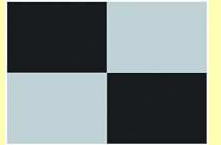


Jan. 10, 2008

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

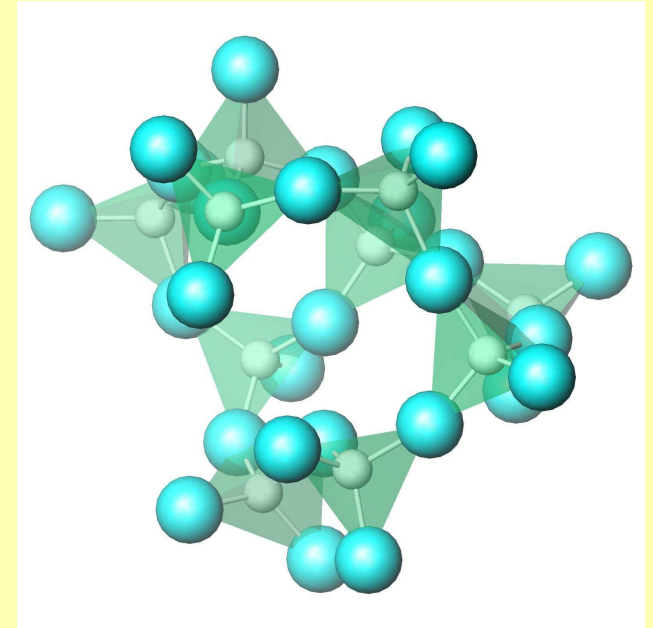
Overview

1. Introduction
2. Structure and optical properties of defects
 - Strained Si-O-Si bonds
 - Network modifiers ($\equiv\text{SiX}$)
 - 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?

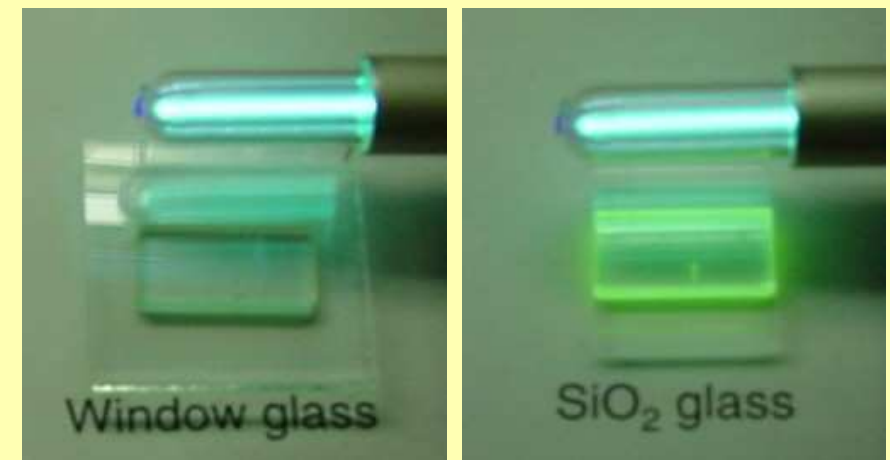
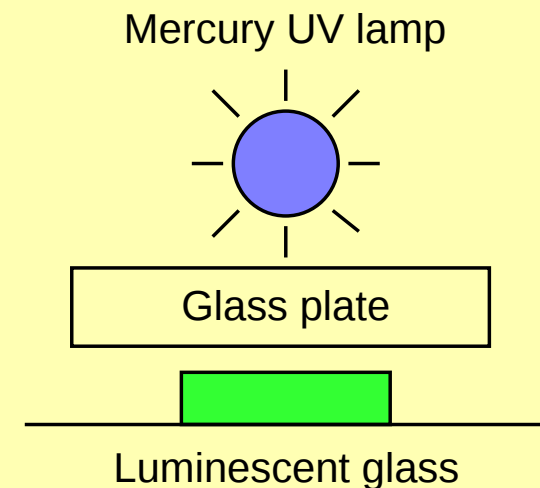
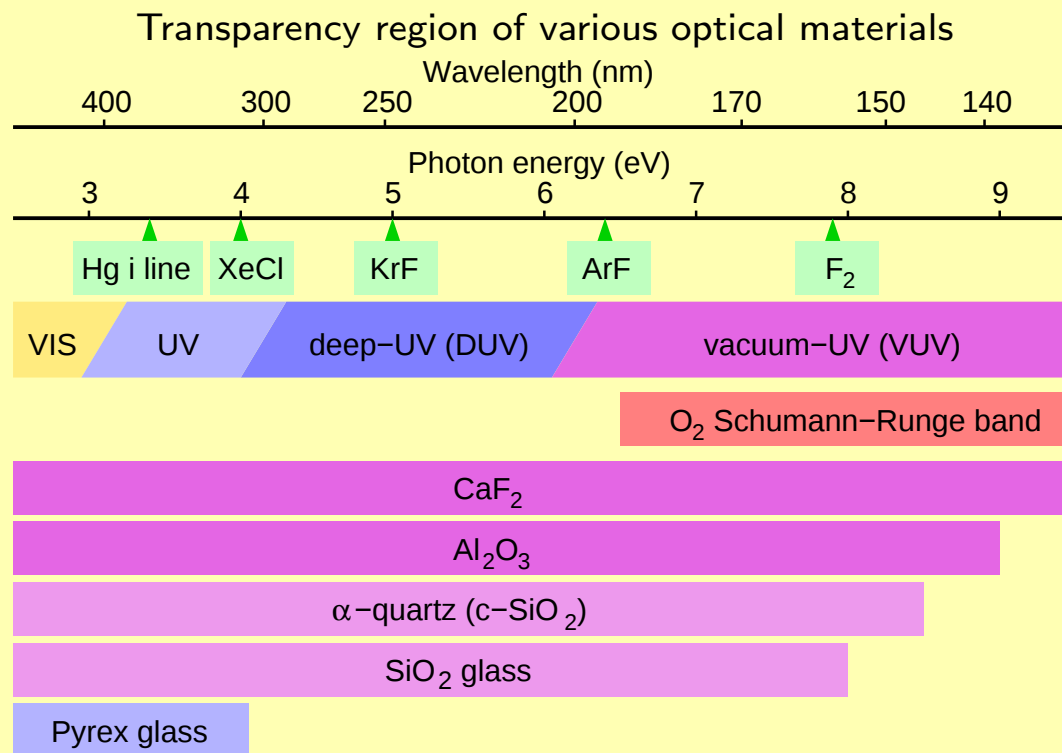
- One of the simplest light metal amorphous oxides
- Large-size crystalline polymorph (α -quartz) is available
- Good mechanical properties and chemical stability
- High purity products are commercially available
- Various practical applications
 - Optical components
 - Gate dielectric films
 - Catalysts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



1. Introduction

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

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



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 ($<5\text{ppm}$) OH concentration.
- Type II Crucible-free $\text{H}_2\text{-O}_2$ flame fusion. Concentrations of metallic impurities are lower than Type I. Medium ($\sim 100\text{ppm}$) OH concentration.

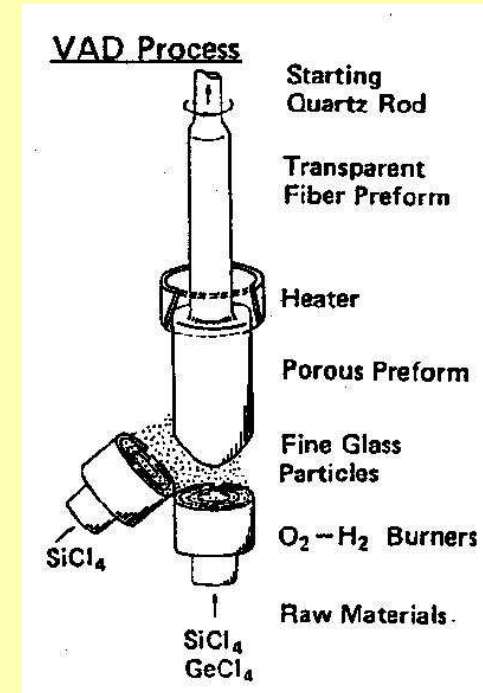


From product catalog,
Covalent Materials Co.

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 $\text{H}_2\text{-O}_2$ hydrolysis.
High ($\sim 1,000\text{ppm}$) OH concentration.
- Type IIIa,b Prepared by “soot”-remelting.
Suitable for dehydration and doping.
- Type IV Prepared by $\text{O}_2\text{-Ar}$ plasma CVD method.
Nealy OH-free but contains O_2 molecules.



There are various types of silica glasses!

1. Introduction

Effect of point defects (color centers)

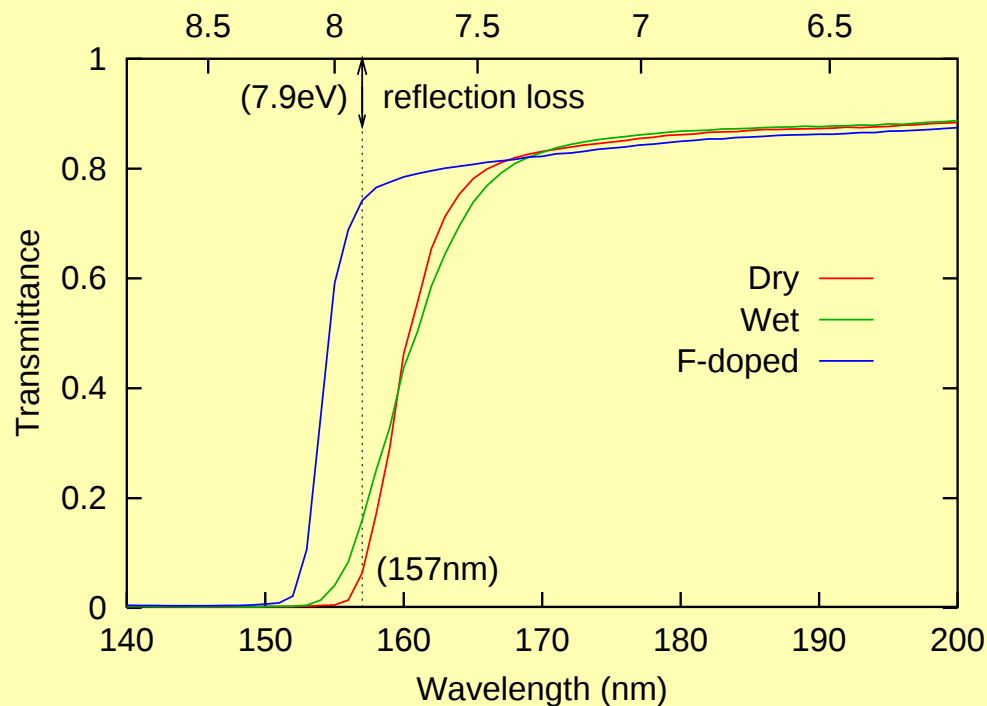
- Different types of silica glasses

different optical properties ... different concentrations of point defects

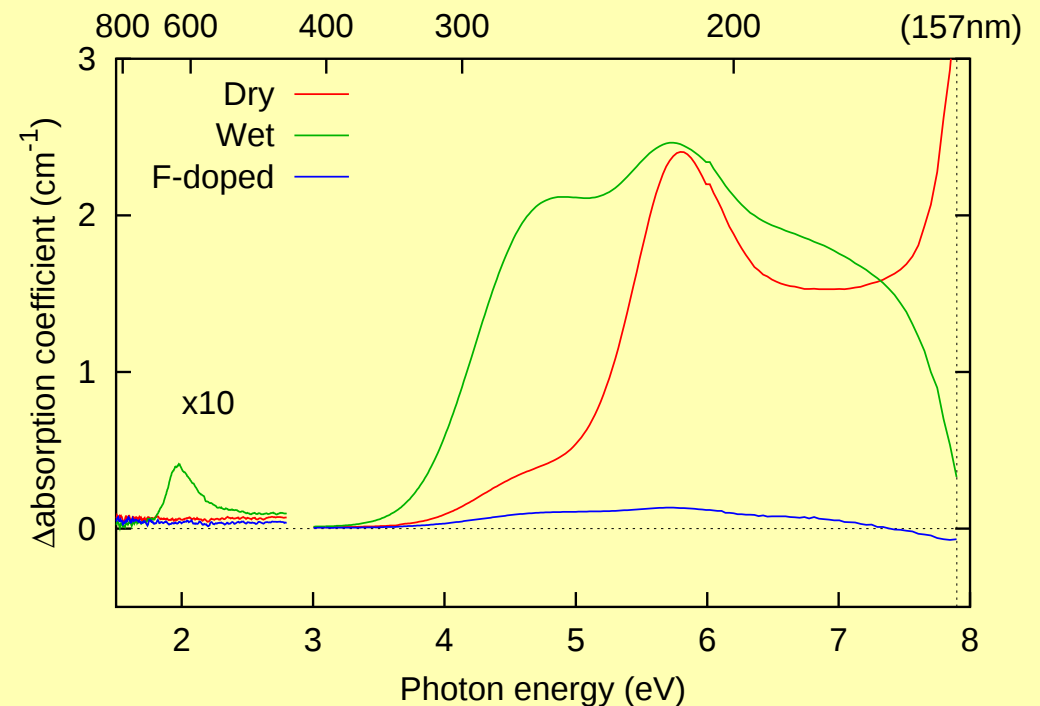
Control of point defects is important!

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

Absorption spectra



Induced absorption spectra



1. Introduction

Defect concentration

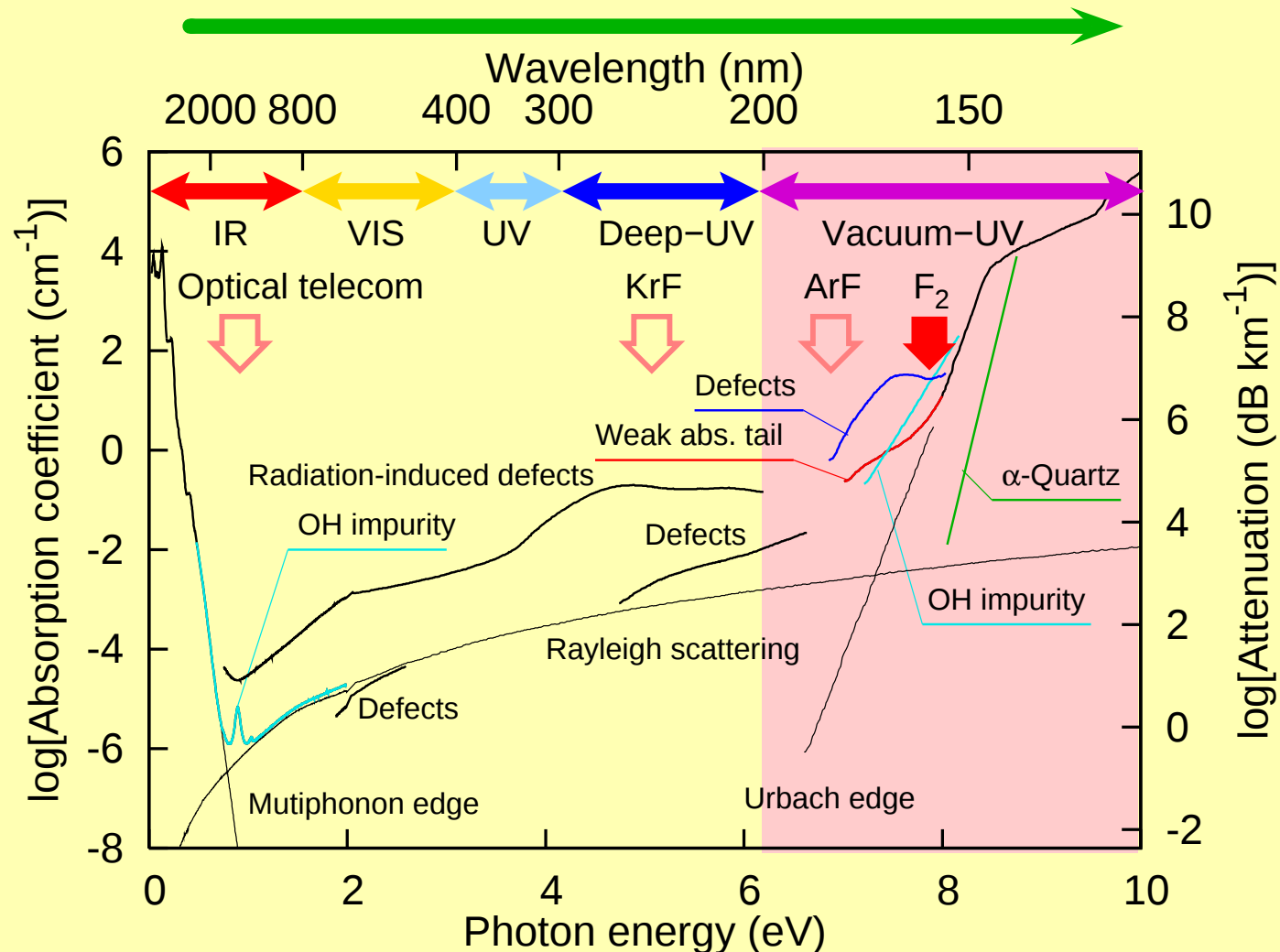
Optical properties of silica glass is often influenced by **trace amounts of defects!**

log[Conc.(cm ⁻³)]	
22	Lattice atom (O: $4.4 \times 10^{22} \text{cm}^{-3}$)
21	Solubility limit of fluorine (SiF) (several wt%)
20	SiOH in “wet” silica glass ($\sim 1000 \text{wtppm}$, $\sim 10^{20} \text{cm}^{-3}$)
	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

