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 $t + \Delta t$

SiO$_2$  Si

SiO$_2$  Si

$\Delta x$  $x$
Oxidation of Silicon

Si is oxidized to form amorphous SiO$_2$ at high temperature in dry (O$_2$) atmosphere or wet (H$_2$O) atmosphere. The oxidation kinetics follows the linear-parabolic law at a constant temperature.

\[ x_0^2 + Ax_0 = B(t + \tau) \]

where \( x_0 \): SiO$_2$ film thickness
\( t \): heat-treatment time; \( \tau \): 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 H₂O) oxidation, \( \tau = 0 \)

Deal and Grove
Traditionally

Linear growth is attributed to the interface reaction-controlled process. Parabolic growth is attributed to diffusion-controlled process. Diffusing species are $\text{H}_2\text{O}$ in wet and $\text{O}_2$ in dry.

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

\[ B = \frac{2D C^*}{N}; \]  
\[ N: \text{number of oxidant in a unit volume of } SiO_2 \text{ (Deal and Grove)} \]  
\[ \text{and } D: \text{Diffusion coefficients} \]
Wet oxidation is faster than dry oxidation even though the diffusion coefficient of water appears smaller than that of oxygen.


Oxidation rate is slower for nano-Si.

Oxidation rate depends upon the orientation of Si crystal.
Oxidation of nano-silicon

SiO\textsubscript{2} film growth rate is slower for smaller silicon particles

Oxidation rate of Si with curved surface

Effect of Si crystal orientation on oxidation rate

Lewis and Irene
(111)>(110)>(100)

Expected water (H$_2$O and OH) diffusion profiles

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

$\text{H}_2\text{O} + \text{SiO}_2 \leftrightarrow \text{2SiOH}$

H$_2$O diffuses and reacts with SiO$_2$ to form SiOH. If the reaction equilibrium holds strictly, H$_2$O and OH (solid line) should have same depth of diffusion. If H$_2$O is not restricted by the equilibrium, it can diffuse deeper.
Diffusion coefficient and solubility

- **Diffusion Coefficient**
  - **D (cm²/sec)**
  - **Molecular diameter (Å)**

- **Solubility**
  - **Solubility (# of mol/cm³)**
  - **Molecular diameter (Å)**
$^{18}\text{O}_2$ diffusion during Si oxidation


Treatment in $^{16}\text{O}_2$ Followed by $^{18}\text{O}_2$

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 SiO$_2$ film
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

\[ y = 0.122 \times x \]

- Wet oxidation, 170 Torr @ 1200 °C
- Wet oxidation, 170 Torr @ 1000 °C
- Step change: 1000 °C to 1200 °C
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 $\rightarrow$ 1.5 in SiO$_x$
Fictive temperature effect on IR silica structural band peak wavenumber

- Absorption data of etched and ion-milled silica film
- Subtracted thin film data of oxide on silicon wafer

- Peak position (cm\(^{-1}\))
- Fictive temperature (°C)

Graph 1: Oxide thickness (nm) vs. Peak position (cm\(^{-1}\))

Graph 2: Fictive temperature (°C) vs. Peak position (cm\(^{-1}\))
Effect of non-stoichiometry on IR silica structural band peak wavenumber

IR peak wavenumber at Si/SiO$_2$ interface


At the interface the composition is estimated to be SiO$_{1.45}$
Si/SiO$_2$ interface structure


Atomistic model based upon experimental data
Three atomic layers average SiO$_{1.46}$ (exp. SiO$_{1.70}$, SiO$_{1.43}$)
Si/SiO$_2$ interface


From medium-energy ion scattering

Iwata and Ishizaka, J. Appl. Phys. 79 (1996) 6653. (from ESCA data)
Si/SiO$_2$ interface structure

Room temperature air, after HF cleaning.
Pulse laser atom probe microanalysis.
Si/SiO$_2$ interface structure

Phase separation of Si/SiO$_2$ (Ge/GeO$_2$) system


Phase Separation of a-SiO

Coherent and Incoherent boundary

After W.D. Callister, Jr. Fundamental of Materials Science And Engineering (2001)
Si/SiO$_2$ interface

Si(001)-SiO$_2$, $\bullet$ : Si, $\bullet$ : O
Effect of coherent energy on phase diagram


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

V: molar volume.
z: mol fraction of one phase
\( \varepsilon \): linear mismatch between phases
Schematic free energy diagram

Coherency strain energy

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\textsubscript{2} or H\textsubscript{2}O) 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\textsubscript{1}.
Flux in the bulk of the film, J\textsubscript{2}.

For thin films, interface flux is important ⇒ a linear growth.
When the film become thicker, bulk flux becomes important ⇒ parabolic growth.
Effect of oxygen vacancy on oxidant diffusion

- Oxygen deficiency $\approx$ Oxygen vacancy $\approx$ Silicon suboxide ($\text{SiO}_x$, $1<x<2$).
- $\text{SiO}_x$ coating on $\text{SiO}_2$ glass can reduce mechanical fatigue of the glass.
- Vacancy annihilation by water diffusion.
- Oxygen vacancies serve as oxidant diffusion traps and diffusion barriers.

Oxygen vacancy annihilation process by oxidants

\[(1/2) \ O_2 + ΞSi - SiΞ \rightleftharpoons ΞSiOSiΞ\]

\[K_1 = \frac{C_{SiOSi}}{(C_{O_2}^{1/2} \ C_V)}\]

\[\frac{\partial C_{O_2}}{\partial t} - \frac{\partial C_V}{\partial t} = \frac{\partial [D_{O_2} \ C]/\partial x]{\partial x}\]

\[H_2O + ΞSi - SiΞ \rightleftharpoons ΞSiOH + HSiΞ\]

\[(SiOH + SiH--> SiOSi + H_2)\]

\[K_2 = \frac{c_{SiHCSiOH}}{C_{H_2O} C_V}\]

\[\frac{\partial C_{H_2O}}{\partial t} + \frac{\partial C_{SiOH}}{\partial t} = \frac{\partial [D_{H_2O} \ C_{H_2O}/\partial x]{\partial x}\]
Oxidant diffusion and reaction

Effective diffusion coefficient,

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

\[ J_1 = J_2 \quad DC_0/(x-\delta) = D_{\text{eff}} \frac{Ci}{\delta} = N \left( \frac{\partial x_0}{\partial t} \right) \]

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

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

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

With \( B = 2D_{O2}C_{O2}/N \)

\( B/A = C_0/\{N \left[ (1/D_{\text{eff}}) - (1/D) \right] \delta \} \approx C_0D_{\text{eff}}/(N \delta) \)

Similar equations for wet (H\(_2\)O) oxidation.
Effect on electrical properties


Effect on electrical properties

Before and after electron irradiation.
Warren et al, APL, 64 (1994) 3452…
O vacancies are the dominant hole trapping sites.

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

PL of oxidized porous Si. Excited with 325 nm. Oxide formed at lower temperature contains OH.
Photoluminescence and electroluminescence, SiO$_{1.4}$ film prepared by rf sputtering, heated at 500ºC. 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.
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