An IMI Video Reproduction of Invited Lectures from the 17th University Glass Conference

OXIDATION OF Si: Role of Si/SiO_2 INTERFACE

M. Tomozawa and S.-R. Ryu

Materials Science and Engineering Department

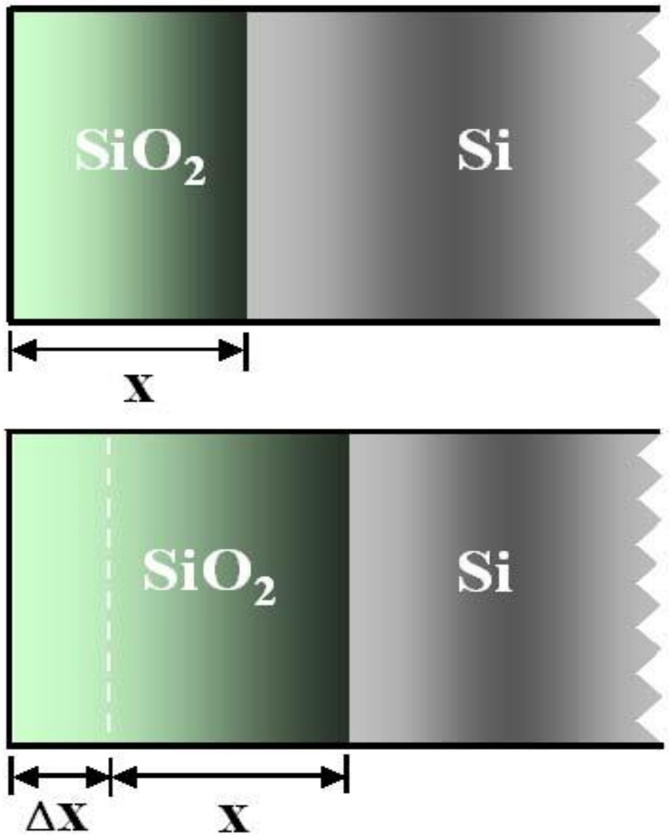
Rensselaer Polytechnic Institute

Troy, NY 12180-3590 USA

Oxidation of Silicon

Heat treated time t

Heat treated time t + Δt



Oxidation of Silicon

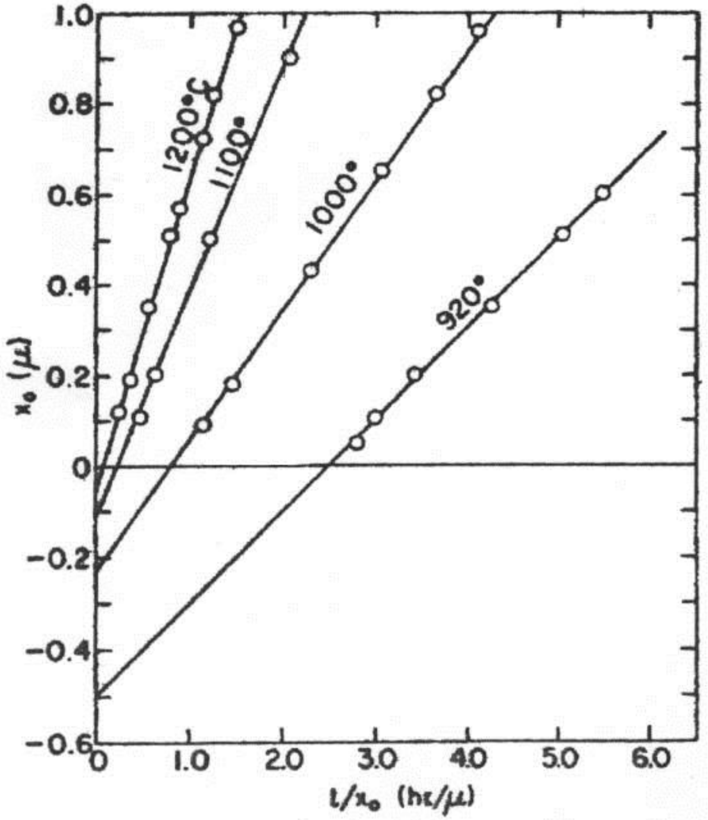
Si is oxidized to form amorphous SiO_2 at high temperature in dry (O_2) atmosphere or wet (H_2O) atmosphere.
The oxidation kinetics follows the linear-parabolic law at a constant temperature.

$$\boxed{x_0^2 + Ax_0 = B(t + \tau)}$$

where x_0: SiO_2 film thickness
t: heat-treatment time; τ: off-set time
B: parabolic rate constant; B/A: linear rate constant

Deal and Grove, J. Appl. 36 (1965) 3770.

Oxidation of Silicon



$X_0 = - A + Bt/x_0$

Wet (95°C H_2O) oxidation, $\tau = 0$

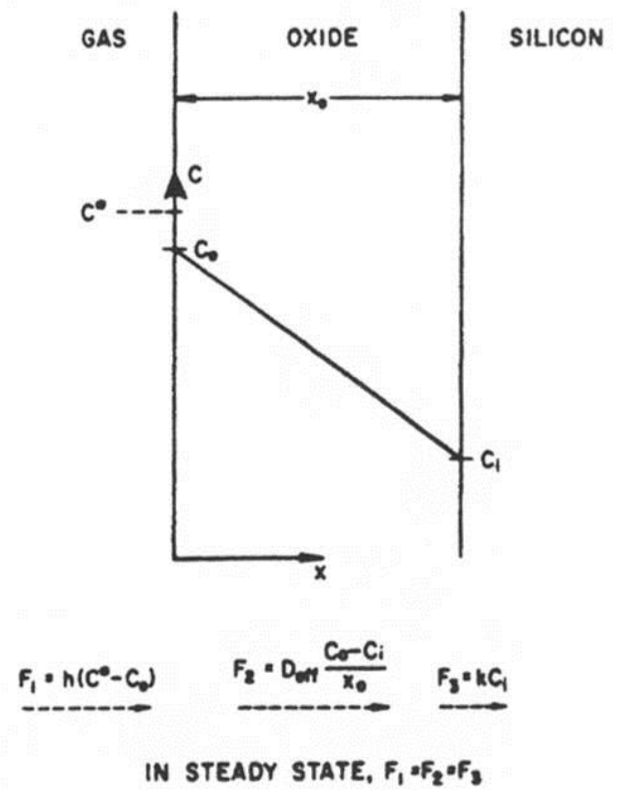
Deal and Grove

Oxidation of Silicon

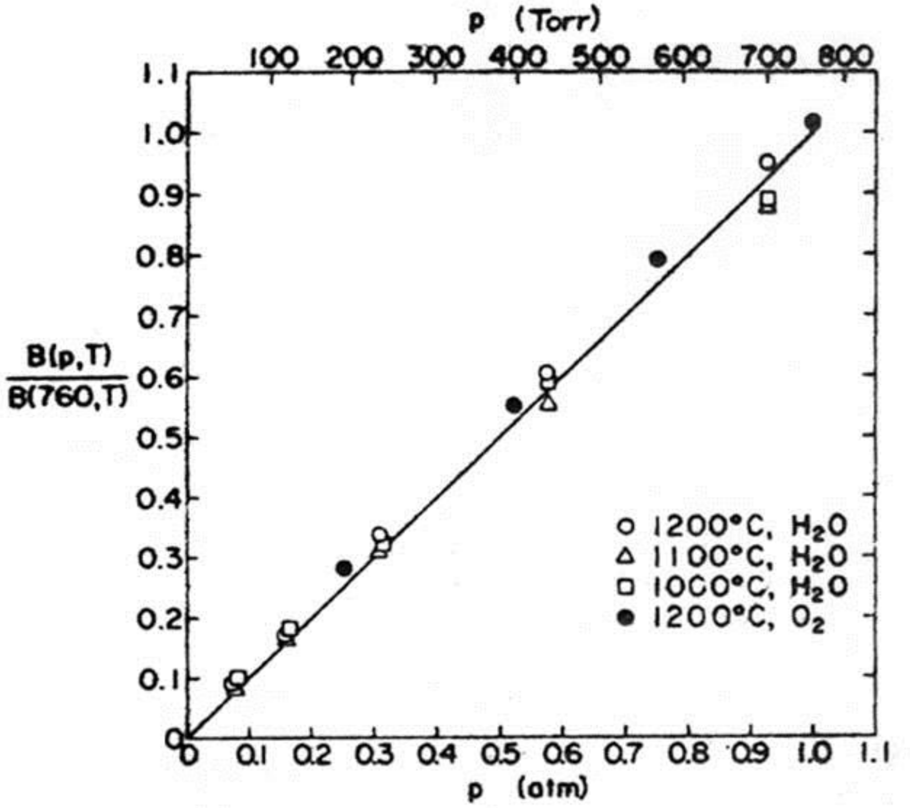
Traditionally

Linear growth is attributed to the interface reaction-controlled process.
Parabolic growth is attributed to diffusion-controlled process.
Diffusing species are H_2O in wet and O_2 in dry.

B.F. Deal and A.S. Grove, J. Appl. Phys. 36, 3770 (1965).



Oxidant pressure effect

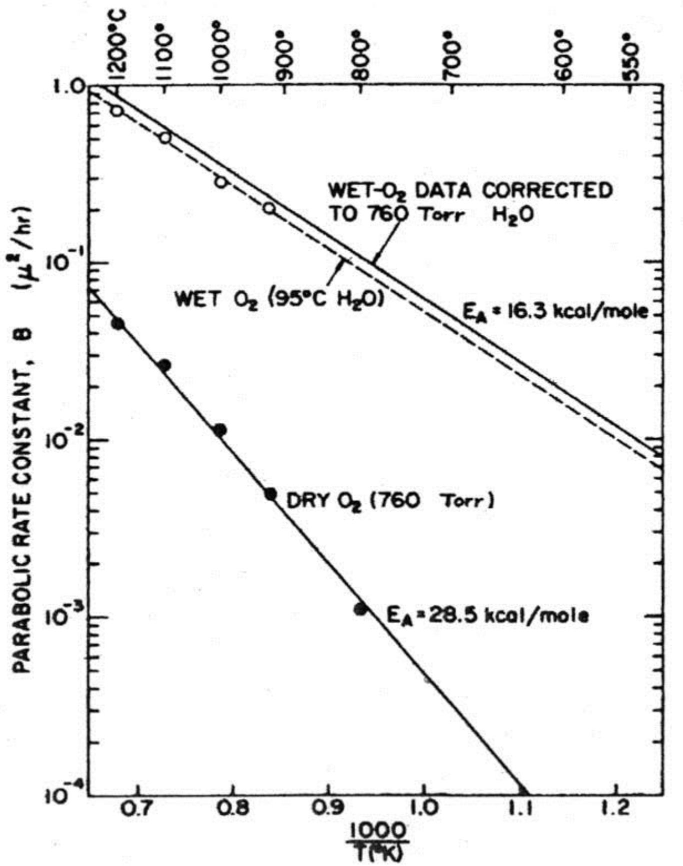


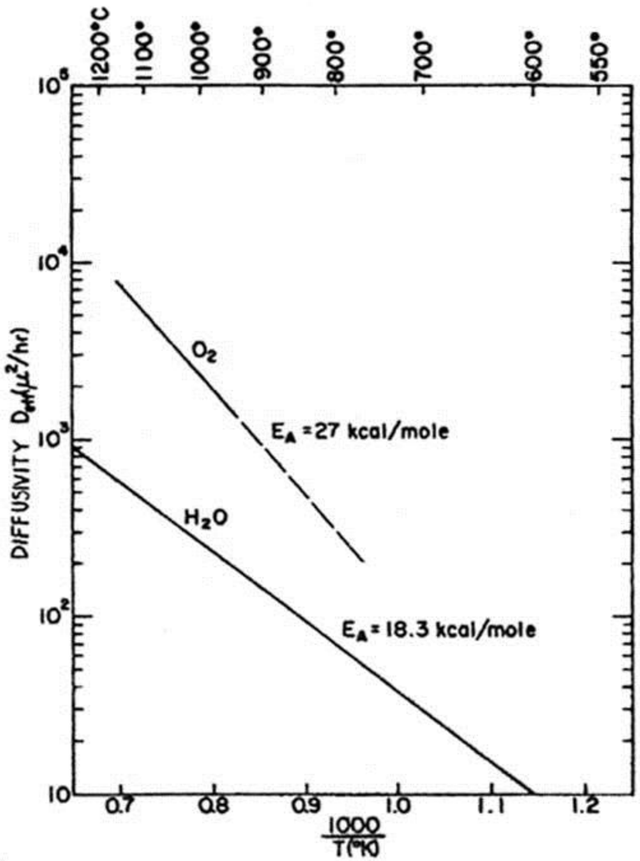
Parabolic rate constant, B, is proportional to vapor pressure.

