

CONTENTS

LECTURE 1

Fundamental aspects of the semiconductor-solution interface by L.M. Peter

1. Electrons in solids.....	1
1.1. The Band Model and Conductivity.....	1
2. Solid state semiconductor junctions.....	3
2.1. The Contact Potential.....	3
2.2. Band Bending.....	3
3. Electrolyte solutions.....	4
3.1. Standard Electrode Potentials and the Vacuum Energy Scale....	4
3.2. Energy Fluctuations in Solution Redox Species.....	5
4. The semiconductor-solution junction.....	6
4.1. Electron Transfer at the Metal Solution Interface.....	6
4.2. Electron Transfer at the Semiconductor Electrolyte Interface....	7
4.3. Space Charge Capacitance: the Mott Schottky Equation.....	8
5. The illuminated semiconductor-electrolyte junction.....	11
5.1. The Gärtner equation.....	11
5.2. Photocorrosion Reactions.....	12
5.3. Photosensitization.....	13
6. Experimental aspects of semiconductor electrochemistry.....	14

LECTURE 2

The silicon/electrolyte interface by J.-N. Chazalviel

1. Introduction.....	17
2. Stable silicon/electrolyte interfaces: the case of organic electrolytes..	17
2.1. Interface energetics.....	18
2.2. Methanol-based regenerative solar cells.....	18
3. Silicon surface chemistry under open-circuit condition.....	19

VIII

3.1. Fluoride media.....	19
3.2. Alkaline media.....	20
3.3. Surface modification by organic reagents.....	21
4. The silicon/aqueous-electrolyte interface.....	22
4.1. Interface energetics: effect of pH.....	22
4.2. Cathodic polarization: hydrogen evolution and hydrogen penetration.....	22
4.3. Anodic polarization and SiO ₂ formation.....	23
5. Anodic dissolution of silicon in fluoride media.....	24
5.1. General behaviour: n and p type, dissolution valence.....	24
5.2. Porous silicon regime: electron/hole participation in the electrochemical process.....	26
5.3. Porous silicon formation: possible mechanisms.....	27
5.4. Electropolishing regime: interfacial film, ionic transport, resonant behaviour.....	29
6. Conclusion.....	30

LECTURE 3

Porous silicon: material processing, properties and applications by A. Halimaoui

1. Porous silicon formation: Anodization cells.....	33
2. Dissolution chemistries.....	35
3. Charge exchange mechanism and reaction selectivity.....	36
4. Porosity and thickness determination.....	38
5. Variation in porosity and thickness as a function of anodization conditions.....	39
6. Material properties.....	43
6.1. Microstructure of the material.....	43
6.2. X-ray diffraction.....	44
6.3. Chemical composition.....	44
6.4. Thermal behavior and oxidation of porous silicon.....	45
6.5. Chemical dissolution and wettability phenomena.....	46
6.6. Optical absorption of free standing porous silicon films.....	49
7. Applications of porous silicon.....	50

LECTURE 4

Luminescence of porous silicon after electrochemical oxidation by R. Herino

1. Introduction.....	54
2. Anodic oxidation of porous silicon.....	53
2.1. Experimental aspects.....	53

2.2. Main characteristics of the electrochemical oxidation.....	54
2.3. Influence of the anodizing current density.....	55
2.4. A phenomenological model for the anodic oxidation of porous film.....	56
3. Luminescence of electro-oxidized porous layers formed on p-doped substrates.....	57
3.1. Main characteristics of the electroluminescence observed under electrochemical oxidation.....	57
3.2. Luminescence modifications under electrochemical oxidation.....	59
3.3. Mechanisms governing the emission efficiency.....	59
3.4. Spectral shifts resulting from anodic oxidation.....	61
3.5. Electroluminescence from porous layers formed on heavily p-doped substrates.....	63
4. Conclusion.....	65

LECTURE 5

Mechanism for light emission from nanoscale silicon by M.S. Hybertsen

1. Introduction.....	67
2. Electronic states.....	70
3. Mechanism for radiative transitions.....	73
4. Discussion of the optical properties of porous silicon.....	79
5. Concluding remarks.....	87

