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

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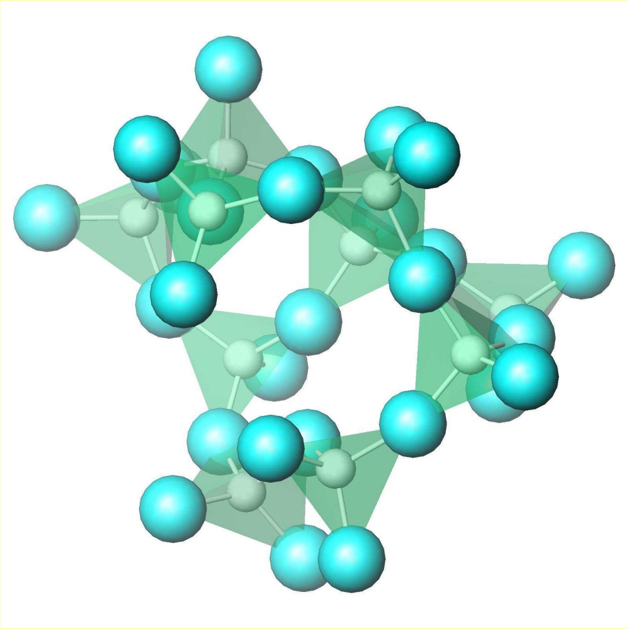
Overview

1. Introduction
2. Structure and optical properties of defects
   - Strained Si-O-Si bonds
   - Network modifiers ($\equiv$SiX)
   - Interstitial hydrogen molecules (H_2)
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 H_2 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?



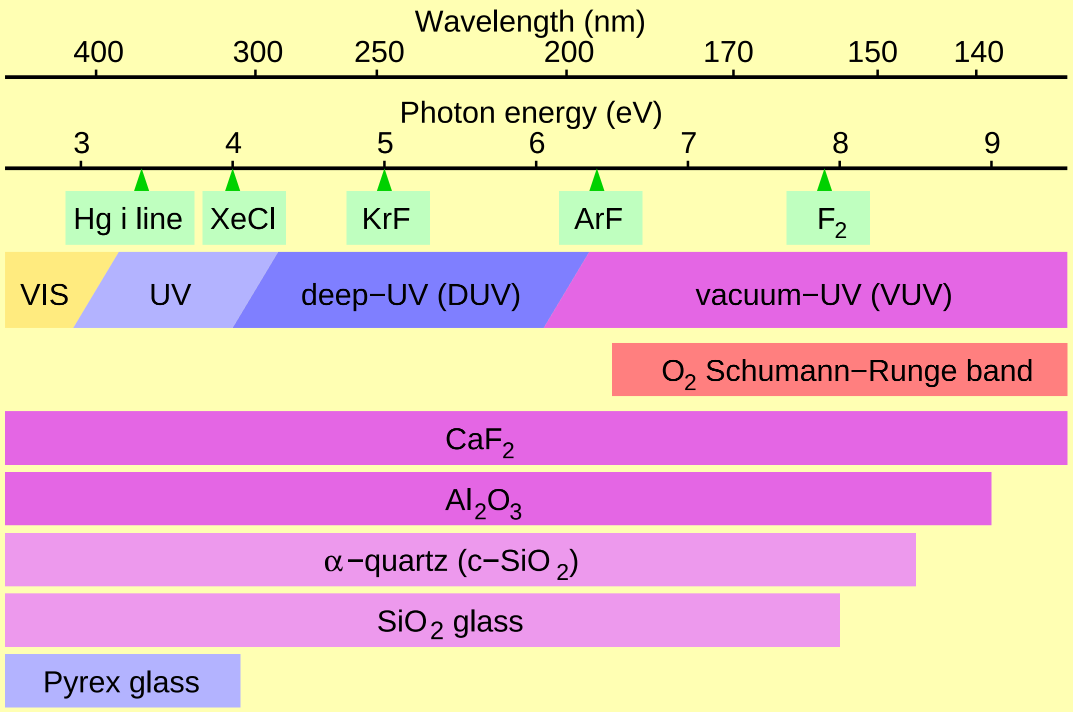
- One of the simplest light metal amorphous oxides
- Large-size crystalline polymorph (α-quartz) is available
- Good mechanical properties and chemical stability
- High purity products are commercially available
- Various practical applications
  - Optical components
  - Gate dielectric films
  - Catalysts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

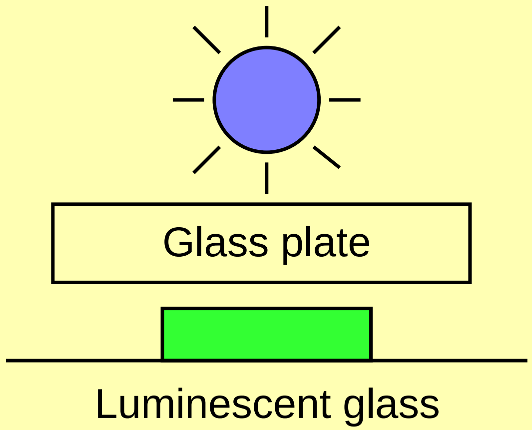
1. Introduction

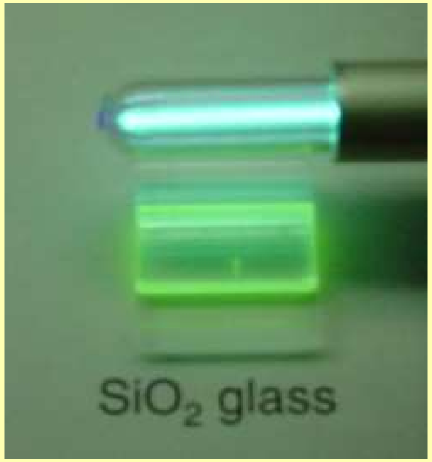
Silica glass (amorphous SiO_2) – A promising UV optical material

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

Transparency region of various optical materials







1. Introduction   Characteristic types of silica glasses [after Brückner(1998)]

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 H_2-O_2 flame fusion. Concentrations of metallic impurities are lower than Type I. Medium (∼100ppm) OH concentration.

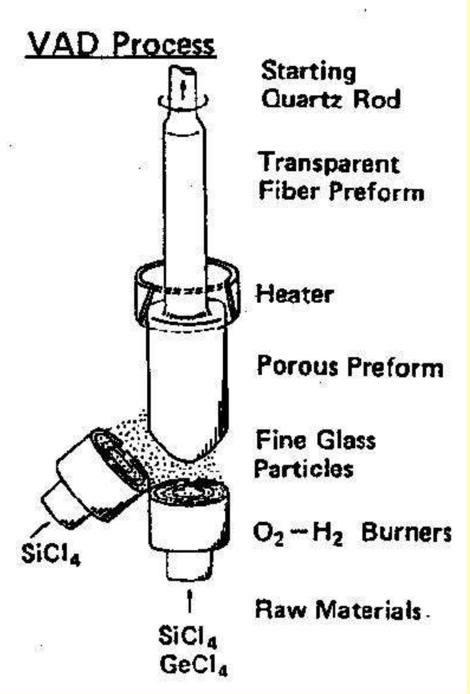
From product catalog, Covalent Materials Co.

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 (∼1,000ppm) OH concentration.
- Type IIIa,b Prepared by "soot"-remelting.
  Suitable for dehydration and doping.
- Type IV Prepared by O_2-Ar plasma CVD method.
  Nealy OH-free but contains O_2 molecules.



There are various types of silica glasses!

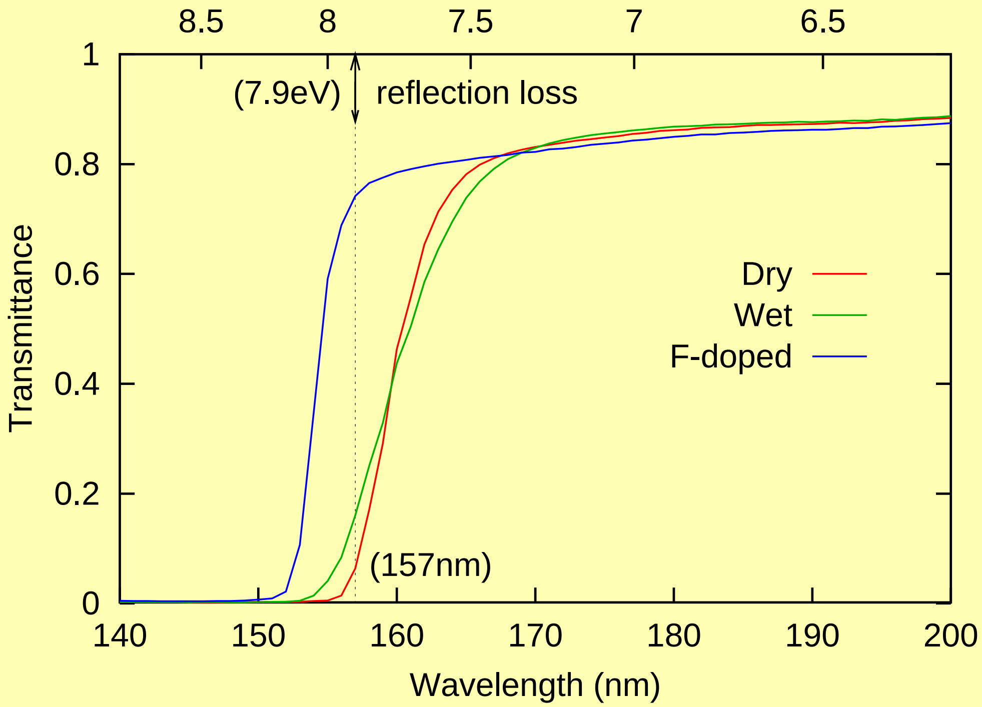
- Different types of silica glasses

different optical properties . . . different concentrations of point defects

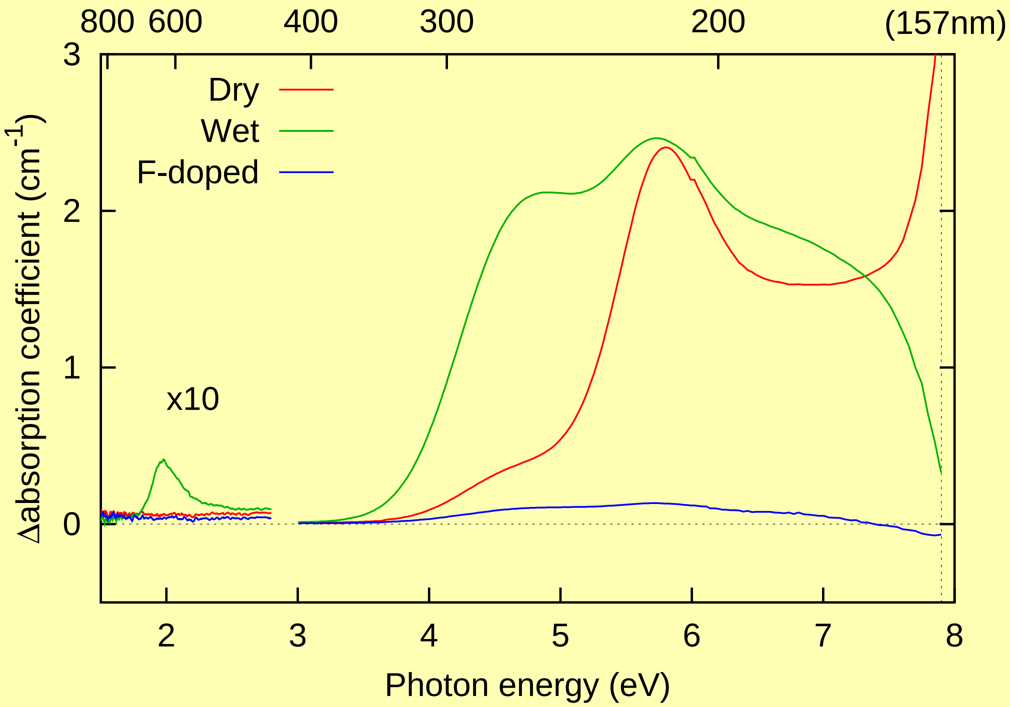
Control of point defects is important!

Mizuguchi et al., Opt. Lett. 24, 863(1999), Hosono et al., APL 74, 2755(1999)

Absorption spectra



Induced absorption spectra

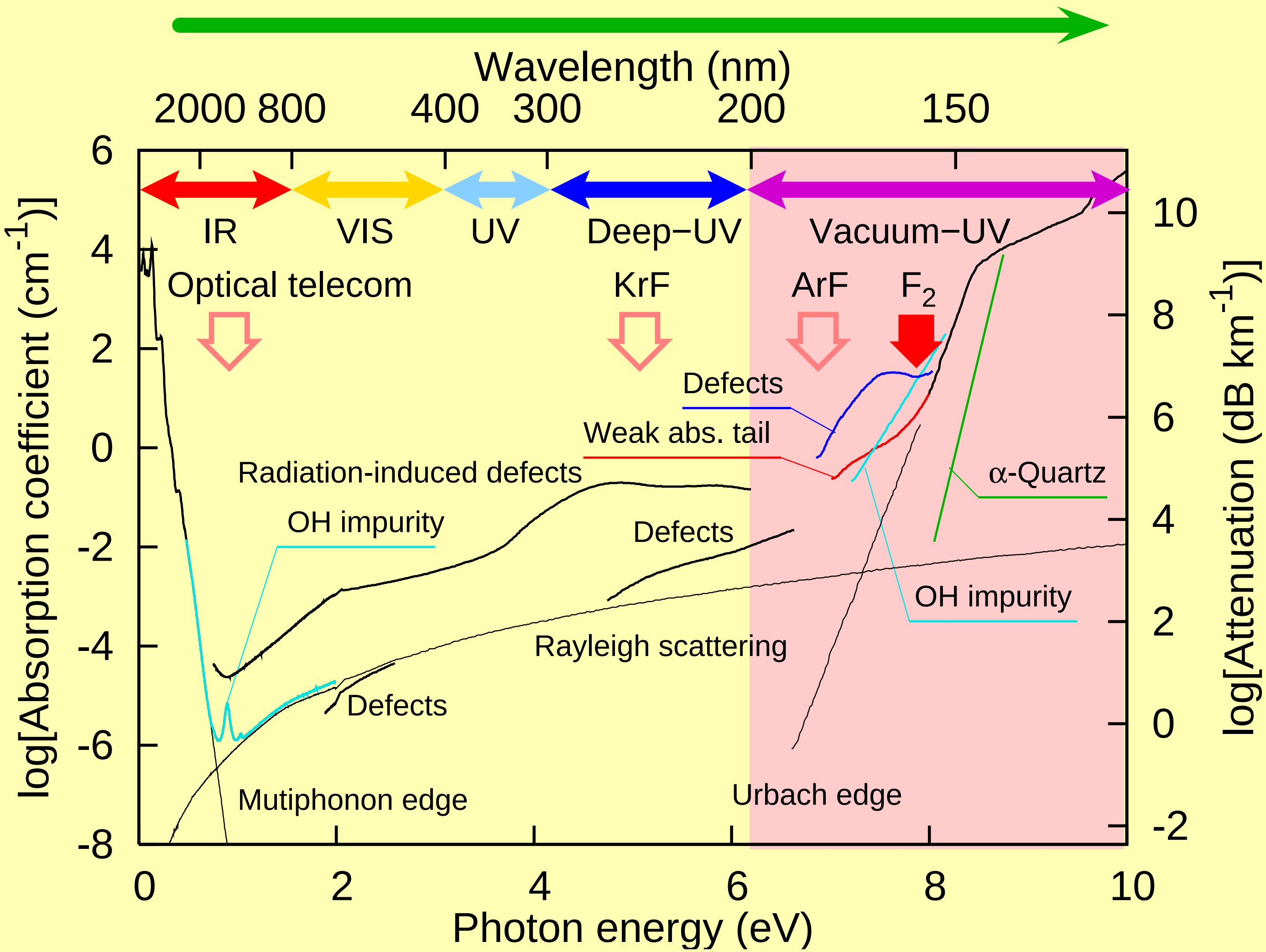


Optical properties of silica glass is often influenced by trace amounts of defects!

log[Conc.(cm^{-3})]	
22	Lattice atom (O: $4.4\times10^{22}cm^{-3}$)
21	Solubility limit of fluorine (SiF) (several wt%)
20	SiOH in "wet" silica glass ($\sim$1000wtppm、 $\sim10^{20}cm^{-3}$)
	Detection limit by X-ray fluorescence spectroscopy
19	H_2 in H_2-loaded silica, chlorine (SiCl) in dry silica
18	SiOH in silica glass for KrF and ArF photolithography (10-100wtppm)
	Metallic impurities (e.g. Al) in fused silica
17-16	Detection limit by IR and Raman spectroscopy (bulk glasses)
17-15	Common radiation-induced defects
15-14	Detection limit by PL and EPR spectroscopy (bulk glasses)
	SiOH in optical telecom fibers
13	Problematic defect concentration for DUV optical fibers