Linear rate constant B/A is proportional to vapor pressure. (Deal and Grove); or proportional to square root of vapor pressure (Deal, Hess, Plummer and Ho, J. Electrochem. Soc., 125, 339)

Parabolic rate constant

B =2DC*/N; N: number of oxidant in a unit volume of SiO_2 (Deal and Grove) and D: Diffusion coefficients





Anomalous phenomena related to S/SiO_2

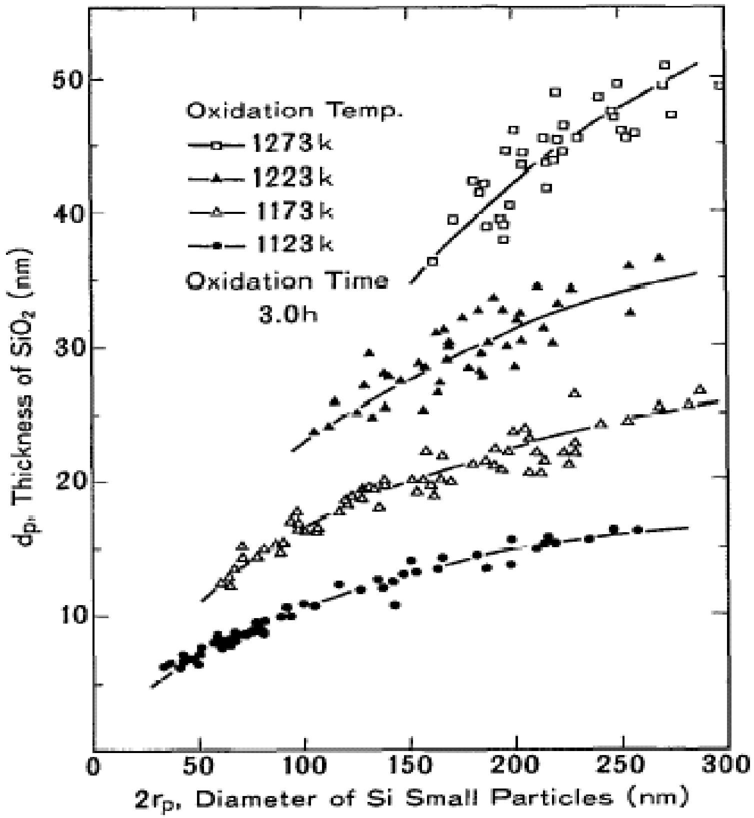
Wet oxidation is faster than dry oxidation even though the diffusion coefficient of water appears smaller than that of oxygen.

Origin of linear rate constant—reaction rate of Si with oxidant is fast. (Doremus, JAP, 66 (1989)4441; Mott, Rigo and Rochet, Philo. Mag. B, 60 (1989) 189; Bongiorno and Pasquarello, Phys. Rev. Letters, 93 (2004) 086102).

Oxidation rate is slower for nano-Si.

Oxidation rate depends upon the orientation of Si crystal.

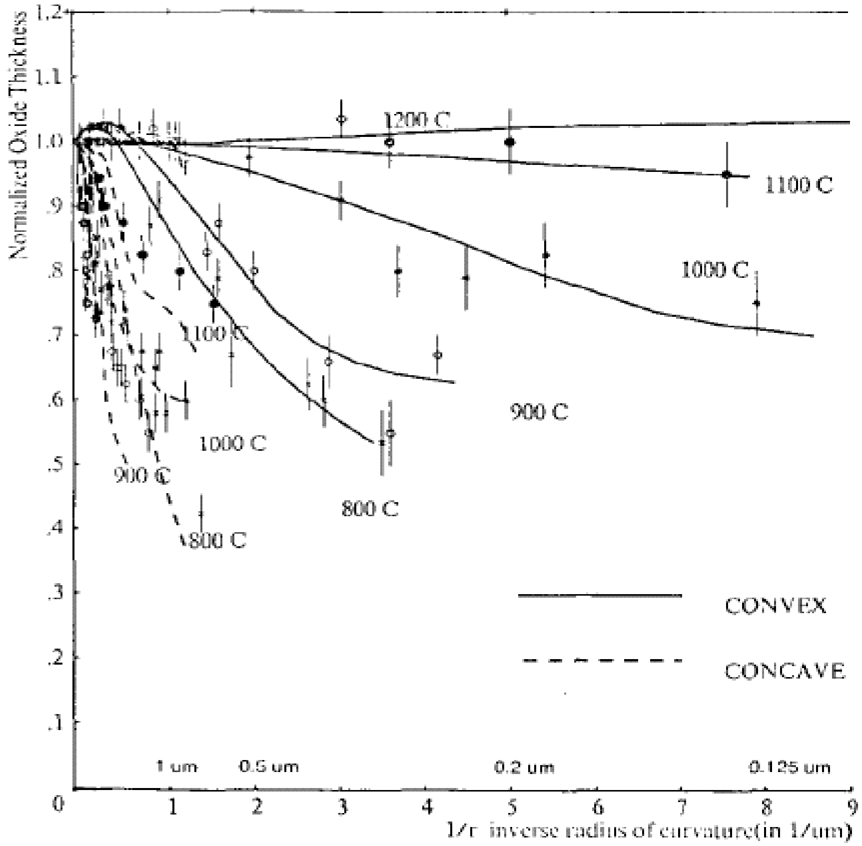
Oxidation of nano-silicon



SiO_2 film growth rate is slower for smaller silicon particles

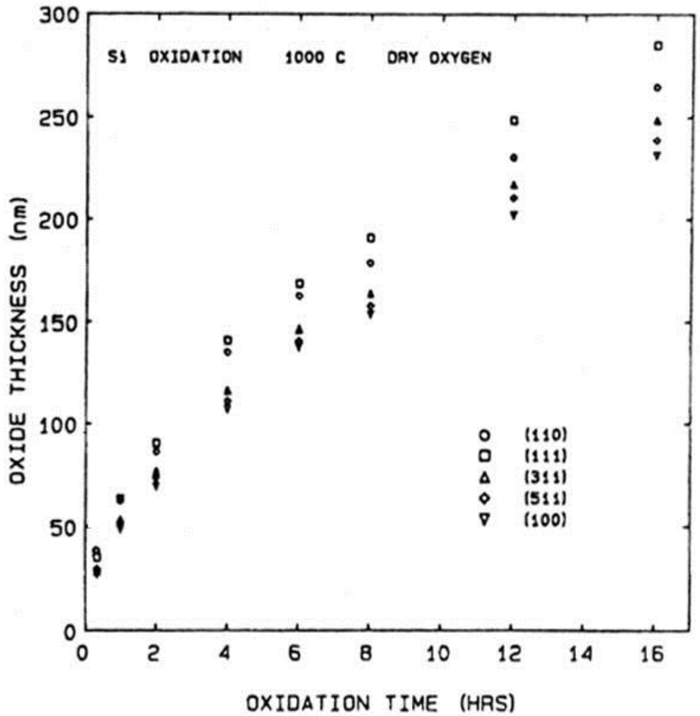
R. Okada and S. IIjima, Appl. Phys. Letters, 58, 1662 (1991).

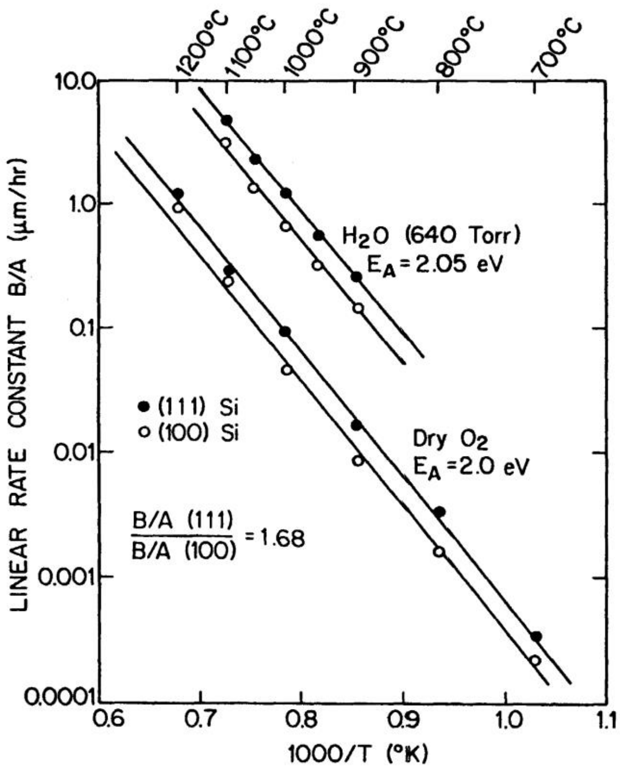
Oxidation rate of Si with curved surface



Kao, McVittie, Nix, and Saraswat, IEEE ED-35, 25(1988).

Effect of Si crystal orientation on oxidation rate

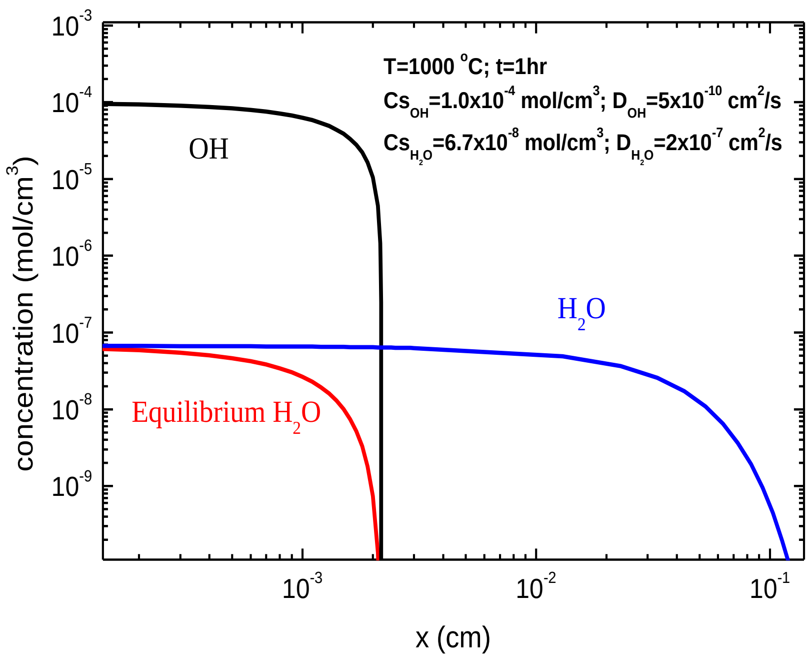




Lewis and Irene
J. Electrochem. Soc., 134 (1987) 2332. Oxidation rate: (111)>(110)>(100)

Deal, J. Electrochem. Soc.125 (1978)576.

Expected water (H_2O and OH) diffusion profiles



Water diffusion, 1000ºC, 355 Torr water vapor, 1 h.

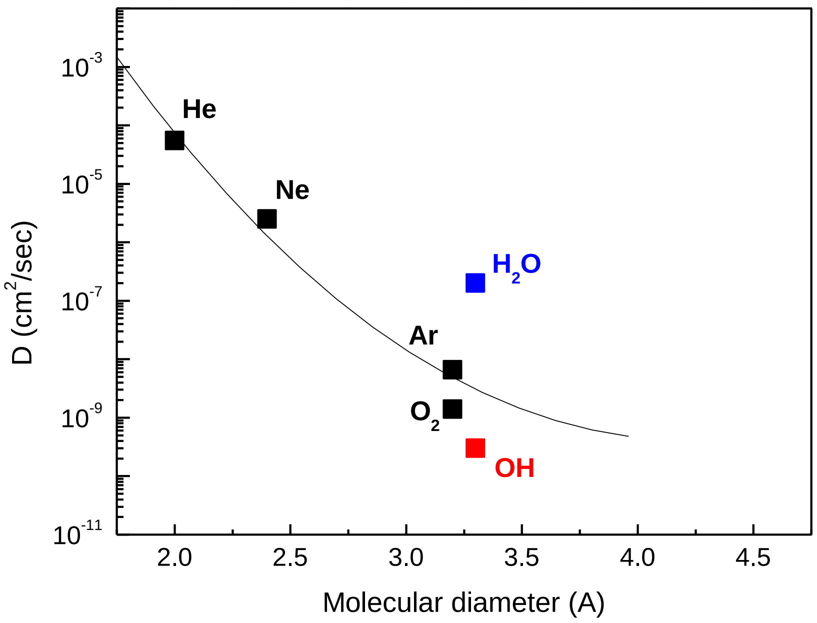
$H_2O + SiO_2 \leftrightarrow 2SiOH$

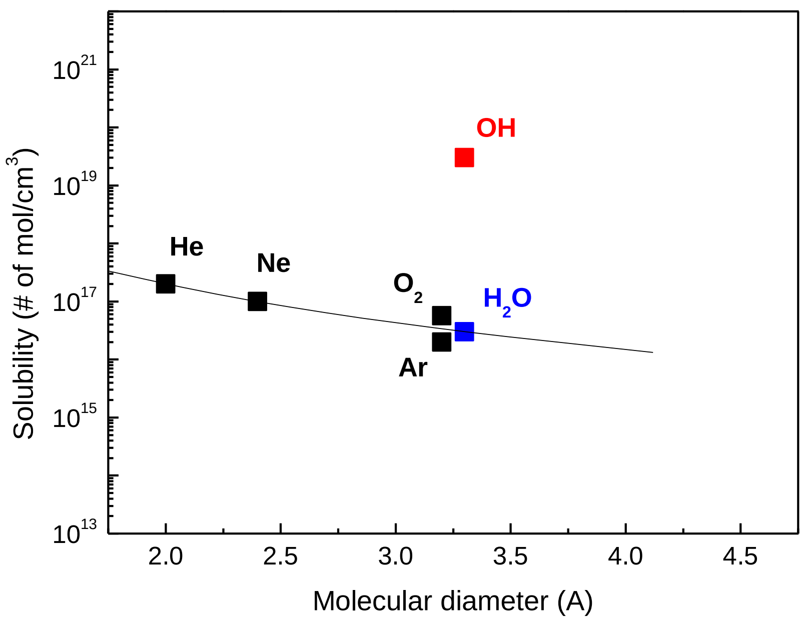
H_2O diffuses and reacts with SiO_2 to form SiOH.

If the reaction equilibrium holds strictly, H_2O and OH (solid line) should have same depth of diffusion.