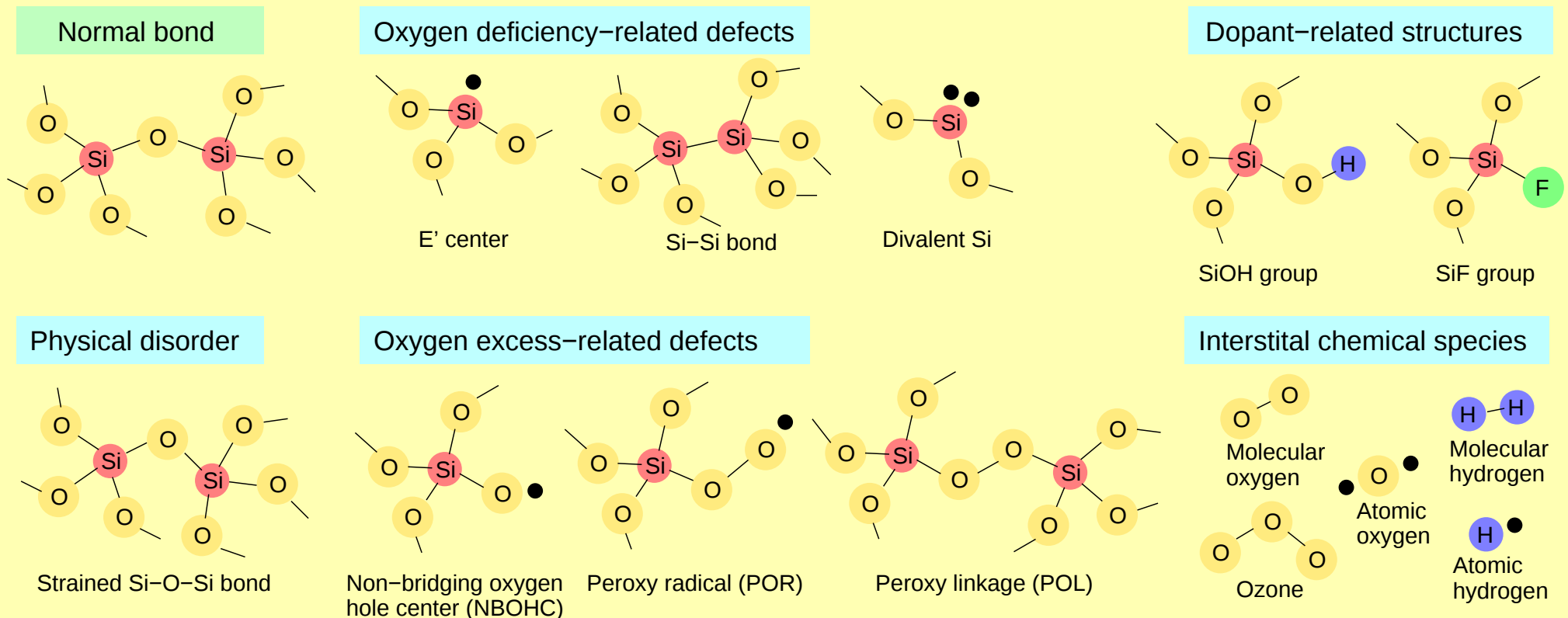


After Griscom,
J.Ceram.Soc.Jpn,
99,923(1991)

2. Structure and optical properties of defects

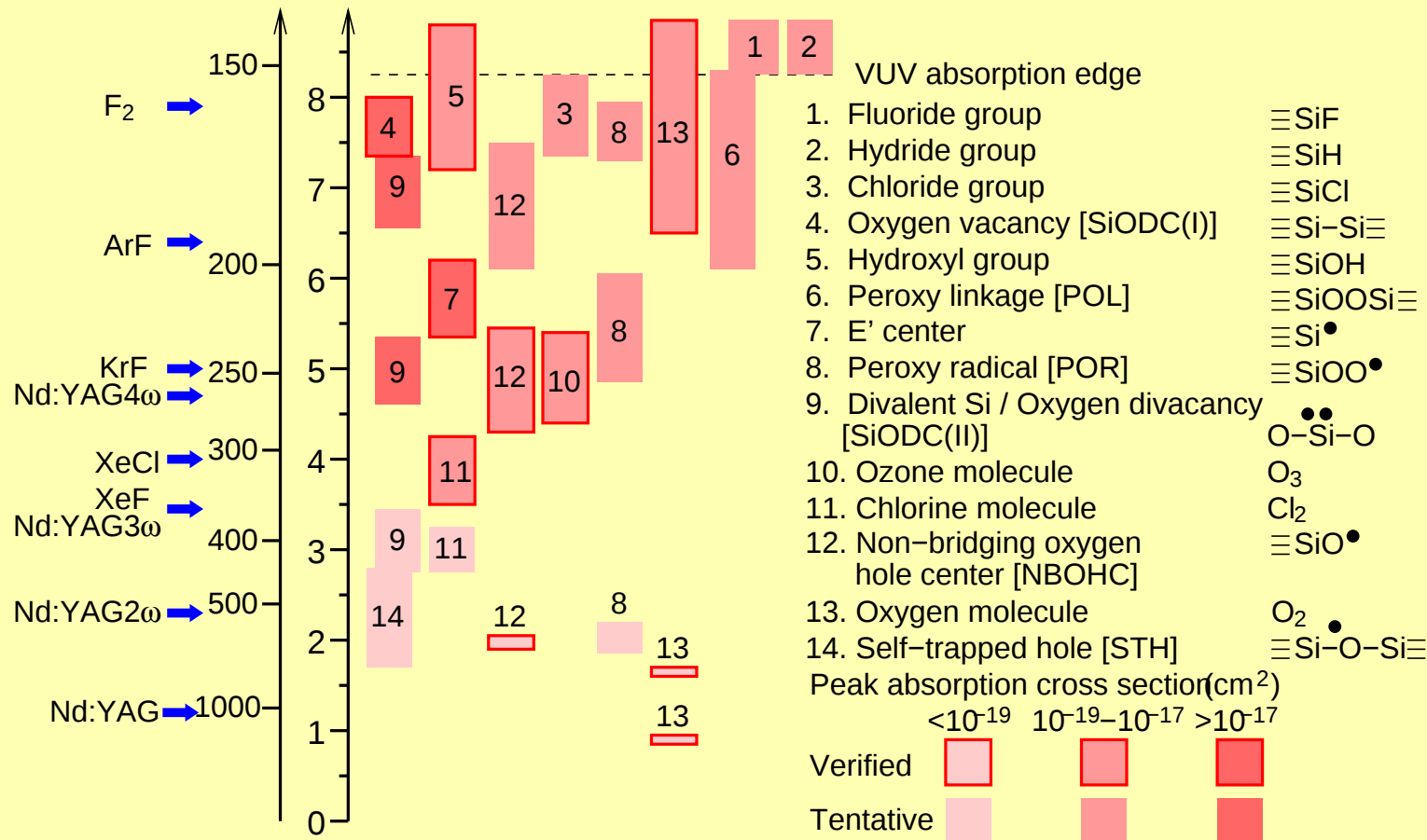
Ideal structure... Corner-shared SiO_4 tetrahedra, built only from Si-O bonds

- 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

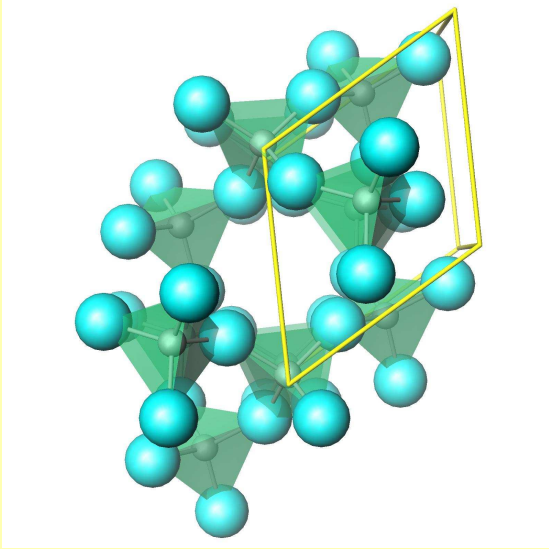


After Skuja et al.,
Proc.SPIE
4347,155(2001)

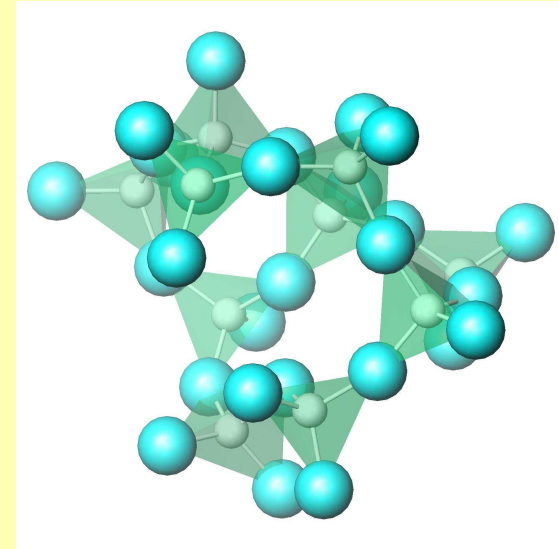
3a. Strained Si-O-Si bonds

A comparison among SiO₂ polymorphs

α -quartz (ordered SiO₄ units)



Silica glass (disordered SiO₄ units)



- Larger bandgap than silica glass
- F₂ laser irradiation does not form persistent defects

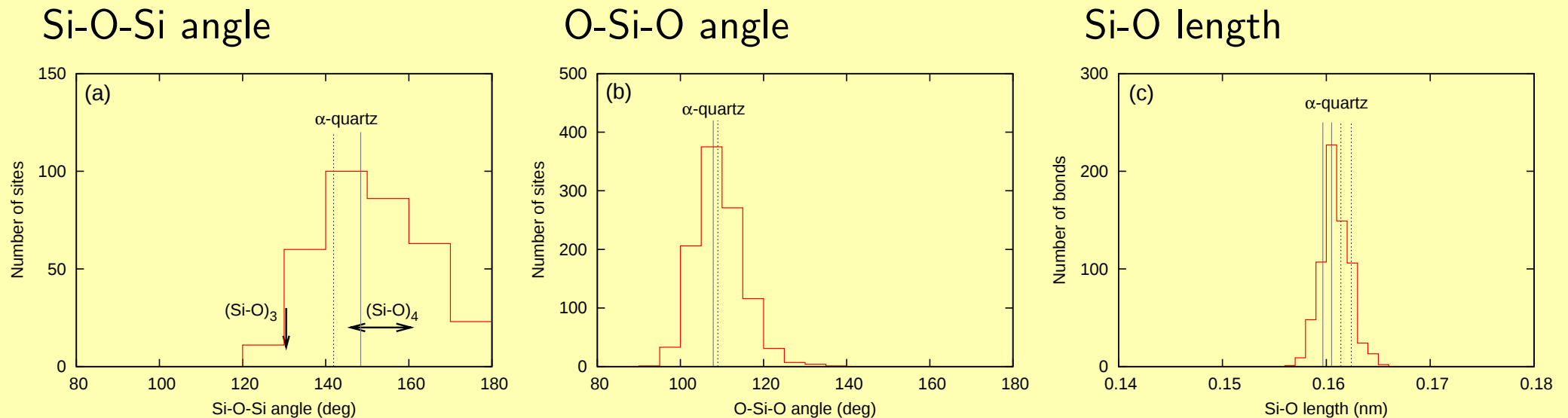
Materials	Band gap	Bandgap excitation causes
Amorphous silicon	~1.7eV	Staebler-Wronski effect
Chalcogenide glasses	~2eV	Photo darkening
Silica glass	~9eV	?

3a. Strained Si-O-Si bonds

Physical disorder in silica glass

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



*Calculated from a periodic silica structure reported in Mukhopadhyay et al., PRB70,195203 (2004)

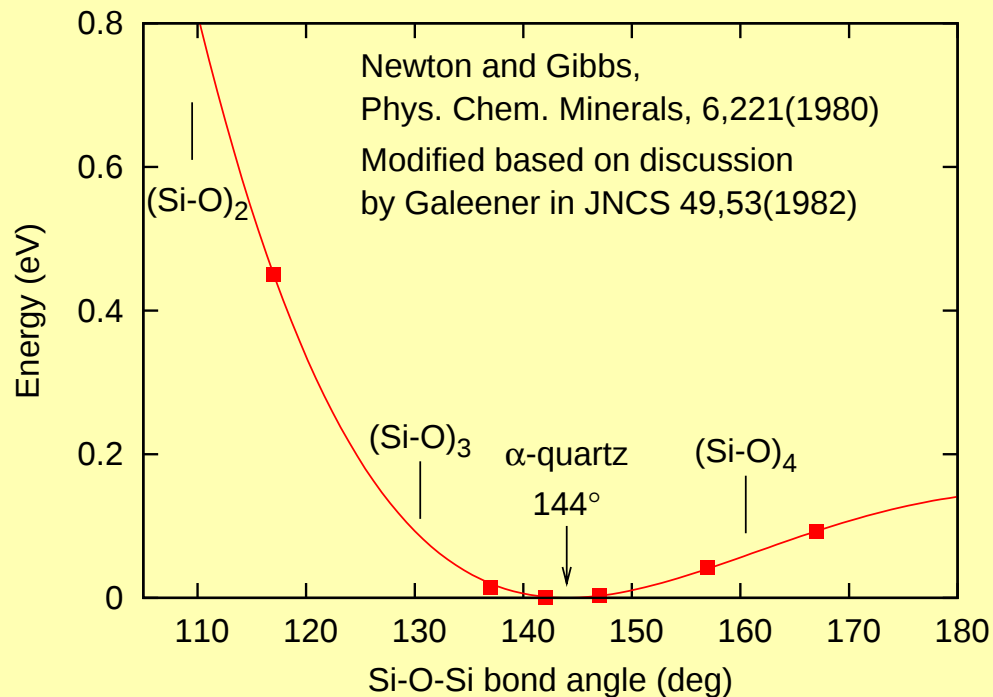
3a. Strained Si-O-Si bonds

Typical strained Si-O-Si bonds

... 3- and 4-membered rings

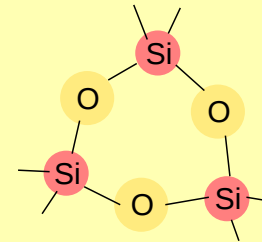
Galeener, JNCS49,53(1982)

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



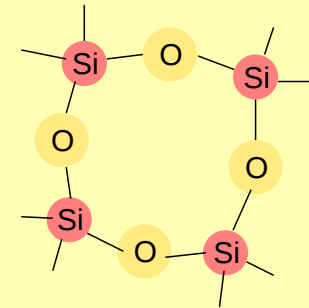
3-membered ring

D₂ band (606cm⁻¹)