LECTURE 6

Theory of silicon crystallites. Part II

by C. Delerue, G. Allan, E. Martin and M. Lannoo

1. Introduction.....	91
2. Tight binding treatment (T.B.).....	91
3. Optical properties of polysilanes.....	96
4. Defects and impurities in crystallites.....	98
4.1. Surface dangling bonds.....	99
4.2. Hydrogenic impurities in silicon crystallites.....	103
5. Exchange splitting and stokes shift of crystallites.....	104
5.1. Calculation of the exchange splitting.....	105
5.2. Calculation of the Stokes shift.....	106
6. Conclusion.....	109

LECTURE 7

Doping of a quantum dot and self-limiting effect in electrochemical etching

by R. Tsu and D. Babic

1. Introduction.....	111
2. Calculation and results.....	112
3. Self-limiting etching in porous silicon.....	117
4. Future work.....	119

LECTURE 8

Electronic and optical properties of semiconductors quantum wells

by R. Ferreira

1. Introduction.....	121
2. Electronic states.....	121
3. Interband optical absorption.....	127
4. Experimental aspects.....	130
5. Conclusion.....	136

LECTURE 9

What can be learned from time resolved measurements on porous silicon luminescence

by J.C. Vial

1. Introduction.....	137
1.1. History.....	137
1.2. The objectives.....	138
1.3. The vocabulary.....	138
1.4. The orders of magnitude.....	138
2. Experimental techniques.....	139
2.1. Short pulse and long pulse excitation.....	139
3. A general presentation of the problem.....	141
3.1. The master equation (in the small flux approximation).....	141
4. General properties of the luminescence decays of porous silicon.....	145
4.1. The line shape, the "selective detection".....	145
4.2. The various parameters which affect the decays.....	145

5. Non radiative processes of porous silicon luminescence.....	146
5.1. The tunneling model.....	146
5.2. W_{nr} dependence on passivation.....	147
5.3. W_{nr} dependence on confinement.....	147
5.4. The decay shapes.....	148
6. Radiative processes.....	150
7. Other practical uses of time resolved measurements.....	152
7.1. Voltage quenching of the photoluminescence.....	152
7.2. The saturation of the excitation of the photoluminescence.....	153
8. General conclusion.....	154

LECTURE 10

Ion beam analysis of thin films. Applications to porous silicon by C. Ortega, A. Grosman and V. Morazzani

Introduction.....	157
1. Rutherford Backscattering Spectrometry.....	158
1.1. Basic physical concepts.....	158
1.1.1. Kinematic factors.....	158
1.1.2. Two-body problem.....	159
1.1.3. Rutherford scattering cross section.....	163
1.1.4. Deviations from Rutherford scattering cross section.....	164
1.2. Rutherford Backscattering Spectrometry.....	164
1.2.1. Experimental setup.....	165
1.2.2. Energy loss. Energy straggling.....	165
1.2.3. Simulated backscattering spectrum.....	167
1.2.4. How to read a RBS spectrum.....	168
1.3. Ion Channeling in crystals [15].....	170
1.4. Elastic Recoil Detection Analysis (ERDA).....	172
1.4.1. Experimental setup.....	172
1.4.2. Simulated recoil spectrum.....	172
1.4.3. Cross section for H and ^2H elastic recoil using MeV ^4He	173
2. Nuclear reaction analysis.....	174
2.1. Q values and kinetic energies.....	174
2.2. Nuclear reaction cross sections.....	175
2.3. Experimental setup.....	177
3. Applications to the case of porous silicon.....	177
3.1. Impurity content in porous silicon.....	177
3.2. Boron content in p+ porous layers.....	180
3.3. Channeling experiments.....	182
3.4. Thermal oxidation and nitridation of porous silicon.....	183
3.5. Anodic oxidation of porous silicon.....	185

