

Lecture 12

Mechanisms of Oxidation and Corrosion

12.1 Surface and Interface reactions in oxidation of metals

- thermal oxidation

12.2 Thermal oxidation of Si: Deal-Grove

12.3 Diffusion in metal oxide thin films

12.4 Corrosion (anodic oxidation)

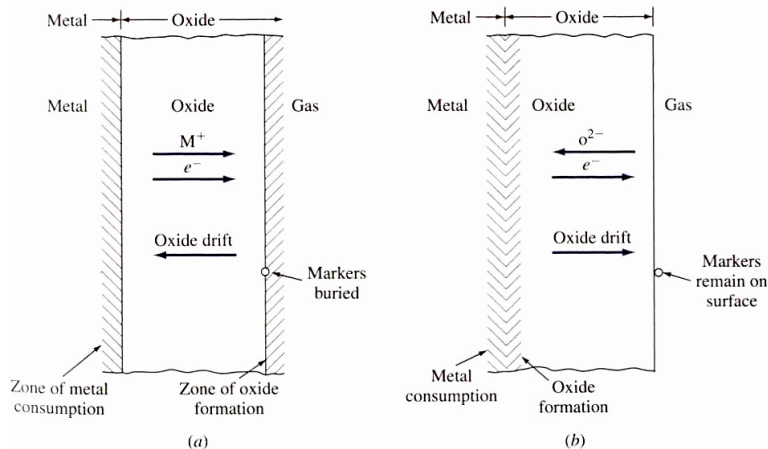
- thermodynamics
- kinetics

References:

- 1) Zangwill, p.104-109
- 2) S.A. Campbell, The Science and Engineering of Microelectronic Fabrication, 1995
- 3) B. E. Deal and A. S. Grove, J. Appl. Phys., 36 (1965) 3770
- 4) C.Y. Chang, S.M. Sze, VLSI Technology, McGraw Hill

1

12.1 Mechanisms of Oxidation



- When cations diffuse, the initially formed oxide drifts towards the metal
- When anions diffuse, the oxide drifts in the opposite direction

2

Microscopic oxidation pathways

TABLE II. Activation energy Q and pre-exponential factor D_0 for oxygen and cation (self-)diffusion in metal oxides. Data are given for volume diffusion D_V , unless D_B is stated to indicate interface diffusion. T_m = melting temperature.

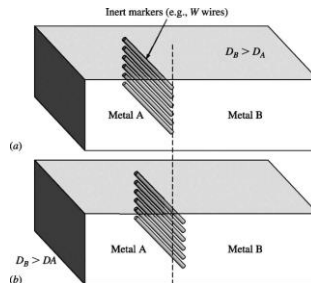
Diffuser	Substrate	Q [eV]	D_0 [m ² /s]	Reference
Oxygen self-diffusion				
¹⁶ O	m-ZrO ₂	D_V 2.29	2.5×10^{-7}	a
¹⁶ O	m-ZrO ₂	D_B 1.95	3.3×10^{-5}	a
¹⁶ O	m-ZrO ₂	2.41	9.73×10^{-7}	c
¹⁶ O	m-ZrO ₂	1.96	2.34×10^{-6}	d
¹⁶ O	Ca(14 mol %)-ZrO ₂	1.35	1.8×10^{-6}	e
¹⁶ O	Y(2.8 mol %)-ZrO ₂	1.24	1.55×10^{-6}	g
¹⁶ O	Y(16 mol %)-ZrO ₂			f
¹⁶ O	Y(9.5 mol %)-ZrO ₂	0.89	1.1×10^{-7}	h
¹⁶ O	n-TiO ₂	D_B 1.5	1.4×10^{-8}	b
¹⁶ O	c-TiO ₂	D_V 2.47	2.0×10^{-7}	r
¹⁶ O	NiO	5.6	5×10^{-3}	u
¹⁶ O	MgO	3.84	1.9×10^{-3}	s
¹⁶ O	MgO	5.55	6.76×10^{-4}	t
¹⁶ O	Al ₂ O ₃	D_V 6.89	5.62×10^{-3}	u
¹⁶ O	Al ₂ O ₃	D_V 6.59	2.06×10^{-3}	o
¹⁶ O	Al ₂ O ₃	D_B 9.54	1.6×10^{22}	p
Cation diffusion				
Ca	Ca(16 mol %)-ZrO ₂	4.34	4.4×10^{-5}	i
Zr	Ca(16 mol %)-ZrO ₂	4.01	3.5×10^{-6}	j
Zr/Y	Y(9.4 mol %)-ZrO ₂	5.3	1.4×10^{-3}	j
Zr/Y	Y(18 mol %)-ZrO ₂	5.3	9.6×10^{-3}	j
Zr	Y-ZrO ₂	4.4	1.5×10^{-5}	v
Zr	Y(9.5 mol %)-ZrO ₂	4.78	9.3×10^{-6}	h
Y	Y(9.5 mol %)-ZrO ₂	4.79	2.5×10^{-5}	h
Zr	Y(8-32 mol %)-ZrO ₂	4.4-5.1	$10^{-6}-10^{-4}$	k
Ca	Y(8-32 mol %)-ZrO ₂	≥ 5.0		k
Al	Al ₂ O ₃	D_V 5.29	1.6×10^{-3}	q
Al	Al ₂ O ₃	D_B 8.81	1.3×10^{10}	q
Mg	MgO	3.46	7.43×10^{-6}	w
Mg	MgO	3.43	2.5×10^{-5}	x
Ni	NiO	D_B 1.78	4.3×10^{-5}	y
Ni	NiO	D_V 2.56	2.2×10^{-6}	m
Ti	TiO ₂	$D_{B,c}$ 2.86	6.5×10^{-4}	l
Ti	TiO ₂	$D_{B,c}$ 2.52	2.0×10^{-6}	l
Ti	TiO ₂	$D_{B,L,c}$ 2.12	2.2×10^{-6}	l