1. Introduction　　Transparency region of silica glass

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

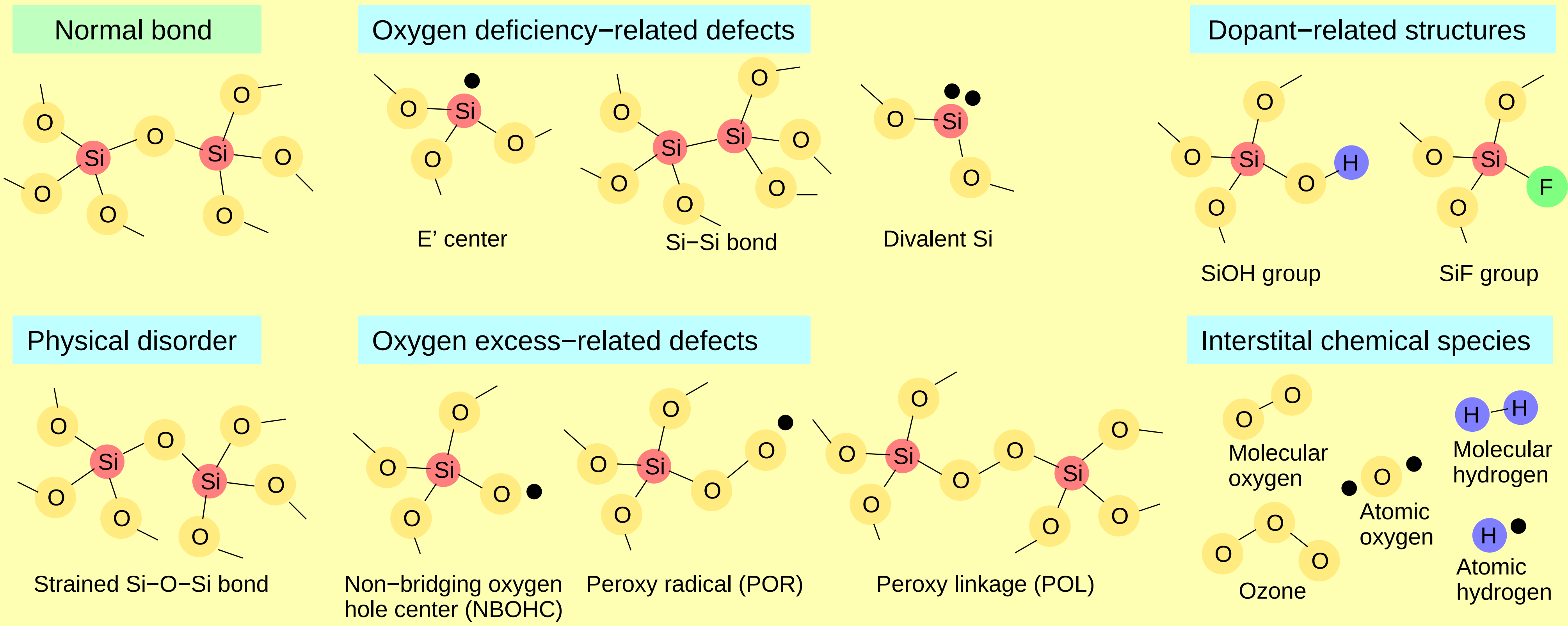


After Griscom, J.Ceram.Soc.Jpn, 99,923(1991)

2. Structure and optical properties of defects

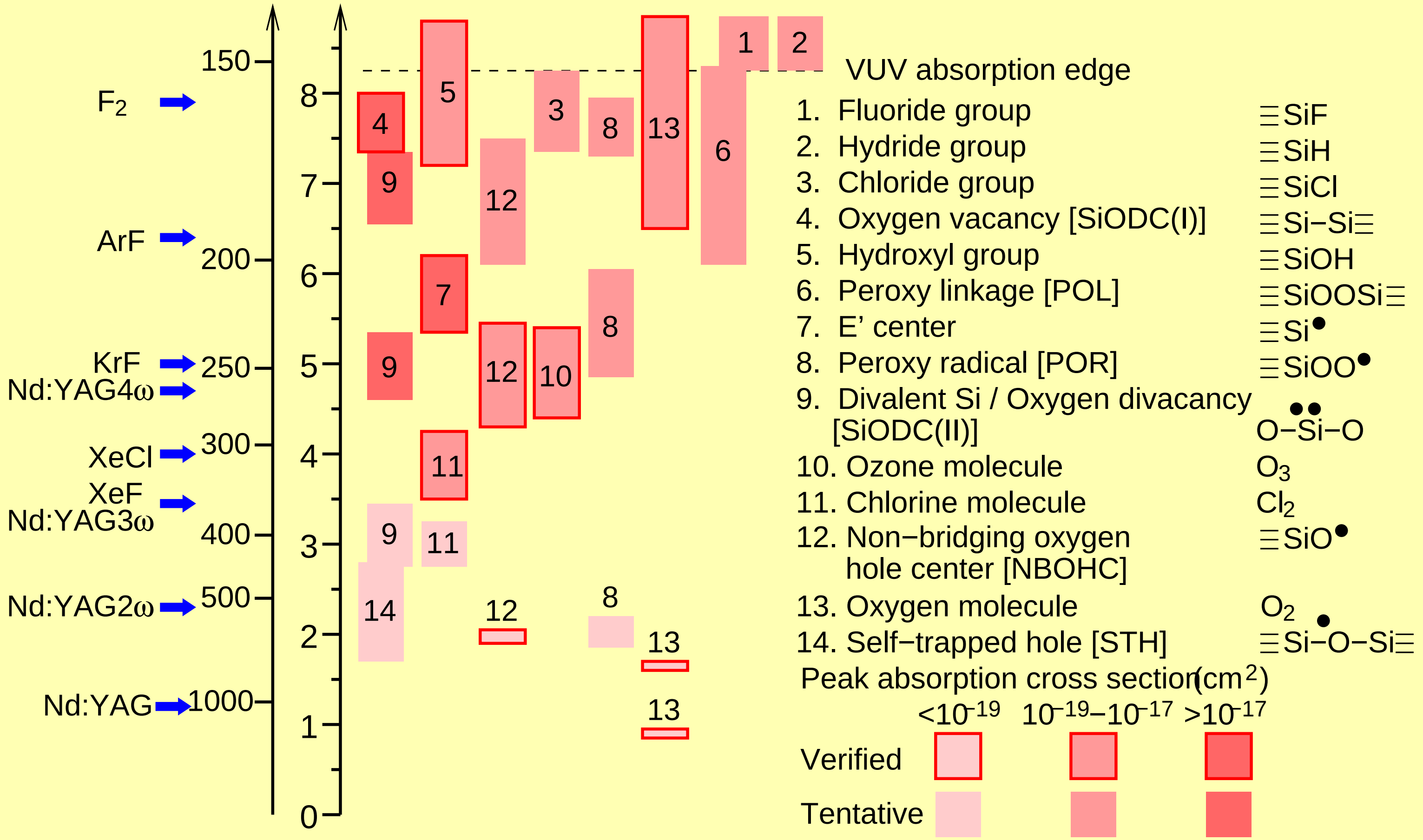
Ideal structure. . . Corner-shared SiO_4 tetrahedra, built only from Si-O bonds

- 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

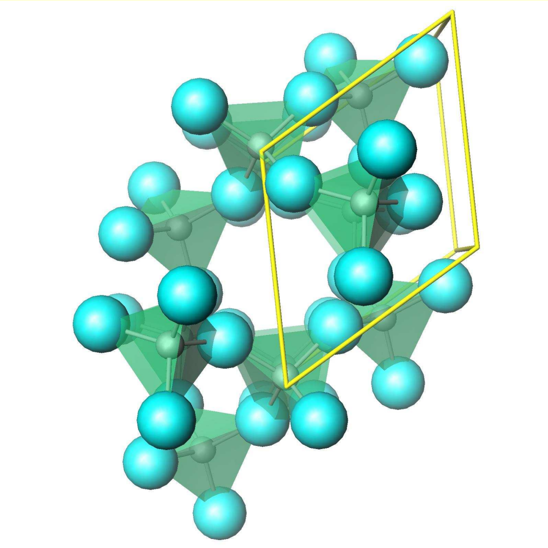
Improvement of transparency and radiation hardness . . . Control of point defects



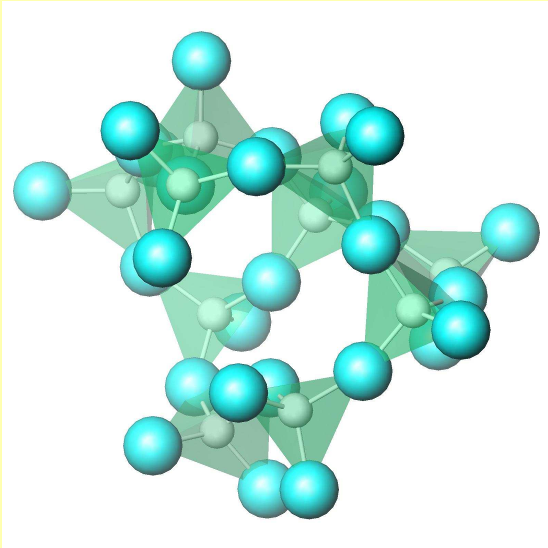
After Skuja et al., Proc.SPIE 4347,155(2001)

3a. Strained Si-O-Si bonds — A comparison among SiO_2 polymorphs

α-quartz (ordered SiO_4 units)



Silica glass (disordered SiO_4 units)



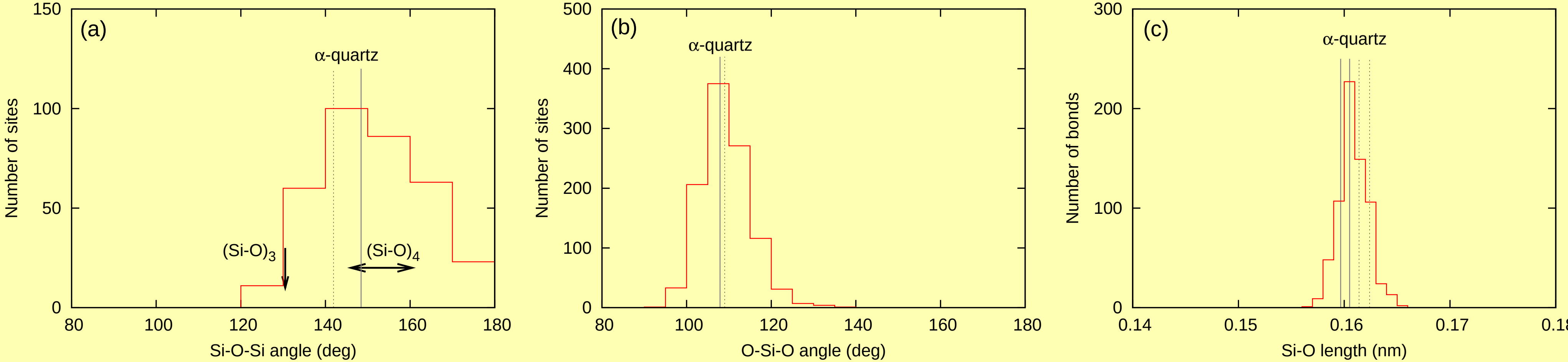
- Larger bandgap than silica glass
- F_2 laser irradiation does not form persistent defects

Materials	Band gap	Bandgap excitation causes
Amorphous silicon	$\sim$1.7eV	Staebler-Wronski effect
Chalcogenide glasses	$\sim$2eV	Photo darkening
Silica glass	$\sim$9eV	?

Short-range physical disorder... Distribution in Si-O-Si angle

c.f. α-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)

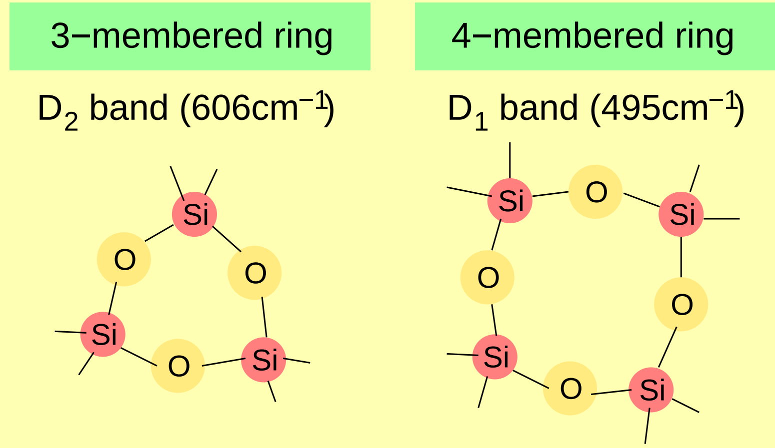
3a. Strained Si-O-Si bonds

Typical strained Si-O-Si bonds

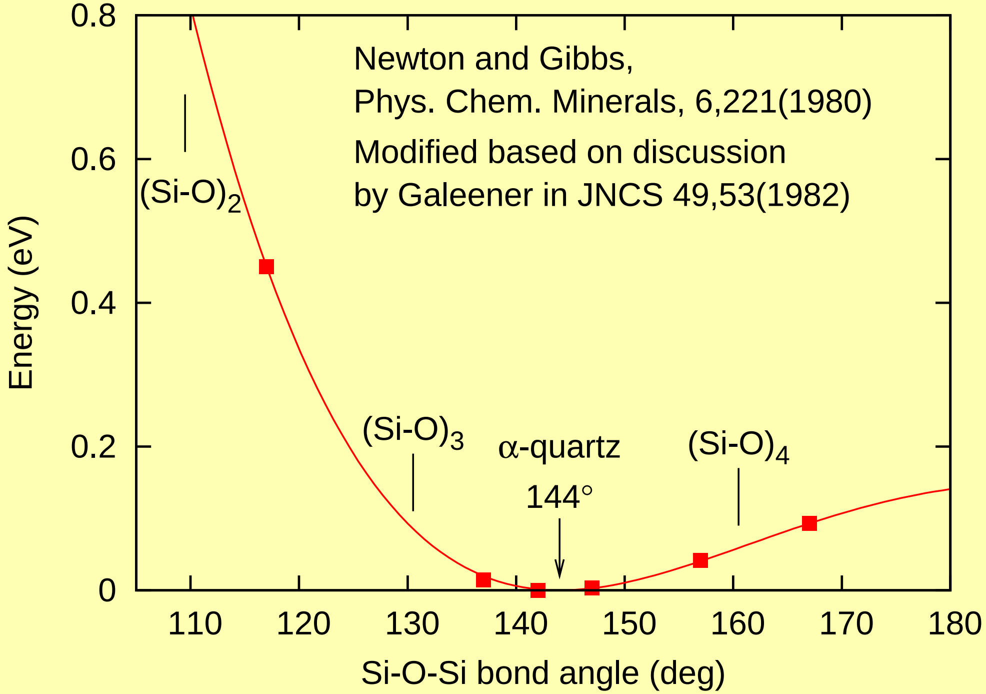
. . . 3- and 4-membered rings

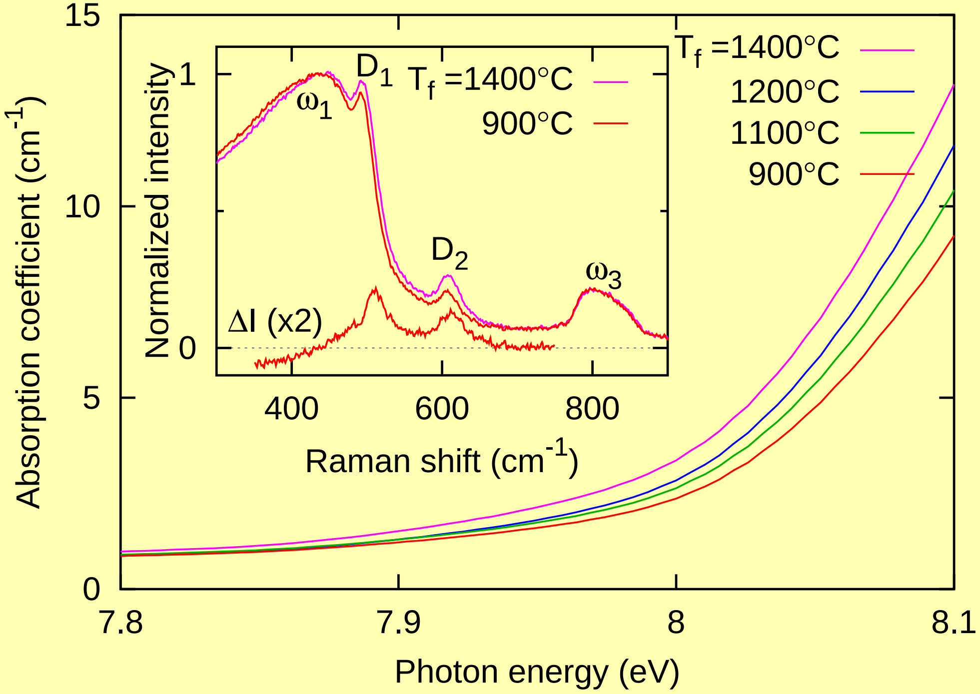
Galeener, JNCS49,53(1982)