LECTURE 11

IR spectroscopy of porous silicon

by W. Theiss

1. Introduction.....	189
2. Theory.....	190
2.1. Excitations by electric fields: dielectric functions.....	190
2.1.1. Dielectric background.....	190
2.1.2. Free charge carriers.....	191
2.1.3. Vibration of atomic cores: oscillator model.....	191
2.2. Wave propagation.....	192
2.2.1. Complex refractive index.....	192
2.2.2. Boundaries.....	193
2.3. Optical properties of layer stacks.....	193
2.4. Porous systems: effective dielectric functions.....	195
3. Instrumentation.....	195
3.1. Fourier transform spectroscopy.....	195
3.2. A typical spectrometer.....	196
3.3. Comparison of various techniques.....	197
3.3.1. Transmission.....	197
3.3.2. Reflection.....	198
3.3.3. Attenuated Total Reflection (ATR).....	198
3.3.4. IR microscopy.....	199
3.3.5. Photoacoustic spectroscopy.....	199
4. Examples.....	200
4.1. Single layers.....	200
4.2. Investigation of photolithography steps.....	202
4.3. Porosity superlattices.....	203
5. Summary.....	204

LECTURE 12

Nano characterization of porous silicon by transmission electron microscopy

by I. Berbezier

Introduction.....	207
1. Introduction to electron diffraction.....	209
1.1. Kinematical approach to electron diffraction from a crystalline specimen.....	209
1.2. Electron diffraction in the TEM.....	211
1.2.1. Selected Area Diffraction (SAD).....	211
1.2.2. Convergent beam diffraction (CBD).....	213
2. Image analysis by conventional T.E.M.....	214
2.1. Bright-field imaging (BF).....	215

2.2. Dark field imaging (DF).....	216
3. High resolution image analysis.....	218
3.1. Dynamical theory of electron diffraction.....	218
3.2. Multislice method.....	219
4. Microanalysis.....	222

LECTURE 13

Electron paramagnetic resonance spectroscopy: Defect and structural analysis of solids

by H.J. von Bardeleben and M. Schoisswohl

1. Introduction.....	225
2. Basic principles of EPR spectroscopy.....	225
2.1. The Spin Hamiltonian.....	225
2.2. EPR spectroscopy.....	228
3. Some instructional examples.....	229
3.1. Intrinsic Defects in GaAs.....	229
3.2. Si/SiO ₂ Interface Defects.....	230
3.3. Intrinsic Defects in Amorphous Silicon.....	234
4. Application of EPR to the case of porous silicon.....	235
4.1. Defect Analysis.....	235
4.1.1. Defects in as Prepared n ⁺ , p ⁺ , p, p ⁻ Layers.....	236
4.1.2. EPR of Photoexcited Free Electrons: an Indication for Spatial Separation of Photoexcited Carriers.....	238
4.1.3. EPR of the Dopants B,P.....	239
4.1.4. Influence of Thermal Annealing under Ultra High Vacuum.....	240
4.1.5. High Temperature (1000 °C) Thermally Oxidized Layers	242
4.1.6. Anodically Oxidized p ⁺ Layers.....	243
4.2. Structure analysis: Monocrystalline/Disordered Si.....	244

LECTURE 14

Raman scattering in silicon nanostructures

by B. Champagnon, I. Gregora, Y. Monin, E. Duval, L. Saviot

1. Photon-phonon interactions in bulk materials.....	247
2. Size effects in quantum dots.....	248
3. LOw Frequency Inelastic Scattering (LOFIS).....	250
4. Luminescence and temperature measurements.....	251
5. Conclusion.....	252

LECTURE 15

Scattering of X-rays

by A. Naudon, P. Goudeau and V. Vezin

1. Introduction.....	255
2. Theoretical aspects of small-angle scattering.....	256
2.1. The scattering problem.....	256
2.2. Particle scattering.....	257
2.2.1. Dilute system: form factor $P(q)$	257
2.2.2. Dense packing: structure factor $S(q)$	258
2.2.3. Two-phase system.....	259
2.3. Correlation function.....	260
2.3.1. The invariant Q_0	260
2.3.2. Radius of gyration.....	261
2.3.3. Porod law [2,3].....	261
2.4. Non-particulate system.....	262
2.4.1. Case of a porous sample.....	262
2.4.2. Chord distribution.....	262
2.4.3. Characteristic dimensions.....	263
3. Experimental technique.....	264
3.1. In a laboratory.....	264
3.2. At a synchrotron radiation source.....	265
4. Application to porous silicon.....	266
4.1. Doping influence on the scattering.....	266
4.2. Photoluminescent P silicon.....	267
4.3. Blue-shift after anodic oxidation.....	269
5. Diffraction of X-rays.....	270
5.1. Small-angle scattering and wide-angle scattering.....	270
5.2. Lattice parameter of porous silicon.....	271
5.3. Scattering around Bragg's peaks.....	272
6. Conclusion.....	273