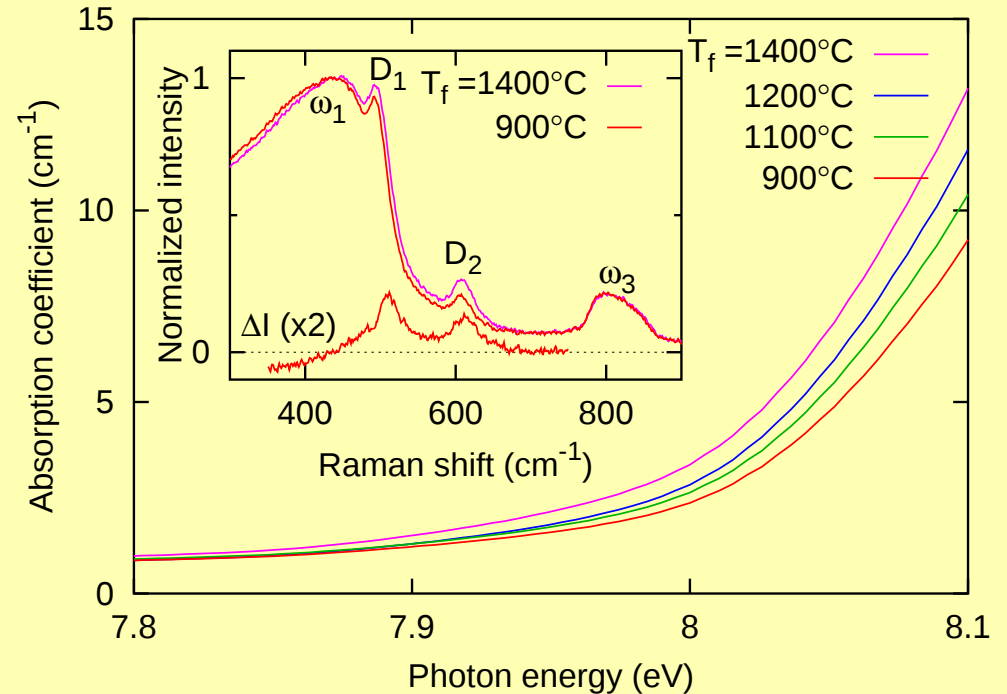


4-membered ring

D₁ band (495cm⁻¹)



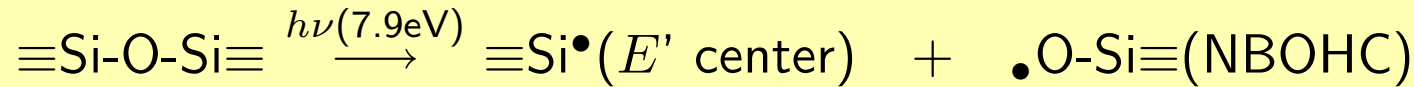
Hosono et al., PRL87, 175501(2001)



3a. Strained Si-O-Si bonds

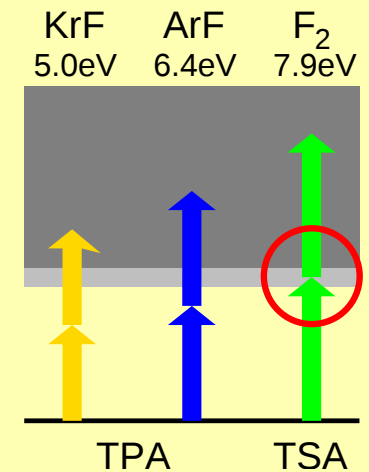
Defect formation

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

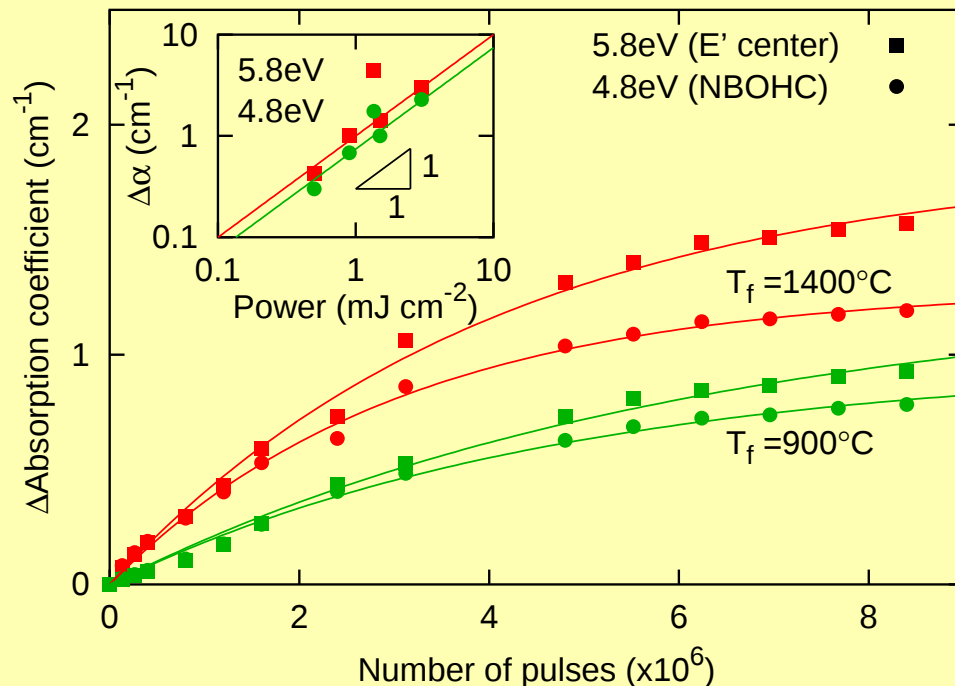


- $> 10 \text{ mJ cm}^{-2}$... Two-photon processes (Yield... $\text{F}_2 \gg \text{KrF}, \text{ArF}$)

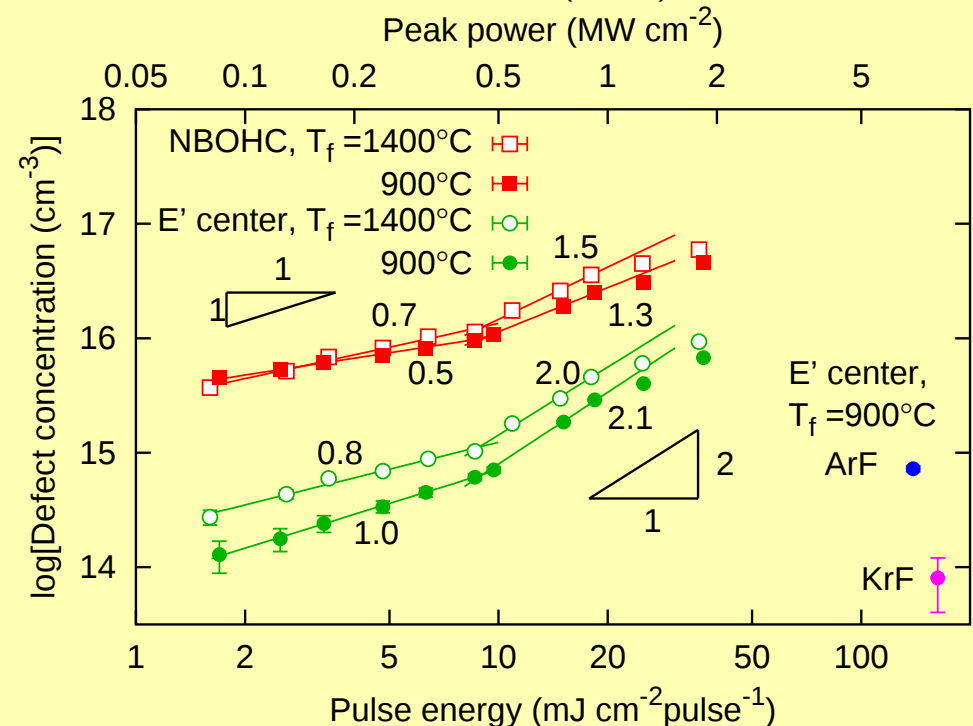
Strained Si-O-Si bonds ... Real intermediate states for defect formation via two-step absorption processes



Hosono et al., PRL87,175501(2001)



Kajihara et al., APL81,3164(2002)



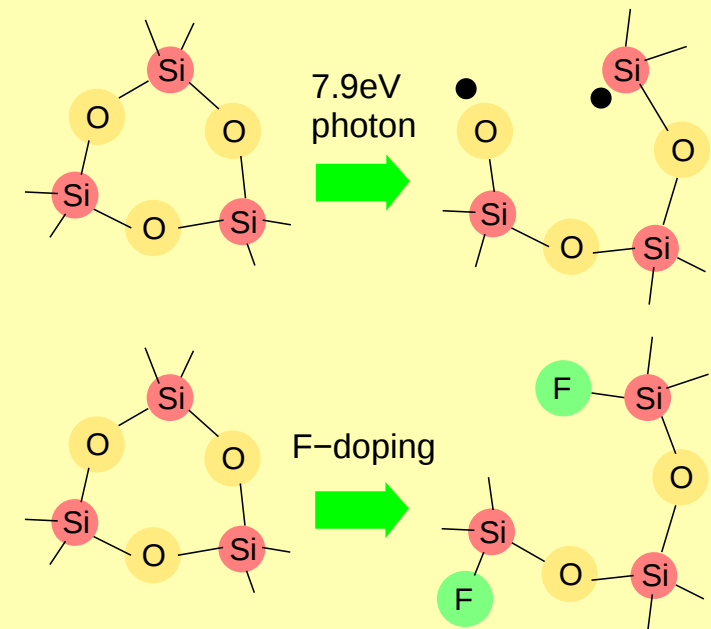
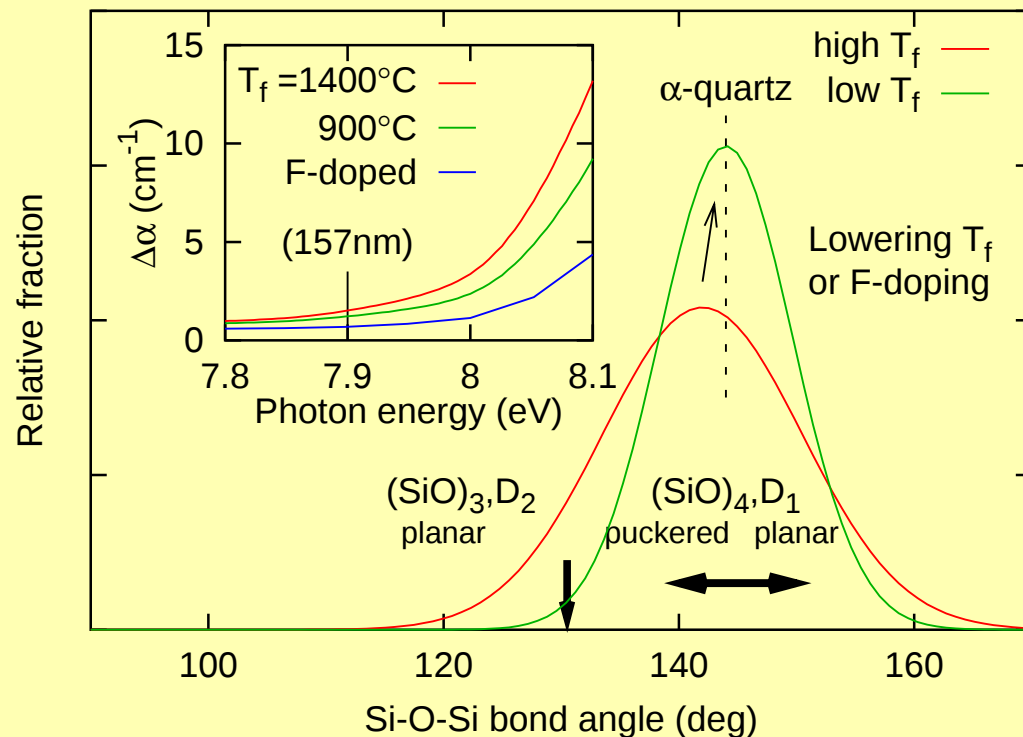
3a. Strained Si-O-Si bonds

Chemical annealing

Elimination of strained Si-O-Si bonds

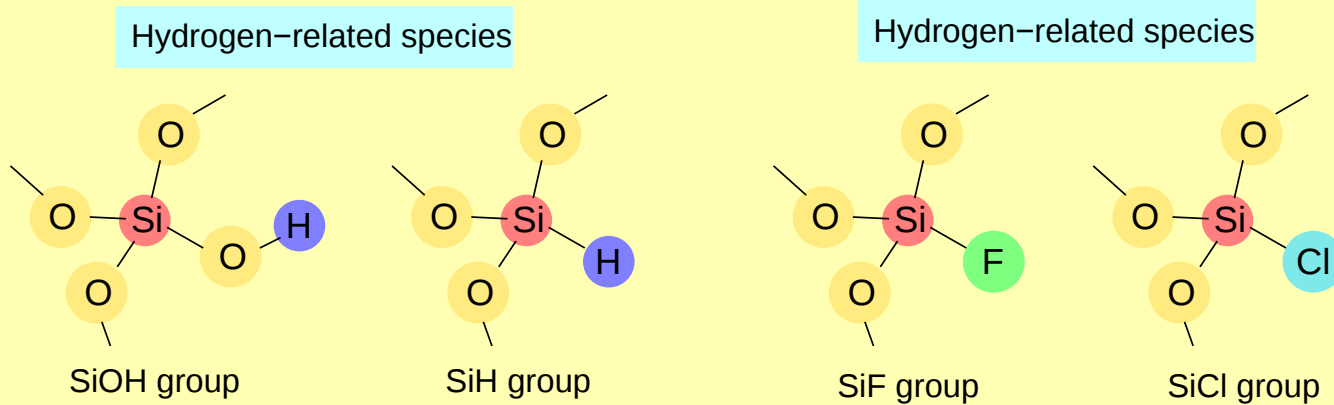
- Low temperature heating (“physical” annealing) . . . time consuming
- Breaking up glass network by network modifiers (SiF, SiCl, SiOH, SiH) (“chemical” annealing) . . . structural relaxation by lowered viscosity

Hosono and Ikuta, NIMB166, 691(2000)



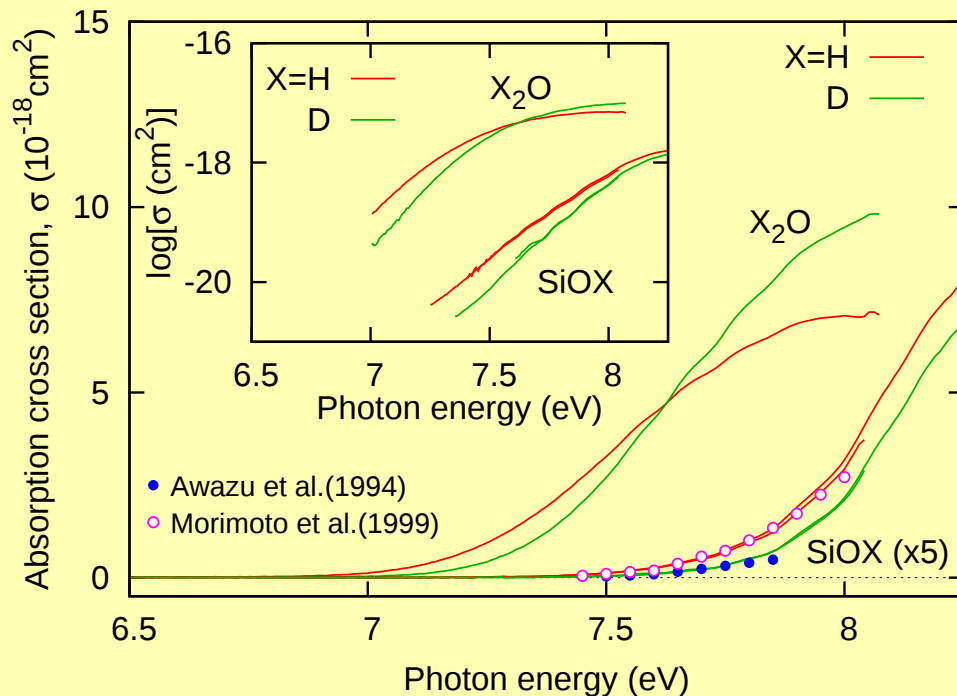
3b. Network modifiers

Types and the VUV absorption bands

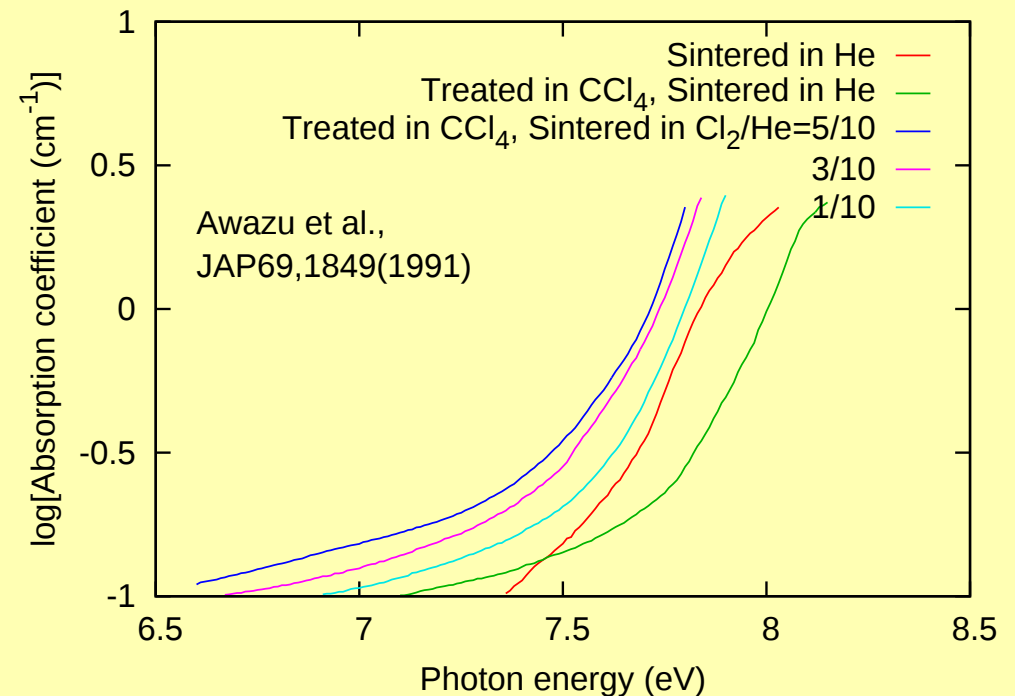


Absorption band	
SiOH	$\gtrsim 7.4\text{eV}$
SiH	Not known ($\gtrsim E_g$)
SiF	Not known ($\gtrsim E_g$)
SiCl	$\gtrsim 7\text{eV}$