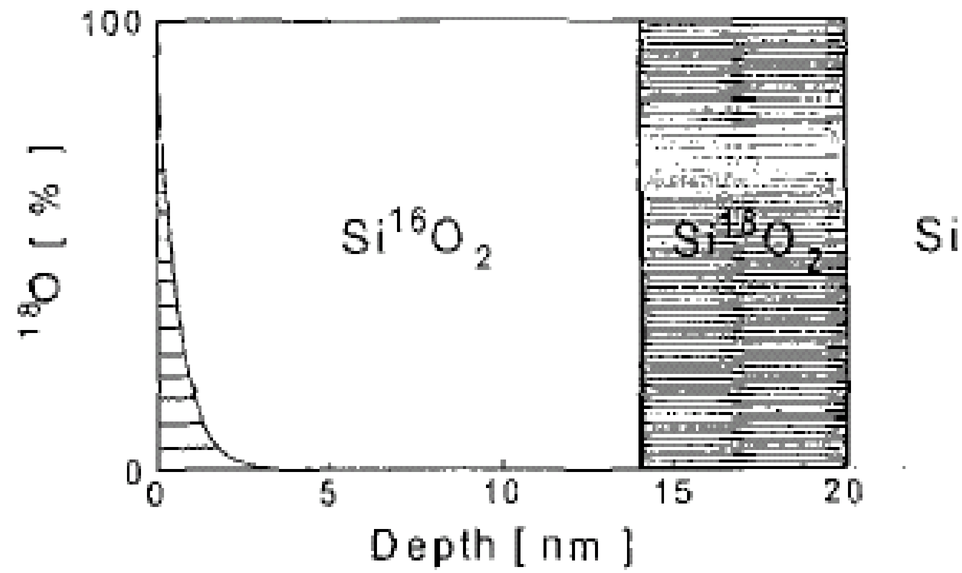
If H_2O is not restricted by the equilibrium, it can diffuse deeper.

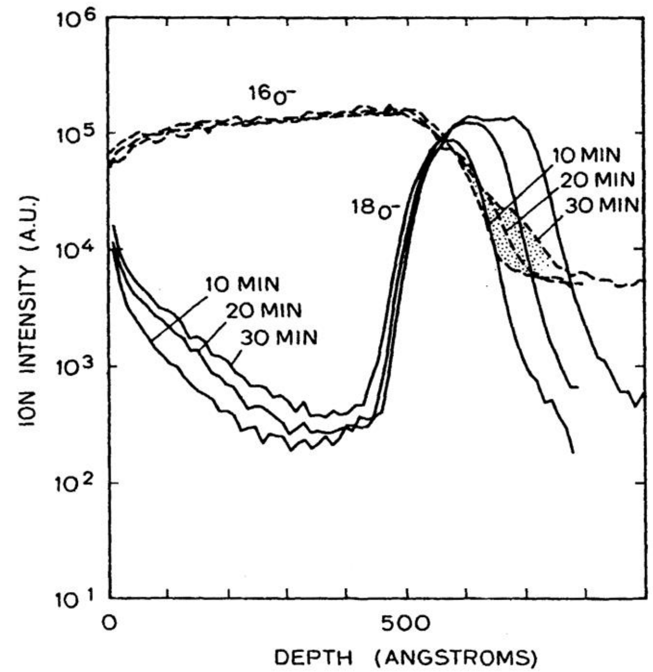
Diffusion coefficient and solubility





$^{18}O_2$ diffusion during Si oxidation



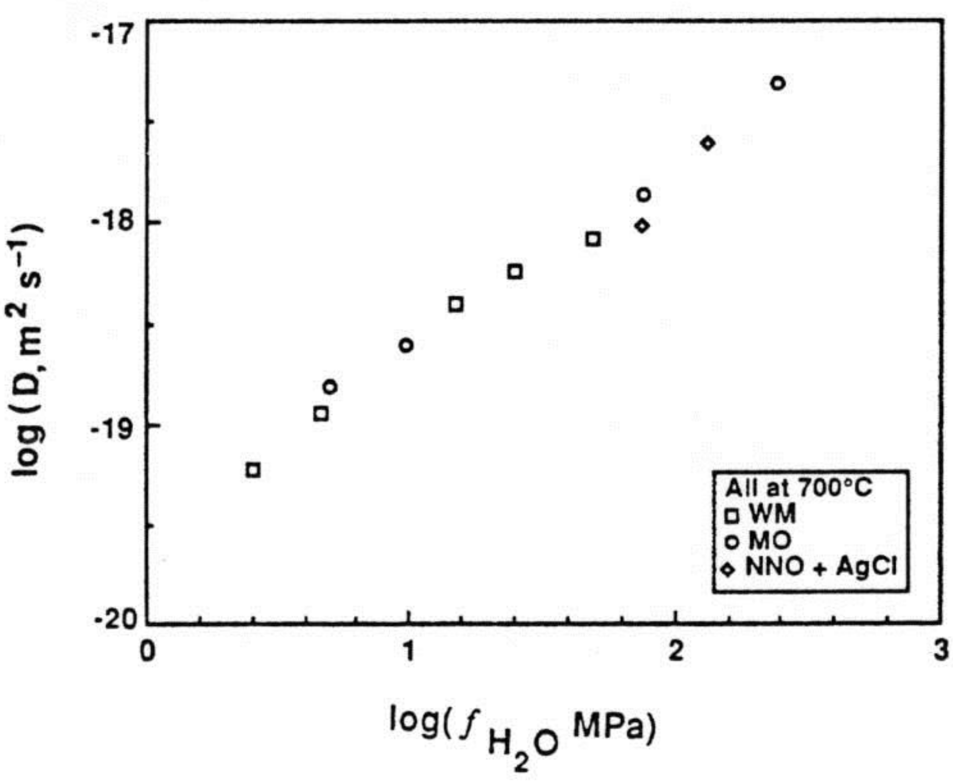


Stedile, Baumvol, Oppenheim, Trimaille, Ganem and Rigo, Nucl. Inst. Method in Phys. Res. B 118 (1996) 493.

Treatment in $^{16}O_2$ Followed by $^{18}O_2$

Han and Helms, JAP, 59 (1986)1768.

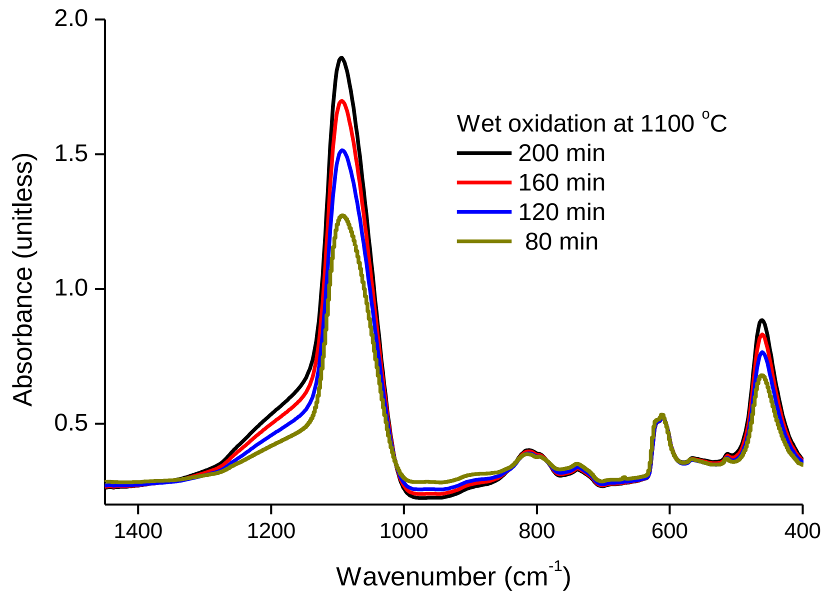
Apparent diffusion coefficient of ^{18}O as a function of water vapor pressure

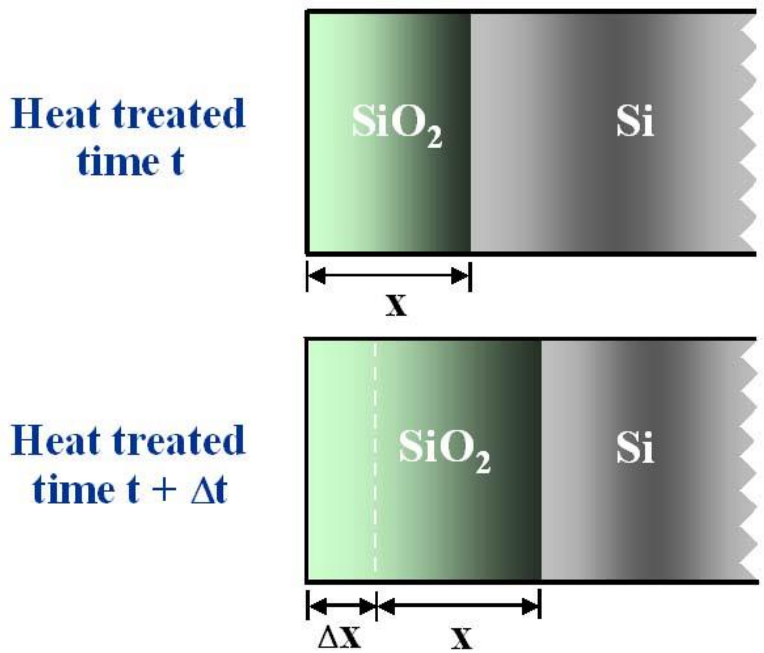


Farver and Yund, Chem. Geology, 90 (1991) 55. Quartz:

Similar analysis was made for SiO2 film By Doremus in Diffusion of Reactive Molecules in Solids and Melts, Wiley (2002).

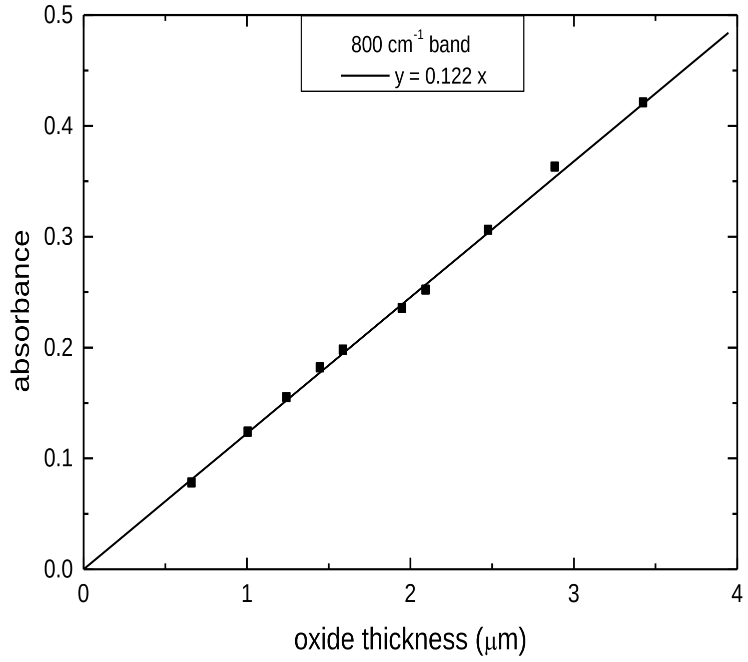
IR absorption of amorphous SiO_2 film

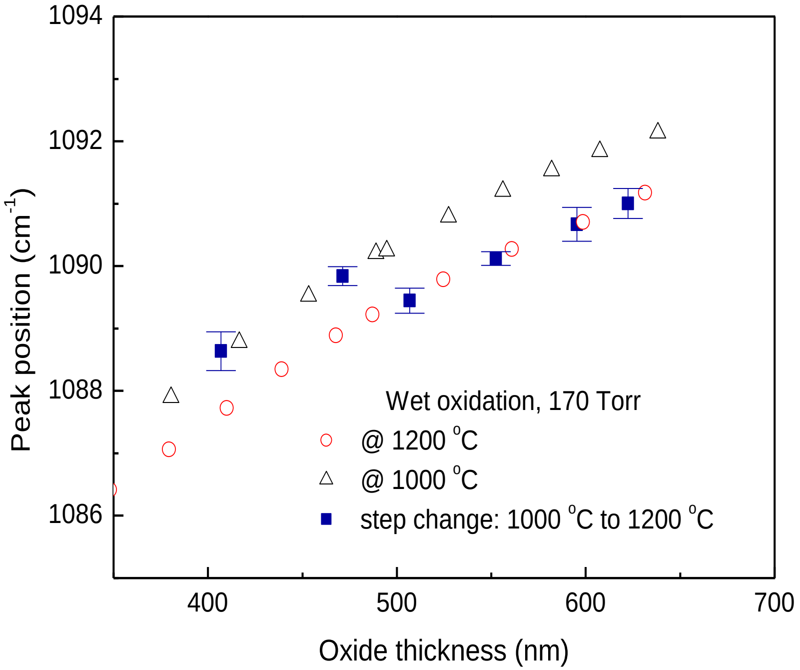




Absorbance of IR SiO_2 structural bands can be used to determine SiO_2 film thickness.