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



Hosono et al., PRL87, 175501(2001)



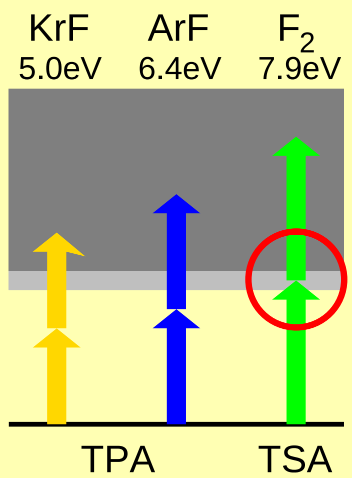


- $<$10mJ cm^{-2}. . . One-photon processes

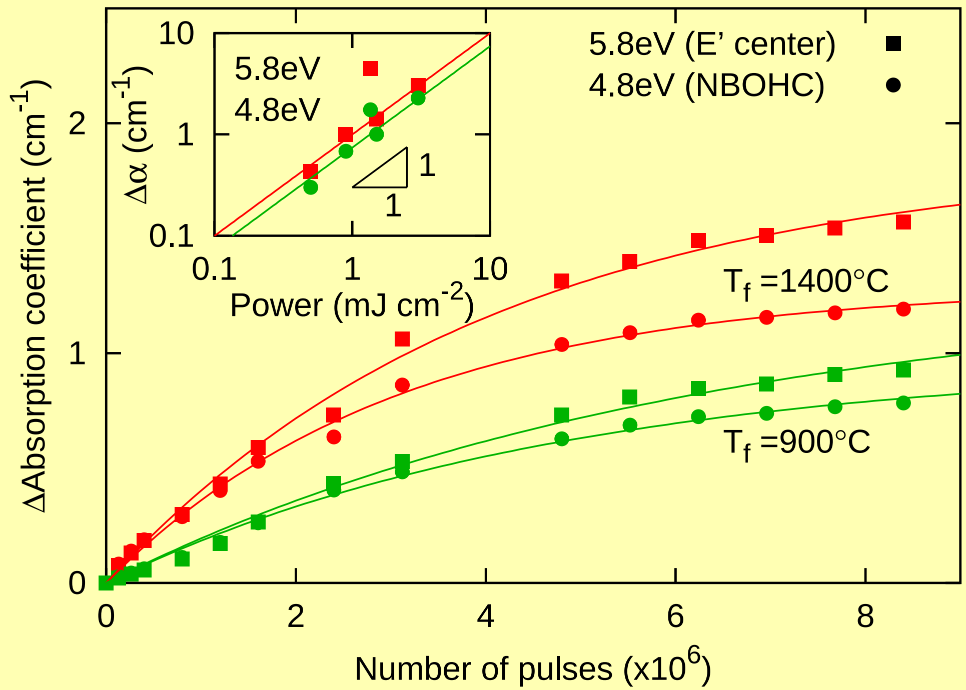
$$\equiv\text{Si-O-Si}\equiv \xrightarrow{h\nu(7.9\text{eV})} \equiv\text{Si}^{\bullet}(E\text{' center}) \quad + \quad {}_{\bullet}\text{O-Si}\equiv(\text{NBOHC})$$

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

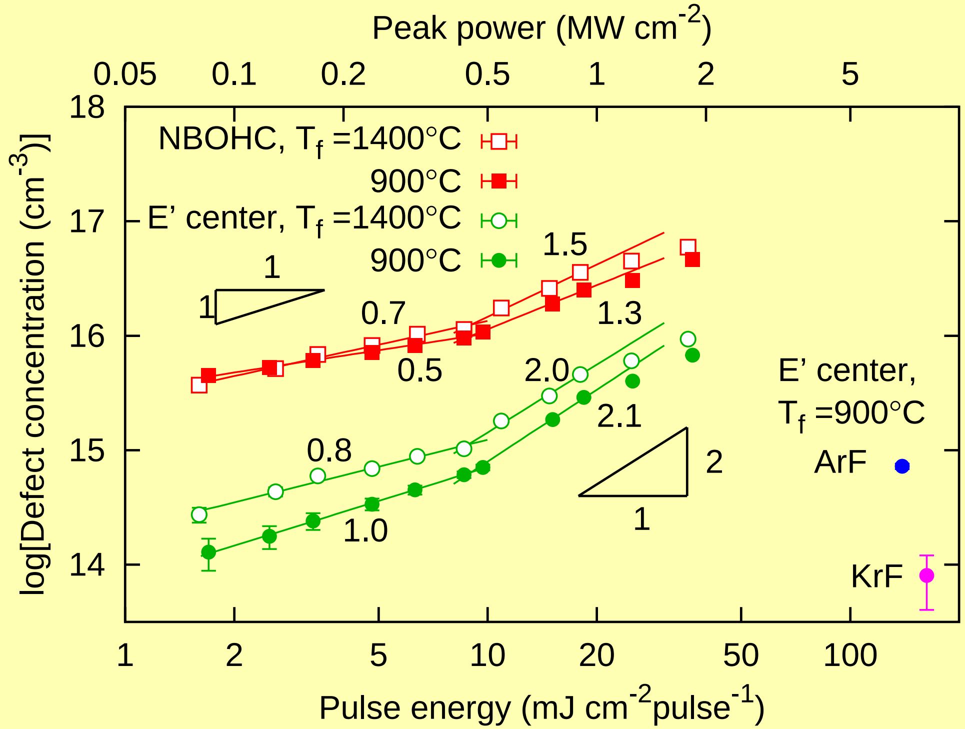
Strained Si-O-Si bonds . . . Real intermediate states for defect formation via two-step absorption processes



Hosono et al., PRL87,175501(2001)



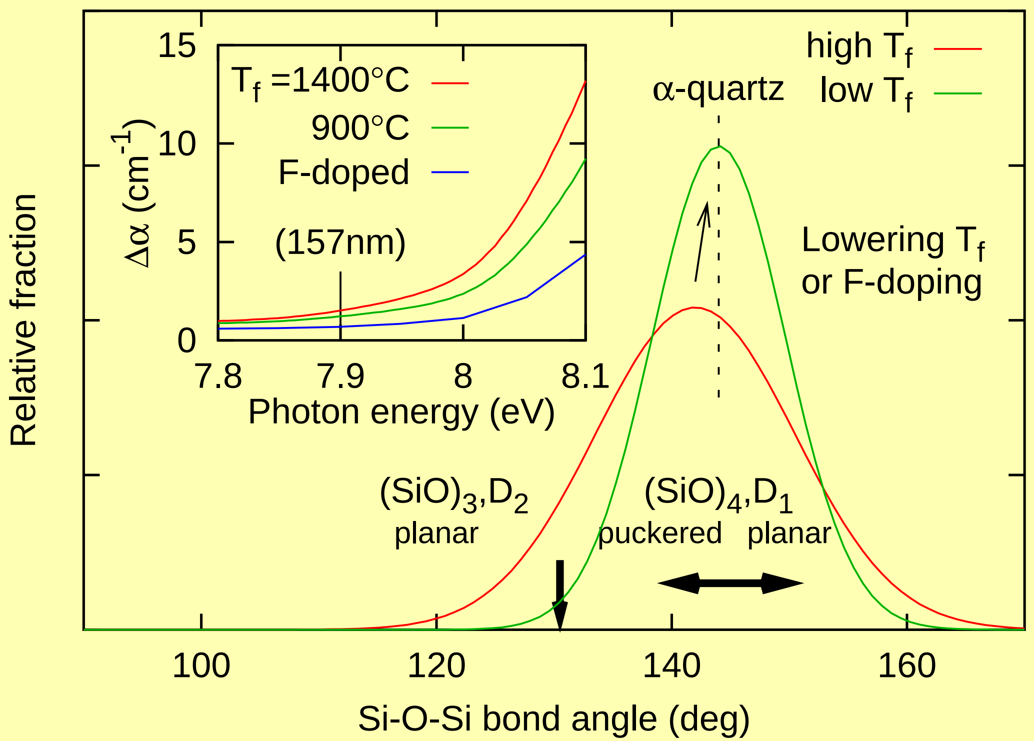
Kajihara et al., APL81,3164(2002)

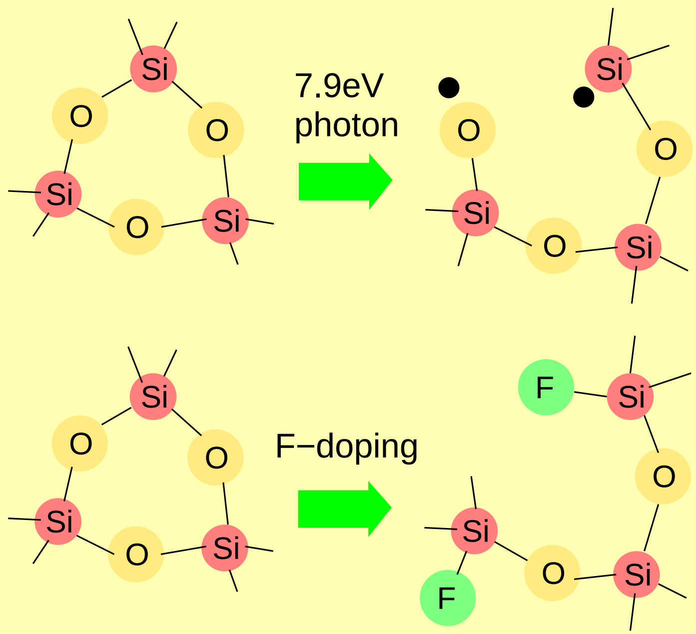


Elimination of strained Si-O-Si bonds

- 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

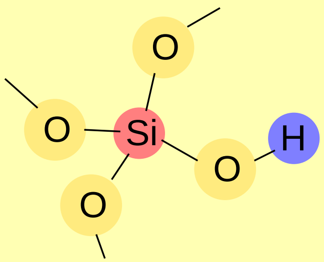
Hosono and Ikuta, NIMB166, 691(2000)



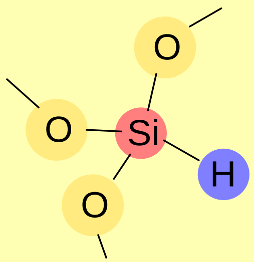


3b. Network modifiers — Types and the VUV absorption bands

Hydrogen−related species

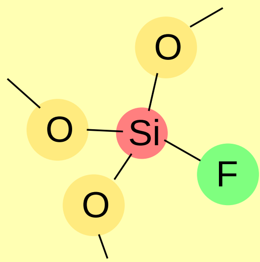


SiOH group

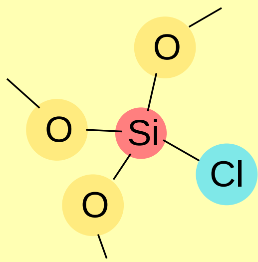


SiH group

Hydrogen−related species



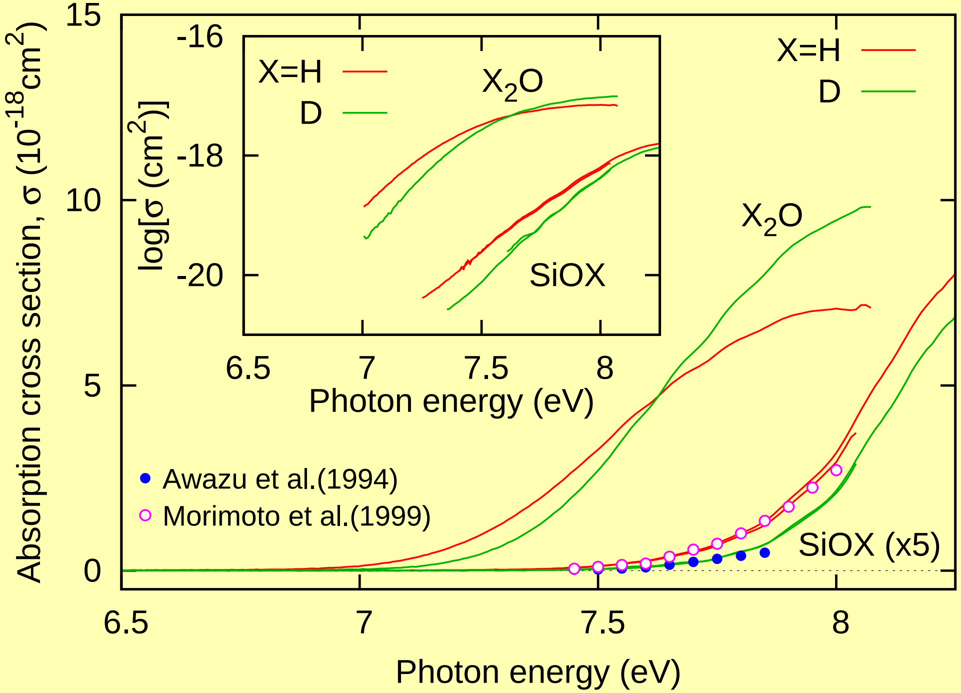
SiF group



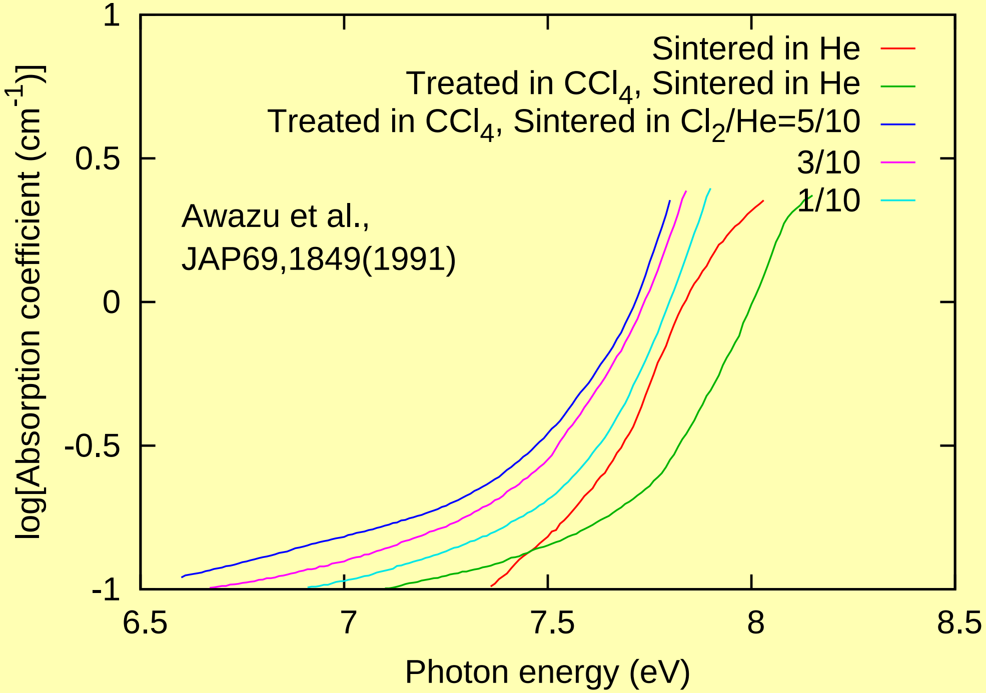
SiCl group

	Absorption band
SiOH	$\gtrsim$7.4eV
SiH	Not known ($\gtrsim E_g$)
SiF	Not known ($\gtrsim E_g$)
SiCl	$\gtrsim$7eV