J. Appl. Phys. 85 (1999) 7646

3

Kirkendall effect

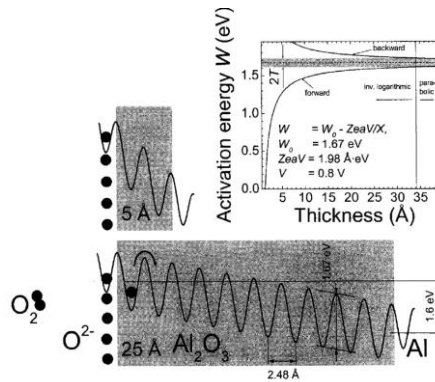
- Marker at the diffusion interface move slightly in the opposite direction to the most rapidly moving species \Rightarrow vacancies can move!



4

Diagram of potential energy maps for O²⁻

- There is thickness dependence of activation energy for ionic transport in the opposite directions

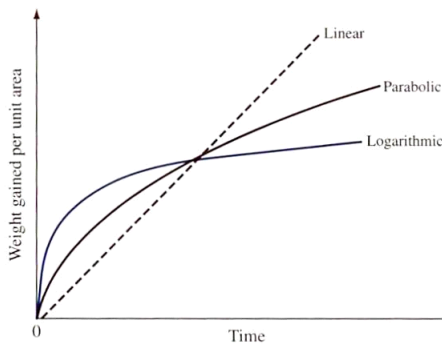


Aside: Electrochemical oxidation of Al (Presentation 2)

7

Oxidation Rate (Kinetics)

- During the oxidation of different metals, various empirical rate laws have been observed



w – weight gain per unit area; or oxide thickness

• Linear law: $w = k_L t$

Typical for metals with porous or cracked oxide films (\Rightarrow transport of reactant ions occurs at faster rates than the chemical reaction), e.g., K, Ta

• Parabolic law: $w^2 = k_p t + C$

Typical for metals with thick coherent oxides, e.g. Cu, Fe

• Logarithmic rate: $w = k_e \log(Ct + A)$

For oxidation at elevated temperature, e.g., Fe, Cu, Al; fast oxidation at the start, the rate decreases to a very low value

• Catastrophic at high T: rapid exothermal reactions, oxides are volatile, e.g. Mo, W, V

8

Oxidation of metals

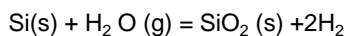
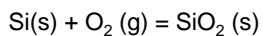
Protective oxide films:

1. The volume ratio of oxide to metal after oxidation should be close to 1:1
or Pilling-Bedworth ratio = 1 (ration of oxide volume produced by oxidation to the volume of metal consumed by oxidation)
2. The oxide film should have good adherence, high-temperature plasticity to prevent fracture
3. The melting point of the oxide should be high
4. The oxide films should have a low vapor pressure and thermal coefficient of expansion comparable to the one of the metal
5. Low conductivity and low diffusion coefficient for metal ions and oxygen are desired

9

12.2 Thermal oxidation of silicon

Si grows a high quality oxide



10

Oxide growth calculator

Important parameters:

- initial SiO₂ thickness
- temperature (700-1200°C)
- Si crystal orientation
- Wet or dry environment

Examples: Initial SiO₂ thickness – 25Å, 1000°C, Si(001), Dry O₂

⇒ **400Å in 1 hour**

initial SiO₂ thickness – 10Å, 1000°C, Si(111), Wet O₂

⇒ **~4500Å in 1 hour**

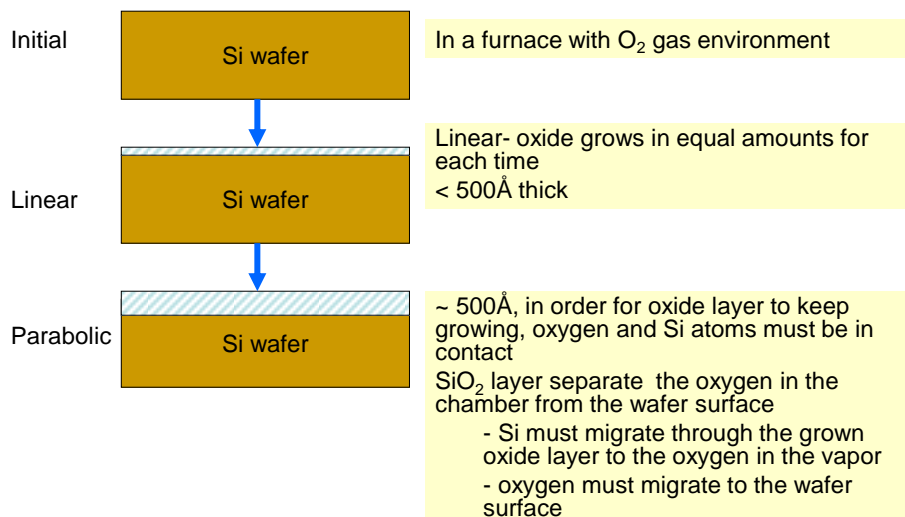
initial SiO₂ thickness – 10Å, 1000°C, Si(100), Wet O₂