IR peak wavenumber silica structural band and thickness of SiO_2 films





Peak wavenumber of IR SiO_2 structural band

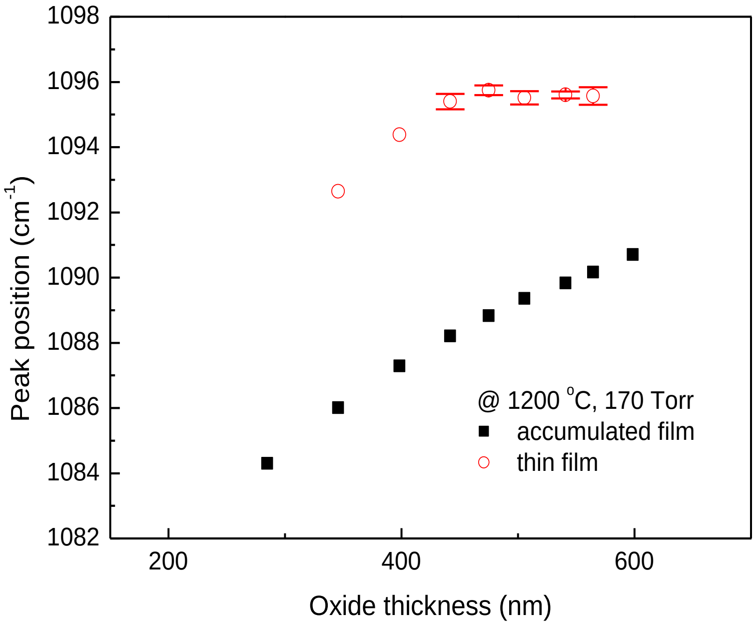
IR Peak wavenumber can change with

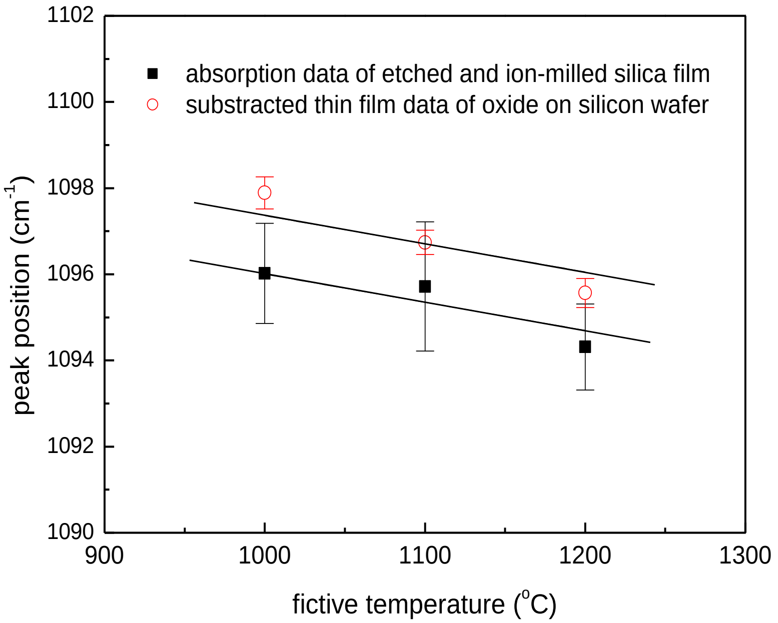
1. SiO_2 fictive temperature—small effect
   ~0.006 cm^{-1} /100ºC change of T_f at 1200 cm^{-1} peak.

2. Stress (density change)-intermediate effect
   <1 cm^{-1}/GPa
   91 cm^{-1} shift for 1 g/cm^3 density change.
   High density of 2.4 g/cm^3 for 1.5 nm film was reported. 18 cm^{-1} for 0.2 g/cm^3 change.

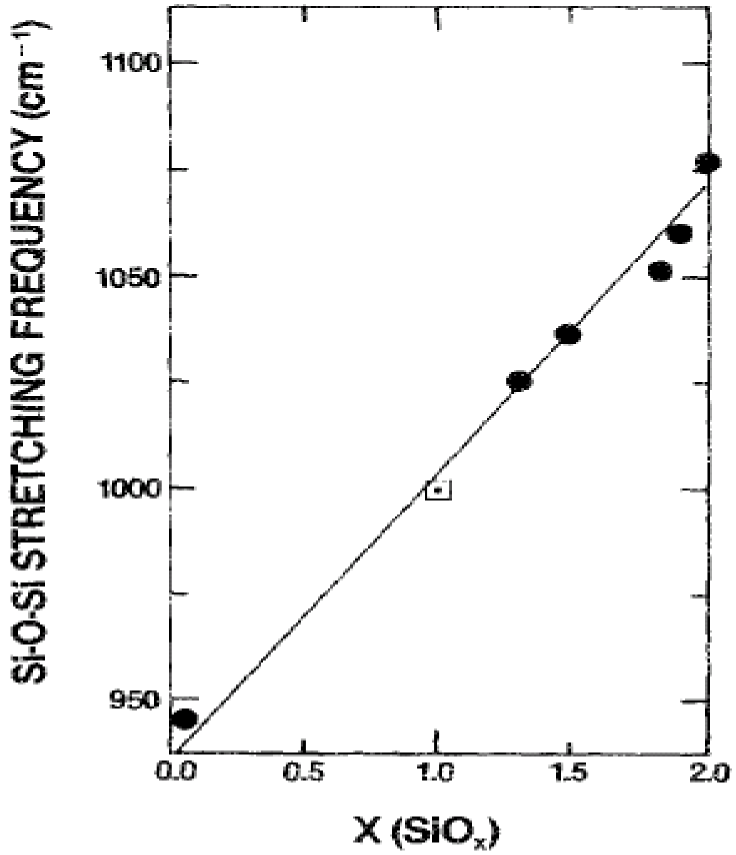
3. Non-soichiometry-large effect
   ~50 cm^{-1} decrease for x= 2 →1.5 in SiO_x

Fictive temperature effect on IR silica structural band peak wavenumber



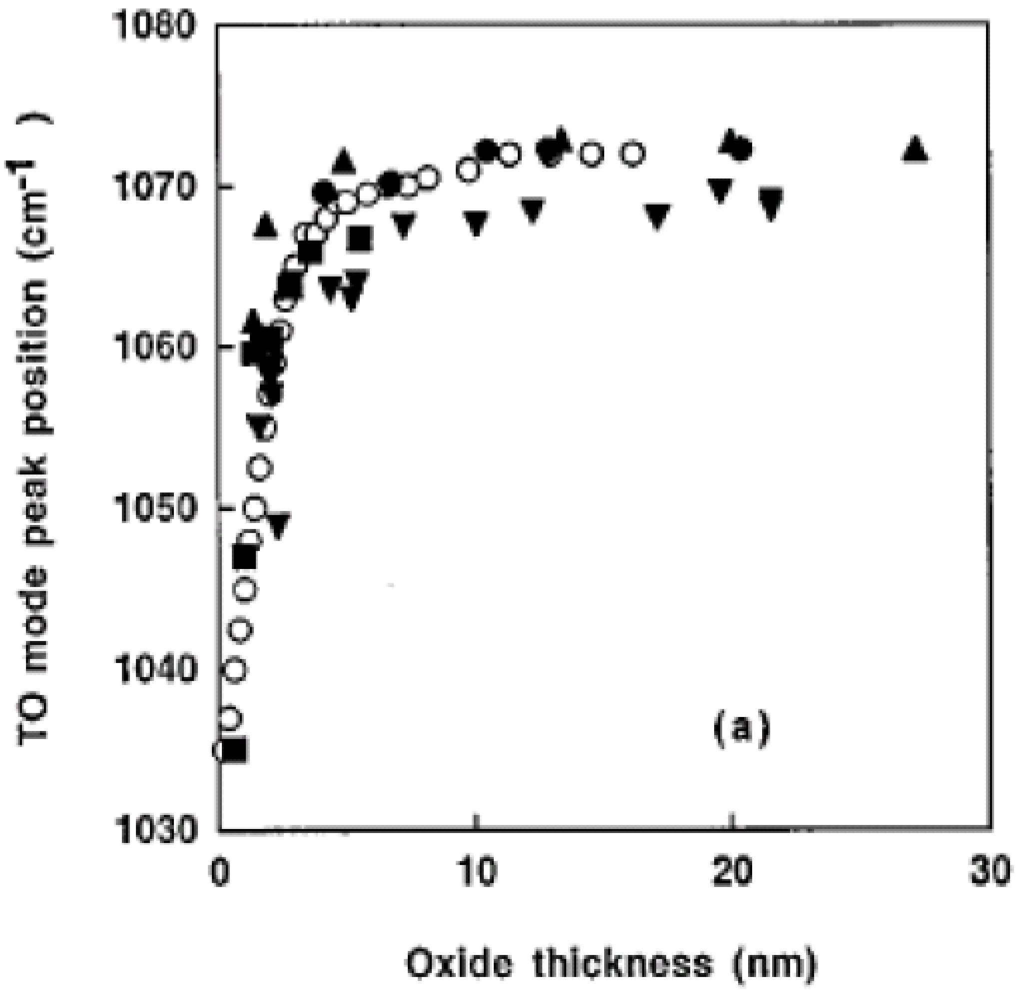


Effect of non-stoichiometry on IR silica structural band peak wavenumber



P.G. Pai, S.S. Chao, Y. Takagi, and G. Lucovsky, J. Vacuum Sci. Technol. 4, 689 (1986).

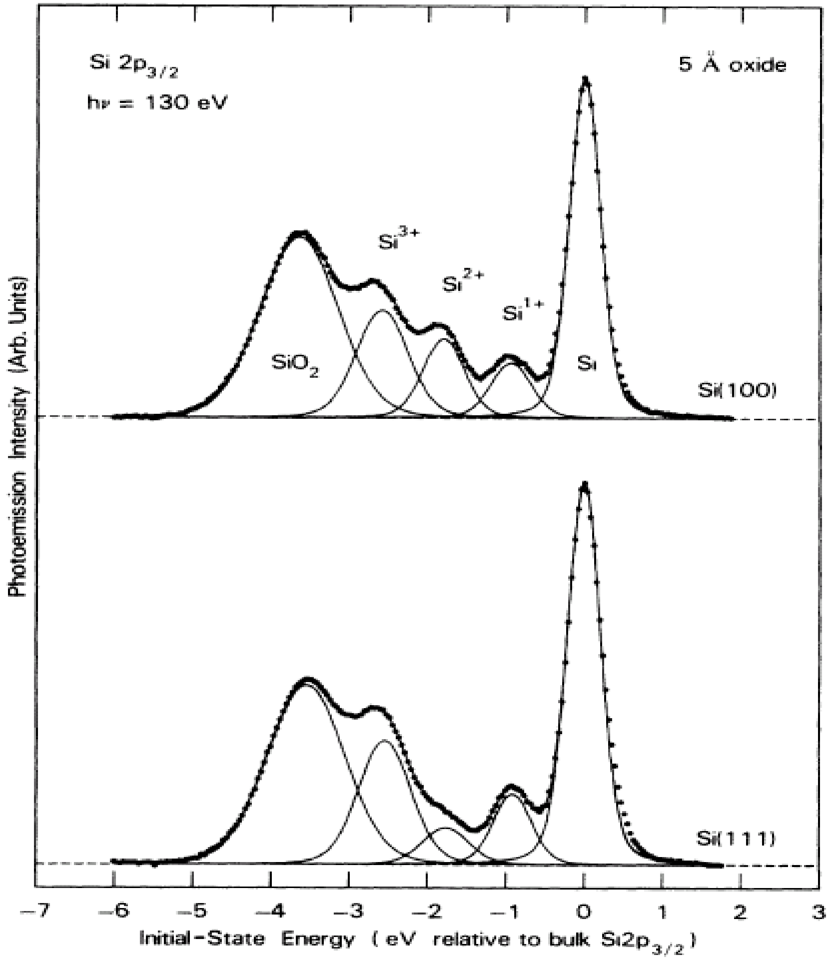
IR peak wavenumber at Si/SiO_2 interface



R.A.B. Devine, Appl. Phys. Lett., 68, 3108 (1996).

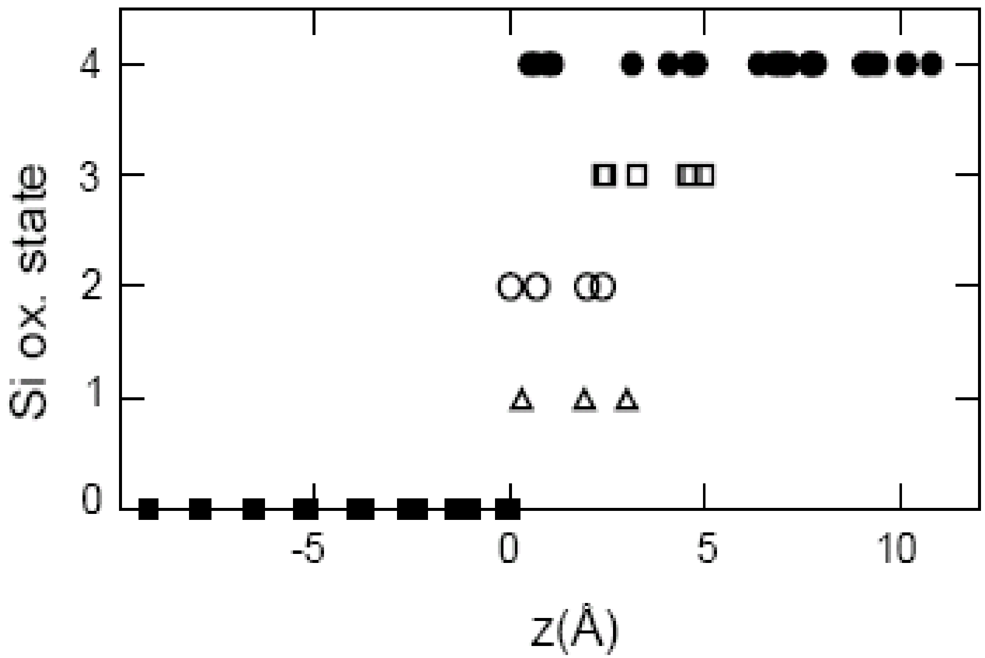
At the interface the composition is estimated to be **$SiO_{1.45}$**

Si/SiO_2 interface structure



Himpsel, McFeely, Taleb-Ibrahimi and Yarmoff, Phys. Rev. B 38 (1988) 6084. Core-level spectroscopy with Synchrotron radiation

Si/SiO_2 interface structure

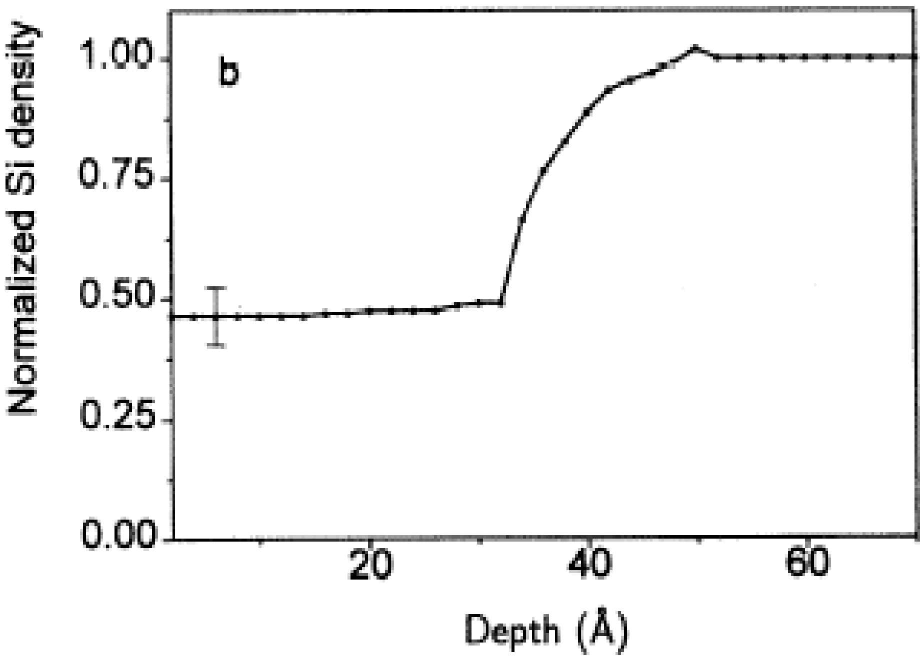


Bongiorno and Pasquarello, Appl. Surf. Sci. 234 (2004) 190.