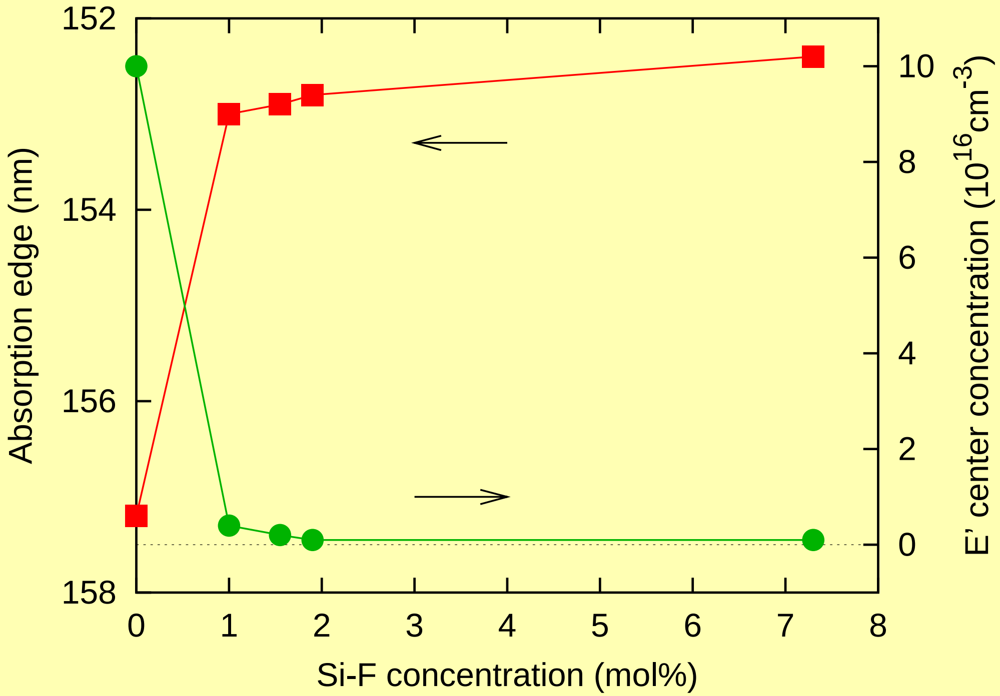
Kajihara et al. PRB72,214112(2005)



Awazu et al. JAP69,1849(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)

	VUV OA	Photolysis	Cost	Applications
SiF (F-doped	No	No	High	Excimer laser lithography, DUV fiber
SiOH (Wet)	$\gtrsim$7.4eV	$SiO^{\bullet} + H^0$	Low-Med.	UV-DUV laser optics
SiCl (Dry)	$\gtrsim$7.7eV	$Si^{\bullet} + Cl^0$	Med	IR optical telecom
SiH	No?	$Si^{\bullet} + H^0$?	–	–

3c. Interstitial H_2 molecules

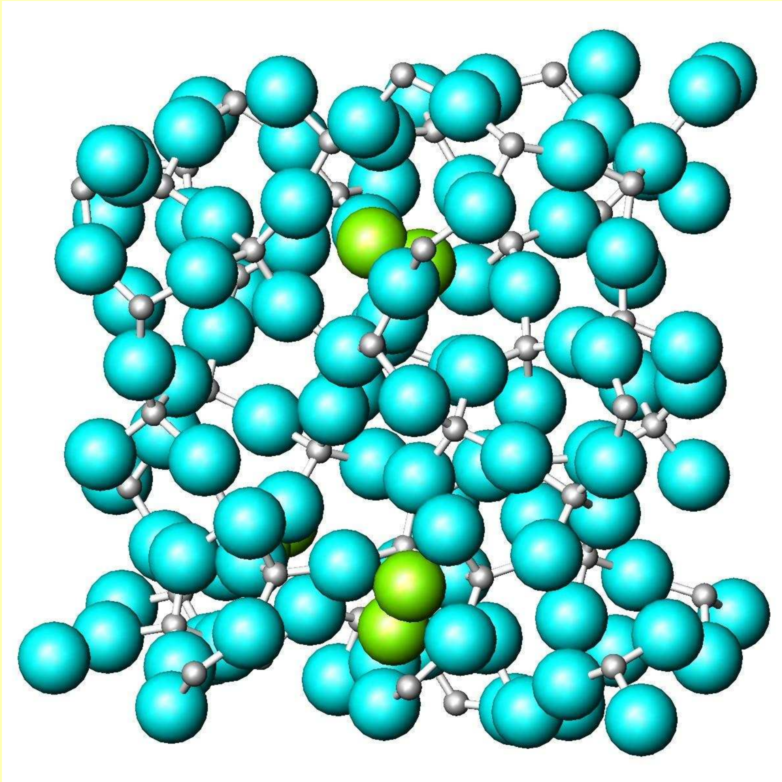
Silica glass

- Low density as compared with crystalline SiO_2, Al_2O_3. . . 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. . . H^0、 H_2
- Oxygen-related . . . O^0、 O_2

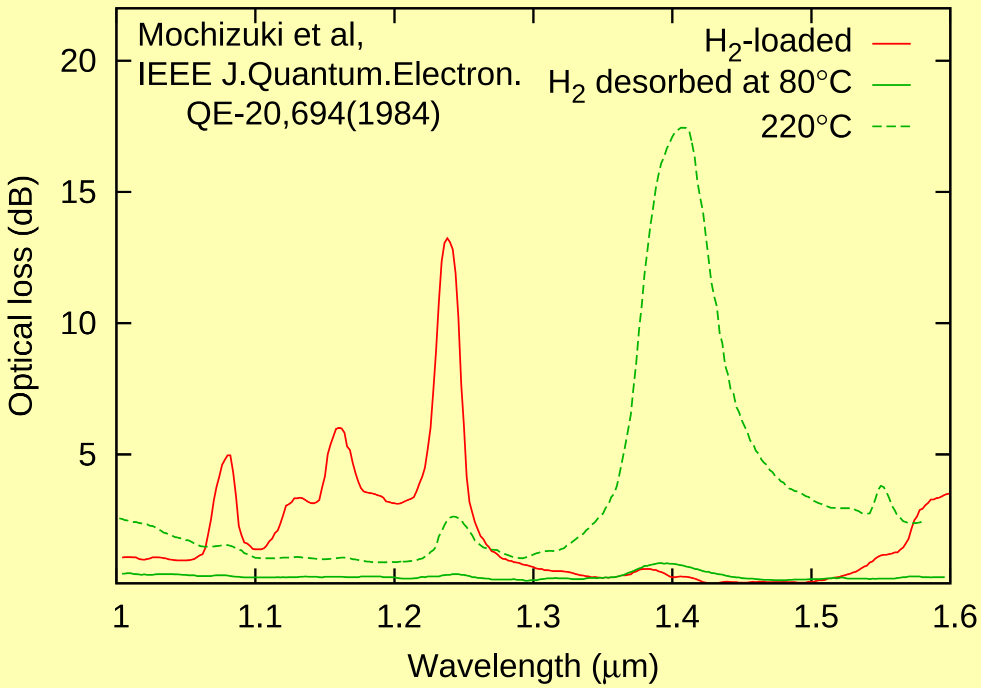
	Density (g cm^{-3})
Silica glass	2.21
Tridymite	2.33
Cristobalite	2.33
α-quartz	2.65
Soda-lime silicate	2.47
Alumina (Al_2O_3)	3.97

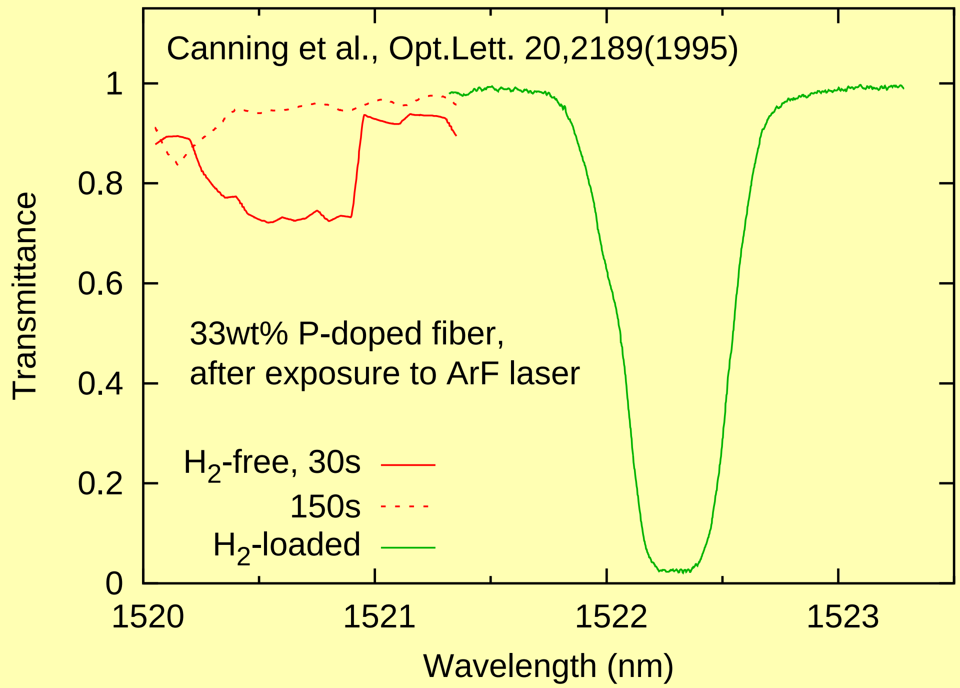


3c. Interstitial H_2 molecules

H_2 in silica glass... fast diffusion (He $>$ H_2 $>$ Ne $\gg$ Ar, H_2O), high reactivity

- Hydrogen corrosion in telecom fibers ($\equiv$Si-O-Si$\equiv$ + H_2 $\rightarrow$ $\equiv$SiOH + $\equiv$SiH)
- Sensitization of photoencoding of Bragg gratings
- Termination of dangling bonds ($R^\bullet + H_2 \rightarrow RH + H^0$)
- Improvement of KrF and ArF laser hardness





3c. Interstitial H_2 molecules — In-situ study of diffusion and reactions

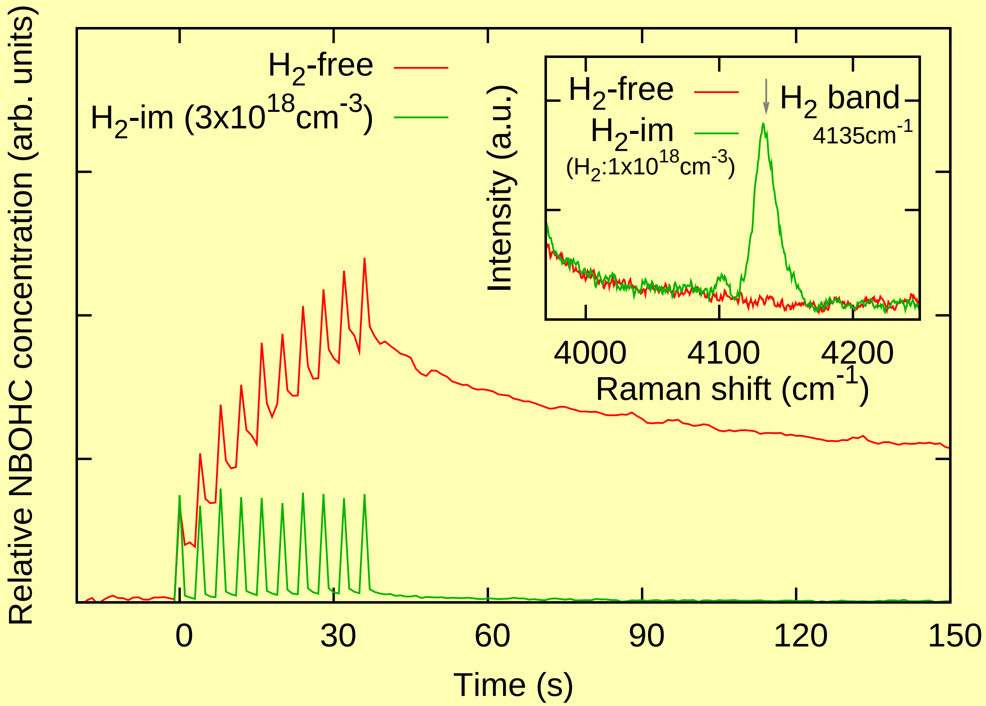
F_2-laser-irradiated "wet" silica glass

F_2 laser (7.9eV) $\equiv$SiO-H $\longrightarrow$ $\equiv$SiO$^\bullet$ + H^0 (quantum yield ~0.1–0.2)

Nd:YAG 4HG (4.7eV) $\equiv$SiO$^\bullet$ $\longrightarrow$ $\equiv$SiO$^\bullet$(1.9eV PL)

- Concentration of radiation-induced NBOHC($\equiv$SiO$^\bullet$) . . . insensitive to H_2 loading
- NBOHC does not accumulate in H_2-loaded glass

Kajihara et al., APL79,1575(2001); NIMB33,323(2004); PRB74,094202(2006)

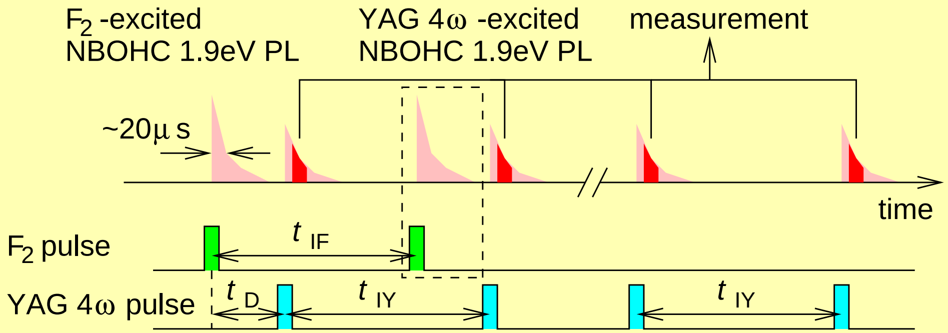


H_2-free

$\equiv$SiOH $\rightleftarrows$ $\equiv$SiO$^\bullet$ + H^0

H_2-loaded

$\equiv$SiOH $\rightleftarrows$ $\equiv$SiO$^\bullet$ + H^0, H_2



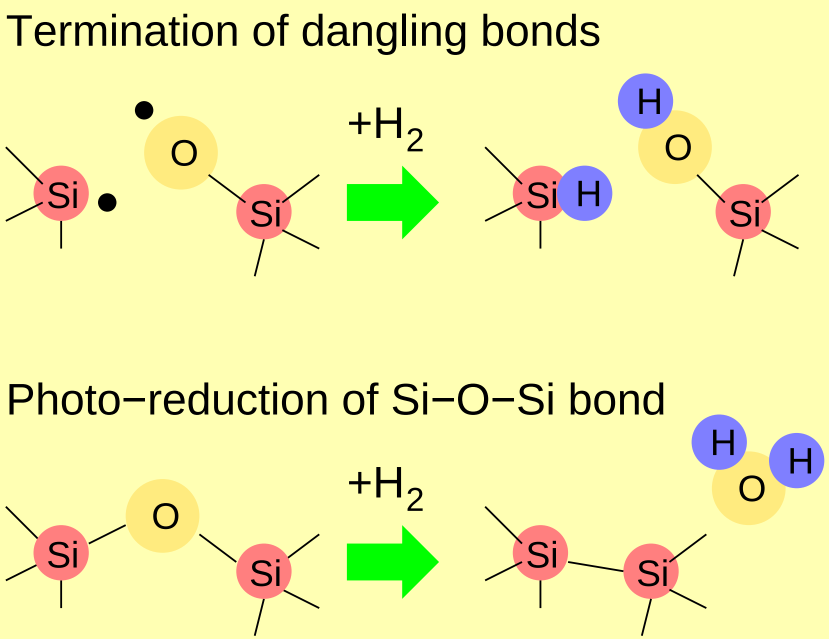
Various effects of interstitial H_2

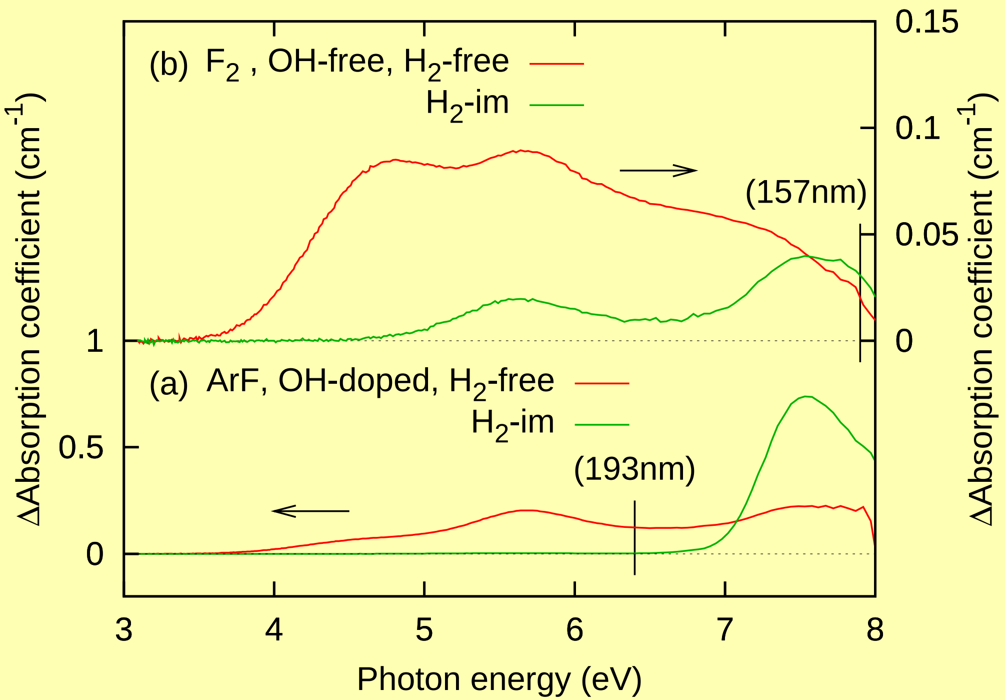
1. Termination of dangling bonds[$\equiv$Si$^\bullet$(5.8eV), $\equiv$SiO$^\bullet$(4.8eV, 6.8eV)]
2. Acceleration of oxygen vacancy formation [$\equiv$Si-Si$\equiv$ (7.6eV)]