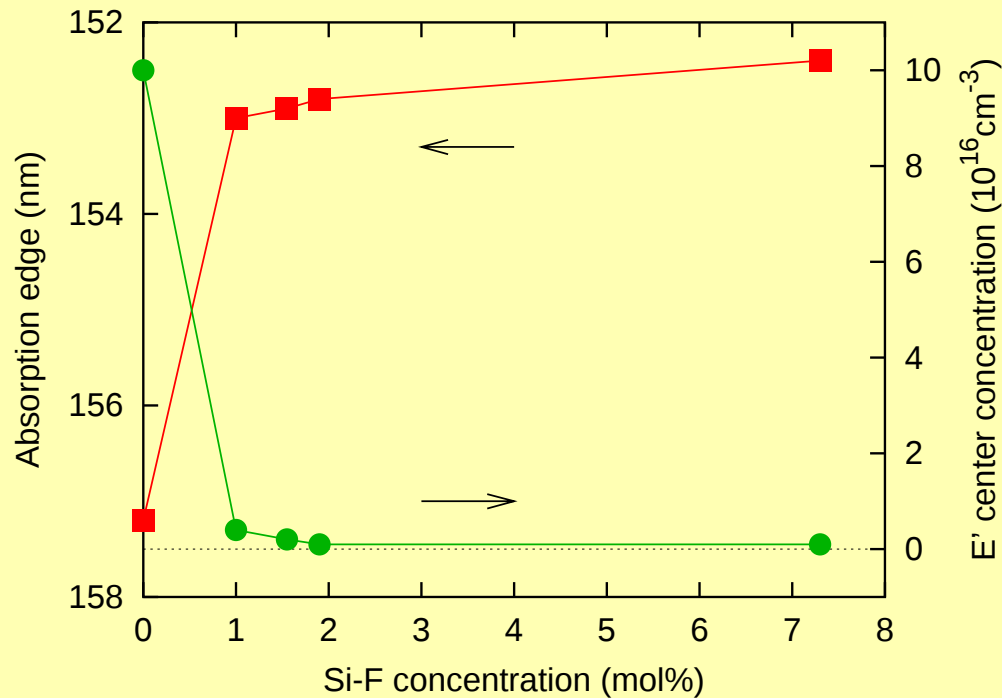
Kajihara et al. PRB72,214112(2005)



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)

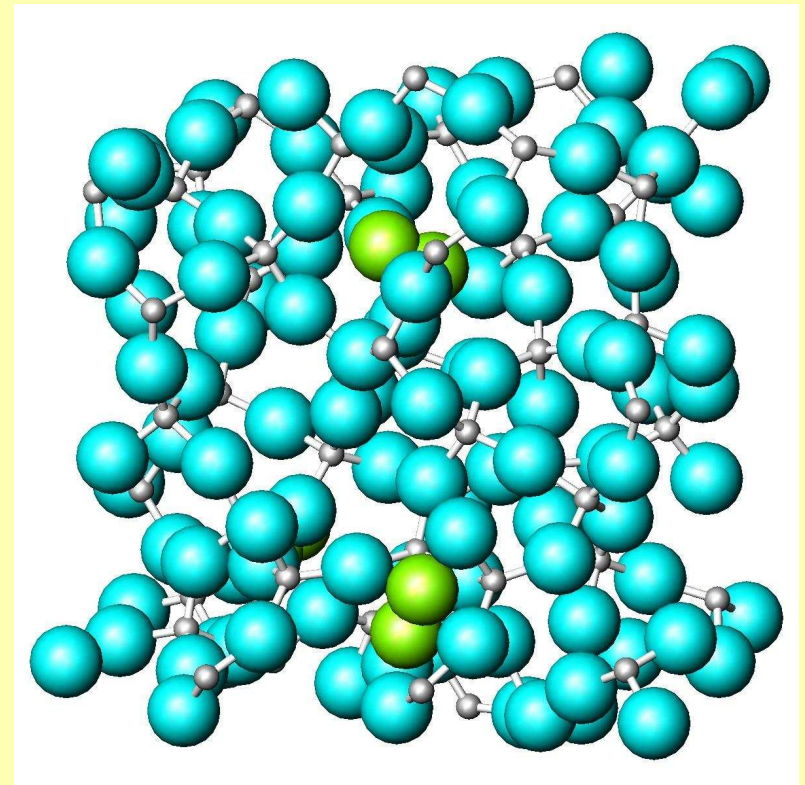
	VUV OA	Photolysis	Cost	Applications
SiF (F-doped)	No	No	High	Excimer laser lithography, DUV fiber
SiOH (Wet)	$\gtrsim 7.4 \text{ eV}$	$\text{SiO}^\bullet + \text{H}^0$	Low-Med.	UV-DUV laser optics
SiCl (Dry)	$\gtrsim 7.7 \text{ eV}$	$\text{Si}^\bullet + \text{Cl}^0$	Med	IR optical telecom
SiH	No?	$\text{Si}^\bullet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

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

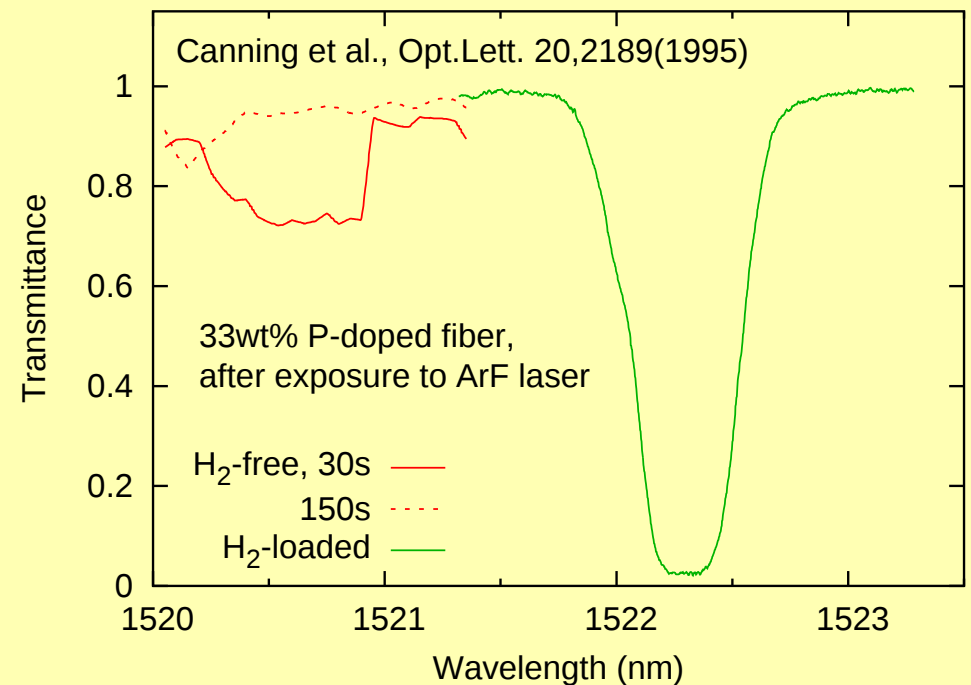
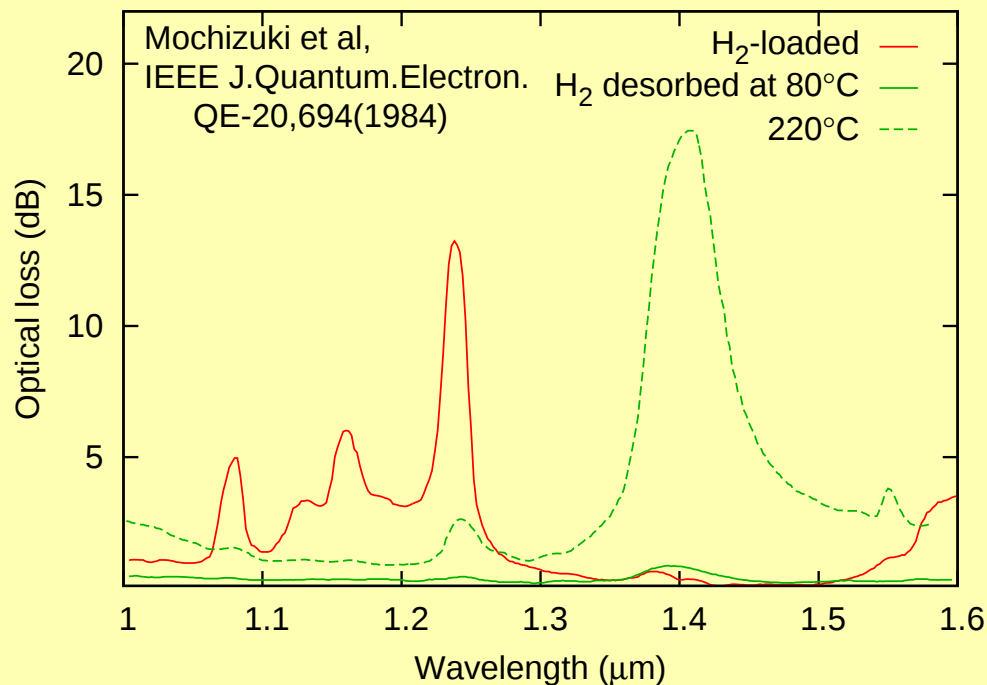
	Density (g cm ⁻³)
Silica glass	2.21
Tridymite	2.33
Cristobalite	2.33
α-quartz	2.65
Soda-lime silicate	2.47
Alumina (Al ₂ O ₃)	3.97



3c. Interstitial H₂ molecules

H₂ in silica glass... fast diffusion ($\text{He} > \text{H}_2 > \text{Ne} \gg \text{Ar}, \text{H}_2\text{O}$), high reactivity

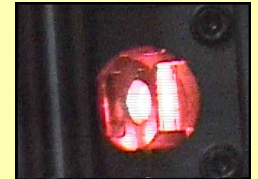
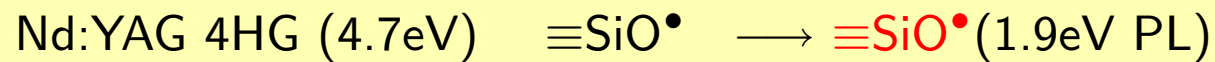
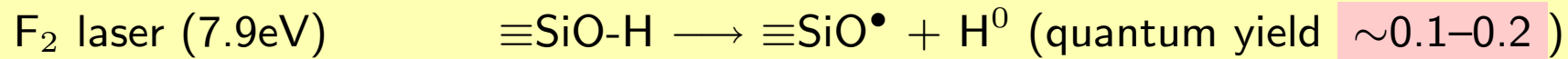
- Hydrogen corrosion in telecom fibers ($\equiv\text{Si}-\text{O}-\text{Si}\equiv + \text{H}_2 \rightarrow \equiv\text{SiOH} + \equiv\text{SiH}$)
- Sensitization of photoencoding of Bragg gratings
- Termination of dangling bonds ($\text{R}^\bullet + \text{H}_2 \rightarrow \text{RH} + \text{H}^0$)
- Improvement of KrF and ArF laser hardness



3c. Interstitial H₂ molecules

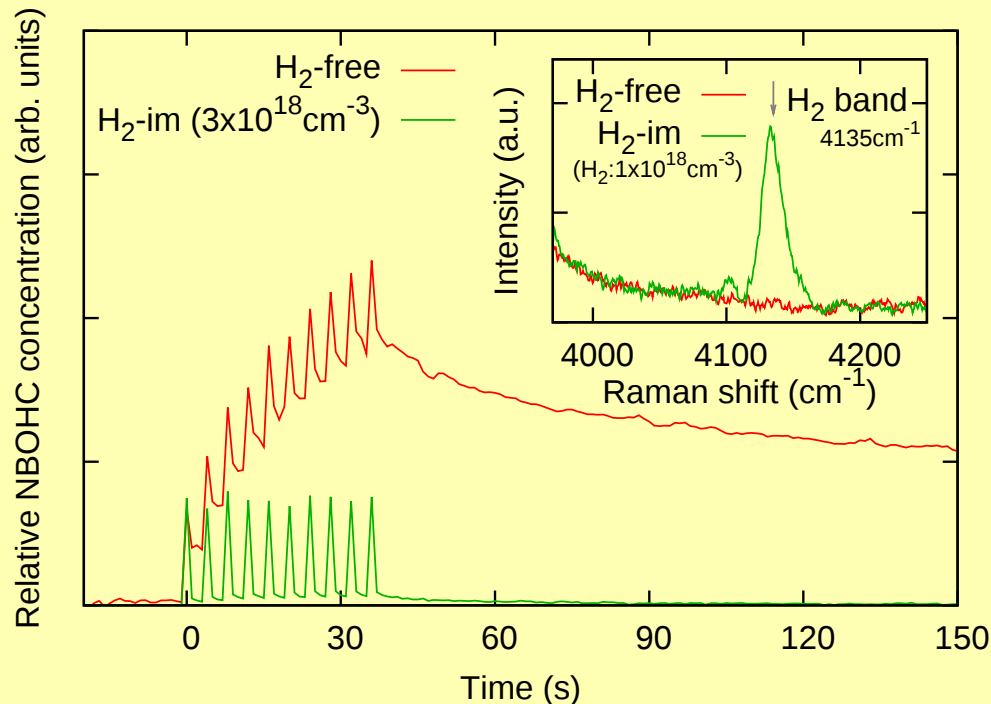
In-situ study of diffusion and reactions

F₂-laser-irradiated “wet” silica glass



- Concentration of radiation-induced NBOHC($\equiv\text{SiO}^\bullet$) ... insensitive to H₂ loading
- NBOHC does not accumulate in H₂-loaded glass

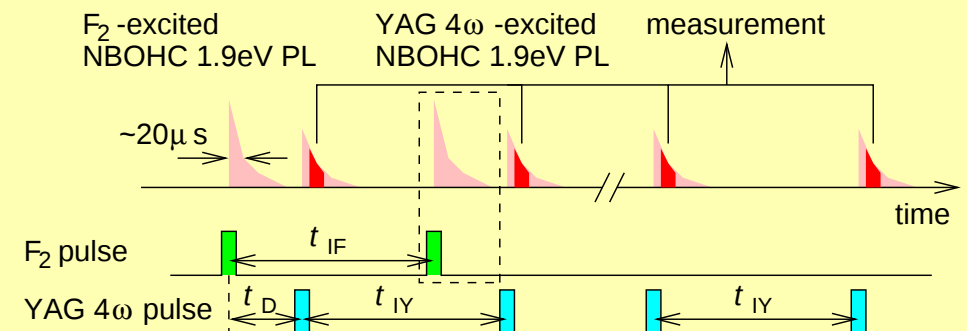
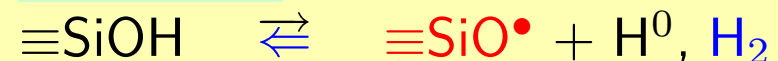
Kajihara et al., APL79,1575(2001); NIMB33,323(2004); PRB74,094202(2006)