LECTURE 16

X-ray photoemission spectroscopy

by H. Mnder

1. Introduction.....	277
2. Electronic structure of solids and surfaces.....	278
3. Physical principles.....	279
4. Instrumentation.....	281
4.1. Light sources.....	281
4.2. Analyzers.....	282
5. Lineshape analysis.....	283
6. Experimental.....	283

7. Results and discussion.....	283
7.1. Si (100).....	283
7.2. Freshly prepared and aged porous Si layers.....	284
7.3. Anodically oxidized porous Si layers.....	287
7.4. Rapid thermal oxidized porous Si.....	290
8. Summary.....	290

LECTURE 17

Optoelectronic properties of porous silicon. The electroluminescent devices

by W. Lang, P. Steiner, F. Kozlowski

1. Introduction.....	293
2. Basic devices.....	294
2.1. Metal contacts.....	294
2.2. ITO and SiC contacts.....	297
3. UV - Type devices.....	298
4. Homojunction devices.....	300
5. Indium treated devices.....	301
6. Main tasks for future work.....	302
6.1. Stability.....	302
6.2. Quantum efficiency.....	303
6.3. EL time constants.....	303

LECTURE 18

Porous silicon luminescence under cathodic polarisation conditions

by A. Bsiesy

1. Introduction.....	307
2. Experimental.....	307
3. The voltage-tunable electroluminescence.....	308
3.1. Why cathodic polarisation conditions?.....	308
3.2. Current and light intensity-potential characteristics.....	308
3.3. Spectral shift of porous silicon EL, a voltage-induced effect.....	311
3.4. EL voltage tunability: a consequence of a possible material inhomogeneity?.....	312
3.5. Origin of the voltage-tunable electroluminescence.....	313
3.6. Relation between the porous silicon VTEL and its morphology	315
4. The electrically-induced quenching of porous silicon photoluminescence.....	317
4.1. Blueshift and narrowing of the PL line.....	317

4.2. Radiative and non-radiative recombination rates evolution under a cathodic polarisation.....	318
4.3. Possible mechanisms at the origin of the decrease of the number of the optically active silicon crystallites.....	320
5. Conclusion.....	320

LECTURE 19

Interrelation between electrical properties and visible luminescence of porous silicon

by N. Koshida

1. Introduction.....	323
2. Experimental.....	323
2.1. Sample Preparation.....	323
2.2. Measurements.....	324
2.2.1. Photoconduction, PL and EL.....	324
2.2.2. Electric field effects on PL.....	324
2.2.3. Formation of a large-area contact.....	324
3. Results and discussion.....	324
3.1. Carrier Transport and Photoconduction.....	324
3.2. Photoconductivity Spectra and Other Optoelectronic Properties..	324
3.3. Electrical modulation of PL intensity.....	326
3.4. Improvement in the EL characteristics.....	327
4. Conclusions.....	328

LECTURE 20

Characteristics of porous n-type silicon obtained by photoelectrochemical etching

by C. Levy-Clement

1. Introduction.....	329
2. Condition of formation of porous silicon.....	329
3. The macroporous Si layer.....	331
3.1. Morphology.....	331
3.2. Optical properties of macroporous Si.....	334
4. The nanoporous Si layer.....	335
4.1. Morphology.....	335
4.2. Nanostructure of the Si nanowire.....	337
4.3. Photoluminescence.....	338
4.4. Macroscopic chemical characterisation.....	339
4.5. Local chemistry of the nanowires.....	340
5. Conclusion.....	342

LECTURE 21**Porous Si: From single porous layers to porosity superlattices**

by M.G. Berger, St. Frohnhoff, W. Theiss, U. Rossow
and H. Mnder

1. Introduction.....	345
2. Single porous silicon layers.....	345
2.1. Raman scattering from nanocrystals.....	345
2.2. Application to porous silicon.....	347
2.3. Experimental.....	348
2.4. Properties of single porous layers.....	349
3. Porosity superlattices.....	350
3.1. Experimental.....	351
3.2. Properties of porosity superlattices.....	352
4. Summary.....	355