⇒ **~3870Å in 1 hour**

- <http://www.cleanroom.byu.edu/OxideThickCalc.phtml>

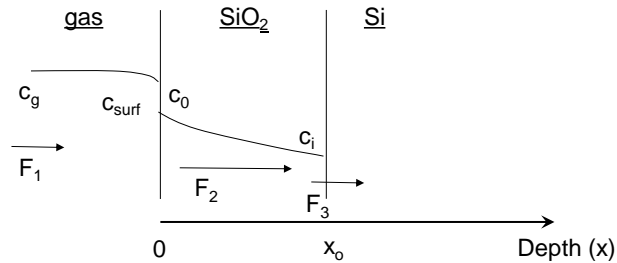
11

SiO₂ growth stages



Thermal oxidation of silicon

- Diffusivity of Si in SiO₂ much smaller than that of O₂
- ⇒ molecular O₂ diffusion
- (opposite to metal oxidation or anodic oxidation of Si, in which cations moves out to surface)



F₁ – incident flux to surface; $F_1 = h_g (C_g - C_s)$ h_g – mass transfer coefficient

F₂ – flux through the oxide; F₃ – reaction flux of oxide growth at interface

13

Deal-Grove model

Recall: from ideal gas law, $C_g = p_g / kT$

Henry's law: $C_0 = H p_s$

$F_1 = h(C^* - C_0)$, where $h = h_g / HkT$

$F_2 = D(O_2) [(C_0 - C_i) / x_0]$ (from Fick's law)

If we let rate at interface be proportional to concentration of oxidant at the SiO₂/Si interface, then:

$F_2 = k_s C_i$

Assuming **steady state approximation**: $F_1 = F_2 = F_3$

$h(C^* - C_0) = D(O_2) [(C_0 - C_i) / x_0] = k_s C_i$

... algebra then, solve for concentration at the interface...

$$C_i = \frac{C^*}{1 + \frac{k_s}{h} + \frac{k_s x_0}{D}}; \quad C_0 = \frac{C^* \left(1 + \frac{k_s x_0}{D}\right)}{1 + \frac{k_s}{h} + \frac{k_s x_0}{D}}$$

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

14

Deal-Grove model (linear-parabolic regime)

Rate of growth $\frac{dx}{dt} = \frac{F_3}{N}$, where N is the number of oxygen atoms incorporated per unit volume ($2.2 \times 10^{22} \text{ cm}^{-3}$ for SiO_2)

$$\frac{dx}{dt} = \frac{F_3}{N} = \frac{Hk_s p_g}{N \left(1 + \frac{k_s}{h} + \frac{k_s x_o}{D} \right)}$$

for $x_0 = x(t=0)$ solution is

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

$$A = 2D \left(\frac{1}{k_s} + \frac{1}{h} \right); B = \frac{2DC^*}{N}; \tau = \frac{x_0^2 + Ax_0}{B}$$

For very thin oxides, we can neglect quadratic term, and we have :

$$x_0 \approx \frac{B}{A}(t + \tau) \quad \text{linear regime}$$

For thick oxides

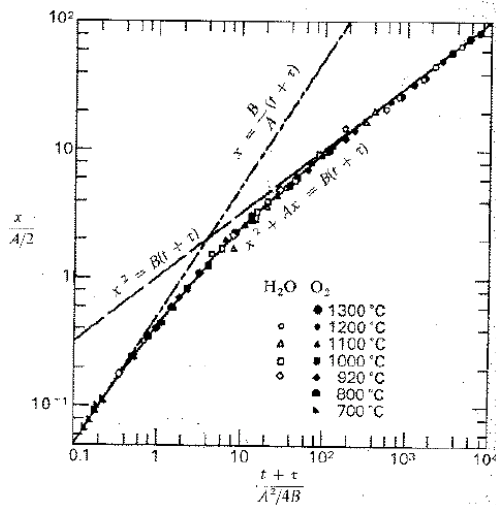
$$x_0^2 \approx B(t + \tau) \quad \text{parabolic regime}$$

15

Deal-Grove Model

Physical significance of 2 regimes:

- in linear regime for thin films, the oxidant concentration is assumed constant throughout the system, $C_0 \sim C_1$, rate is controlled by interface (surface) reaction;
- in the parabolic (thick film) regime, $C_1 \rightarrow 0$, and $C_0 \sim C^*$; and $B \propto D$, and diffusion through the oxide dominates growth kinetics



16

Problems with DG model:

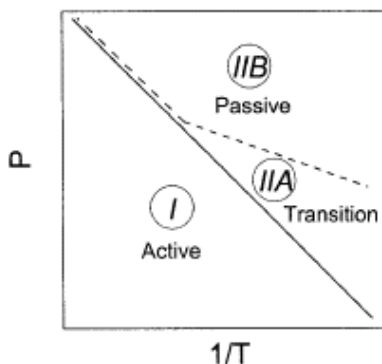
- Steady state growth?
- Interface growth assumes first order gas phase type reaction, why?
- What is the true O_2 profile?
- Is the interface a sharp well-phase-segregated plane (strain in Si, suboxides, roughness?)
- No good physical interpretation of accelerated initial growth
- Ions, radicals, surface reaction/exchange?