   . . . Photoreduction ($\equiv$Si-O*-Si$\equiv$ + H_2 $\rightarrow$ $\equiv$Si-Si$\equiv$ + H_2O)
3. Crack formation . . . Stress corrosion ($\equiv$Si-O-Si$\equiv$ + H_2O $\rightarrow$ 2$\equiv$SiOH)

H_2 conc. should be strictly optimized

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



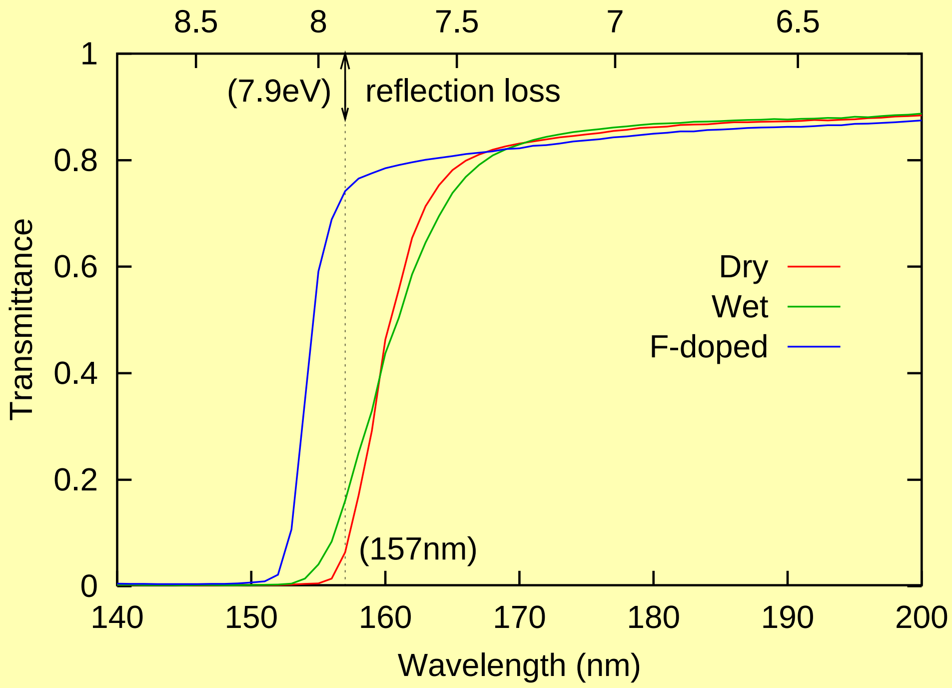


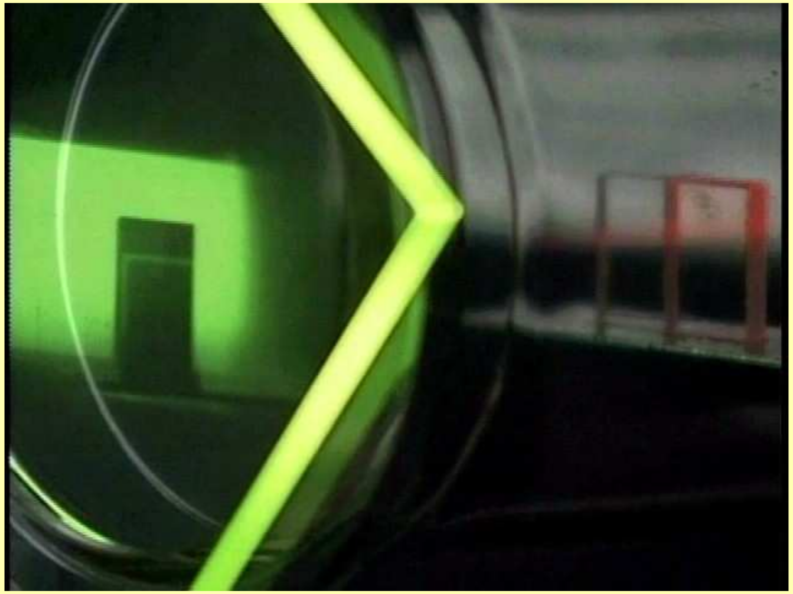
4. Silica glasses for UV-VUV spectral region F_2 laser optics

Type	Defect species	Conventional applications	7.9eV Transparency
Wet	SiOH	UV optics	Poor(OA by SiOH)
Dry	SiCl, Si-Si	IR telecom. fibers	Poor(OA by Si-Si)
F-doped	SiF	X- and γ-resistant fibers	Good

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

Hosono et al. APL74,2755(1999), Mizuguchi et al. JVSTB17,3280(1999)



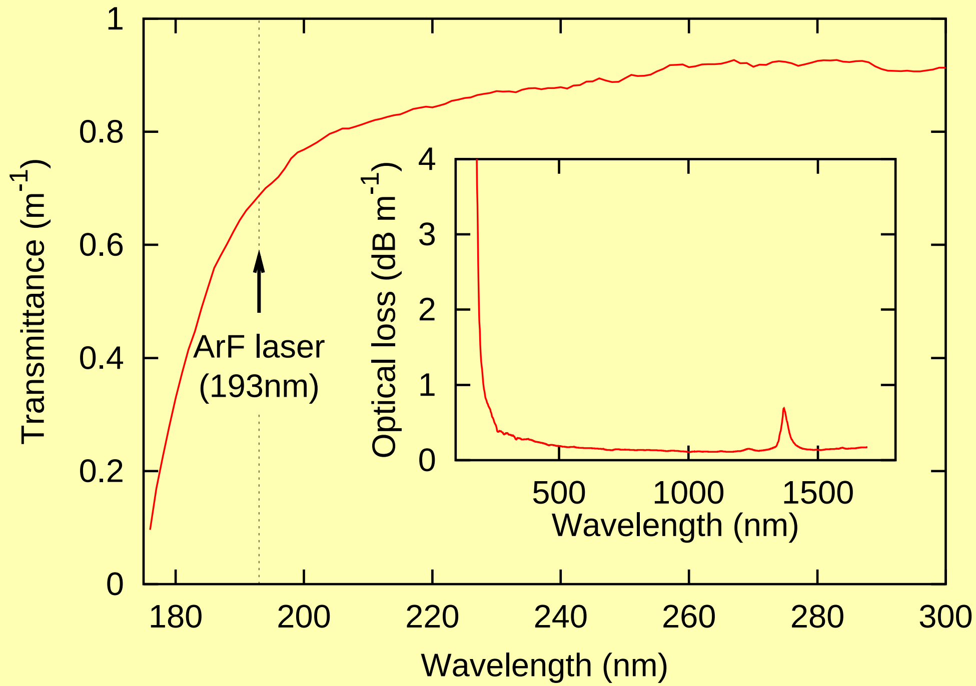


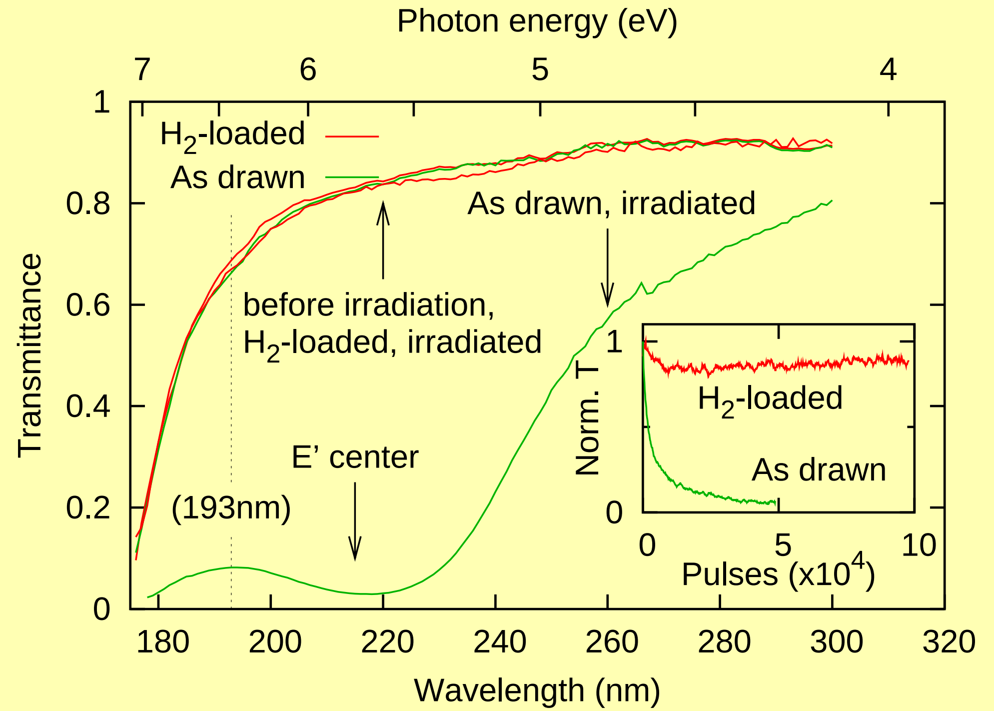
Conventional fibers (Ge-doped core and pure-silica cladding)

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

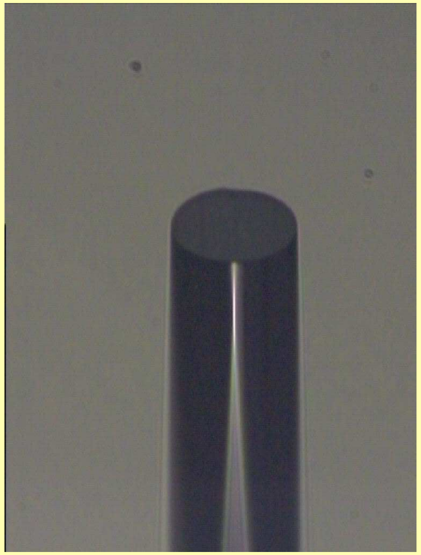
⇒
1. F-doped core and cladding
2. Defect annihilation by H_2 impregnation

Oto et al, IEEE Photo. Technol. Lett. 13, 978(2001); J. Non-Cryst. Solids 349,133(2004)





- End sharpening by chemical etching in hydrofluoric acid
  . . . Possible application to scanning nearfield optical microscopy (SNOM)



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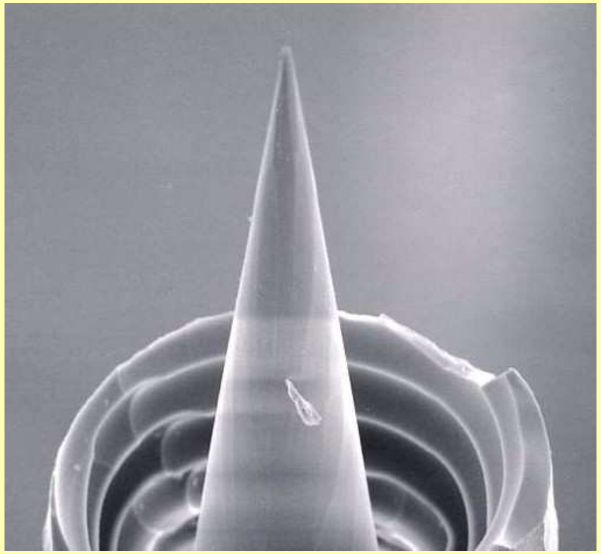
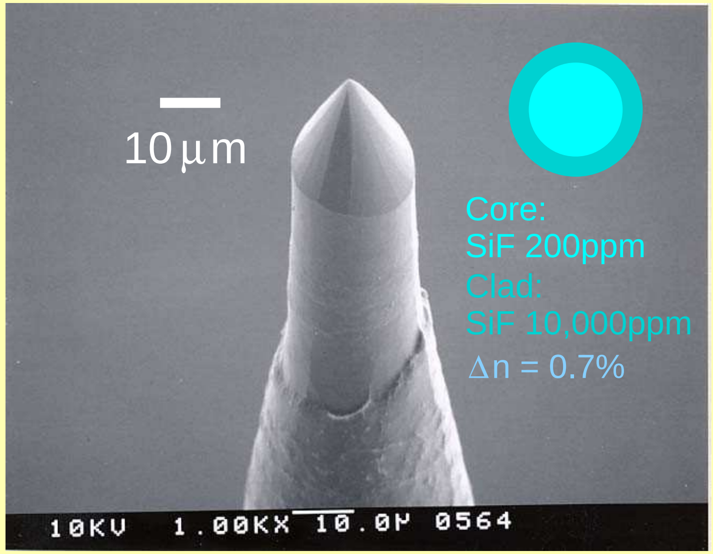
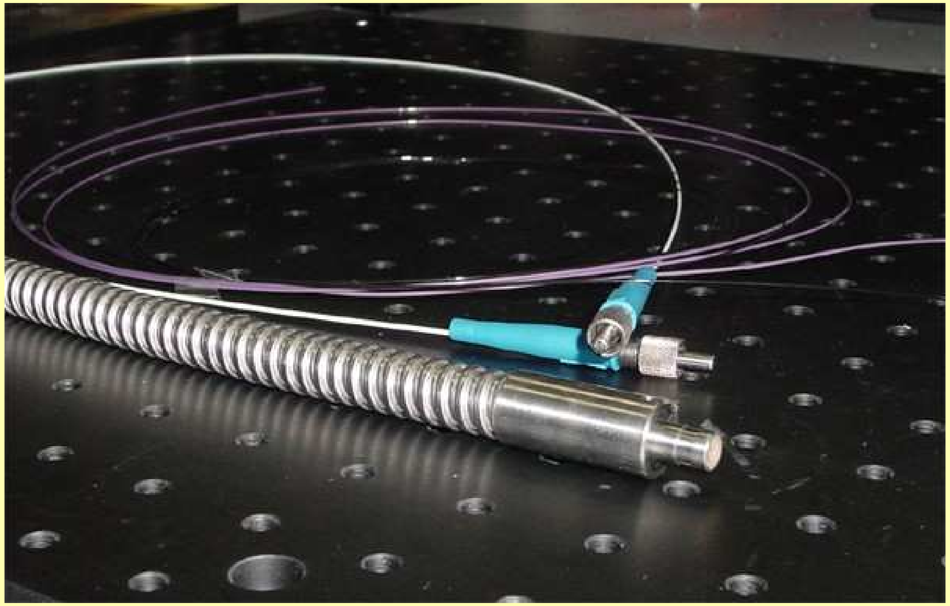
HF etching