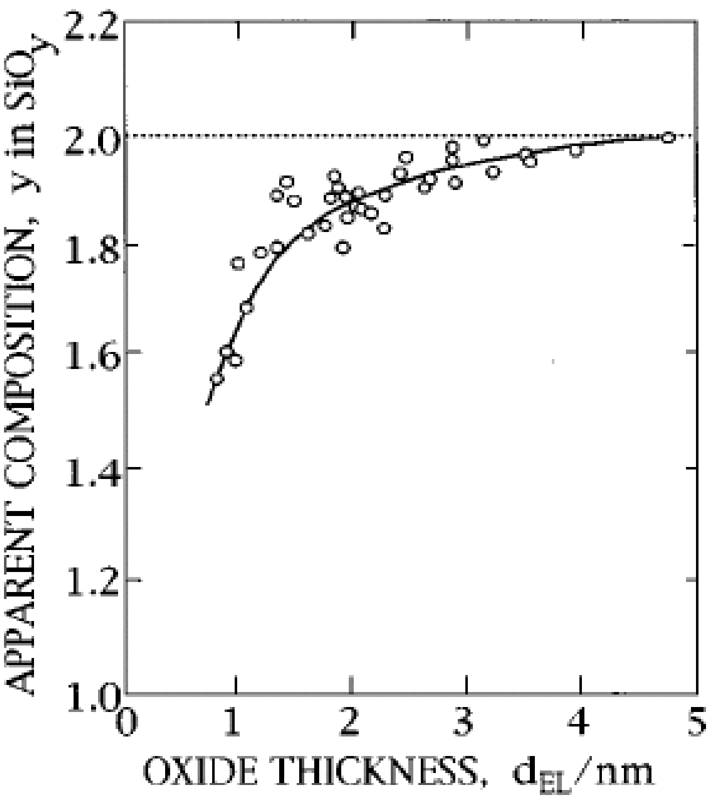
Atomistic model based upon experimental data

Three atomic layers average $SiO_{1.46}$ (exp. $SiO_{1.70}$, $SiO_{1.43}$)

Si/SiO$_2$ interface

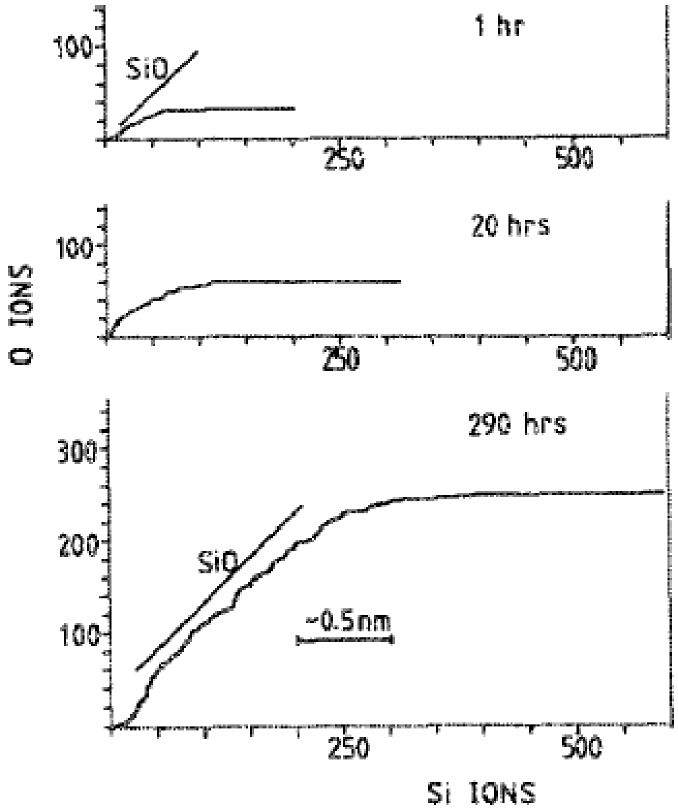


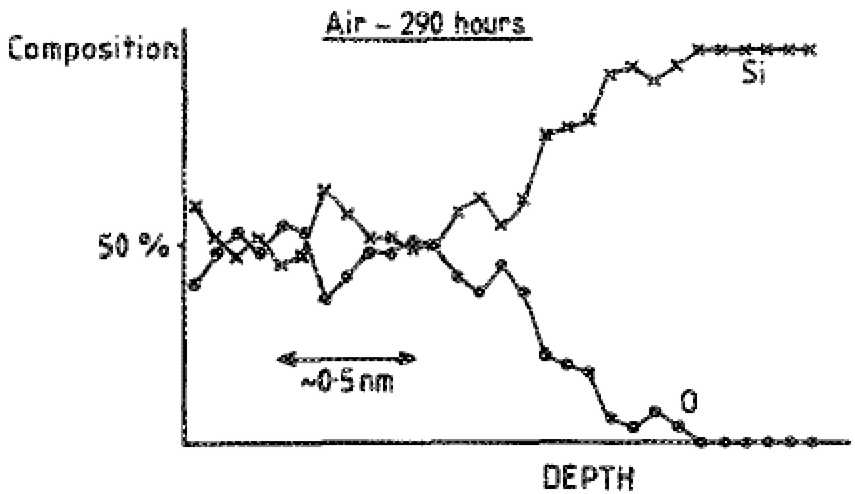
Gusev, Lu, Gustafsson, and Garfunkel, Phys. Rev. B 52 (1995) 1753.
From medium-energy ion scattering



Iwata and Ishizaka, J. Appl. Phys. 79 (1996) 6653. (from ESCA data)

Si/SiO_2 interface structure



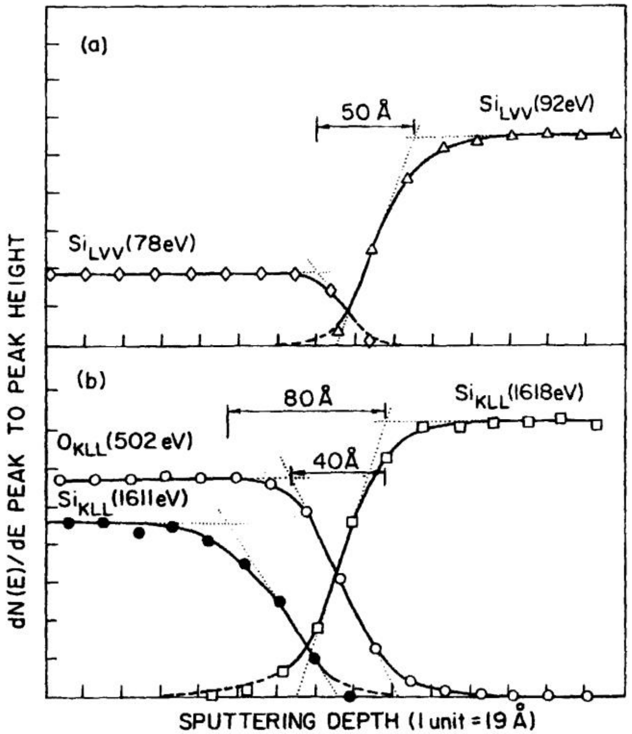


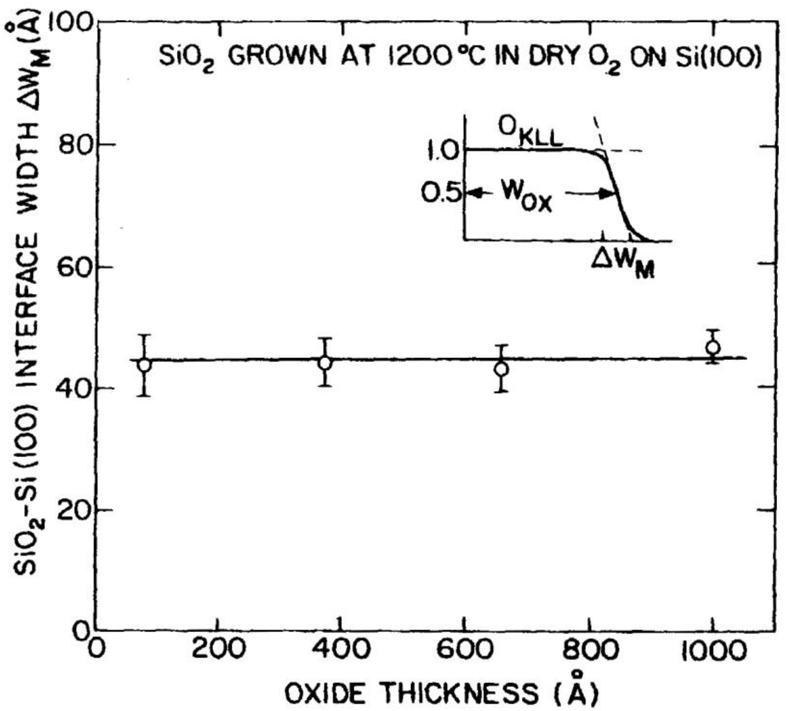
Grovenor and Cerezo, J. Appl. Phys. 65 (1989) 5089.

Room temperature air, after HF cleaning.

Pulse laser atom probe microanalysis.

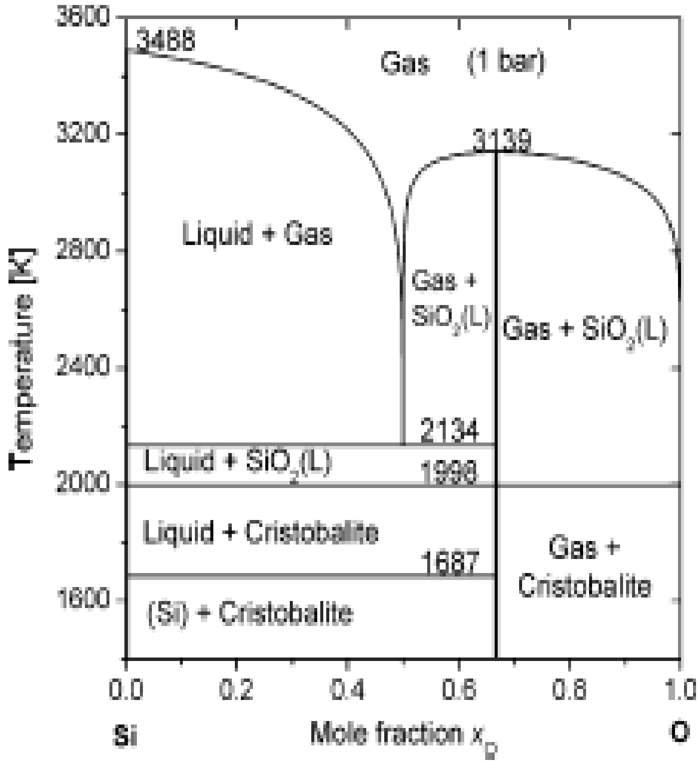
Si/SiO$_2$ interface structure



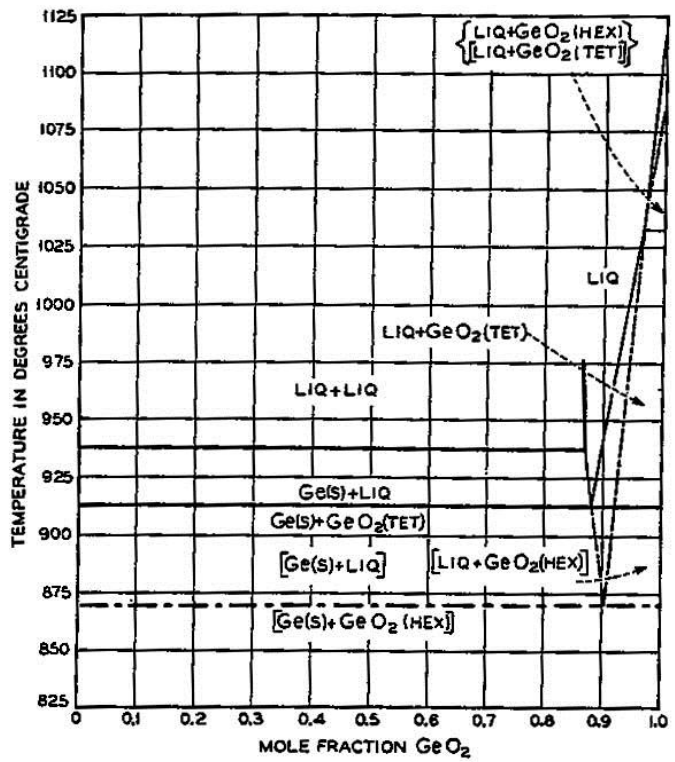


Johannessen and Spicer, and Spicer, JAP, 47 (1976) 3028.
Auger Analysis.

