

Contents

1	Introduction	1
2	Principles of Reaction Kinetics	5
2.1	Equilibria of Chemical Reactions	6
2.2	Structure of Reaction Models	9
2.2.1	Reaction Partial Steps	10
2.2.2	Rate Equations of Partial Reactions	10
2.2.3	Combining the Partial Steps	12
2.2.4	Mathematical Solution of the Problem	12
2.2.5	Steady-State Conception	13
2.2.6	Rate Determining Step	13
2.2.7	Concluding Remarks	14
2.3	Characteristics of Reaction Partial Steps	15
2.3.1	Molecular Adsorption or Physisorption	15
2.3.2	Chemisorption	18
2.3.3	Formation of Lattice Defects	22
2.3.4	Formation of the Reaction Product	23
2.3.5	Diffusion Processes	23
2.3.6	Electronic Currents	25
2.3.7	Ionic Fluxes	26
2.3.8	Initial Stage of Oxidation	26
3	Experimental Techniques	28
3.1	Initial State of Metal Surfaces and UHV Experiments	28
3.2	Volumetric and Manometric Methods	29
3.3	Quartz Crystal Microbalance	31
3.4	Ellipsometry	32
3.5	Energetic Ion Scattering	33
3.5.1	Rutherford Backscattering Spectroscopy	34
3.5.2	Elastic Recoil Detection Analysis	35
3.5.3	Nuclear Reaction Analysis	36
3.6	X-Ray Reflectivity	38
3.7	Surface-Analytical Methods	39
4	Hydrogen Reactions	41
4.1	Experimental Results	42
4.1.1	Metal-Hydrogen Systems	42
4.1.2	Hydrogen Solution in Metals	45
4.1.3	Hydride Formation	47
4.2	Hydrogen Solution in Metals	51
4.2.1	Reaction Mechanism, Partial Steps	51

4.2.2	Transport of H ₂ Molecules in the Gas Phase	52
4.2.3	Desorption of Physisorbed Molecules	53
4.2.4	Dissociation of Physisorbed H ₂ Molecules	53
4.2.5	Recombination and Desorption of Chemisorbed Hydrogen Atoms	54
4.2.6	Surface Penetration, Forward Reaction	55
4.2.7	Surface Penetration, Backward Reaction	56
4.2.8	Diffusion in the Metal Phase	56
4.3	Hydride Formation	57
4.3.1	Reaction Mechanism, Partial Steps	57
4.3.2	Physisorption and Chemisorption	58
4.3.3	Transition from Chemisorption to the Hydride Subsurface	58
4.3.4	Diffusion in the Hydride Phase	59
4.3.5	Formation of the Hydride Phase	62
4.4	Computer Simulation of Advanced Models	63
4.4.1	Structure of the Model	64
4.4.2	Procedure of the Numeric Solution	67
4.4.3	Discussion of Results for Absorption	70
4.4.4	Conclusions	74
4.4.5	Desorption	74
5	Low-Temperature Oxidation	78
5.1	Experimental Results	79
5.2	Rate Laws Proposed in the Literature	82
5.2.1	Parabolic Law	83
5.2.2	Inverse Logarithmic Law	83
5.2.3	Linear Law	83
5.2.4	Logarithmic Law	84
5.3	Partial Steps of the Oxidation Reaction	84
5.3.1	Reaction Mechanisms	84
5.3.2	Charge Distribution and Electric Fields	85
5.3.3	Reactions at the Metal/Oxide Interface	87
5.3.4	Reactions at the Oxide Surface	87
5.4	Relations and Constants Used in Model Calculations	88
5.4.1	Equation of Continuity	88
5.4.2	Steady-State Condition	89
5.4.3	Principle of Coupled Currents	89
5.4.4	Structure of the Models	91
5.4.5	Numerical Procedures	91
5.5	Example of a Model Considering Space Charges	92
5.5.1	Equilibria of the Interface Reactions	93
5.5.2	Ion Currents	93
5.5.3	Electronic Currents	93
5.5.4	Mathematical Treatment	94
5.6	Models Neglecting Space Charges	95
5.6.1	Ion Current in the Homogeneous Field	95
5.6.2	Electrostatic Phenomena	95
5.6.3	Surface Penetration	96