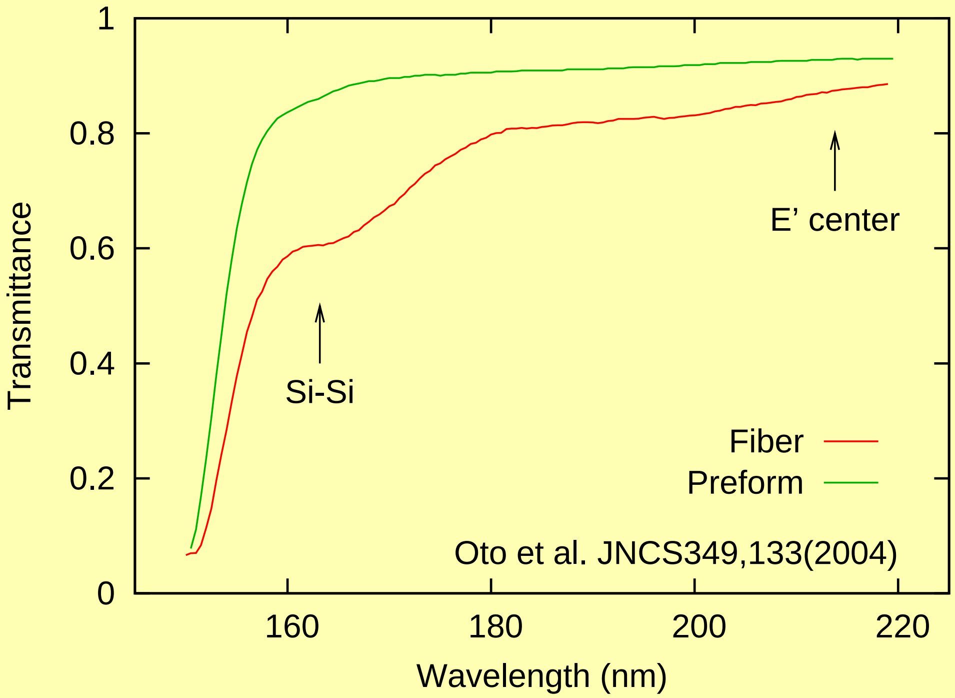




5. Interstitial oxygen in silica glass

- Oxygen-deficiency related defects. . . Si-Si, $\equiv$Si$^\bullet$, –$\ddot{\text{Si}}$–, . . .
  - Main color centers in DUV fibers
- Oxygen-excess related defects. . . $\equiv$SiOO$^\bullet$, O_2, Si-O-O-Si, . . .
  - May be used to oxidize oxygen-deficiency related color centers
  - Chemical and optical properties remain largely unclear

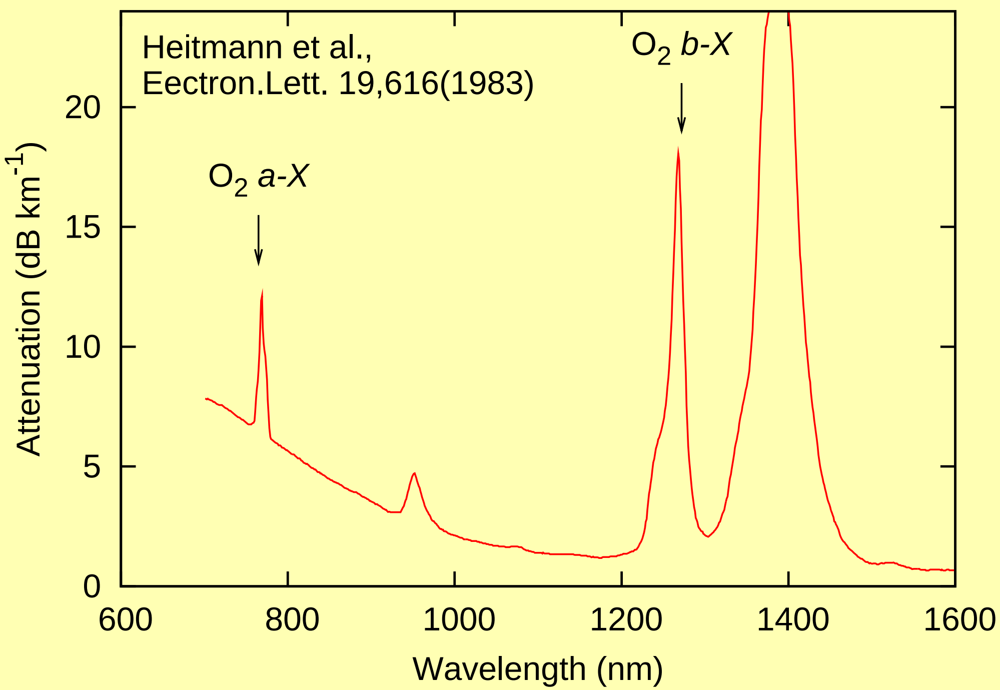


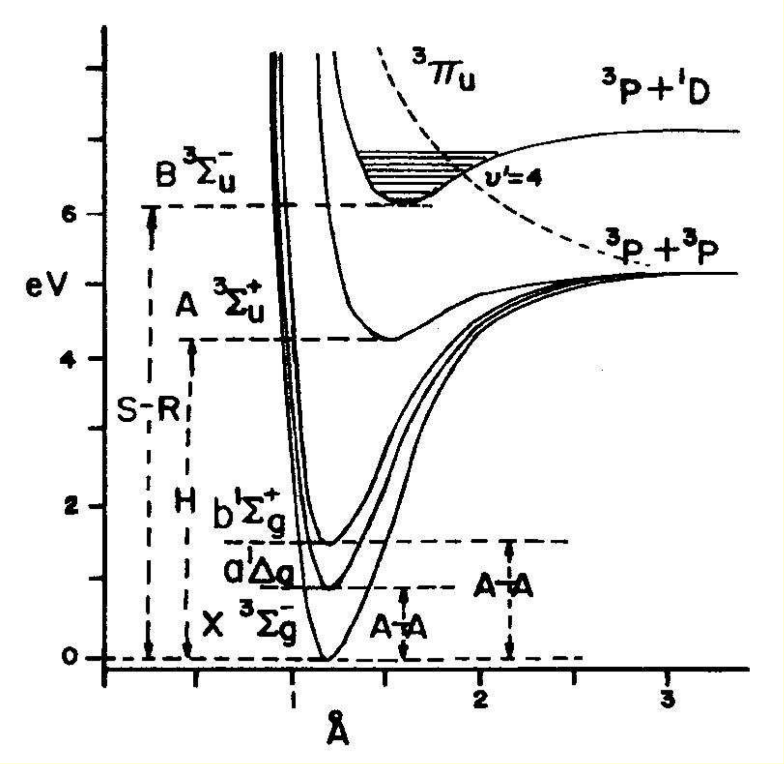


5. Interstitial oxygen in silica glass

Interstitial O_2... The most common form of excess oxygen in silica glass

- Nassau and Shiever (1975) Preparation of low-OH a-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

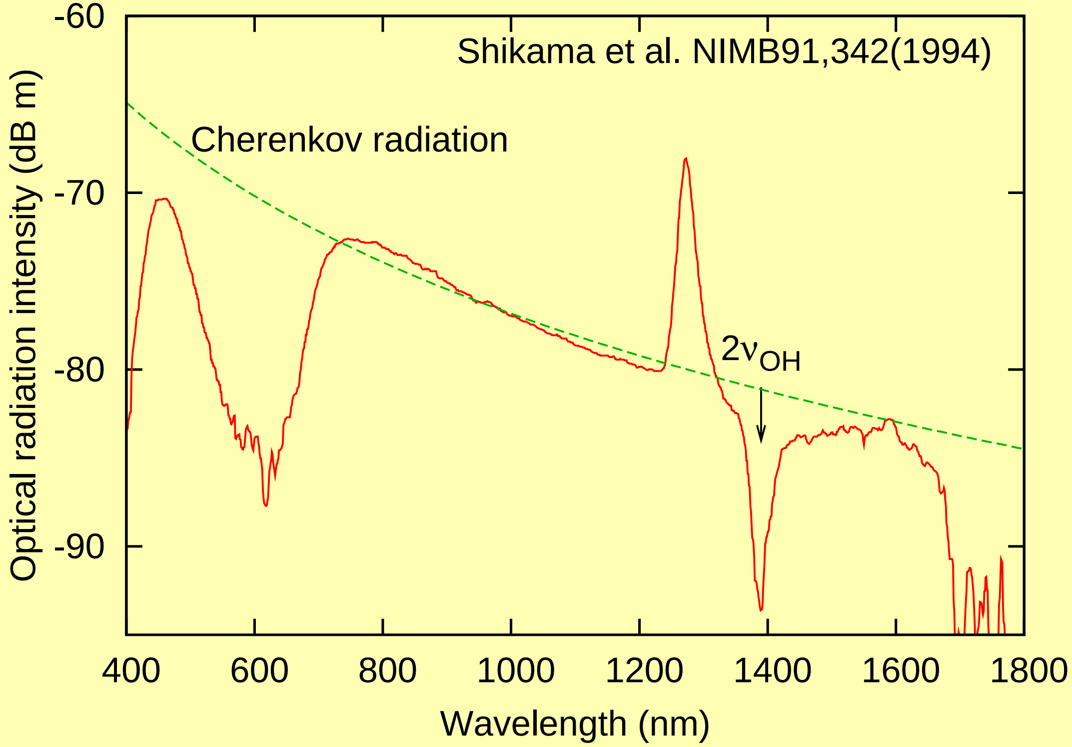


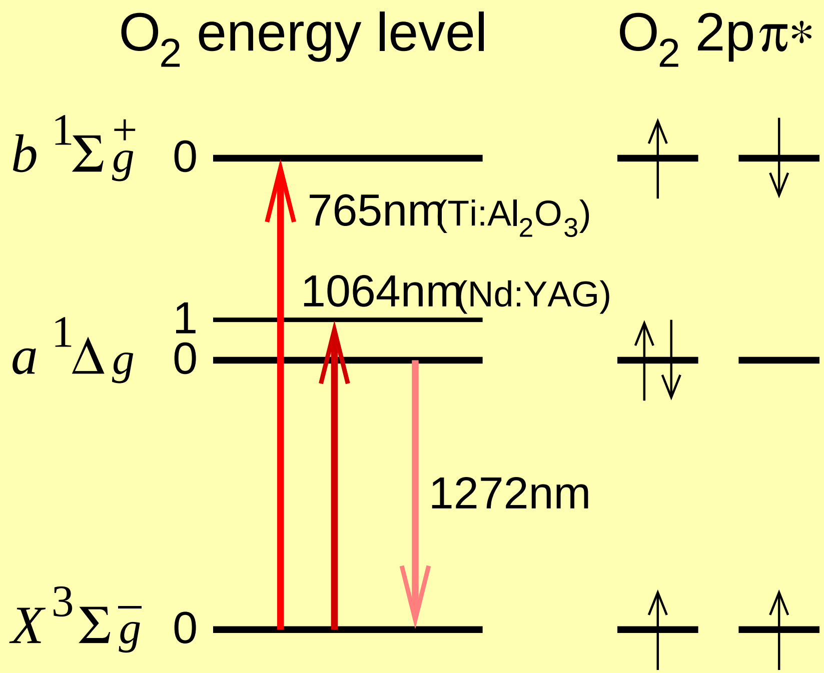


5. Interstitial oxygen in silica glass Detection by photoluminescence

- 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_2 via 1064nm excitation
- Skuja et al.(1998) PL detection of interstitial O_2 via 765nm excitation

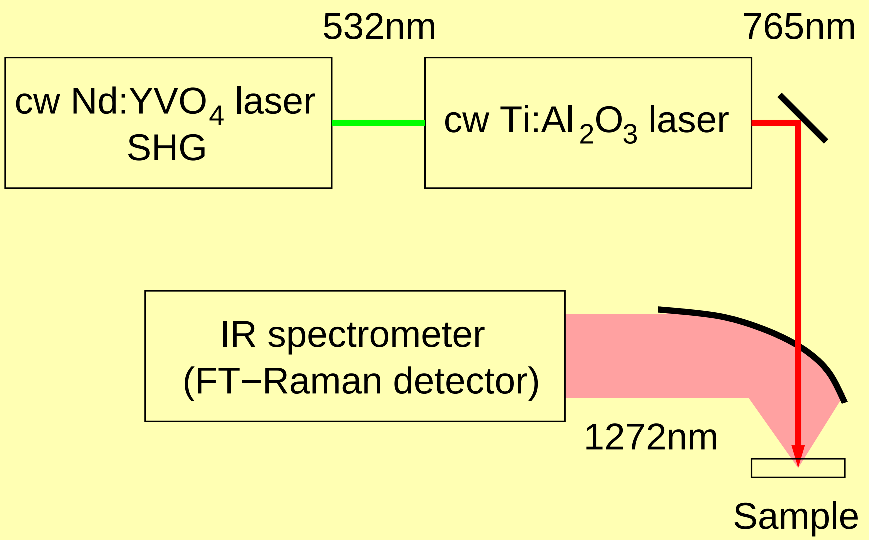
Sensitive, selective, and non-destructive detection of interstitial O_2 in a-SiO_2

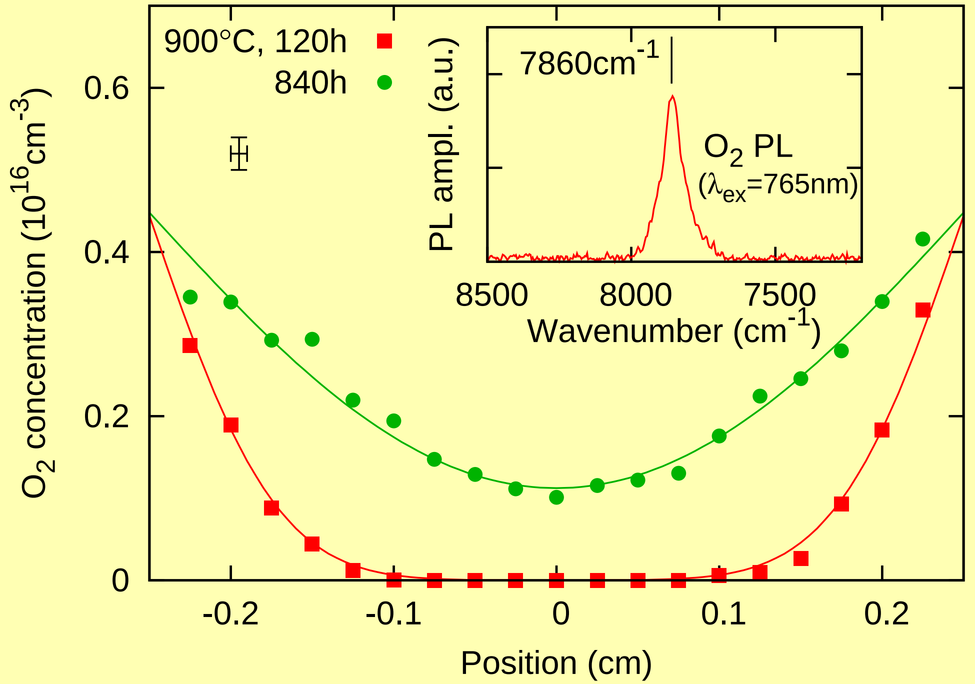




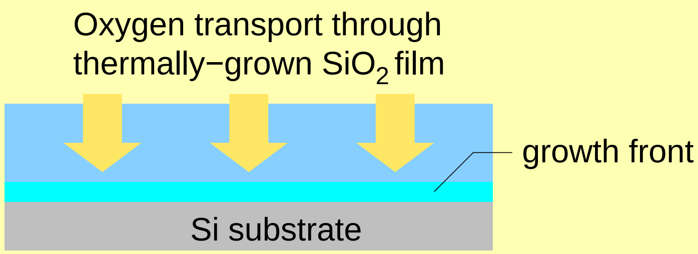
- O_2 PL measurements of silica glasses thermally annealed in air
  ... Solubility and diffusion coefficient of interstitial O_2 in silica glass

Kajihara et al. J.Ceram.Soc.Jpn.112,559(2004); JAP98,013529(2005)





Oxidant in the thermal oxidation of silicon is interstitial O_2

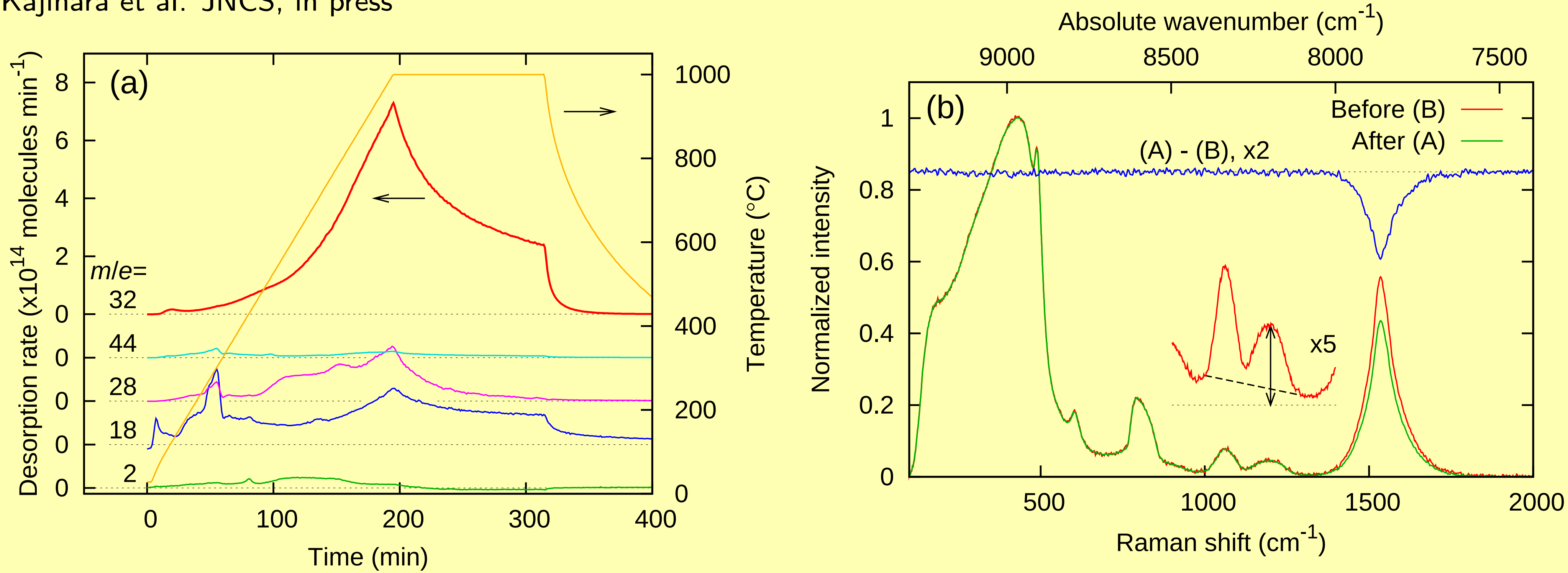


- Thermal desorption spectroscopy

8.3×10^{16} molecules $\sim$ 22 % decrease of PL intensity

O_2 concentration $\sim$ 2.7×10^{16} cm^{-3} $\Delta A_{\text{PL peak}}/A_{\text{Raman@1200cm}^{-1}}$

