
- Heitmann et al. (1983) Sharp loss bands of unknown origin in telecom fibers by PCVD
- Carvalho et al. (1985) Identification of interstitial O$_2$ by Raman spectroscopy
- Awazu et al. (1990) Observation of VUV absorption band of interstitial O$_2$

![Graph](image-url)
5. Interstitial oxygen in silica glass

Detection by photoluminescence

- Shikama et al. (1994) Discovery of 1270nm PL band in optical fiber in an nuclear reactor
- Skuja et al. (1996) PL detection of interstitial O\textsubscript{2} via 1064nm excitation
- Skuja et al. (1998) PL detection of interstitial O\textsubscript{2} via 765nm excitation

Sensitive, selective, and non-destructive detection of interstitial O\textsubscript{2} in $\alpha$-SiO\textsubscript{2}

[Diagram of optical radiation intensity vs. wavelength with energy level transitions for O\textsubscript{2}]
5. Interstitial oxygen in silica glass  

- O₂ PL measurements of silica glasses thermally annealed in air

... **Solubility and diffusion coefficient** of interstitial O₂ in silica glass


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**Oxidant in the thermal oxidation of silicon is interstitial O₂**

---

**Diagram:**

- cw Nd:YVO₄ laser (SHG) 532nm
- cw Ti:Al₂O₃ laser 765nm
- IR spectrometer (FT–Raman detector) 1272nm
- Sample

**Graph:**

- Oxygen transport through thermally–grown SiO₂ film
- Si substrate
- Growth front

**Graph:**

- O₂ concentration (10¹⁶ cm⁻³)
- Position (cm)
- Wavenumber (cm⁻¹)
- PL ampl. (a.u.)
5. Interstitial oxygen in silica glass

Concentration calibration

- Thermal desorption spectroscopy

\[ 8.3 \times 10^{16} \text{ molecules} \sim 22\% \text{ decrease of PL intensity} \]

\[ \text{O}_2 \text{ concentration} \sim 2.7 \times 10^{16} \text{ cm}^{-3} \]

\[ \Delta A_{\text{PL peak}}/A_{\text{Raman@1200 cm}^{-1}} \]

Kajihara et al. JNCS, in press
5. Interstitial oxygen in silica glass

- Simultaneous measurement of VUV absorption and O$_2$ concentration changes
  1. Red-shift of VUV absorption edge
  2. Increase in absorption intensity

$$\Rightarrow$$ Weak attractive interaction between O$_2$ and $a$-SiO$_2$ framework

Kajihara et al. JAP98,013527(2005)

![Graph showing absorption coefficient vs. photon energy with O$_2$-loaded and O$_2$-desorbed samples.](graph1.png)

![Graph showing log(Absorption cross section) vs. photon energy with O$_2$ band at 1539 cm$^{-1}$.](graph2.png)

(b) This study

Gaseous O$_2$
5. Interstitial oxygen in silica glass

- Reaction of $\alpha$-SiO$_2$ with H$_2$... Cracking of Si-O bond
  \[ \equiv \text{Si-O-Si} \equiv + \text{H}_2 \rightarrow \equiv \text{SiOH} + \text{HSi} \equiv \]

- Shelby (1980) SiOH creation with little accompanying SiH formation in O$_2$-rich $\alpha$-SiO$_2$

  Two-step reactions
  1. \[ \frac{1}{2} \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} \]
  2. \[ \equiv \text{Si-O-Si} \equiv + \text{H}_2\text{O} \rightarrow \equiv \text{SiOH} \]

Shelby, JAP51, 2589(1980)

Kajihara, JAP98, 043515(2005)

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

Normalized emission intensity

Absorption coefficient (cm$^{-1}$) vs. Wavenumber (cm$^{-1}$)

Normalized emission intensity vs. Raman shift (cm$^{-1}$)
5. Interstitial oxygen in silica glass

Reactions (2)

- Reaction with Si-Si bonds \( \equiv \text{Si-Si} \equiv + 1/2 \text{O}_2 \rightarrow \equiv \text{Si-O-Si} \equiv \)
- Reaction with \( E' \) center \( \equiv \text{Si}^\bullet + \text{O}_2 \rightarrow \equiv \text{SiOO}^\bullet \)
- Reaction with SiCl \( 1/2 \text{O}_2 + 2\equiv \text{SiCl} \rightarrow \equiv \text{Si-O-Si} \equiv + \text{Cl}_2 \)
- Reaction with \( \text{H}^0 \) \( \text{O}_2 + \text{H}^0 \rightarrow \text{HO}_2^\bullet \)