5.6.4	Configuration of the Models	96
5.7	Detailed Presentation of a Model with Metal Interstitials as Mobile Defects	98
5.7.1	Equilibrium and Rate Equations	98
5.7.2	Surface Charges	99
5.7.3	The Potential V Across the Layer	100
5.7.4	Calculation of Concentrations, Currents, and the Oxide Growth Curve	100
5.7.5	Standard Oxide Growth Curve	100
5.7.6	Concentration of Reacting Species and Partial Fluxes	102
5.8	Results of Model Calculations, Parameter Variations	103
5.8.1	Effective Charge of Metal Interstitials	103
5.8.2	Ion Current	104
5.8.3	Surface Penetration	104
5.8.4	Effective Electron Mass	105
5.8.5	Energy U of the Conduction Band Distance	107
5.8.6	Energy W of the Chemisorption Level	107
5.8.7	Equilibrium Constant of Physisorption	107
5.8.8	Oxygen Pressure	107
5.8.9	Temperature	108
5.9	Effects of the Defect Structure of the Oxide	109
5.9.1	Models with Oxygen Interstitials, Space Charge Effects	109
5.9.2	Effect of the Oxygen Pressure	111
5.9.3	Models with Oxygen Vacancies and Metal Vacancies	112
5.10	Simulation of Experiments with the Volumetric Method	113
5.10.1	Reaction Model	113
5.10.2	Results of Model Calculations	114
5.11	Reaction Mechanisms of Low-Temperature Oxidation	115
5.11.1	Fundamentals of the Mechanism	116
5.11.2	Physisorbed Oxygen	117
5.11.3	Defect Formation and Oxide Formation	118
5.11.4	Electronic Structure and Electronic Currents	118
5.11.5	Effects not Considered by the Models	118
5.11.6	Approximations for Estimated Oxidation Curves	119
5.11.7	Experimental Results and Model Calculations	120
5.11.8	Conclusions	122
6	Poisoning of Hydrogen Reactions	123
6.1	Experimental Results	124
6.1.1	Wire Samples	124
6.1.2	Film Samples	126
6.1.3	Powder Samples	131
6.1.4	General Trends	133
6.2	✓ Stability of Oxide Layers at Elevated Temperatures	134
6.2.1	Structure of the Model	134
6.2.2	Results	135
6.2.3	Conclusions	136
6.3	Surface Layer of Constant Thickness	137
6.3.1	Absorption, Dissociation and Permeation Control	138

6.3.2	Discussion of the Mechanism	143
6.3.3	Desorption, Surface and Permeation Controlled.	145
6.3.4	Absorption, Permeation and Diffusion Control	147
6.4	Contamination Layers Growing During Exposure	148
6.4.1	Poisoning by Chemisorption Layers	149
6.4.2	Poisoning by Oxide Layers	150
6.4.3	Hydrogen Absorption in H ₂ /O ₂ Gas Mixtures	154
6.4.4	Estimate of Exposure Time and H ₂ Absorption Before Poisoning	154

Appendices

A	Chemical Potentials and Standard States	156
A.1	Chemical Potentials	156
A.1.1	Definitions	156
A.2	Standard States and Standard Reactions	158
A.2.1	Elements	158
A.2.2	Oxides M _x O _y	159
A.2.3	Physisorption	160
A.2.4	Molecular Chemisorption	161
A.2.5	Atomic Chemisorption	162
A.2.6	Metal Interstitials.	162
A.2.7	Metal Vacancy	163
A.2.8	Oxygen Interstitials	163
A.2.9	Oxygen Vacancy	164
A.2.10	Other Compounds	164
B	Equilibria of Charged Species	165
B.1	Poisson Equation	165
B.2	Dipole Layers.	166
B.3	Space Charges	166
B.3.1	Thick Layers, $l \gg \lambda$	168
B.3.2	Thin Layers, $l < \lambda$	168
B.3.3	Conclusions	171
B.4	Mott Potential.	171
B.4.1	Oxygen Molecules as Acceptors	172
B.4.2	Oxygen Atoms as Acceptors	174
B.4.3	Pressure Independent Acceptor Sites	174
B.4.4	Conditions for the Existence of a Mott Equilibrium Potential	175
B.5	Equilibria in Oxide Layers	175
C	Electronic Currents	180
C.1	Tunneling	180
C.2	Hopping Mechanism	182
C.3	Semiconduction.	183
D	Ionic Currents	186
D.1	Basic Equations	186
D.1.1	Zero Concentration Gradient	186
D.1.2	Zero Field Current	187

D.1.3	High Field Transport Equation	187
D.1.4	Steady State Current in a Homogeneous Field	188
D.2	Space Charge Effects	189
D.3	Coupled Currents.	190
E	Units, Material Constants	192
Symbols	194
References	197
Subject Index.	202