17

The role of SiO formation during the SiO_2 growth

Overall reaction route is dependent on the oxygen (water) pressure and temperature used

- at low T, high $p_{O_2} \Rightarrow Si(s) + O_2(g) = SiO_2(s)$ - "passive" oxidation regime
- at high T, low $p_{O_2} \Rightarrow Si(s) + O_2(g) = 2SiO(g)$ - "active" oxidation



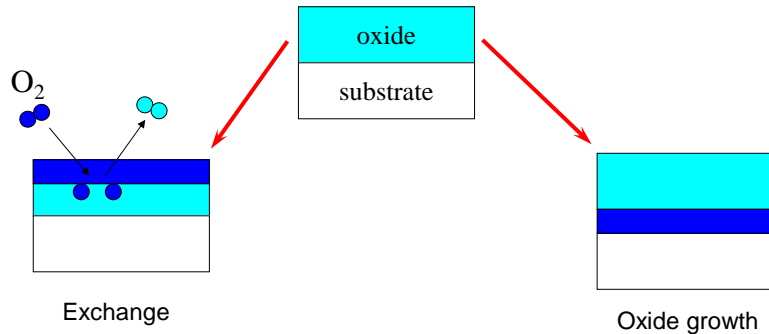
Starodub D. Surf. Rev. Lett. 6 (1999) 45-52

18

Oxygen reactions with oxide films

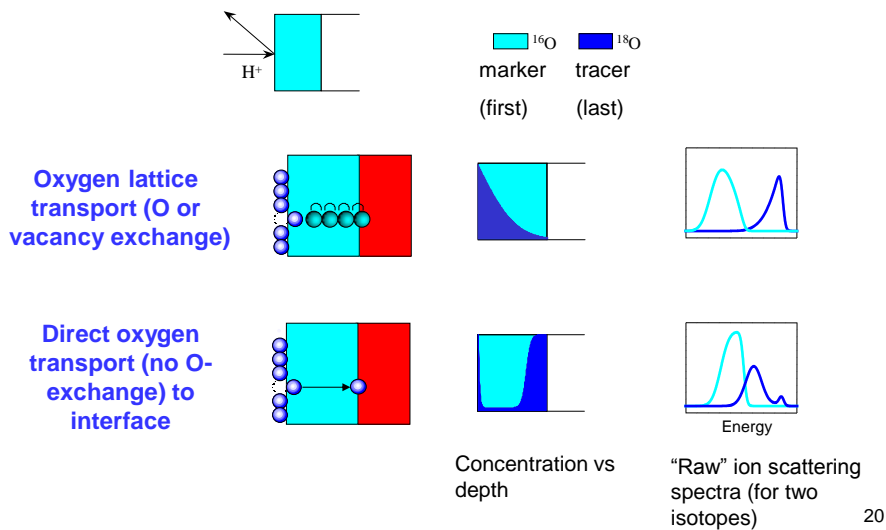
Some possible types of reactions:

- (i) exchange without a change in total oxygen concentration
- (ii) Oxide growth with additional O incorporation



19

Oxygen transport mechanisms examined by ion scattering and isotopes



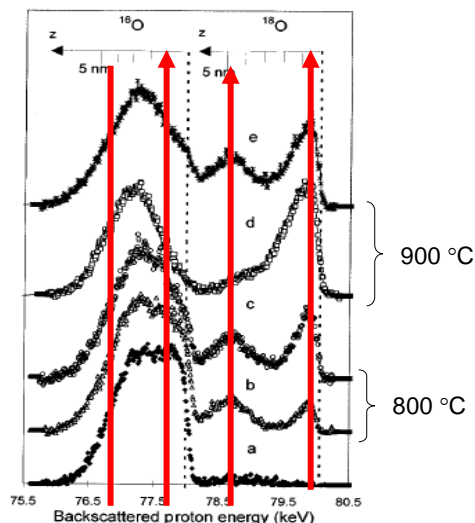
20

Oxygen isotope experiments: SiO₂ growth mode

Q: Why use isotopes?

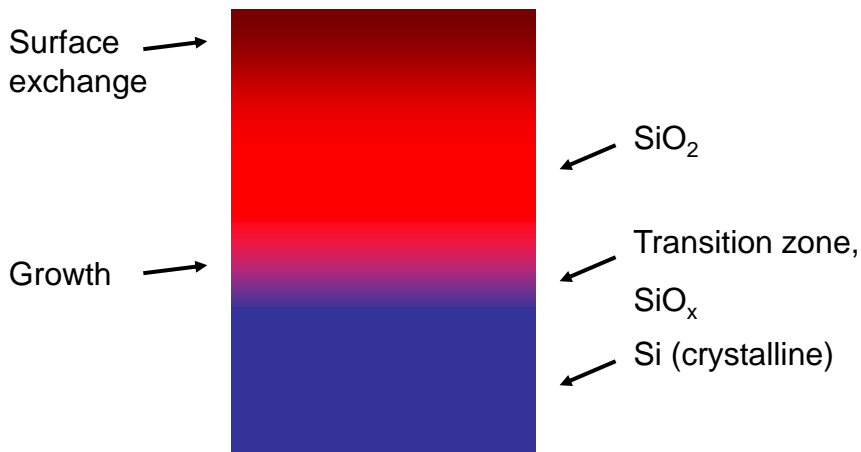
A: To study processes, not just structures!!

1. ¹⁸O uptake at the surface!
2. Growth at the interface
3. ¹⁶O loss at the surface
4. ¹⁶O movement at the interface!