Pfeffer (1998)

Kajihara, JAP98,043515(2005)
5. Interstitial oxygen in silica glass

Configuration... Peroxy linkage form

e.g. Hamann, PRL81,3447(1998)
Szymanski et al. PRB63,224207(2001)

Formation

1. Radiolytic decomposition of Si-O-Si bonds
   \[ \equiv \text{Si-O-Si} \rightarrow h\nu \rightarrow \equiv \text{Si-Si} + \text{O}^0 \] (or 1/2O\(_2\))
2. VUV photolysis of interstitial O\(_2\)
   \[ \text{O}_2 \rightarrow h\nu \rightarrow 2\text{O}^0 \]
3. UV photolysis of peroxy radical
   \[ \equiv \text{SiOO}^\bullet \rightarrow h\nu \rightarrow \equiv \text{SiO}^\bullet + \text{O}^0 \]

Interstitial oxygen atoms

- Anion part of the Frenkel pair
- Low-temperature oxidant of silicon

\[
\begin{array}{cccccccc}
\text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ \\
\text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- \\
\end{array}
\]

\[
\begin{array}{cccccccc}
\text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- \\
\text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ \\
\end{array}
\]

\[
\begin{array}{cccccccc}
\text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- \\
\text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ \\
\end{array}
\]

\[
\begin{array}{cccccccc}
\text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- \\
\text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ \\
\end{array}
\]

\[
\begin{array}{cccccccc}
\text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- \\
\text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ \\
\end{array}
\]

\[
\begin{array}{cccccccc}
\text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- \\
\text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ \\
\end{array}
\]

\[
\begin{array}{cccccccc}
\text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- \\
\text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ \\
\end{array}
\]

\[
\begin{array}{cccccccc}
\text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- \\
\text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ \\
\end{array}
\]

\[
\begin{array}{cccccccc}
\text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- \\
\text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ & \text{O}^2- & \text{M}^2+ \\
\end{array}
\]
5. Interstitial oxygen in silica glass

Optical absorption and diffusivity

\[ \text{O}_2 \xleftrightarrow{\text{Heat}} 2\text{O}^0 \]

- Optical absorption… Use O\(^0\)-rich sample prepared by F\(_2\) laser irradiation
- Diffusivity … Probe O\(_2\) generated by recombination of O\(^0\)

Skuja et al. NIMB191,127(2002)


![Graph showing absorption coefficient vs. photon energy and concentration of O\(_2\) vs. annealing temperature](image)

\[ \Delta \text{Absorption coefficient (cm}^{-1}) \]

\[ \text{Photon energy (eV)} \]

\[ \text{Absorption coefficient (cm}^{-1}) \]

\[ \text{Concentration of O}_2 \(10^{17} \text{cm}^{-3}\) \]

\[ \text{Annealing temperature (K)} \]

\[ D = D_0 \exp(-\Delta E/kT) \]

\[ D_0 = 1 \times 10^{-3} \text{cm}^2\text{s}^{-1} \]

\[ \Delta E = 1.1\text{eV} \]
5. Interstitial oxygen in silica glass

Conversion of dangling bonds

\[ \equiv \text{SiOO}^\bullet \xrightarrow{h\nu(\sim 5\text{eV})} \text{SiO}^\bullet + \text{O}^0 \]

Kajihara et al. PRL 92, 015504 (2004)


Graphs showing concentration changes and absorption coefficients before and after F₂ laser irradiation.
5. Interstitial oxygen in silica glass

Absorption cross section “map”
Summary

- **Optical isotropy**
  - Process engineering
    - Raw material
    - Production method
    - Fiber drawing
  - Deep-UV optics
    - Photomasks
    - Hard pellicles
    - Lenses
  - Optical fibers
  - DUV fibers
  - Bragg grating devices
  - Fiber lasers

- **Wide-gap**
  - Workability
  - α-quartz
  - Optical spectroscopy
  - EPR
  - Simulation
  - Network topology
  - Stoichiometry
  - Doping (H, F, P, RE, ...)

- **Fundamental research**
  - Structural modification
  - Simulation
Acknowledgment

This work has been made in collaboration with

- Professor Hideo Hosono
  (Japan Science and Technology Agency, Tokyo Institute of Technology)
- Professor Masahiro Hirano
  (Japan Science and Technology Agency, Tokyo Institute of Technology)
- Dr. Linards Skuja (University of Latvia)
- Dr. Yoshiaki Ikuta (Asahi Glass Company Co. Ltd.)
- Dr. Masanori Oto (Showa Device Technology Co. Ltd.)