Phase separation of Si/SiO_2 (Ge/GeO_2) system

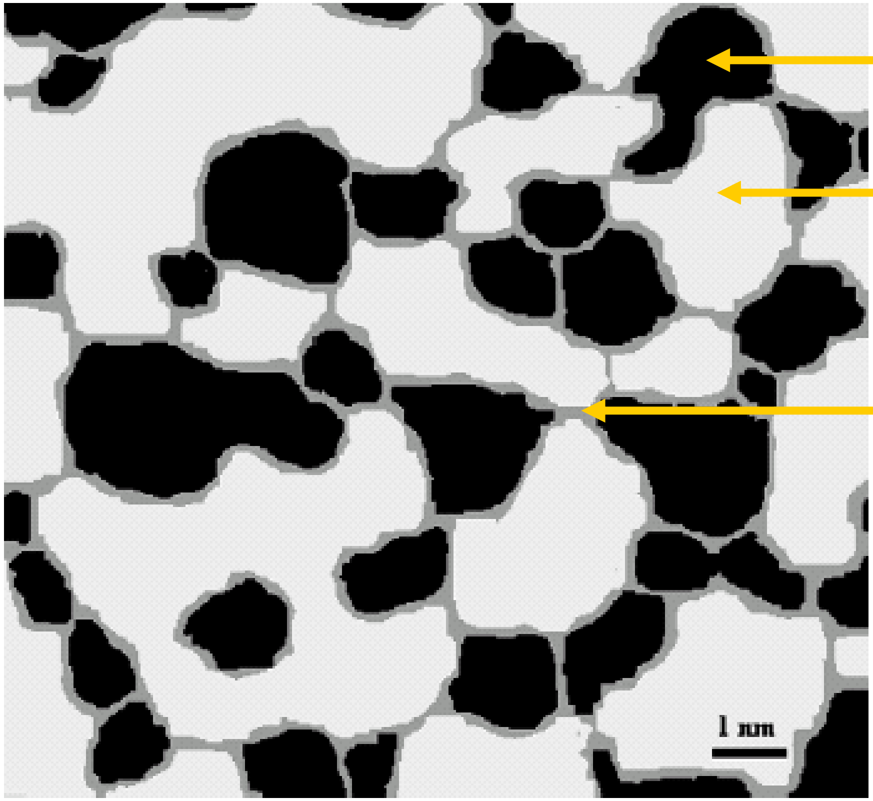


Schmure et al., J. Non-Cryst. Solids, 336 (2004) 1.



Trumbone et al. J. Chem. Phys. 24 (1956) 1112.

Phase Separation of a-SiO



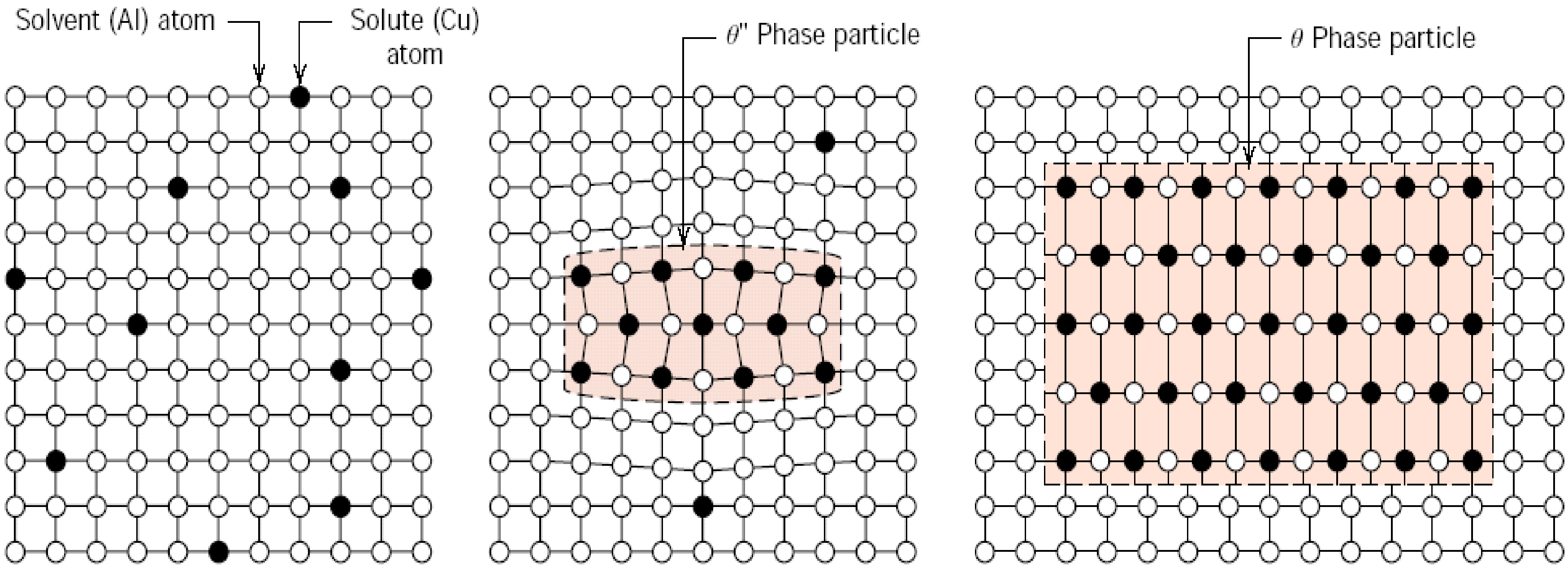
Black: Si

Light Gray: SiO_2

Gray: Suboxide, SiOx

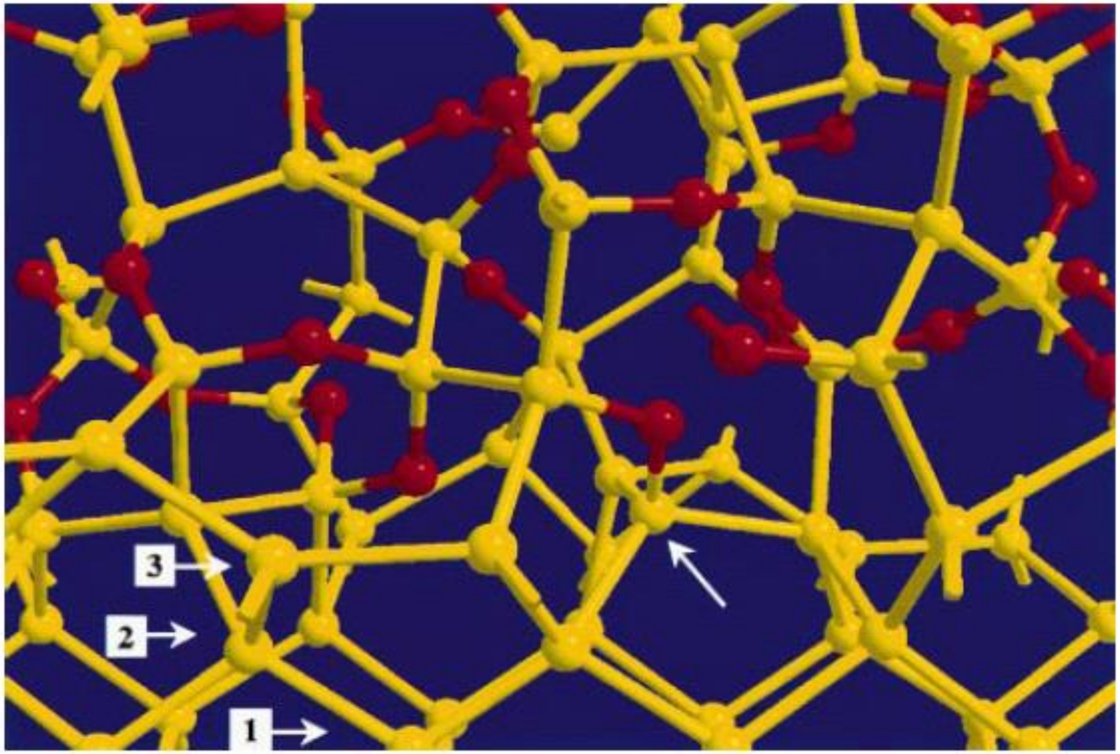
Hohl, Wieder, van Aken, Weirich, Denninger, Vidal, Oswald, Deneke, Mayer and Fuess, J. Non-Cryst. Solids, 320 (2003) 255.

Coherent and Incoherent boundary



After W.D. Callister, Jr. Fundamental of Materials Science And Engineering (2001)

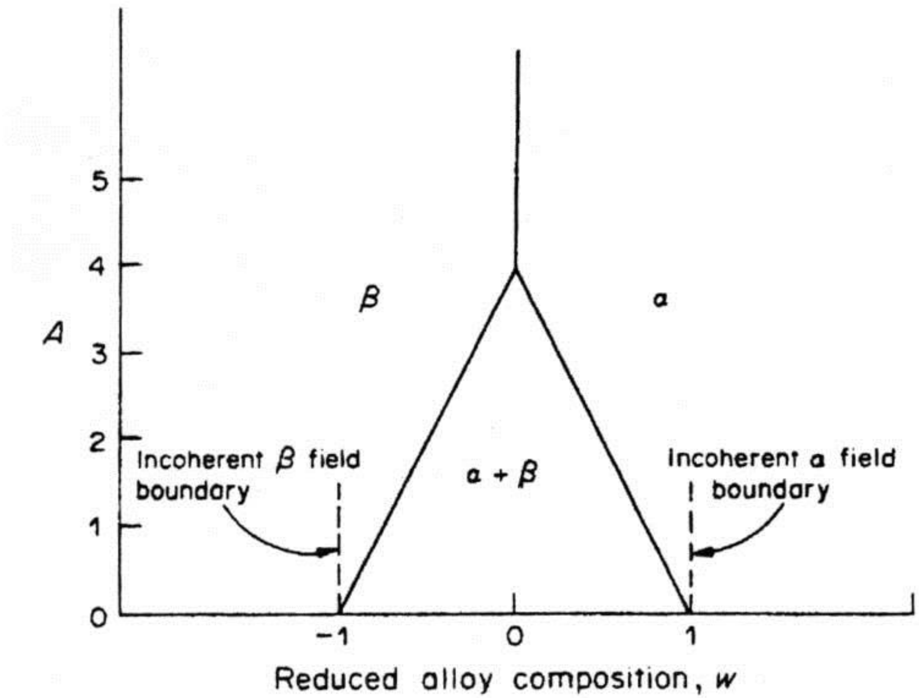
Si/SiO_2 interface

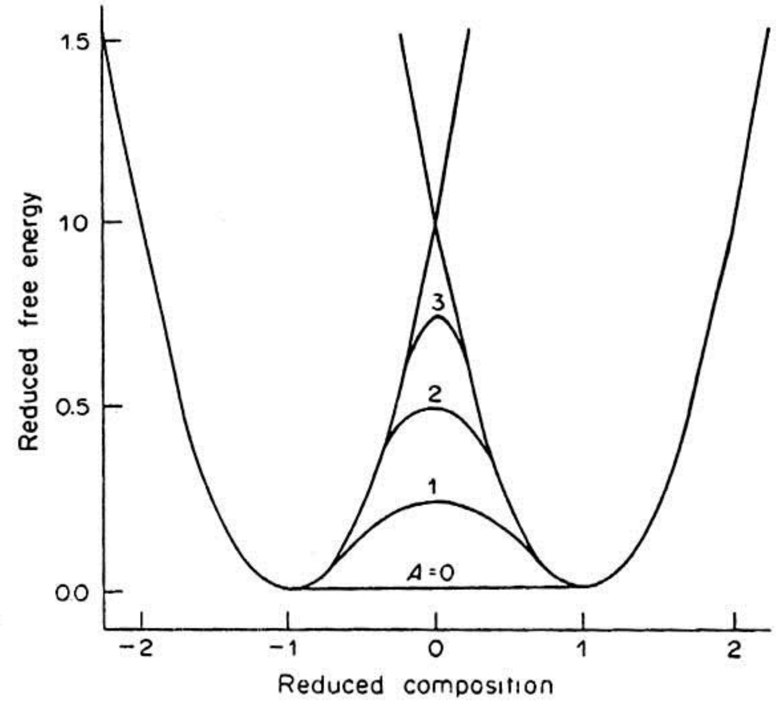


Pasquarello, Hybestsen and Car, Nature, 396 (1998) 58.

Si(001)-SiO_2, : Si, : O

Effect of coherent energy on phase diagram





Cahn and Larche, Acta Met. 32 (1984) 1915.