Gusev, Lu, Gustafsson, Garfunkel, PRB 52, 1759 (1995)

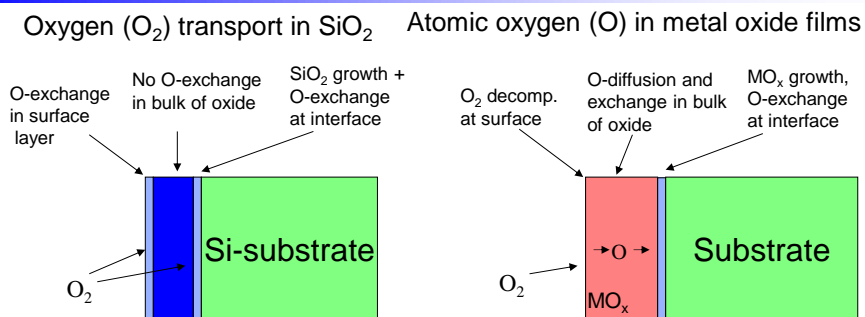
Schematic model for ultra-thin films



Deal and Grove

22

12.3 Diffusion in metal oxide thin films



SiO_2 films:

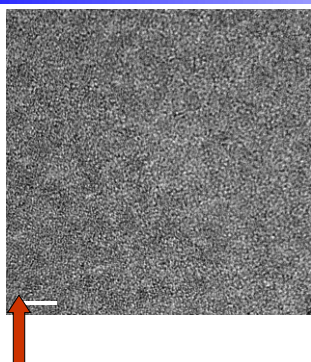
- amorphous after annealing
- molecular O_2 transport in SiO_2
- decomposition by SiO desorption

(Many) transition metal and lanthanide films:

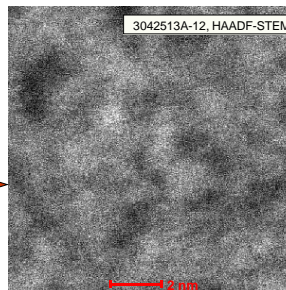
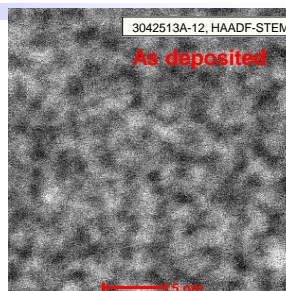
- tend to crystallize at low T
- high oxygen mobility

23

Plan-view HRTEM and HAADF-STEM



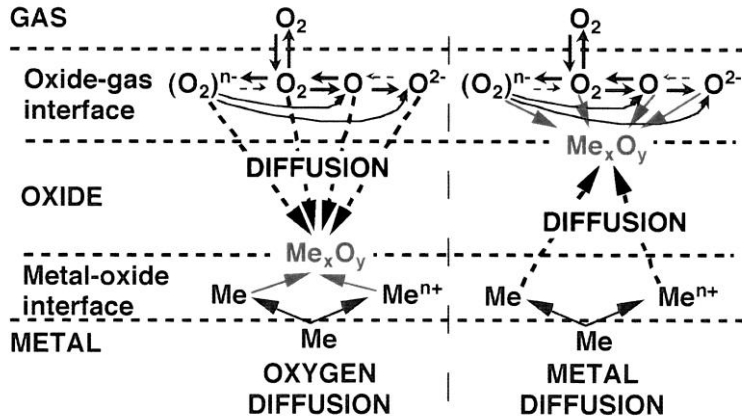
$ZrO_2/Si(001)$



HRTEM shows no discrete crystallization, though some regions do show lower-ordering structure

HAADF-STEM shows density variations suggestive of either roughening or partial phase-separation

Elementary steps during metal oxidation



25

Microscopic oxidation pathways

TABLE II. Activation energy Q and pre-exponential factor D_0 for oxygen and cation (self-)diffusion in metal oxides. Data are given for volume diffusion D_V , unless D_S is stated to indicate interface diffusion. T_m = melting temperature.

Diffusor	Substrate		Q [eV]	D_0 [m ² /s]	Reference
Oxygen self-diffusion					
¹⁶ O	<i>m</i> -ZrO ₂	D_V	2.29	2.5×10^{-7}	a
¹⁸ O	<i>m</i> -ZrO ₂	D_V	1.95	3.3×10^{-5}	a
¹⁶ O	<i>m</i> -ZrO ₂		2.41	9.73×10^{-7}	c
¹⁶ O	<i>m</i> -ZrO ₂		1.96	2.34×10^{-6}	d
¹⁶ O	Ca(14 mol %)-ZrO ₂		1.35	1.8×10^{-6}	e
¹⁶ O	Y(2.8 mol %)-ZrO ₂		1.24	1.55×10^{-6}	g
¹⁶ O	Y(16 mol %)-ZrO ₂		0.89	1.1×10^{-7}	h
¹⁶ O	Y(9.5 mol %)-ZrO ₂		0.89	1.4×10^{-8}	h
¹⁶ O	<i>n</i> -TiO ₂	D_S	1.5	1.4×10^{-11}	b
¹⁶ O	<i>c</i> -TiO ₂	D_V	2.47	2.0×10^{-7}	r
¹⁶ O	NiO		5.6	5×10^{-8}	u
¹⁶ O	MgO		3.84	1.9×10^{-8}	s
¹⁶ O	MgO		5.55	6.76×10^{-4}	t
¹⁶ O	Al ₂ O ₃	D_V	6.89	5.62×10^{-2}	u
¹⁶ O	Al ₂ O ₃	D_V	6.59	2.06×10^{-2}	o
¹⁶ O	Al ₂ O ₃	D_S	9.54	1.6×10^{23}	p
Cation diffusion					
Ca	Ca(16 mol %)-ZrO ₂		4.34	4.4×10^{-5}	i
Zr	Ca(16 mol %)-ZrO ₂		4.01	3.5×10^{-6}	i
Zr/Y	Y(9.4 mol %)-ZrO ₂		5.3	1.4×10^{-3}	j
Zr/Y	Y(18 mol %)-ZrO ₂		5.3	9.6×10^{-3}	j
Zr	Y-ZrO ₂		4.4	1.5×10^{-3}	v
Zr	Y(9.5 mol %)-ZrO ₂		4.78	9.3×10^{-6}	h
Y	Y(9.5 mol %)-ZrO ₂		4.79	2.5×10^{-5}	h
Zr	Y(8-32 mol %)-ZrO ₂		4.4-5.1	$10^{-6}-10^{-4}$	k
Ca	Y(8-32 mol %)-ZrO ₂		>5.0		k
Al	Al ₂ O ₃	D_V	5.29	1.6×10^{-5}	q
Al	Al ₂ O ₃	D_S	8.81	1.3×10^{10}	q
Mg	MgO		3.46	7.43×10^{-6}	w
Mg	MgO		3.43	2.5×10^{-5}	x
Ni	NiO	D_S	1.78	4.3×10^{-5}	y
Ni	NiO	D_V	2.56	2.2×10^{-6}	m
Ti	TiO ₂	$D_{ c}$	2.86	6.5×10^{-4}	l
Ti	TiO ₂	$D_{\perp c}$	2.52	2.0×10^{-6}	l
Ti	TiO ₂	$D_{\perp Lc}$	2.12	2.2×10^{-6}	l