H₂-free



H₂-loaded



3c. Interstitial H₂ molecules

Various effects of interstitial H₂

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

H₂ conc. should be strictly optimized

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

Termination of dangling bonds

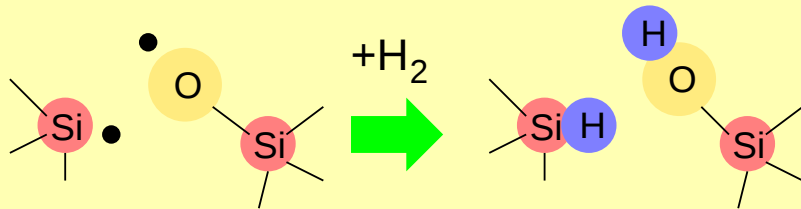
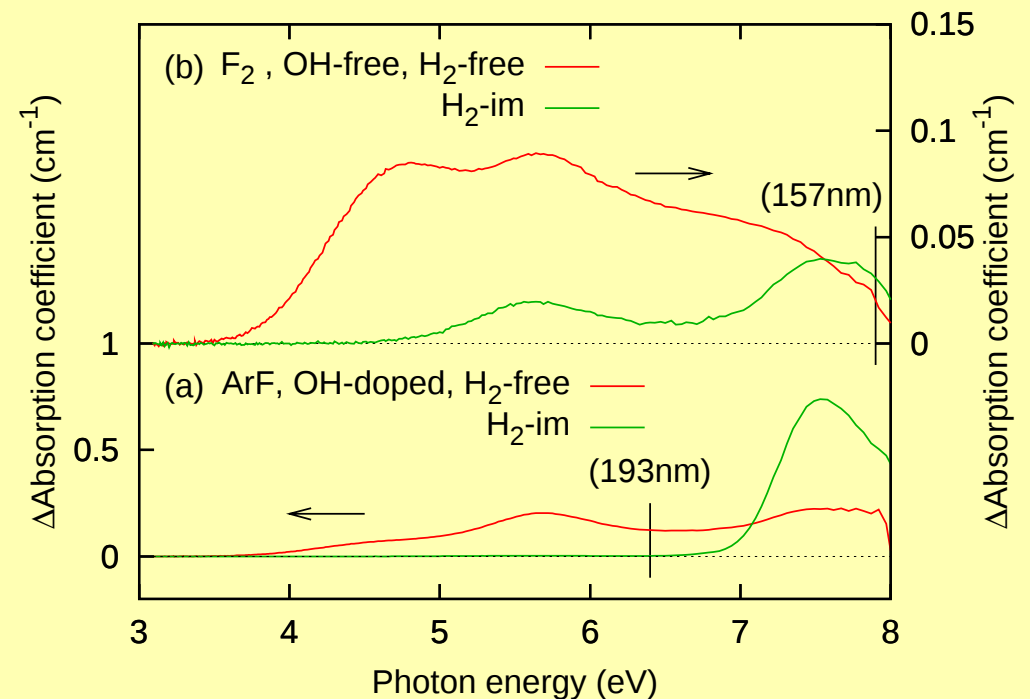
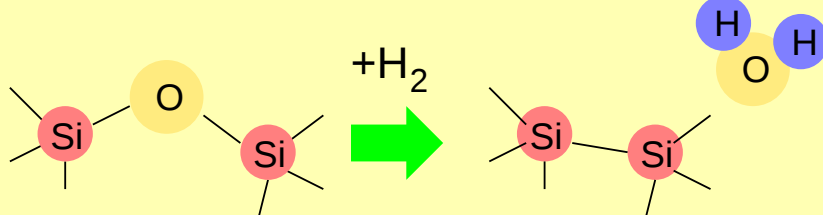


Photo-reduction of Si-O-Si bond



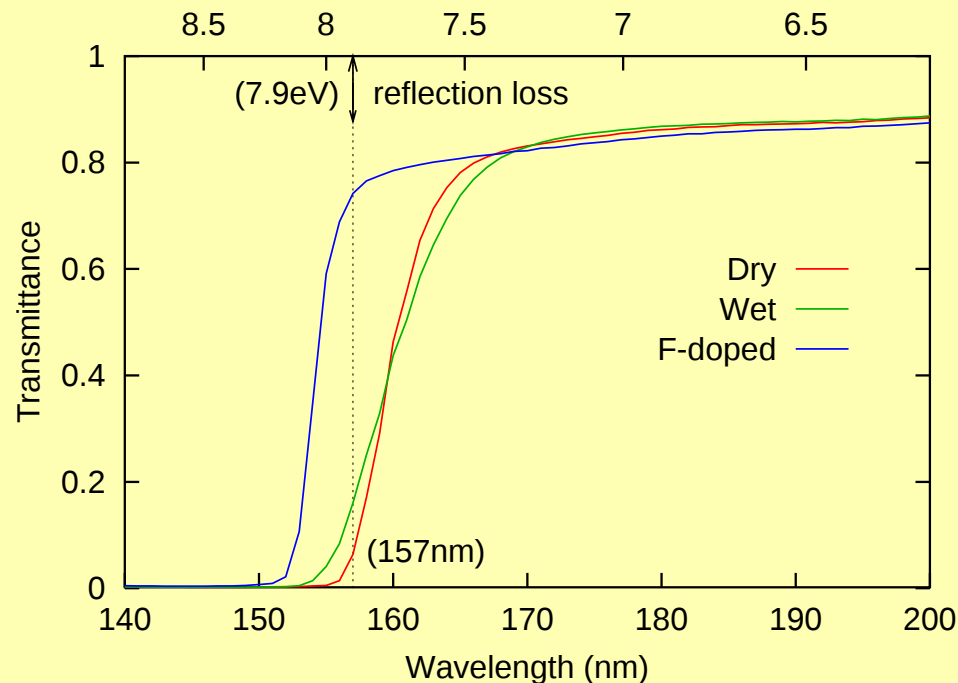
4. Silica glasses for UV-VUV spectral region

F₂ 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 F₂ laser photolithography

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



4. Silica glasses for UV-VUV spectral region

DUV optical fibers

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

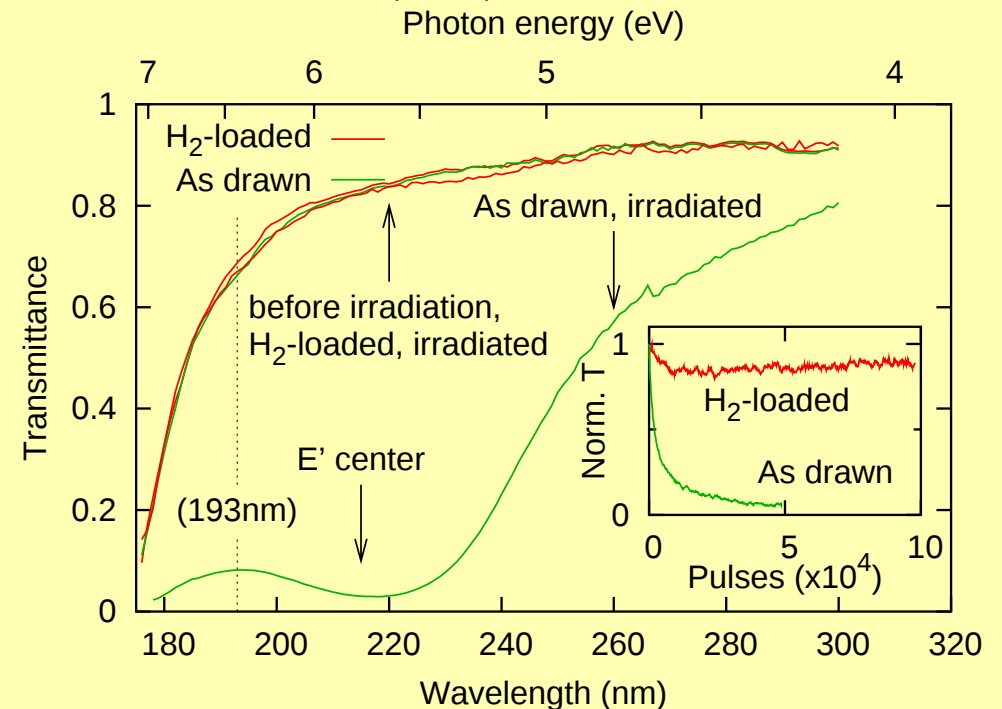
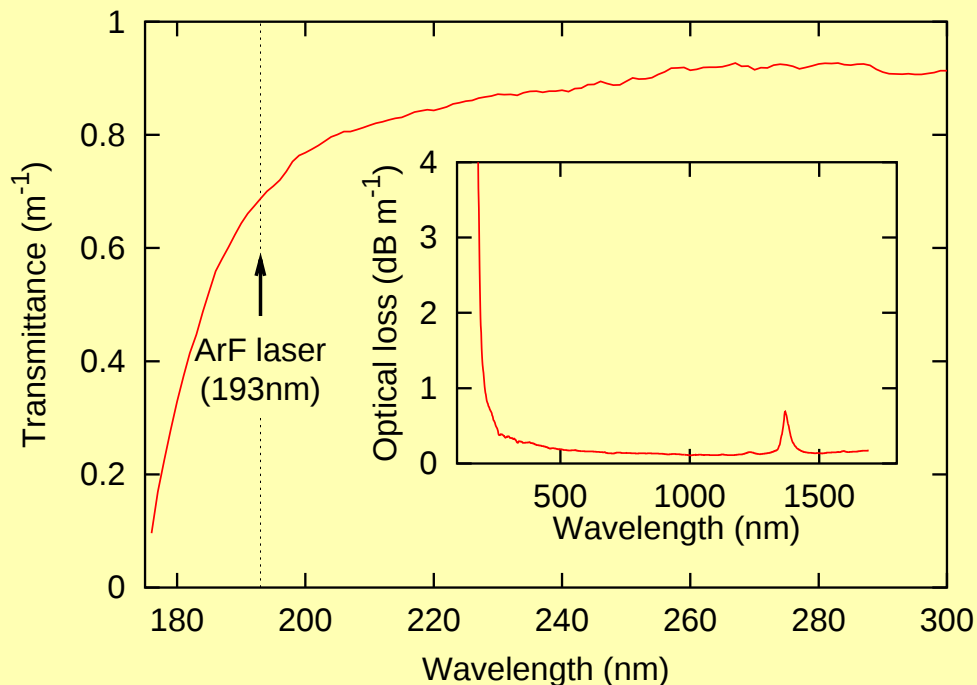
- Not transparent for UV light
- High viscosity – drawing-induced defects
- High radiation sensitivity

⇒

1. F-doped core and cladding
2. Defect annihilation by H₂ impregnation



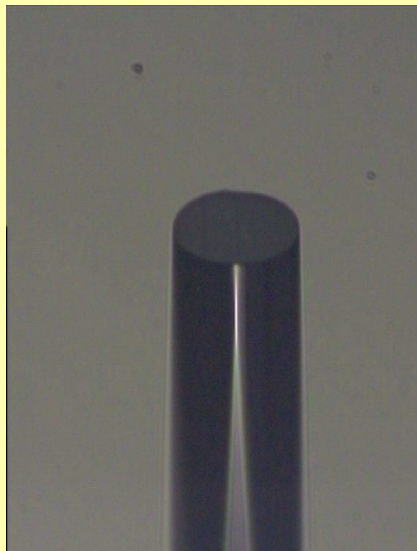
Oto et al, IEEE Photo. Technol. Lett. 13, 978(2001); J. Non-Cryst. Solids 349,133(2004)



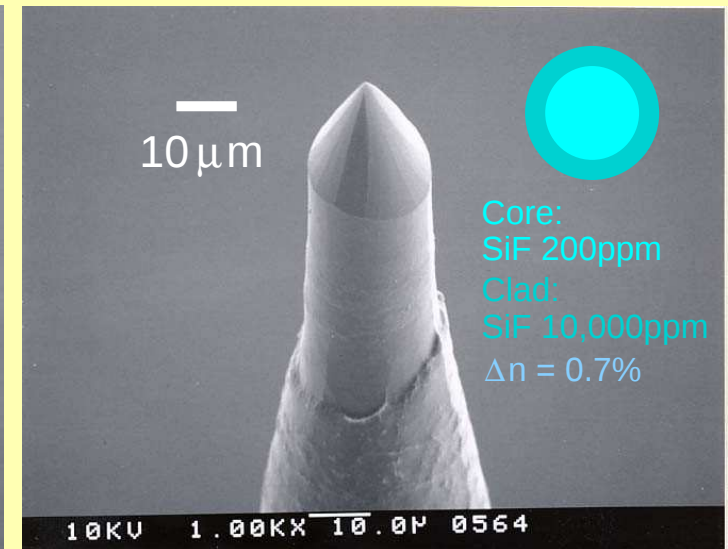
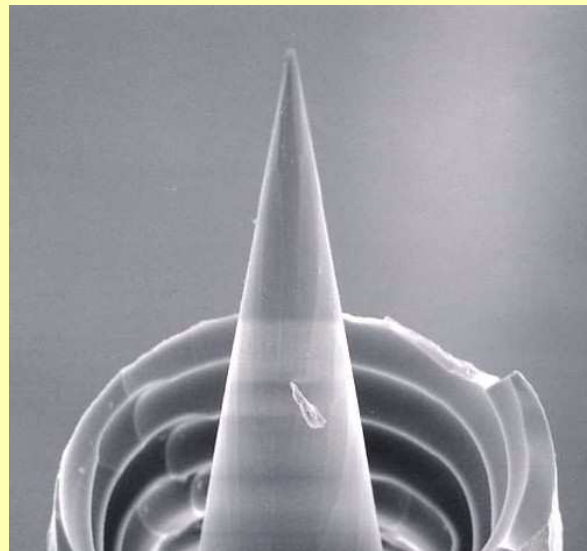
4. Silica glasses for UV-VUV spectral region