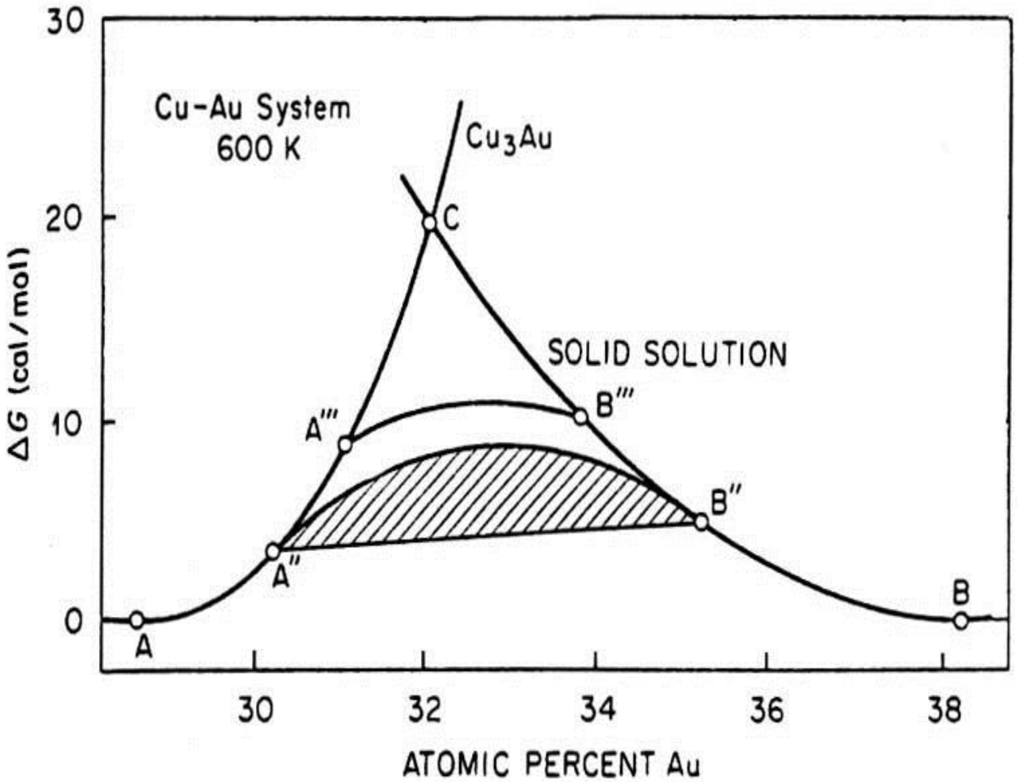
$A = 4VE\varepsilon^2/[(1\text{-}\nu)F''(C^e_\beta - C^e_\alpha)2]$; Elastic energy $F_e = z(1\text{-}z)VE\varepsilon^2/(1\text{-}\nu)$

V: molar volume.

z: mol fraction of one phase

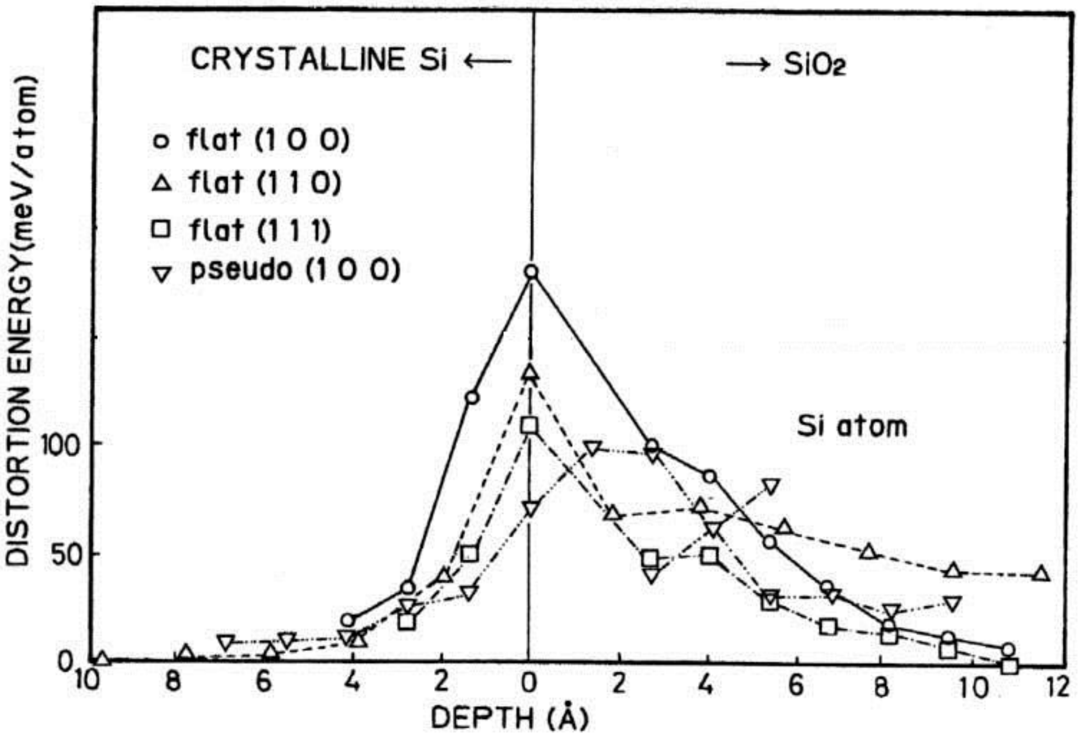
ε: linear mismatch between phases

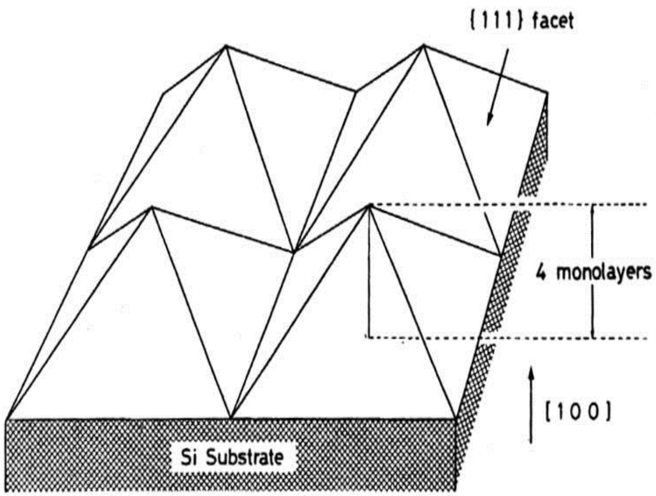
Schematic free energy diagram



Williams, R.O, Met. Trans, 11A (1980) 247.

Coherency strain energy





Ohdomari, Akatgsu, Yamakoshi and Kishimoto, J. Non-Crystalline Solids, 89 (1987) 239. (100)>(110)>(111).

High energy (100) plane tends to create (111) surfaces.

Effect of oxygen deficiency on oxidant diffusion

Oxidation of Si is controlled by the transport of oxidant (O_2 or H_2O) through the oxide film being formed. Oxygen deficiency at the interface becomes diffusion traps of these oxidants, slowing down the diffusion.

Flux at the interface, J_1.

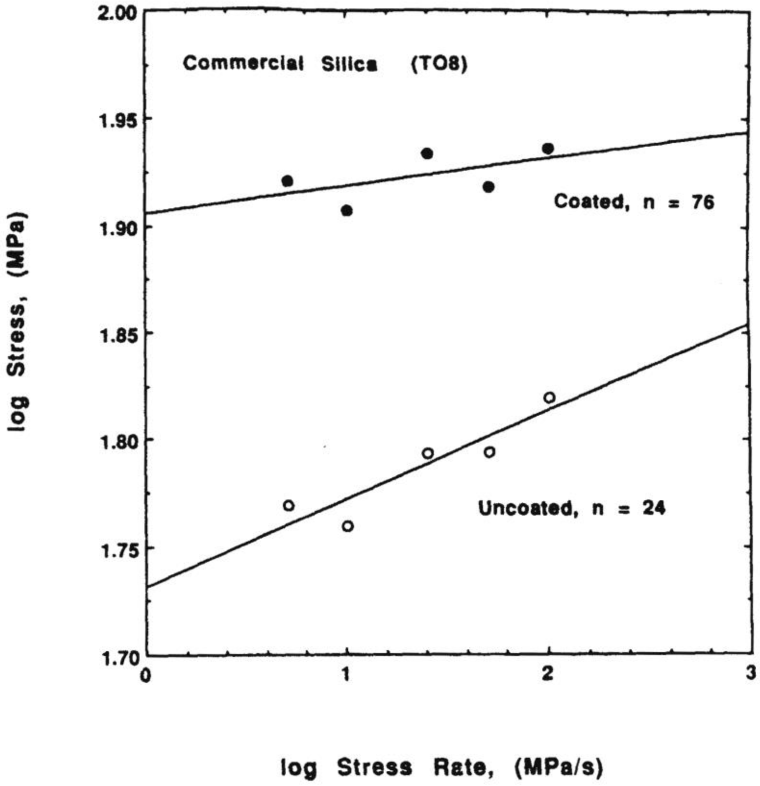
Flux in the bulk of the film, J_2.

For thin films, interface flux is important $\Rightarrow$ a linear growth.

When the film become thicker, bulk flux becomes important $\Rightarrow$ parabolic growth.

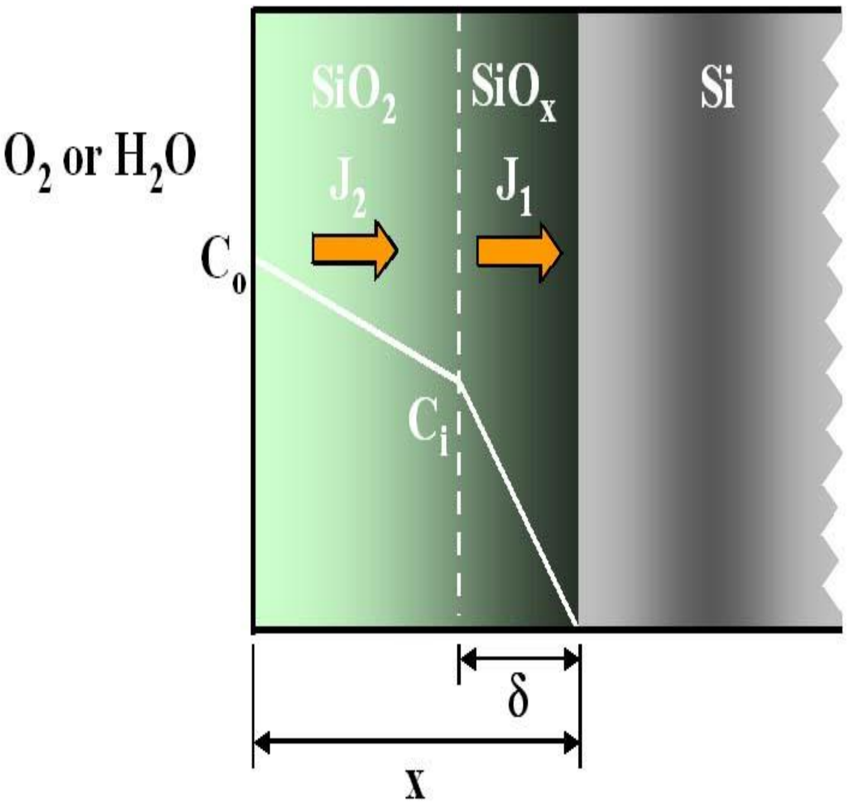
Effect of oxygen vacancy on oxidant diffusion

- Oxygen deficiency ≈ Oxygen vacancy ≈ Silicon suboxide (SiO_x, 1<x<2).
- SiO_x coating on SiO_2 glass can reduce mechanical fatigue of the glass.
- Vacancy annihilation by water diffusion.
- Oxygen vacancies serve as oxidant diffusion traps and diffusion barriers.



Tomozawa, Han and Davis, SPIE 1590 (1991) 160.

Oxygen vacancy annihilation process by oxidants



$(1/2)\ O_2 + \equiv Si - Si\equiv \leftrightarrows \equiv SiOSi\equiv$

$K_1 = C_{SiOSi}/(C_{O2}{}^{1/2}\ C_V)$

$\partial C_{O2}/\partial t - \partial C_V/\ \partial t = \partial[D_{O2}\partial C/\partial x]\partial x$

$H_2O + \equiv Si - Si\equiv \leftrightarrows \equiv SiOH$
$+HSi\equiv$

$(SiOH + SiH \text{-->}\ SiOSi + H_2)$

$K_2 = {}_{CSiHCSiOH}/C_{H2O}C_V$

$\partial C_{H2O}/\partial t + \partial C_{SiOH}/\partial t =$
$\partial[D_{H2O}\partial C_{H2O}/\partial x]\partial x$

Oxidant diffusion and reaction

Effective diffusion coefficient,

$$D_{eff} = D_{O2}/[1 + (C_V/4C_{O2})] \approx D_{O2}/(C_V/4C_{O2})$$

$$J_1 = J_2 \qquad DC_0/(x\text{-}\delta) = D_{eff}\, Ci/\delta = N\,(\partial x_0/\partial t)$$

$$x_0^2 + 2[(D_{O2}/D_{eff}) - 1]N\,\delta x_0$$

$$= 2(D_{O2}C_0/N)t + [(2D_{O2}/D_{eff}) - 1]\delta^2$$

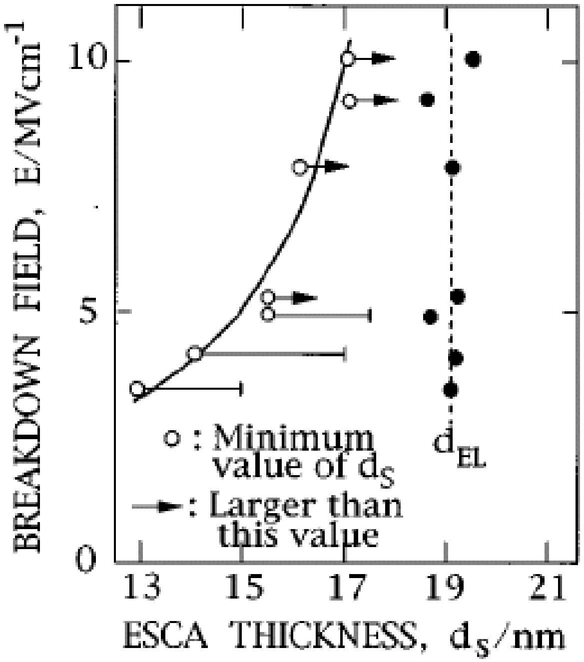
Similar to Deal and Grove equation, $x^2 + Ax = B\,(t + \tau)$

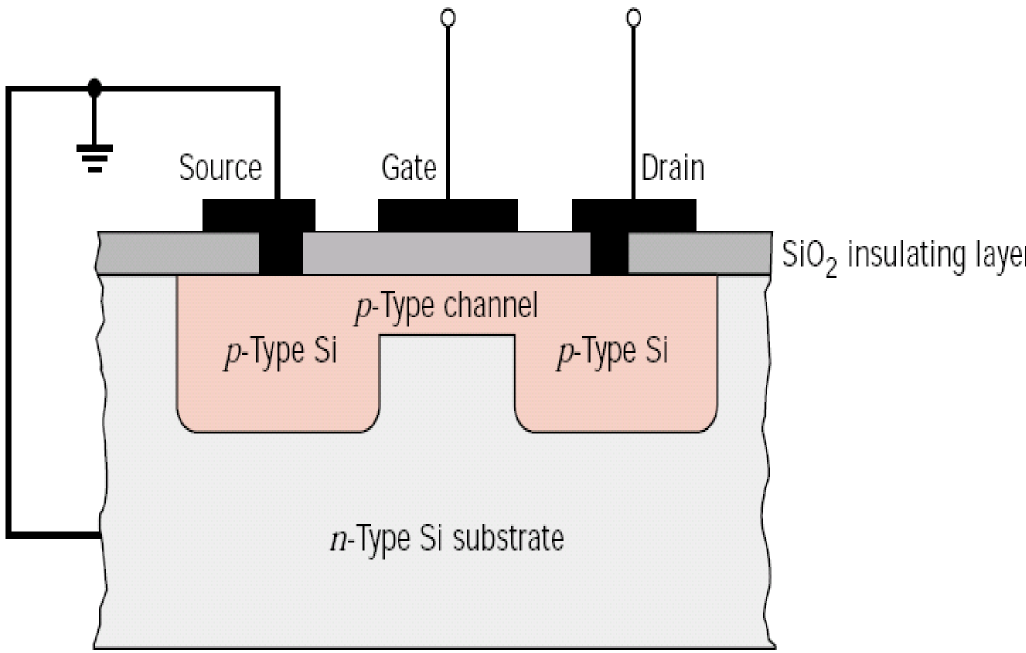
With $B = 2D_{O2}C_{O2}/N$

$B/A = C_0/\{N\,[(1/_{Deff}) - (1/D)]\,\delta\} \approx C_0D_{eff}/(N\,\delta\,)$

Similar equations for wet (H_2O) oxidation.