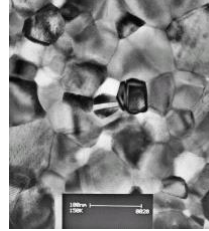
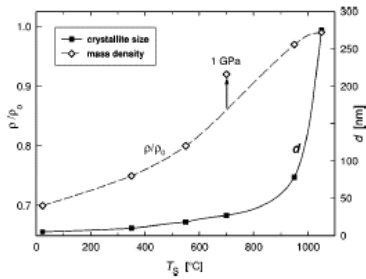
J. Appl. Phys. 85 (1999) 7646

26

Oxygen diffusion in ultrafine grained monoclinic ZrO₂

Objective: find the difference in diffusivities of O in crystalline ZrO₂ and grain-boundary region

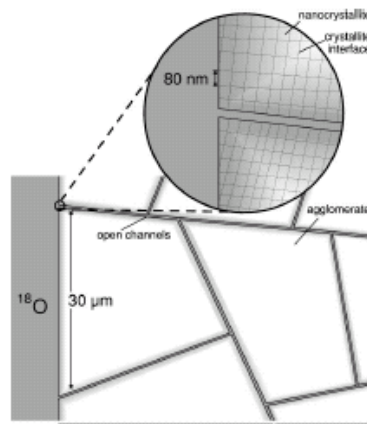
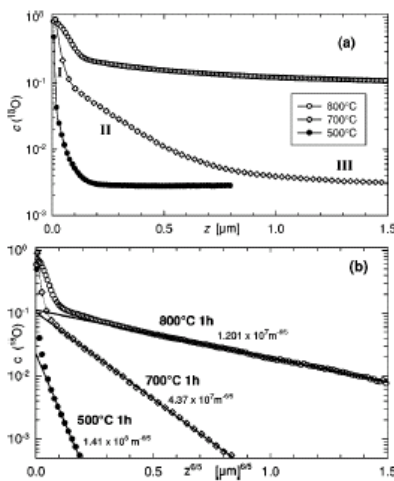
- prepare samples with different grain-to-grain boundary ratio,
- analyze by SIMS



J. Appl. Phys. 85 (1999) 7646

27

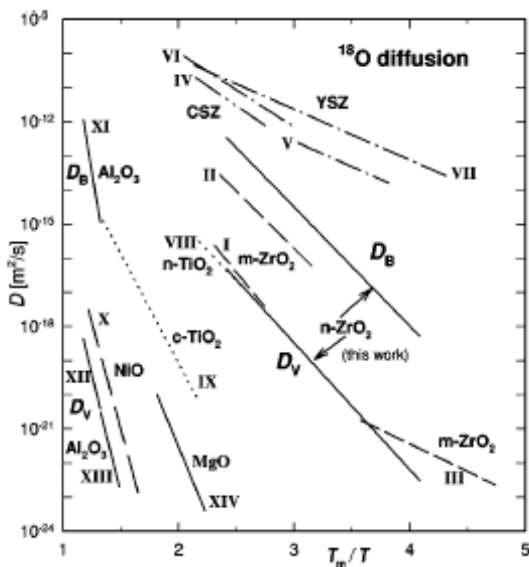
¹⁸O profiles in crystalline ZrO₂



- $D_v = 2.5 \times 10^{-7} \text{ m}^2/\text{s}$;
- $D_b = 3.3 \times 10^{-5} \text{ m}^2/\text{s}$;

28

Comparison of ^{18}O diffusion in metal oxides



J. Appl. Phys. 85 (1999) 7646

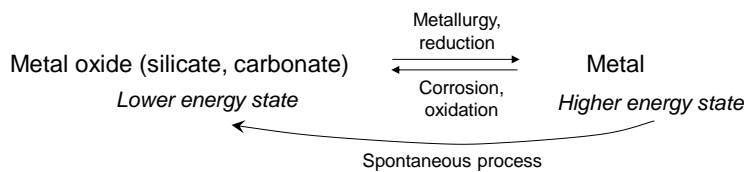
29

12.4 Corrosion

Corrosion is the deterioration of a material resulting from chemical reaction with its environment