Kajihara et al. JNCS, in press

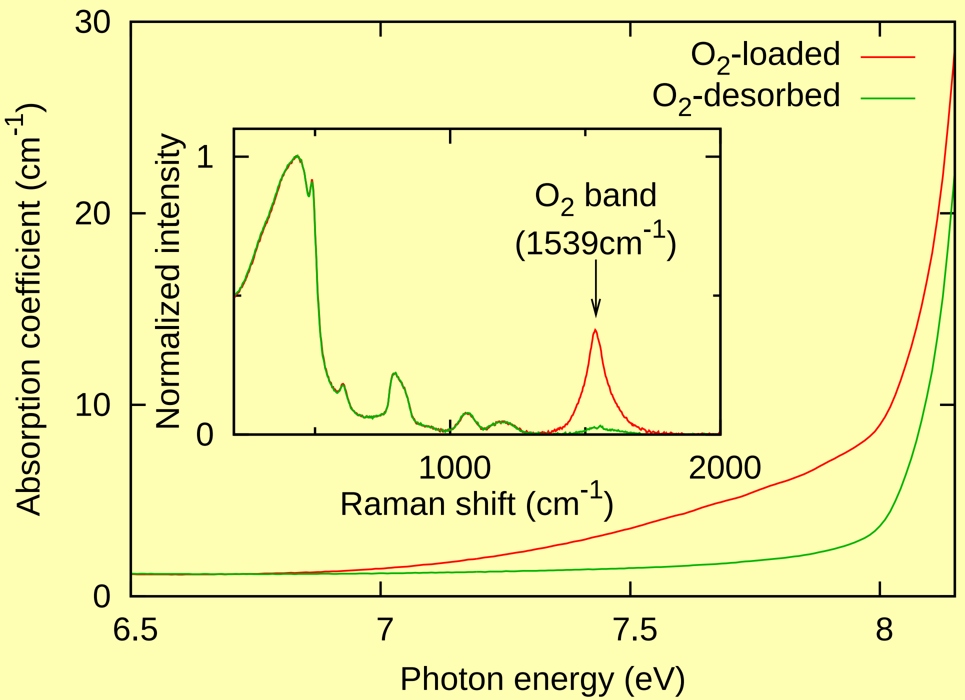


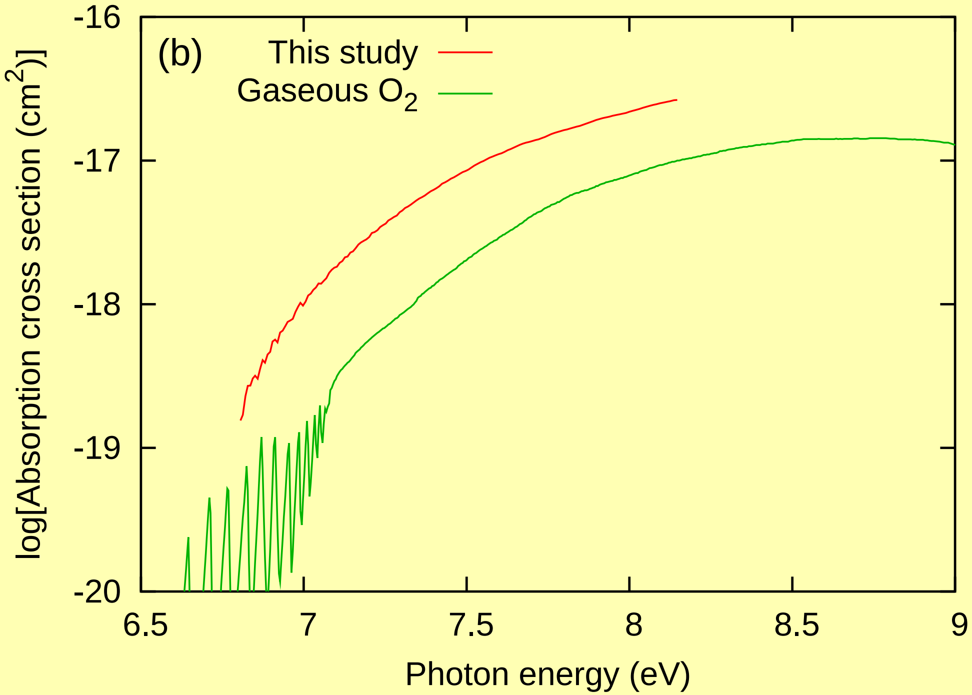
5. Interstitial oxygen in silica glass — VUV OA cross section

- 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)





- Reaction of a-SiO_2 with H_2... Cracking of Si-O bond

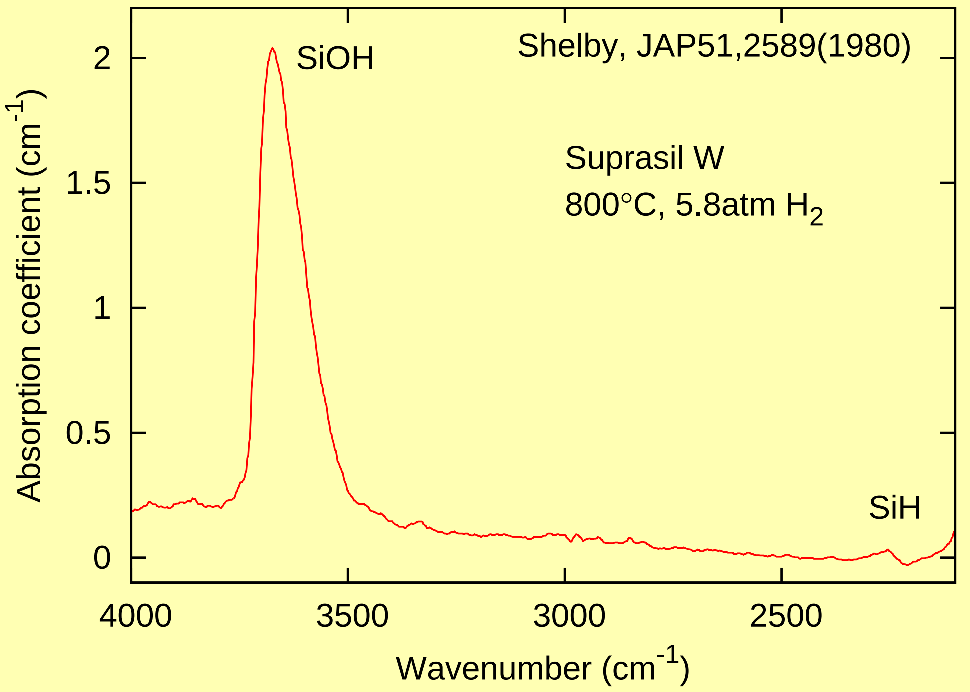
$$\equiv\text{Si-O-Si}\equiv + H_2 \longrightarrow \equiv\text{SiOH} + \text{HSi}\equiv$$

- Shelby(1980) SiOH creation with little accompanying SiH formation in O_2-rich a-SiO_2

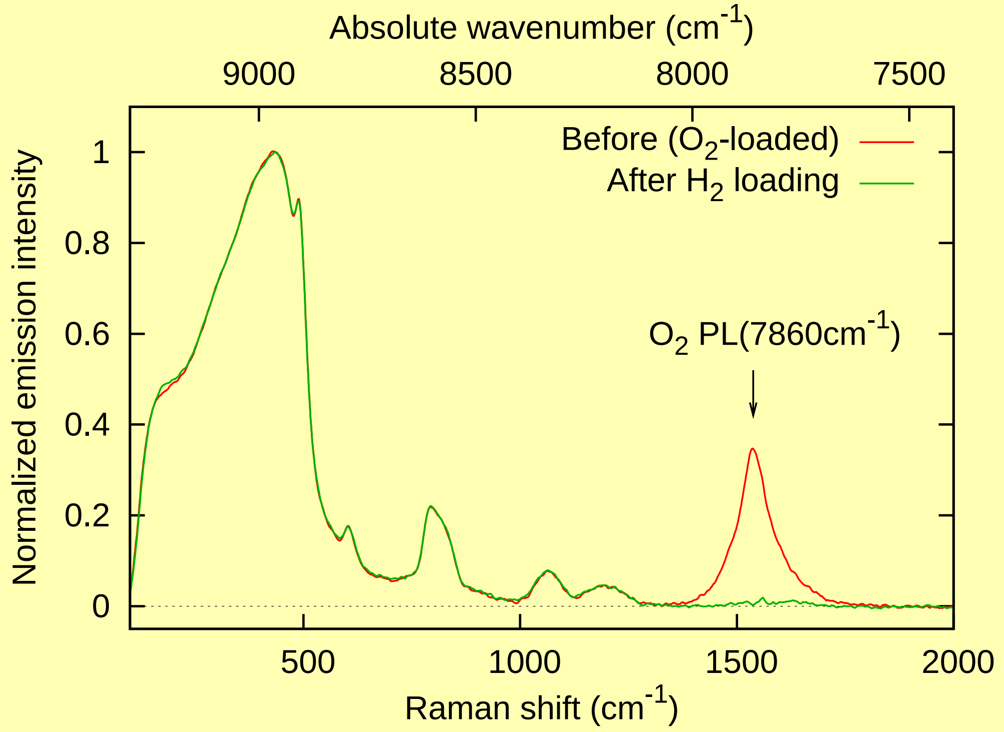
Two-step reactions

1. $1/2O_2 + H_2 \longrightarrow H_2O$
2. $\equiv\text{Si-O-Si}\equiv + H_2O \longrightarrow \equiv\text{SiOH}$

Shelby, JAP51,2589(1980)



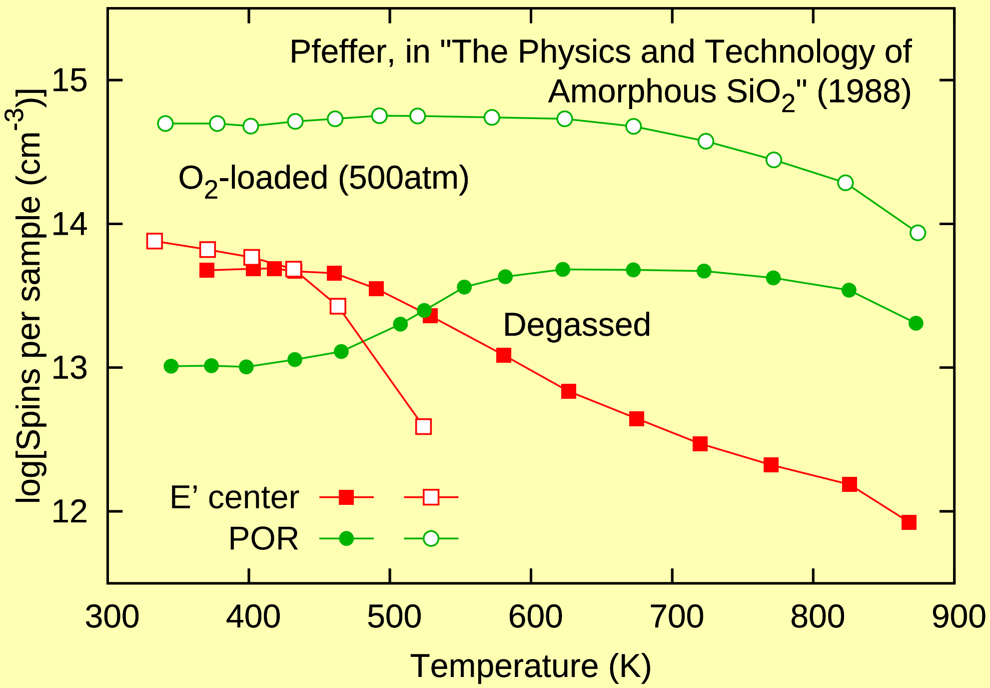
Kajihara, JAP98,043515(2005)



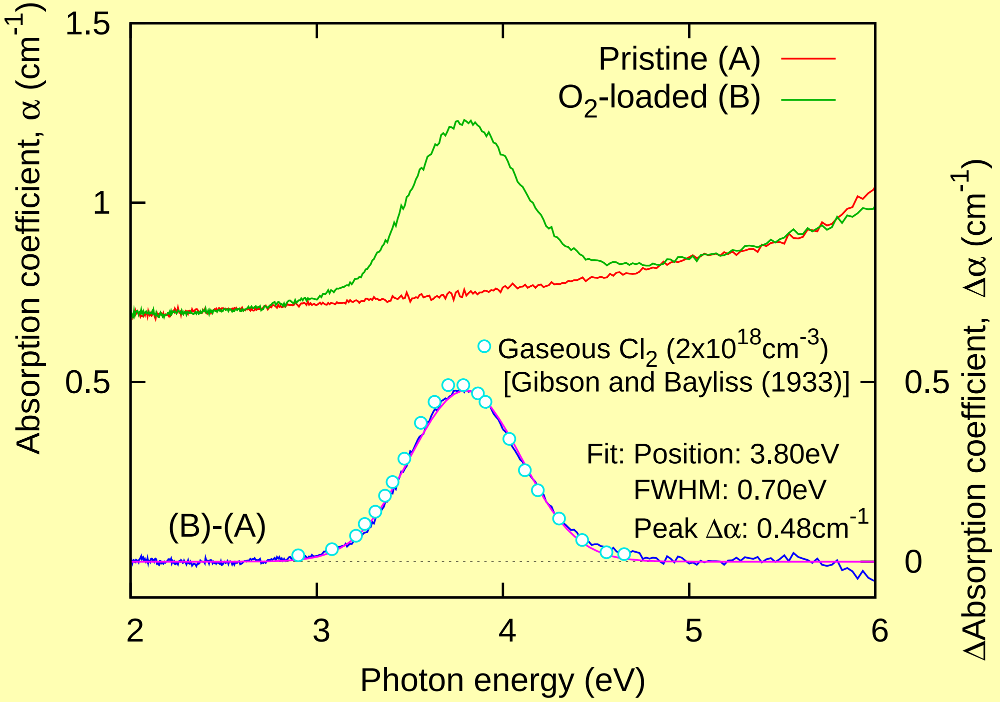
5. Interstitial oxygen in silica glass — Reactions (2)

- Reaction with Si-Si bonds $\equiv$Si-Si$\equiv + 1/2O_2 \longrightarrow \equiv$Si-O-Si$\equiv$
- Reaction with E' center $\equiv Si^{\bullet} + O_2 \longrightarrow \equiv SiOO^{\bullet}$
- Reaction with SiCl $1/2O_2 + 2\equiv SiCl \longrightarrow \equiv$Si-O-Si$\equiv + Cl_2$
- Reaction with H^0 $O_2 + H^0 \longrightarrow HO_2{}^{\bullet}$

Pfeffer (1998)

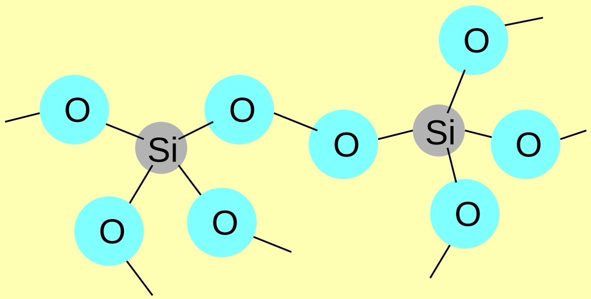


Kajihara, JAP98,043515(2005)