Effect on electrical properties

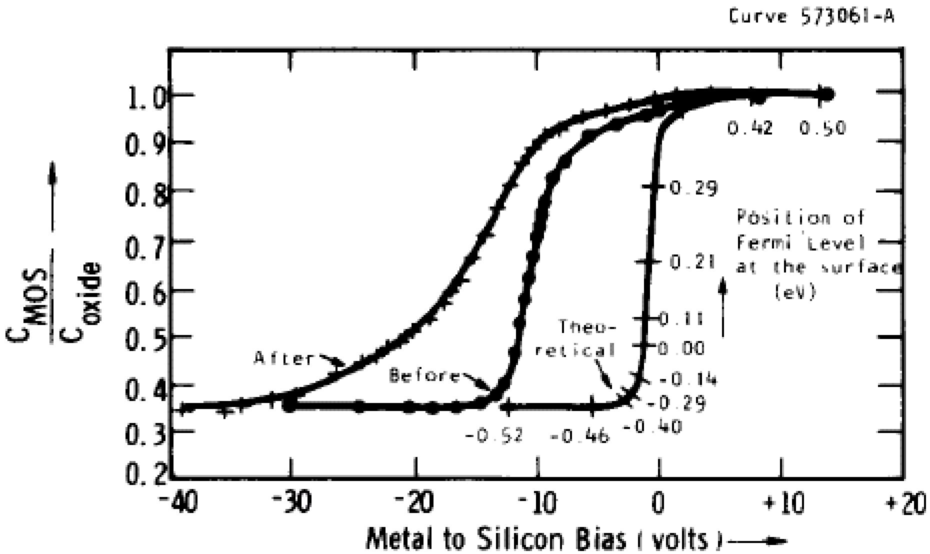


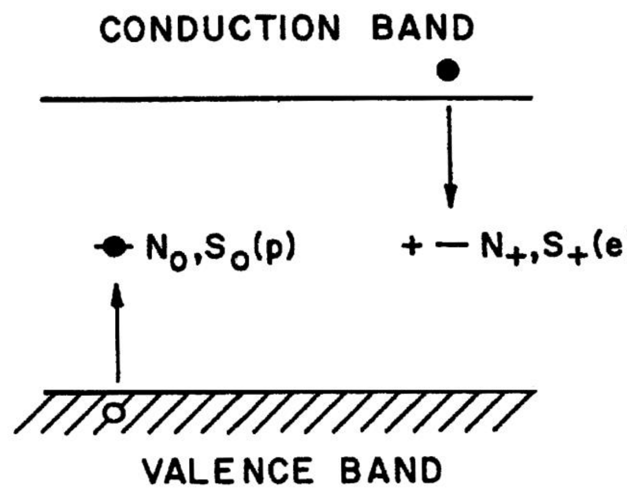


Iwata and Ishizaka, J. Appl. Phys. 79 (1996) 6653.
Si-Si is responsible-Hasegawa et al., J. Electrochem. Soc. 142 (1995) 273.

Callister, <u>Fundamental of Materials Science and Engineering</u>, Wiley (2001).

Effect on electrical properties

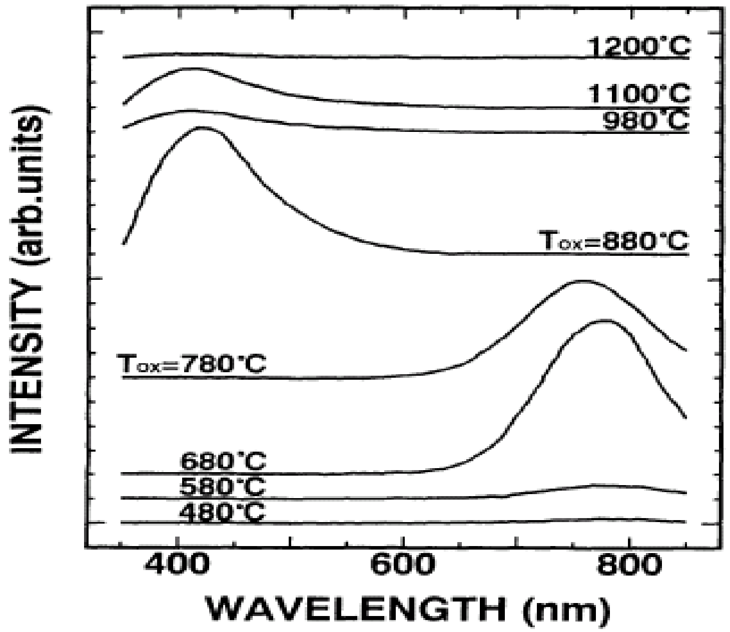


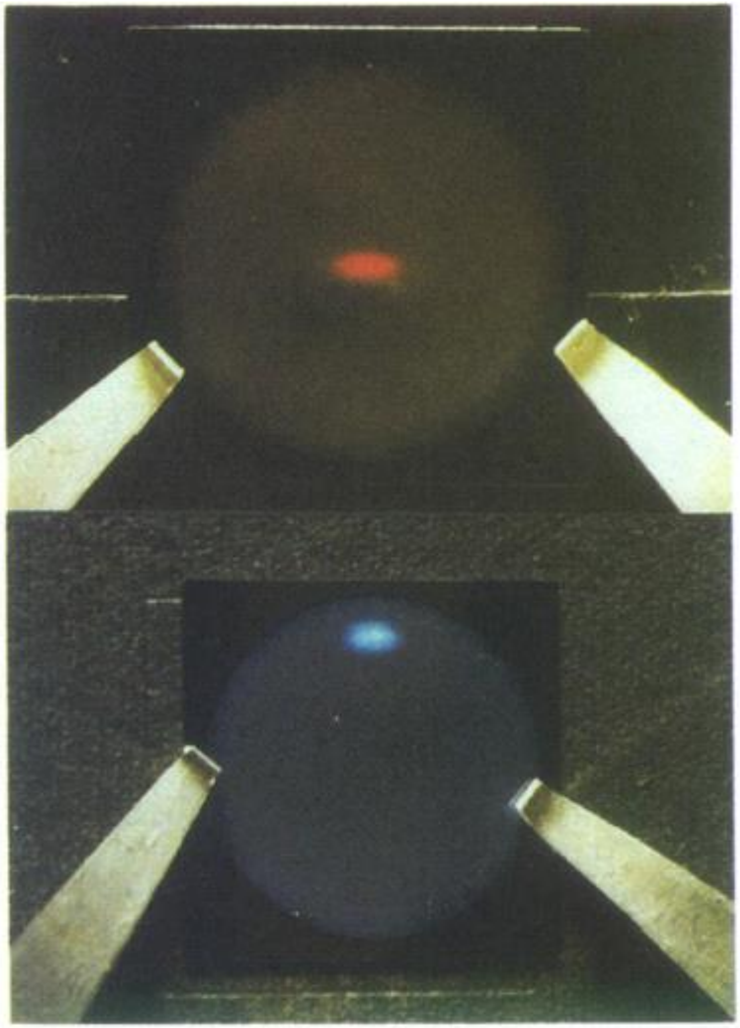


Szedon and Sandor, Appl. Phys. Letters, 6 (1965) 181.
Before and after electron irradiation.
Warren et al, APL, 64 (1994) 3452…
O vacancies are the dominant hole trappping sites.

Si band diagram with hole traps.
Woods and Williams, JAP, 47 (1976) 1082.

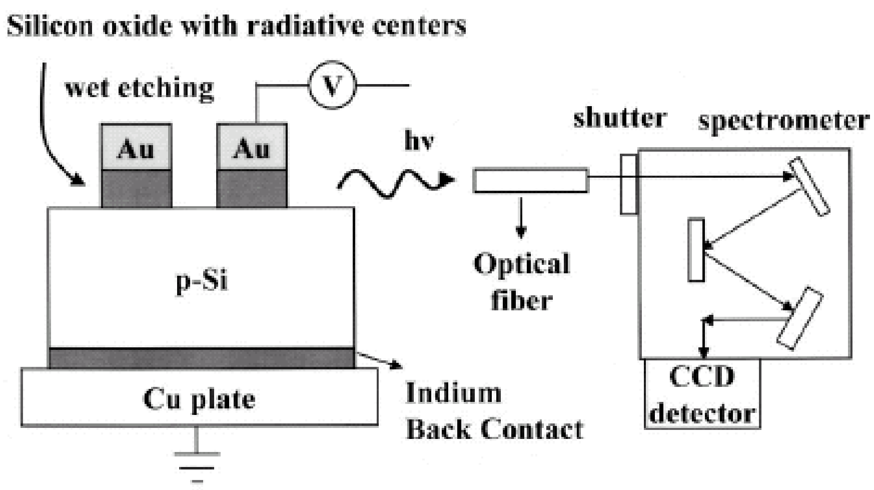
Effect on optical properties



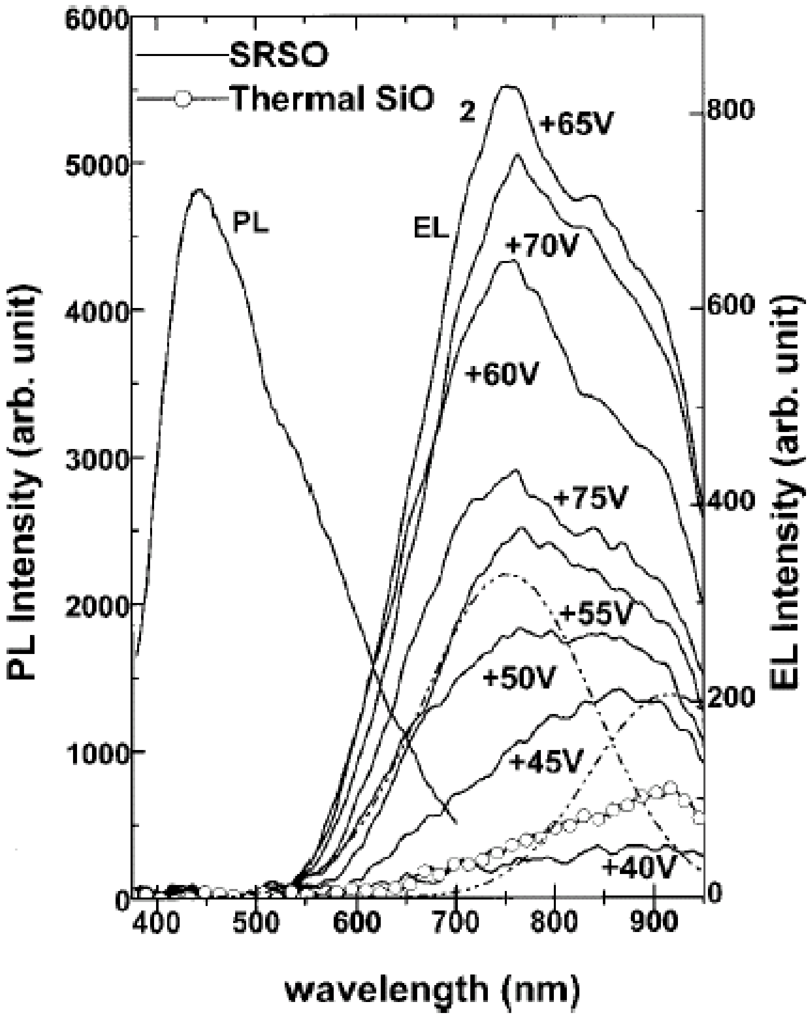


Futagi, Matsumoto and Mimura, Phys. Rev. B 49 (1994) 14732.
PL of oxidized porous Si. Excited with 325 nm. Oxide formed at lower temperature contains OH.

Effect on optical properties



Photoluminescence and electo-Luminescence, $SiO_{1.4}$ film prepared by rf sputtering, heated at 500°C. PL excited with 351 nm. PL: blue and EL:red.



Conclusions

- It is suggested that the linear growth of silica by oxidation of silicon is due to the diffusion and reaction process at the Si/SiO_2. The oxygen vacancies in SiO_{2-x} at the Si/SiO_2 interface work as the oxidant diffusion traps. The slow oxidation rate of nano-silicon and effect of different Si crystalline orientation can be attributed to different oxygen vacancy concentration at the interface.
- Oxygen vacancy influences both optical and electrical properties of Si/SiO_2 systems.

Acknowledgement

Financial support of NSF under contract, DMR-0352773.

We appreciate discussion with Professor R.H. Doremus of Rensselaer Polytechnic Institute