- temperature, pressure
- concentration of the reactions and products
- mechanical stress and erosion

Can be regarded as reverse extractive metallurgy

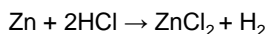


Metals: electrochemical process

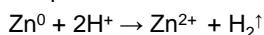
Nonmetals: direct chemical reaction (with salts, water, organic solvents, oxygen plus UV)

30

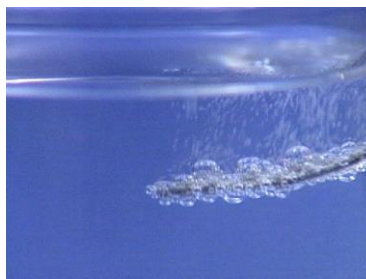
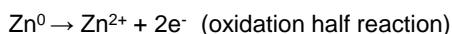
Oxidation Reduction Reactions of Metals



Simplified ionic form:



Two "half reactions":



1. **Oxidation reaction:** metals form ions that go into aqueous solution, also called the **anodic reaction**; electrons are produced and remain in the metal

2. **Reduction reaction:** metals or nonmetals consume electrons and they are reduced into zero-charge state, also called the **cathodic reaction**

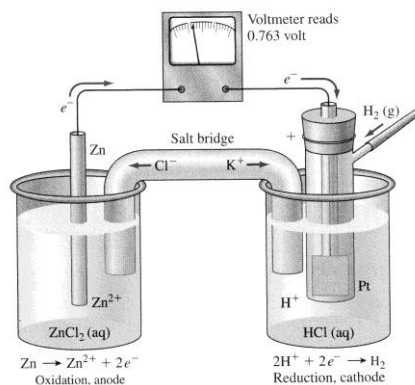
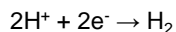
Both oxidation and reduction reactions must occur at the same time

31

Standard Electrode Half-Cell Potential for Metals

- Every metal has a different tendency to corrode in a particular environment
- **Standard Electrode Half-Cell Potential** for metals gives a universal way to compare the tendency for metals to form ions
 - if the potential is negative, metal oxidizes to ions
 - If the potential is positive, less tendency to corrode
 - measured against "standard hydrogen electrode"

Assign 0V to the reaction:



2

Standard electrode potentials at 25°

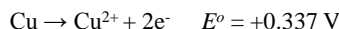
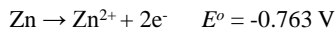
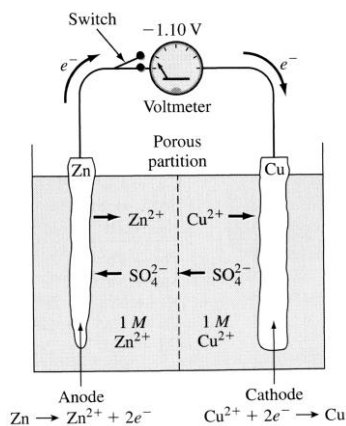
	Oxidation (corrosion) reaction	Electrode potential (E°) (volts versus standard hydrogen electrode)
↑ More cathodic (less tendency to corrode)	$\text{Au} \rightarrow \text{Au}^{3+} + 3e^-$	+ 1.498
	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$	+ 1.229
	$\text{Pt} \rightarrow \text{Pt}^{2+} + 2e^-$	+ 1.200
	$\text{Ag} \rightarrow \text{Ag}^+ + e^-$	+ 0.799
	$2\text{Hg} \rightarrow \text{Hg}_2^{2+} + 2e^-$	+ 0.788
	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$	+ 0.771
	$4(\text{OH})^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^-$	+ 0.401
	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$	+ 0.337
	$\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e^-$	+ 0.150
	$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$	0.000
↓ More anodic (greater tendency to corrode)	$\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$	- 0.126
	$\text{Sn} \rightarrow \text{Sn}^{2+} + 2e^-$	- 0.136
	$\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$	- 0.250
	$\text{Co} \rightarrow \text{Co}^{2+} + 2e^-$	- 0.277
	$\text{Cd} \rightarrow \text{Cd}^{2+} + 2e^-$	- 0.403
	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$	- 0.440
	$\text{Cr} \rightarrow \text{Cr}^{3+} + 3e^-$	- 0.744
	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$	- 0.763
	$\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$	- 1.662
	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$	- 2.363
$\text{Na} \rightarrow \text{Na}^+ + e^-$	- 2.714	

*Reactions are written as anodic half-cells. The more negative the half-cell reaction, the more anodic is the reaction and the greater the tendency for corrosion or oxidation to occur.

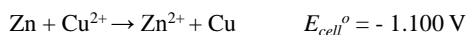
33

Galvanic cells

- Galvanic couple (cell):** is constructed with two dissimilar metal electrodes each immersed in a solution of their own ions, and separated by a porous wall (membrane) to prevent their mechanical mixing and an external wire to connect the two electrodes



Overall reaction:



Recall: Nernst equation connects half-cell reaction potentials with the metal ion concentrations