Configuration. . . Peroxy linkage form

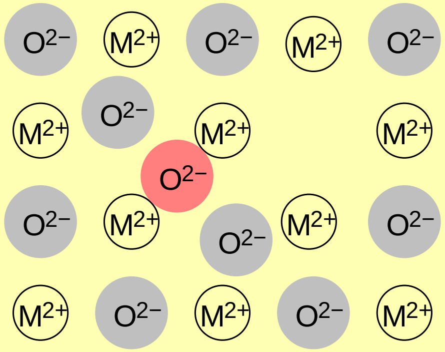
e.g. Hamann, PRL81,3447(1998)
Szymanski et al. PRB63,224207(2001)



Formation

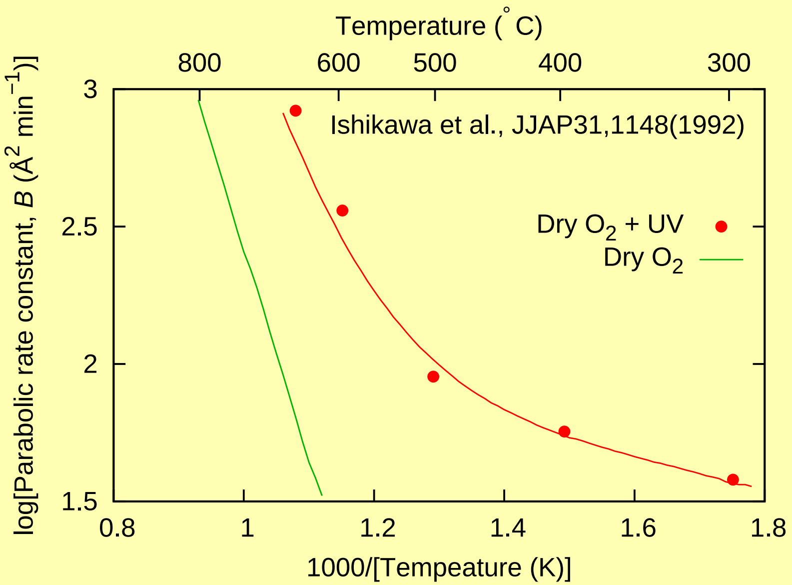
1. Radiolytic decomposition of Si-O-Si bonds
$\equiv$Si-O-Si$\equiv \xrightarrow{h\nu} \equiv$Si-Si$\equiv + O^0$ (or $1/2O_2$)
2. VUV photolysis of interstitial O_2
$O_2 \xrightarrow{h\nu} 2O^0$
3. UV photolysis of peroxy radical
$\equiv SiOO^\bullet \xrightarrow{h\nu} \equiv SiO^\bullet + O^0$

- Anion part of the Frenkel pair



- Low-temperature oxidant of silicon

e.g. Ishikawa et al. JJAP31,1148(1992)

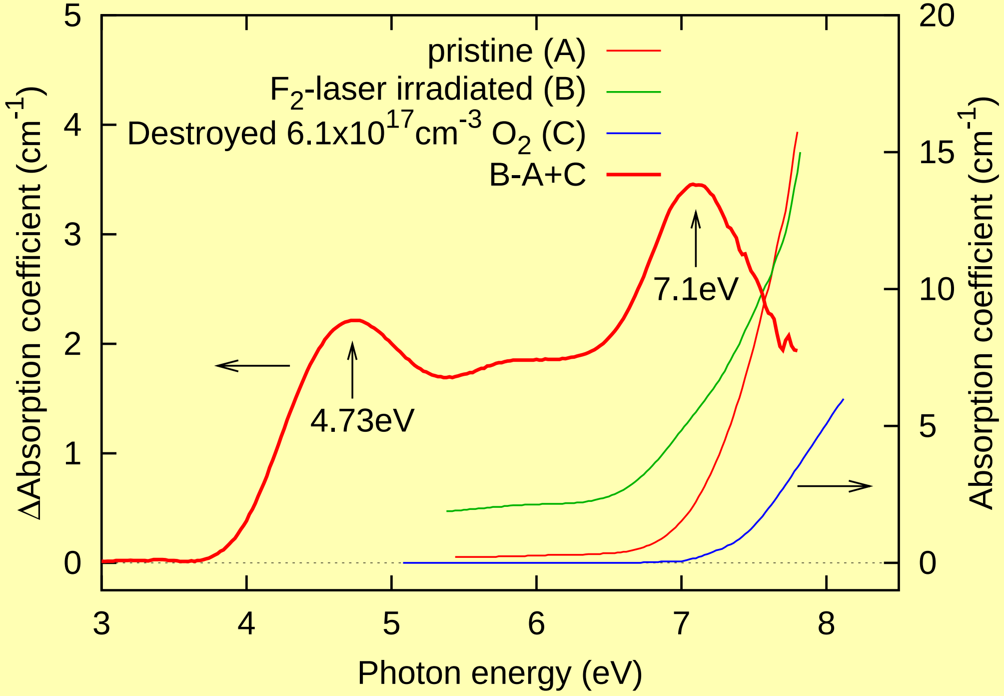


5. Interstitial oxygen in silica glass — Optical absorption and diffusivity

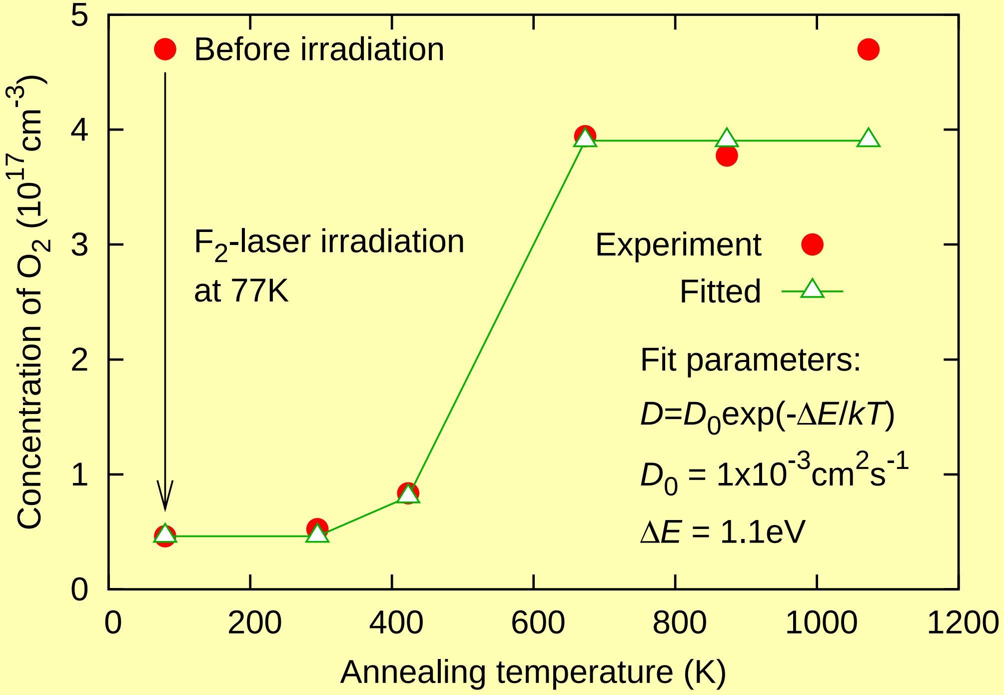
$$O_2 \underset{\text{Heat}}{\overset{h\nu}{\rightleftarrows}} 2O^0$$

- 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)



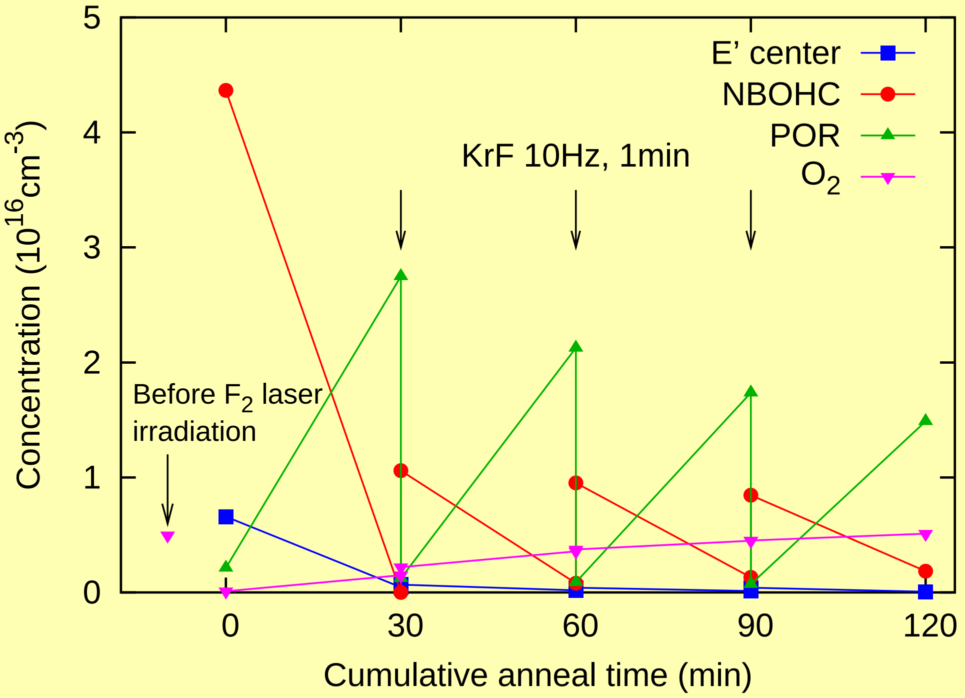
Skuja et al. PCG43C,145(2002)



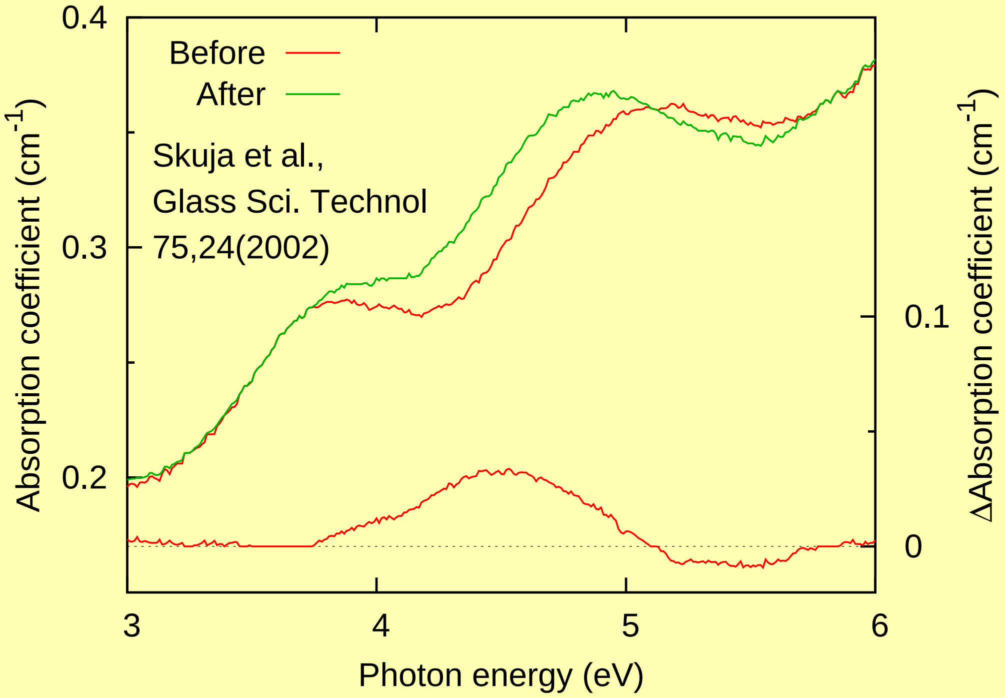
5. Interstitial oxygen in silica glass — Conversion of dangling bonds

$$\equiv\text{SiOO}^\bullet \underset{\text{Heat}}{\overset{h\nu(\sim 5\text{eV})}{\rightleftarrows}} \equiv\text{SiO}^\bullet + \text{O}^0$$

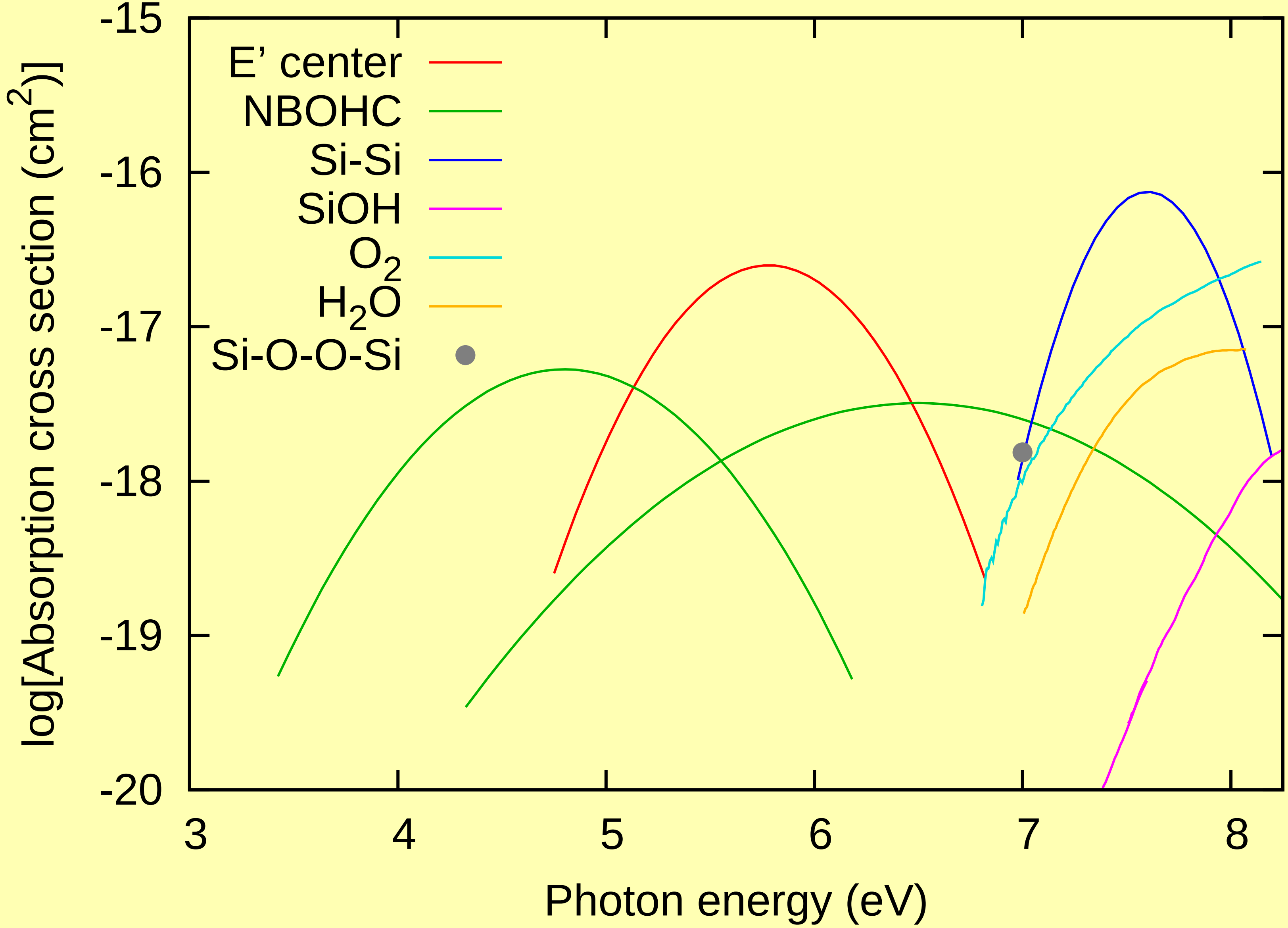
Kajihara et al. PRL92,015504(2004)



Skuja et al. Glass.Sci.Technol. 75,24(2002)



Absorption cross section "map"



Summary

Optical isotropy

Wide−gap
α−quartz

Workability

Process engineering

- Raw material
- Production method
- Fiber drawing

Fundamental research

- Optical spectroscopy
- EPR
- Simulation

Structural modification

- Network topology
- Stoichiometry
- Doping(H,F,P,RE, ...)

Deep−UV optics

Photomasks
Hard pellicles
Lenses

Optical fibers

DUV fibers
Bragg grating devices
Fiber lasers

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  (Japan Science and Technology Agency, Tokyo Institute of Technology)
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  (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.)