Processing of fiber ends

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

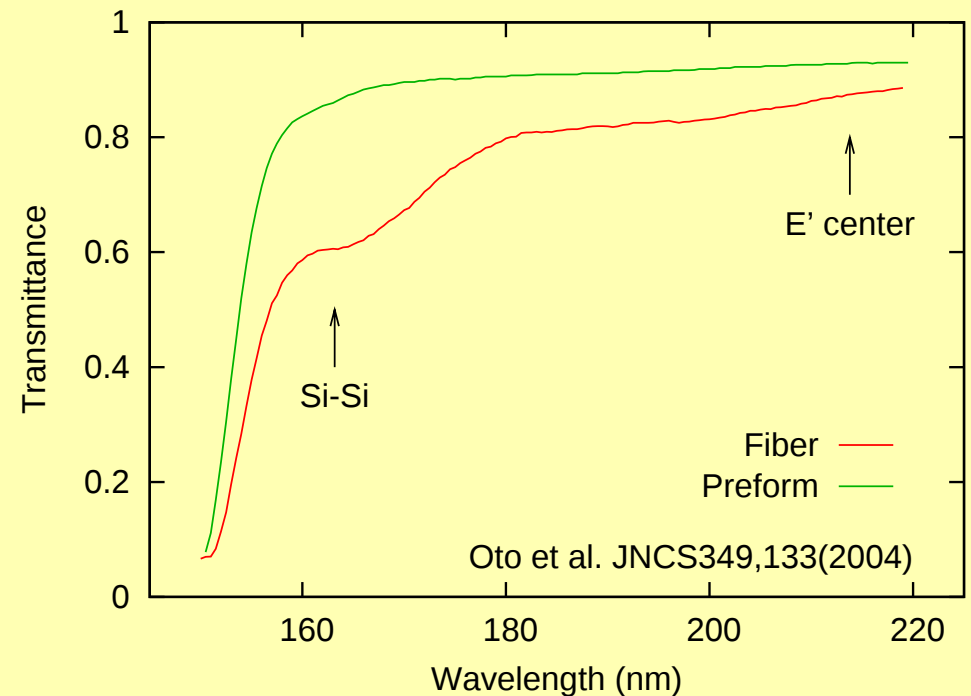


→
HF etching



5. Interstitial oxygen in silica glass

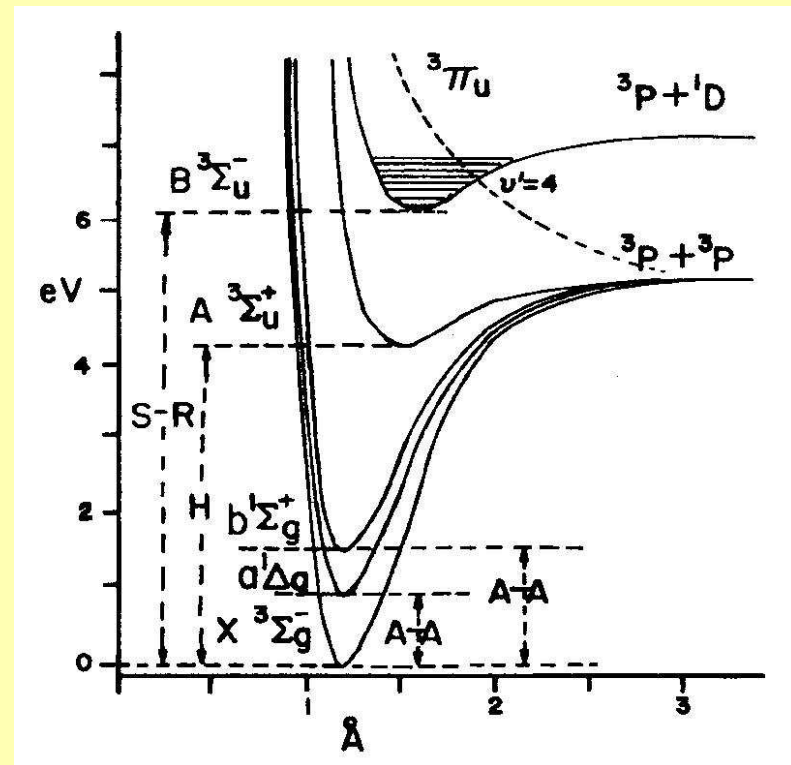
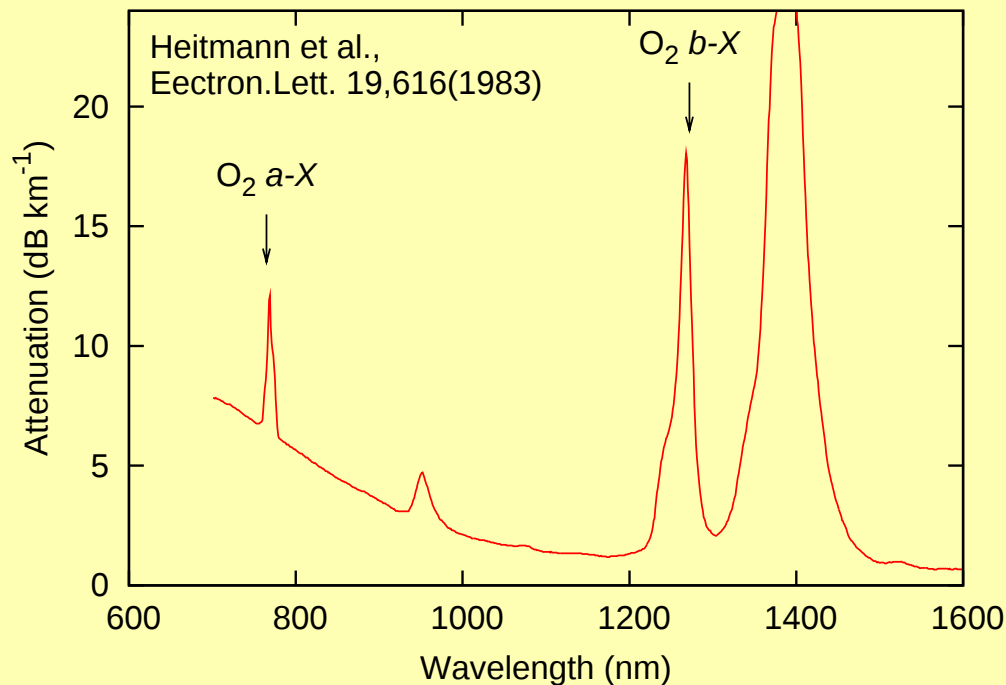
- Oxygen-deficiency related defects. . . Si-Si , $\equiv\text{Si}^\bullet$, $-\ddot{\text{Si}}-$, . . .
 - Main color centers in DUV fibers
- Oxygen-excess related defects. . . $\equiv\text{SiOO}^\bullet$, O_2 , Si-O-O-Si , . . .
 - May be used to oxidize oxygen-deficiency related color centers
 - Chemical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

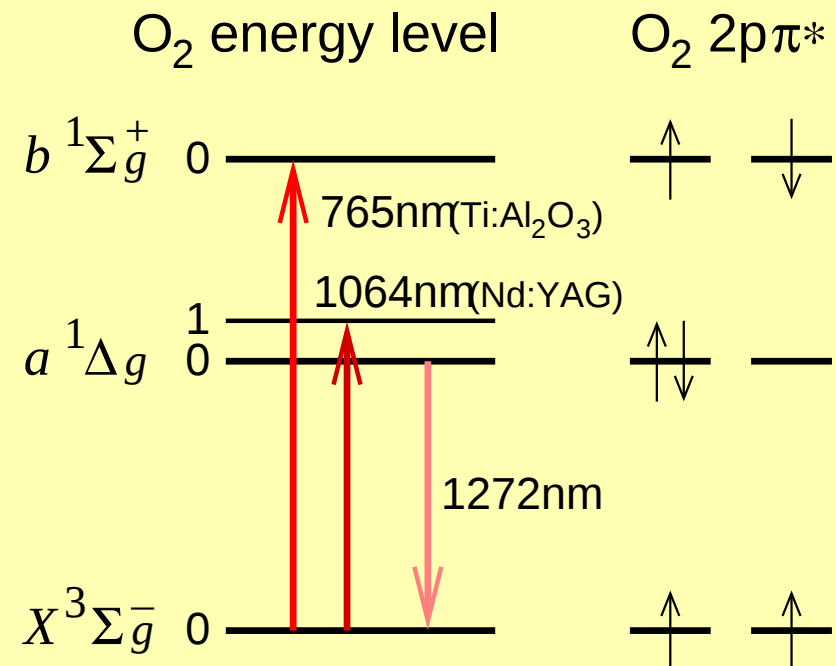
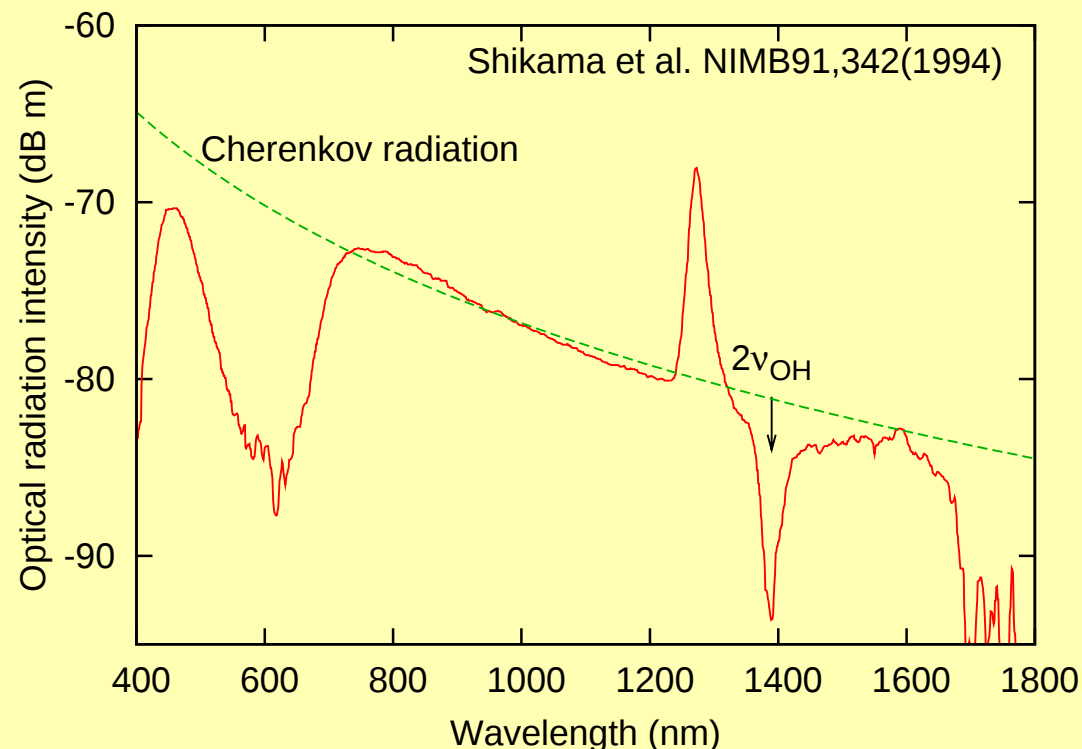


5. Interstitial oxygen in silica glass

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 O₂ via 1064nm excitation
- Skuja et al.(1998) PL detection of interstitial O₂ via 765nm excitation

Sensitive, selective, and non-destructive detection of interstitial O₂ in *a*-SiO₂

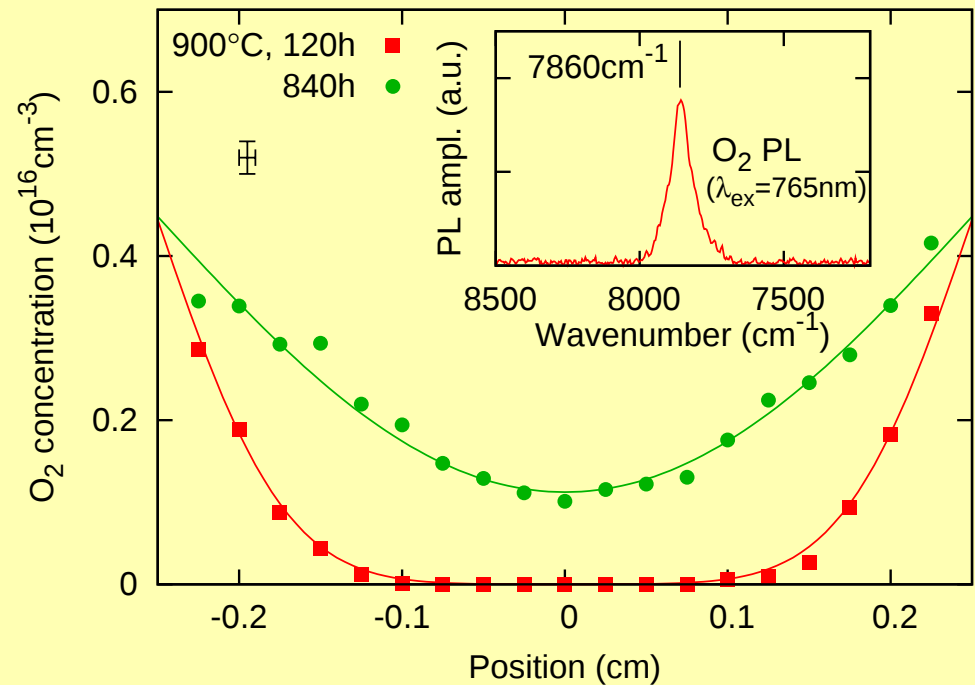
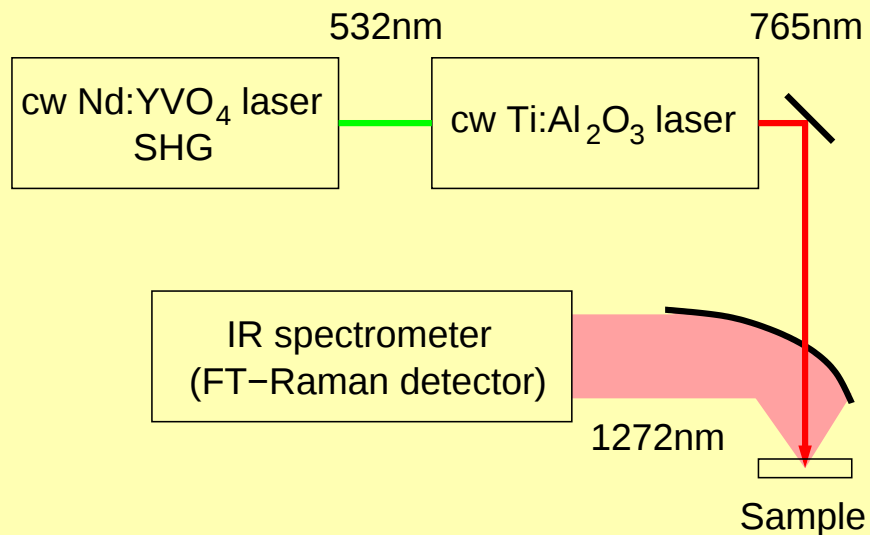


5. Interstitial oxygen in silica glass

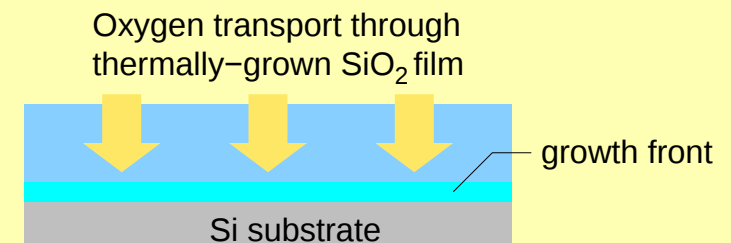
Thermal diffusion

- O₂ PL measurements of silica glasses thermally annealed in air
... **Solubility** and **diffusion coefficient** of interstitial O₂ 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 O₂**