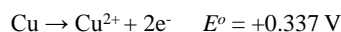
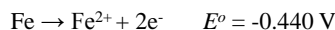
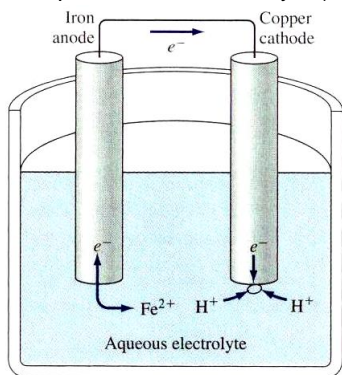
$$E = E^\circ + \frac{0.0592}{n} \log C_{ion}$$

where C_{ion} is molar concentration of ions

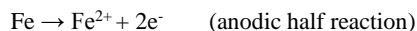
34

Galvanic Cells with NO metal ions present

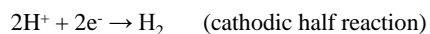
Consider a galvanic cell in which Fe and Cu electrodes are immersed in an aqueous acidic electrolyte (no metals ions present)



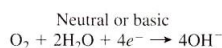
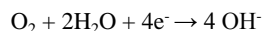
Fe has the more negative half-cell potential, will oxidize



If acidic:



If neutral or basic solution:



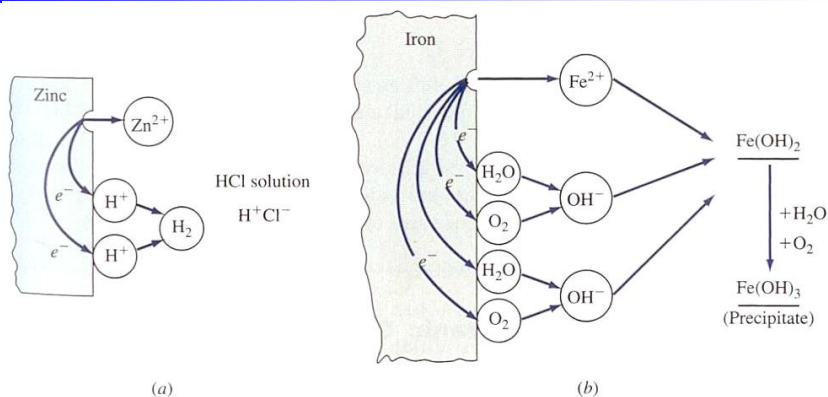
35

Common cathode reactions for aqueous galvanic cells

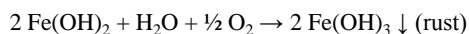
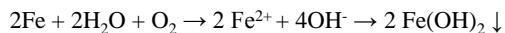
Cathode reaction	Example
1. Metal deposition: $\text{M}^{n+} + ne^- \rightarrow \text{M}$	Fe-Cu galvanic couple in aqueous solution with Cu^{2+} ions; $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$
2. Hydrogen evolution: $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	Fe-Cu galvanic couple in acid solution with no copper ions present
3. Oxygen reduction (acid solutions): $\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$	Fe-Cu galvanic couple in oxidizing acidic solution with no copper ions present
4. Oxygen reduction (neutral or basic solutions): $\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$	Fe-Cu galvanic couple in neutral or alkaline solution with no copper ions present

36

Microscopic Galvanic Cell Corrosion



Electrochemical reactions for (a) Zn in dilute hydrochloric acid; (b) Fe immersed in oxygenated neutral water solution (**rusting of iron**)



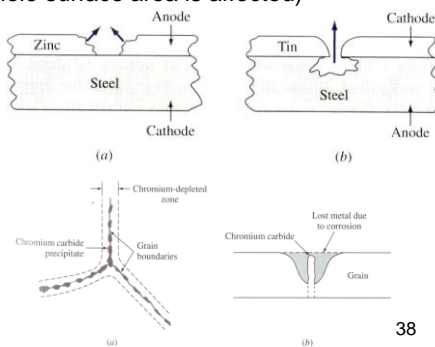
37

Galvanic Cells created by differences in Composition, Structure, and Stress

1. Grain – grain-boundary galvanic cell (grain boundaries are typically more chemically active (anodic) than the grain matrix)
2. Multiple-phase galvanic cells (e.g. Fe and Fe₃C in gray cast iron)
3. Impurity cells (higher corrosion resistance for purer metals)

Types of corrosion

- Uniform chemical attack corrosion (whole surface area is affected)
- Galvanic or two-metal pair corrosion
- Pitting and perforation
- Intergranular
- Stress and Erosion
- Cavitation
- Selective leaching or dealloying



38

Corrosion Rate (Kinetics)

- So far we discussed equilibrium conditions and thermodynamic tendencies of metals to corrode
- Corroding systems are not at equilibrium

Kinetics - Faraday's equation (electrochemistry)

$$w = \frac{ItM}{nF} = \frac{iAtM}{nF};$$

where w is weight of corroded or electroplated metal in time t ;

I = current flow, A; M = atomic mass of the metal, g/mol;

n = number of electrons produced or consumed, $F = 96500\text{C/mol}$;

i = current density, A/cm²; A = area of electrode, cm²

How to measure corrosion rate:

- a weight loss per unit area;
- change in thickness of material per unit time;
- as a current density

39

Acceleration of Corrosion

- Physical Characteristics
 - exposed area (less, increases corrosion rate)
 - time of exposure (more time, more corrosion)
- Environmental Characteristics
 - acidic environment
 - sulfur gas environment
 - temperature (high temps, more corrosion)
 - moisture (oxygenated moisture)

40

Passivation

- A protective film in oxidizing atmospheres
 - chromium, nickel, titanium, aluminum
- Metal oxide layer adheres to parent metal
 - barrier against further damage
 - self-healing if scratched
- Sensitive to environmental conditions
 - passivated metal may have high corrosion rates

41

Corrosion Prevention

- Coatings
- Barrier films
- Inhibitive pigments
- Sacrificial treatments
- Paint
- Active cathodic protection

42