5. Interstitial oxygen in silica glass

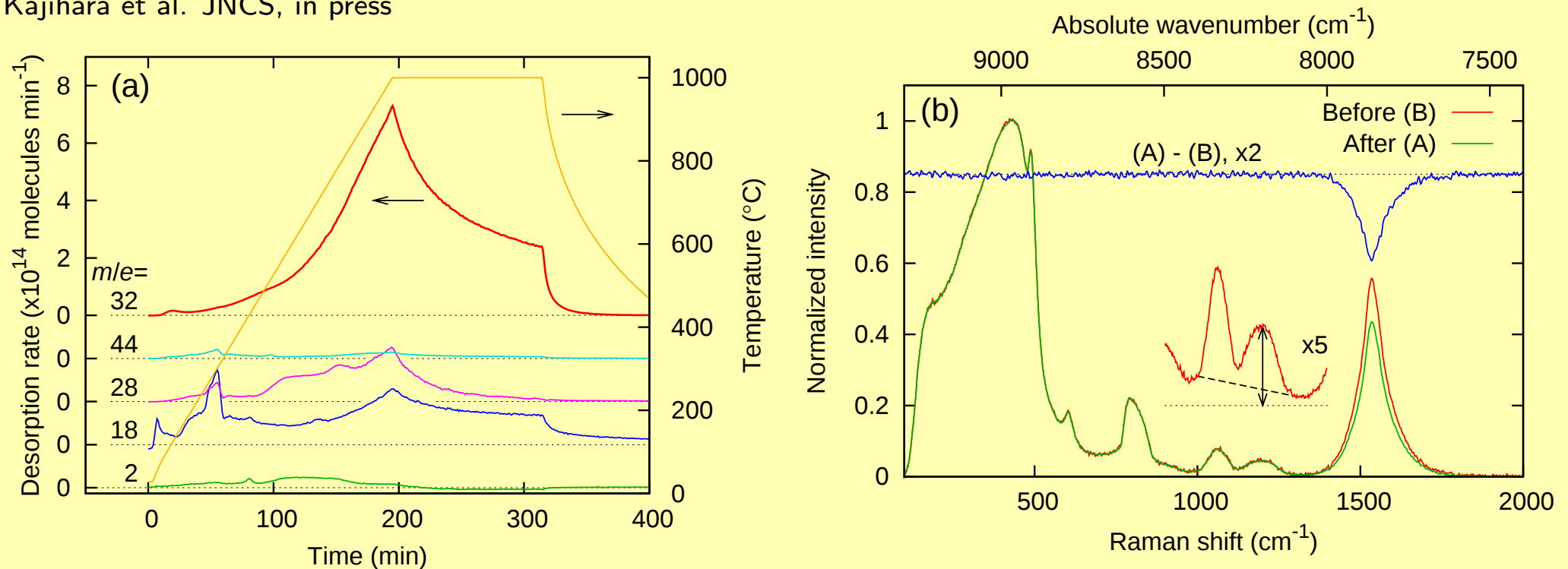
Concentration calibration

- Thermal desorption spectroscopy

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

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

Kajihara et al. JNCS, in press



5. Interstitial oxygen in silica glass

VUV OA cross section

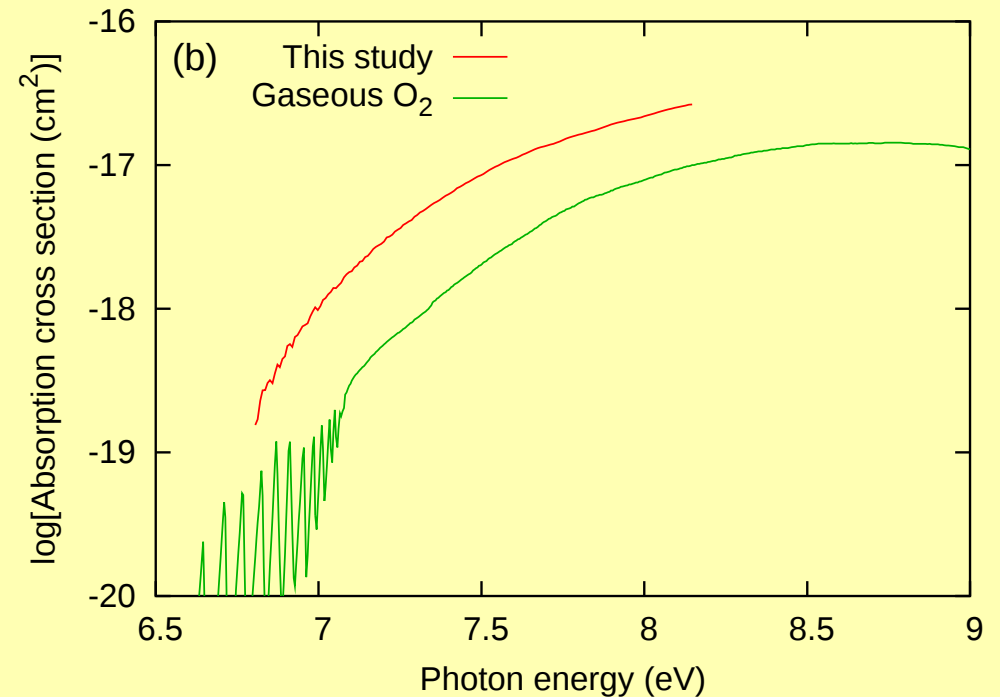
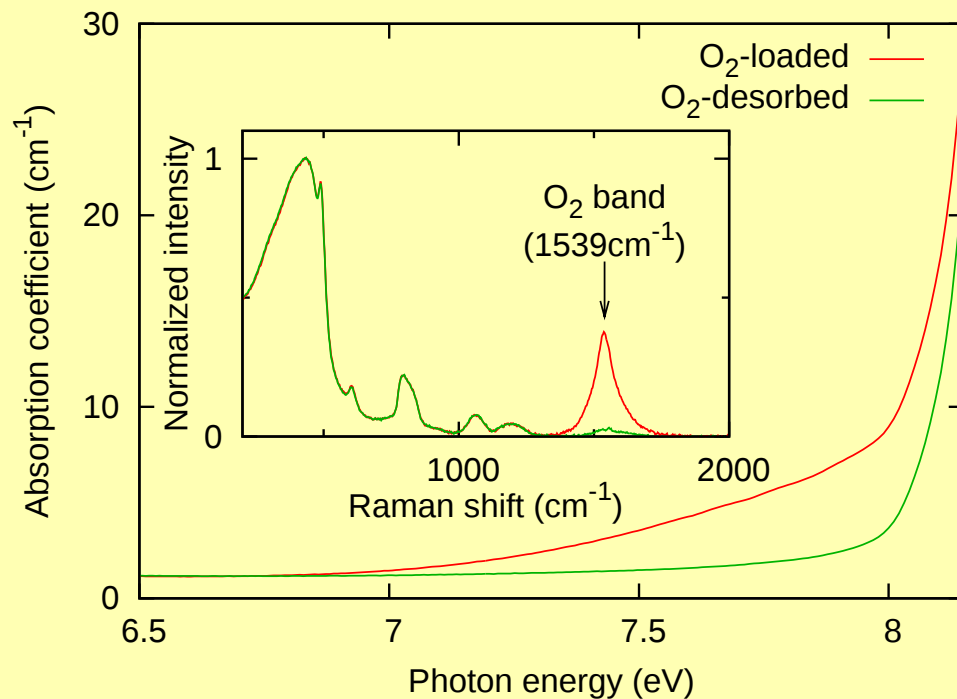
- Simultaneous measurement of VUV absorption and O₂ concentration changes

- Red-shift of VUV absorption edge
- Increase in absorption intensity



Weak attractive interaction between O₂ and *α*-SiO₂ framework

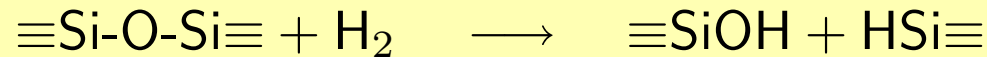
Kajihara et al. JAP98,013527(2005)



5. Interstitial oxygen in silica glass

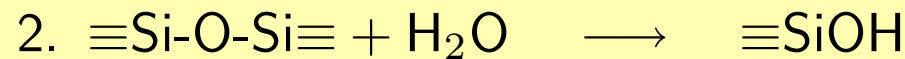
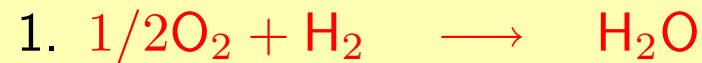
Reactions (1)

- Reaction of α -SiO₂ with H₂... Cracking of Si-O bond

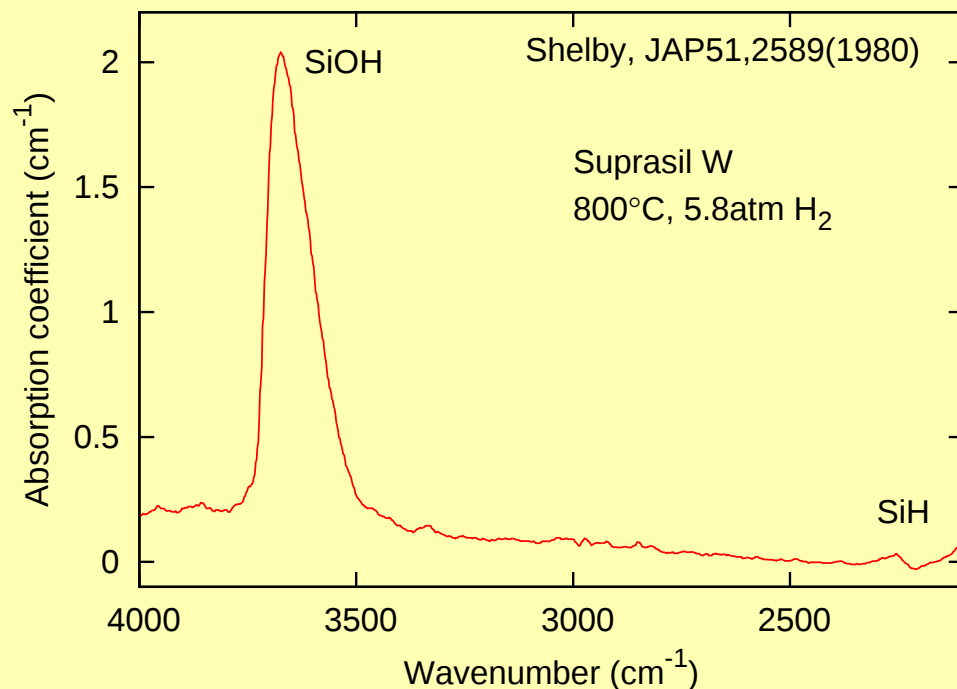


- Shelby(1980) SiOH creation with little accompanying SiH formation in O₂-rich α -SiO₂

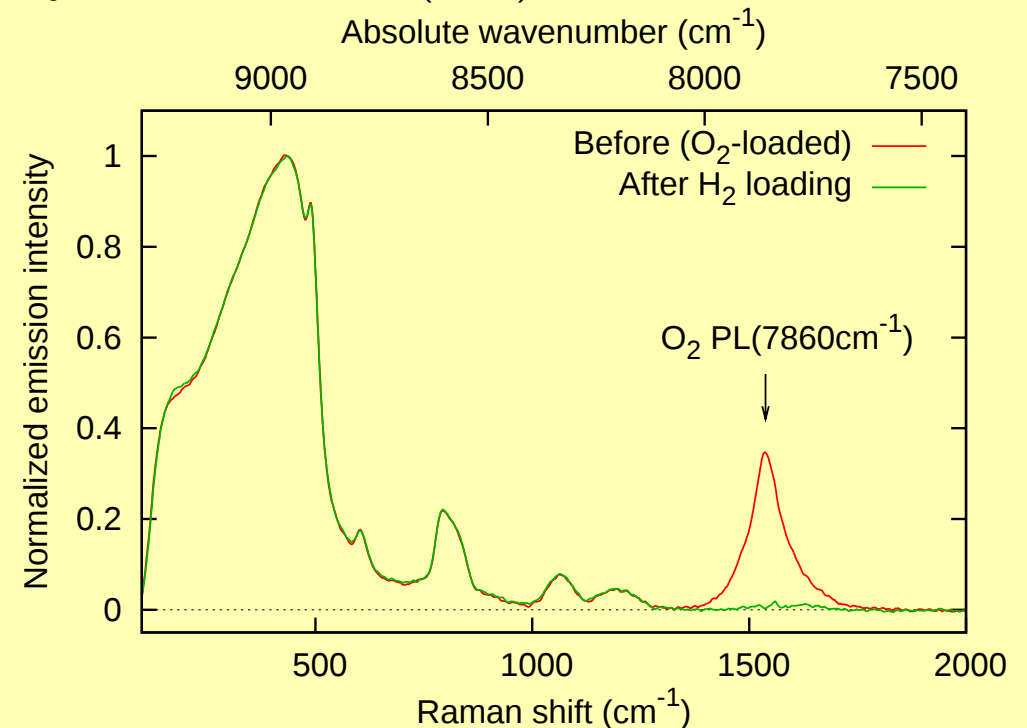
Two-step reactions



Shelby, JAP51,2589(1980)



Kajihara, JAP98,043515(2005)

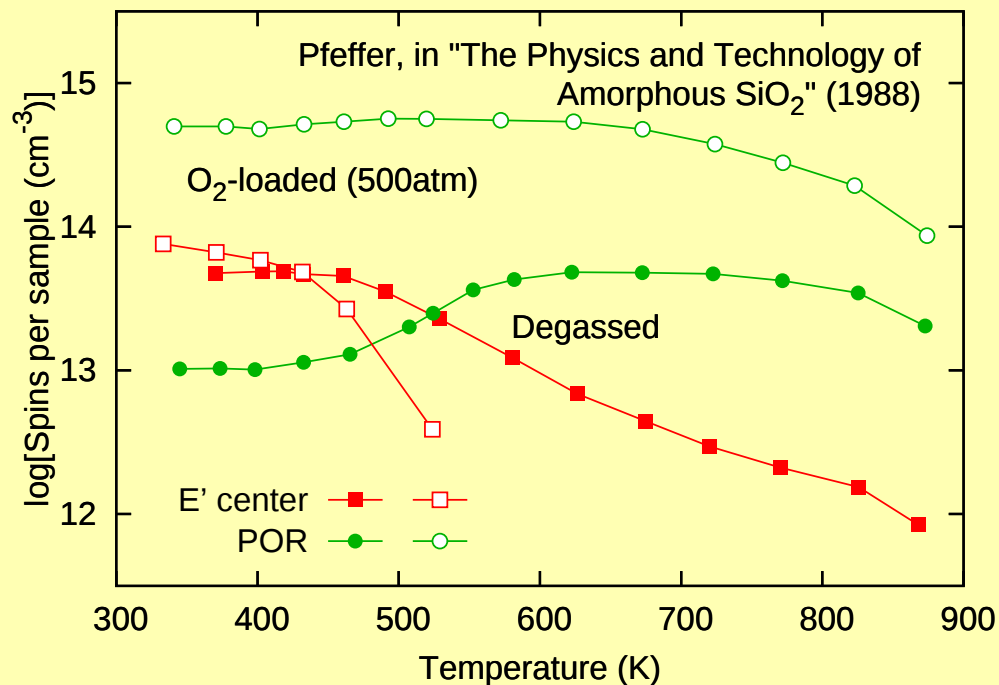


5. Interstitial oxygen in silica glass

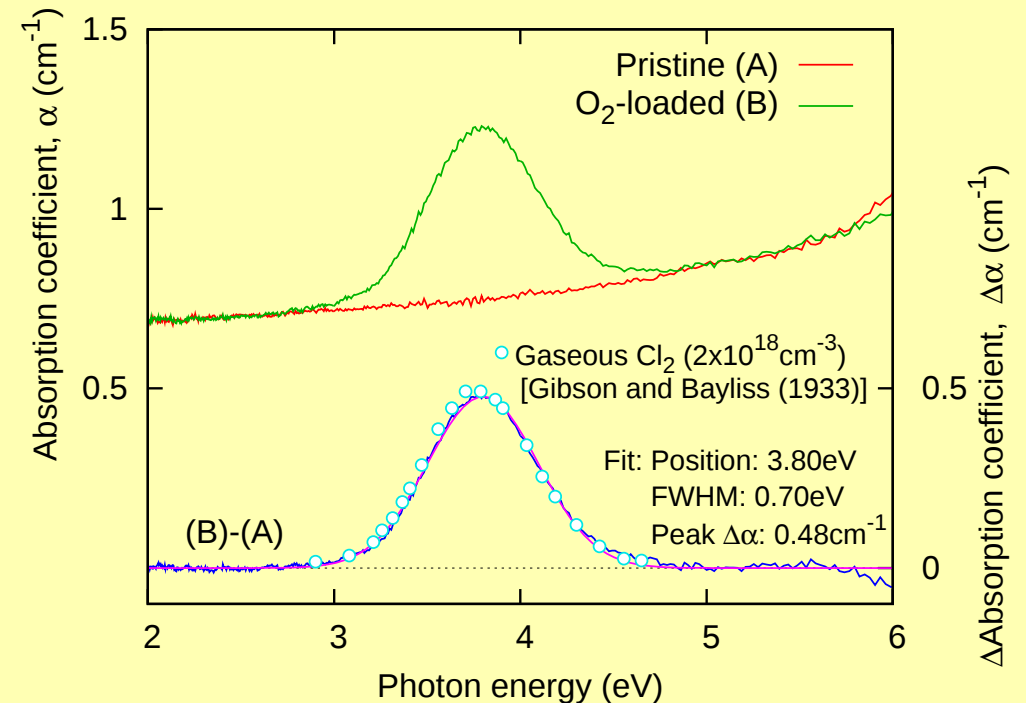
Reactions (2)

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

Pfeffer (1998)



Kajihara, JAP98,043515(2005)

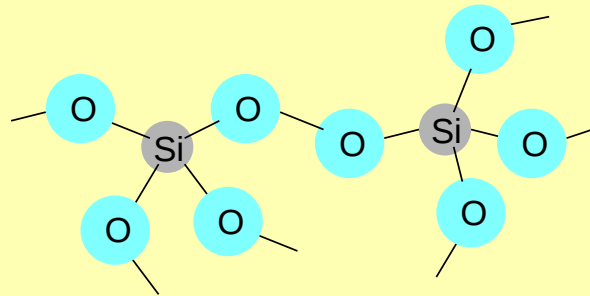


5. Interstitial oxygen in silica glass

Configuration... Peroxy linkage form

e.g. Hamann, PRL81,3447(1998)

Szymanski et al. PRB63,224207(2001)



Formation

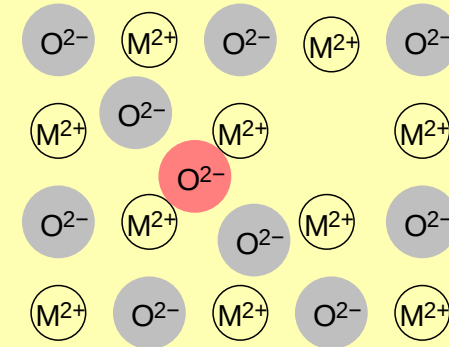
1. Radiolytic decomposition of Si-O-Si bonds
 $\equiv\text{Si-O-Si}\equiv \xrightarrow{h\nu} \equiv\text{Si-Si}\equiv + \text{O}^0 \text{ (or } 1/2\text{O}_2\text{)}$

2. VUV photolysis of interstitial O_2
 $\text{O}_2 \xrightarrow{h\nu} 2\text{O}^0$

3. UV photolysis of peroxy radical
 $\equiv\text{SiOO}\bullet \xrightarrow{h\nu} \equiv\text{SiO}\bullet + \text{O}^0$

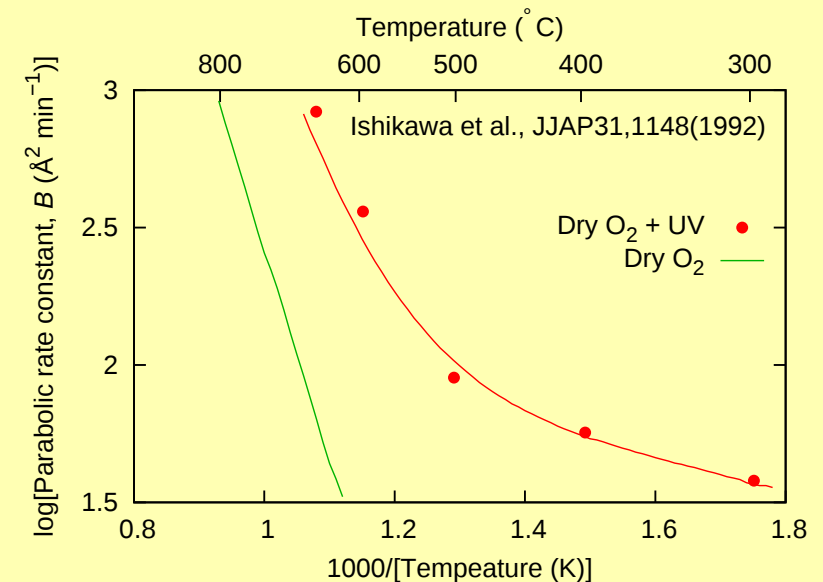
Interstitial oxygen atoms

- Anion part of the Frenkel pair



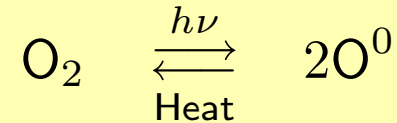
- Low-temperature oxidant of silicon

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



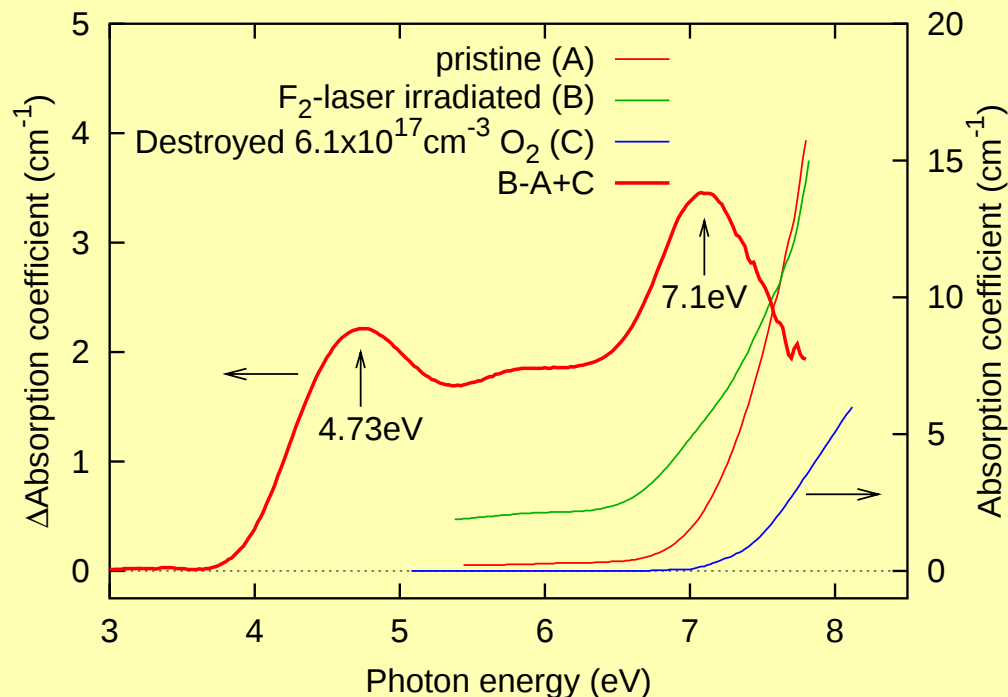
5. Interstitial oxygen in silica glass

Optical absorption and diffusivity

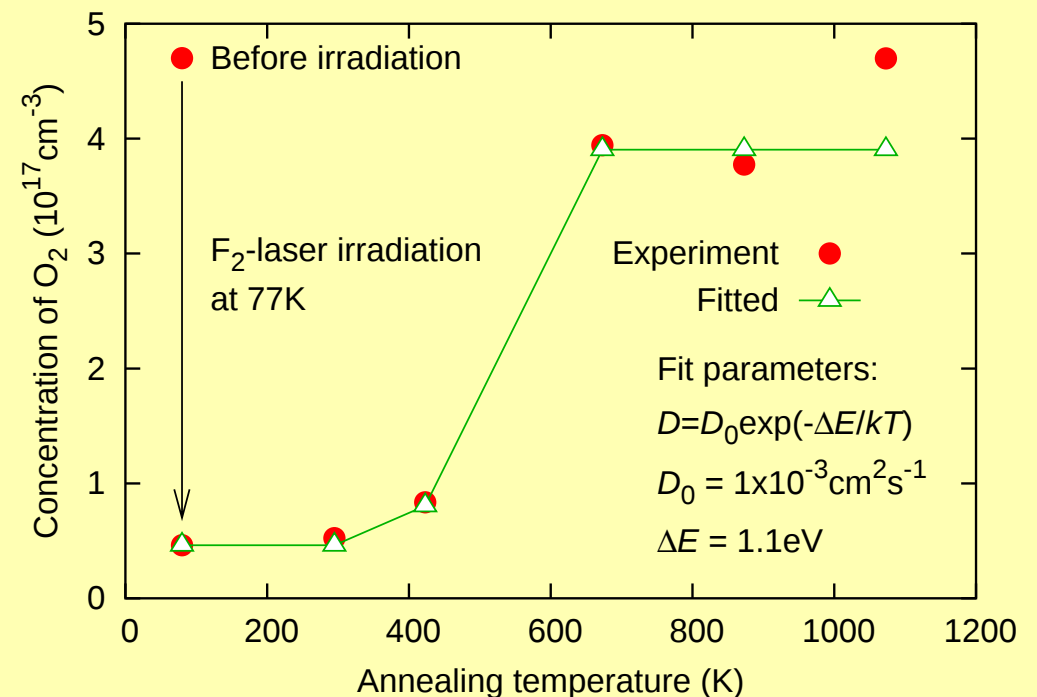


- Optical absorption... Use O^0 -rich sample prepared by F_2 laser irradiation
- Diffusivity ... Probe O_2 generated by recombination of O^0

Skuja et al. NIMB191,127(2002)

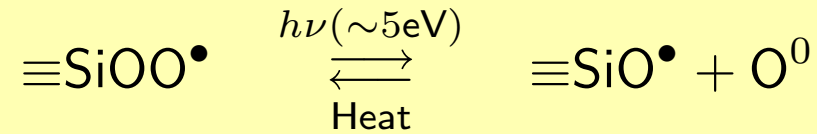


Skuja et al. PCG43C,145(2002)

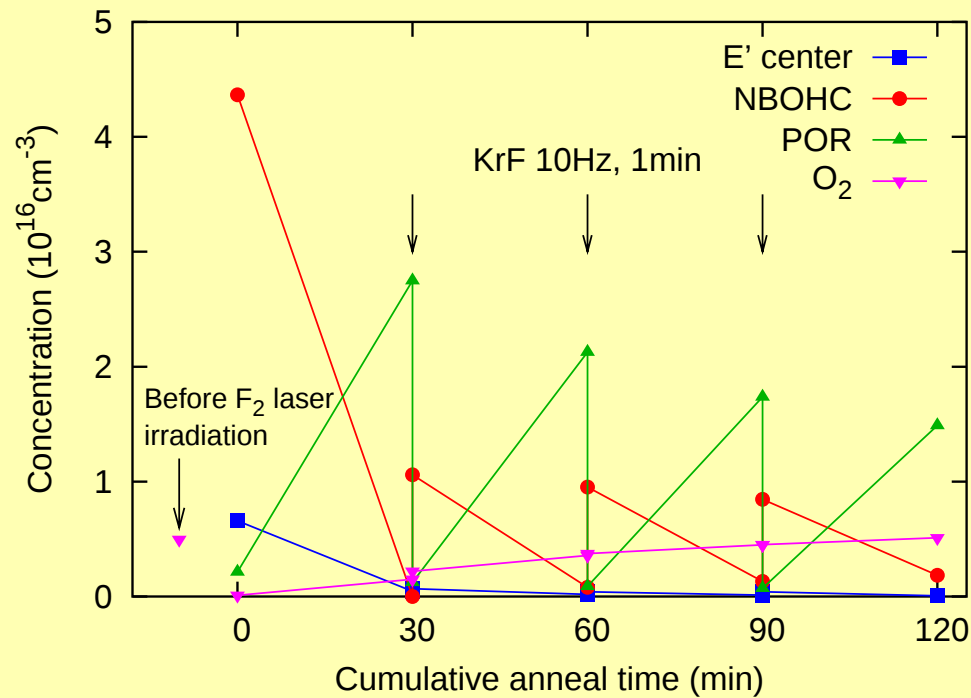


5. Interstitial oxygen in silica glass

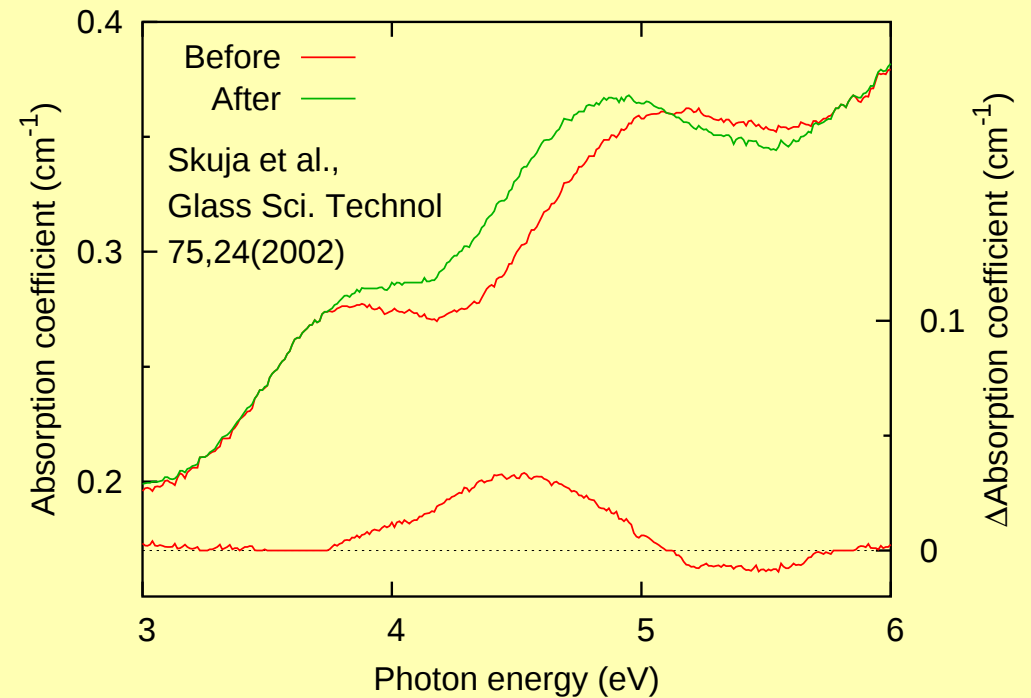
Conversion of dangling bonds



Kajihara et al. PRL92,015504(2004)

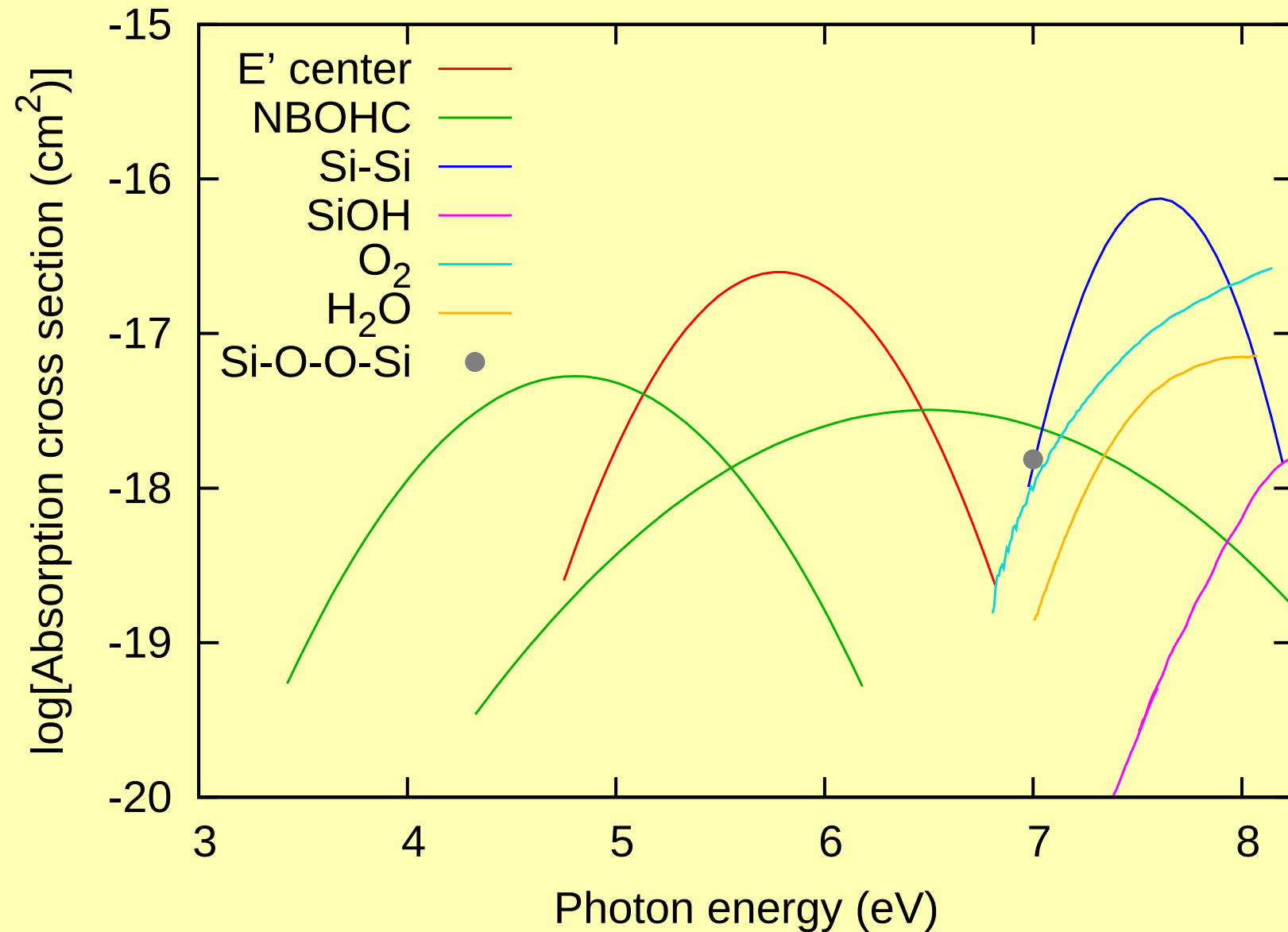


Skuja et al. Glass.Sci.Technol. 75,24(2002)



5. Interstitial oxygen in silica glass

Absorption cross section “map”



Summary

Optical
isotropy

Wide-gap
 α -quartz

Workability

Process
engineering

Fundamental
research

Structural
modification

- Raw material
- Production method
- Fiber drawing

- Optical spectroscopy
- EPR
- Simulation

- 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.)