

Edited by  
**Peter Capper**

# **Bulk Crystal Growth**

of Electronic, Optical  
and Optoelectronic  
Materials



 **WILEY**

Wiley Series  
in Materials for  
Electronic  
& Optoelectronic  
Applications

# Contents

<b>Series Preface</b>	<b>xv</b>
<b>Preface</b>	<b>xvii</b>
<b>Acknowledgements</b>	<b>xxi</b>
<b>List of Contributors</b>	<b>xxiii</b>
<b>Abbreviations</b>	<b>xxvii</b>
<b>1 Silicon</b>	<b>1</b>
<i>Taketoshi Hibiya and Keigo Hoshikawa</i>	
1.1 Introduction	1
1.2 Crystal-growth method and technology	3
1.2.1 High-purity polycrystalline silicon	3
1.2.2 CZ-Si growth apparatus and related furnace parts	6
1.2.3 CZ-Si crystal growth	11
1.2.4 FZ (float-zone) Si crystal growth	13
1.2.5 Wafer processing	16
1.3 Melt process	18
1.3.1 Analysis of heat- and mass-transfer processes	18
1.3.2 Oxygen transportation process and mechanism	24
1.3.3 Control of oxygen concentration by application of cusp magnetic field	27
1.4 Defect and wafer quality	30
1.4.1 Oxygen precipitation and gettering	30
1.4.2 Grown-in defects	33
1.5 Concluding remarks	39
References	40
<b>2 Growth of Gallium Arsenide</b>	<b>43</b>
<i>M.R. Brozel and I.R. Grant</i>	
2.1 Introduction	43
2.2 Doping considerations	45
2.3 Growth techniques	48
2.3.1 Horizontal Bridgman and horizontal gradient freeze techniques	48

2.3.2	Liquid encapsulated Czochralski (LEC) technique	49
2.3.3	Vertical gradient freeze (VGF) technique	53
2.4	Crystalline defects in GaAs	54
2.4.1	Defects in melt-grown, semi-insulating GaAs	54
2.5	Impurity and defect analysis of GaAs (chemical)	59
2.6	Impurity and defect analysis of GaAs (electrical)	61
2.6.1	Introduction to the electrical analysis of defects in GaAs	61
2.7	Impurity and defect analysis of GaAs (optical)	65
2.7.1	Optical analysis of defects in GaAs	65
2.8	Conclusions	67
	Acknowledgments	68
	References	69
<b>3</b>	<b>Computer Modelling of Bulk Crystal Growth</b>	<b>73</b>
	<i>Andrew Yeckel and Jeffrey J. Derby</i>	
3.1	Introduction	74
3.2	Present state of bulk crystal growth modelling	75
3.3	Bulk crystal growth processes	77
3.4	Transport modelling in bulk crystal growth	79
3.4.1	Governing equations	79
3.4.2	Boundary conditions	83
3.4.3	Continuum interface representation	84
3.4.4	Radiation heat-transfer modelling	86
3.4.5	Noninertial reference frames	88
3.4.6	Magnetic fields	88
3.4.7	Turbulence	89
3.5	Computer-aided analysis	89
3.5.1	Discretization	89
3.5.2	Numerical interface representation	90
3.5.3	Deforming grids and ALE methods	92
3.5.4	A simple fixed-grid method	94
3.5.5	Quasi-steady-state models	96
3.6	Modelling examples	98
3.6.1	Float-zone refinement of silicon sheets	98
3.6.2	Bridgman growth of CZT: axisymmetric analysis	102
3.6.3	Bridgman growth of CZT: three-dimensional analysis	104
3.6.4	Morphological stability in solution growth of KTP	106
3.7	Summary and outlook	112
	Acknowledgments	113
	References	113
<b>4</b>	<b>Indium Phosphide Crystal Growth</b>	<b>121</b>
	<i>Ian R. Grant</i>	
4.1	Introduction	121
4.2	Material properties	122
4.3	Hazards	123
4.4	Crystal structure	124

4.5 Synthesis	125
4.6 Single-crystal growth	129
4.7 Defects	132
4.7.1 Twins	132
4.7.2 Dislocations	133
4.8 Dislocation reduction	135
4.9 VGF growth	136
4.10 Crystal-growth modelling	139
4.11 Dopants	141
4.11.1 N-type InP	141
4.11.2 P-type InP	142
4.11.3 Semi-insulating InP	142
4.12 Conclusion	145
Acknowledgements	145
References	145
<b>5 Bulk Growth of InSb and Related Ternary Alloys</b>	<b>149</b>
<i>W.F.H. Micklethwaite</i>	
5.1 Introduction—a little history	149
5.2 Why the interest?	150
5.3 Key properties	151
5.3.1 Crystallography	151
5.3.2 Growth-critical material parameters	154
5.3.3 Common growth conditions	154
5.3.4 Impurities and dopants	154
5.4 Czochralski growth	155
5.4.1 Challenges	156
5.4.2 Choice and implications of growth axis	162
5.4.3 Size evolution and its drivers	163
5.5 Bridgman and VGF growth	164
5.6 Other bulk growth methods	165
5.7 InSb-related pseudobinary (ternary) alloys	165
5.7.1 (Ga,In)Sb	166
5.7.2 (In,Tl)Sb	168
5.7.3 In(As,Sb)	168
5.7.4 In(Bi,Sb)	168
5.8 Conclusion	169
References	169
<b>6 GaN Bulk Substrates Grown under Pressure from Solution in Gallium</b>	<b>173</b>
<i>I. Grzegory, M. Boćkowski and S. Porowski</i>	
6.1 Introduction	173
6.2 Phase diagrams and growth method	175
6.2.1 Thermodynamic properties of GaN-Ga-N <sub>2</sub> system	175
6.2.2 The role of high pressure	178
6.2.3 Crystallization of GaN from solution	179
6.2.4 Experimental	182

6.3	Results of spontaneous crystallization in temperature gradient: crystals and physical properties of the crystals	183
6.3.1	Morphology	183
6.3.2	Physical properties of the pressure-grown GaN crystals	185
6.4	Discussion of crystallization in a temperature gradient	188
6.5	Crystallization on the free gallium surface	192
6.6	Directional crystallization on GaN and foreign substrates	194
6.6.1	Seeded growth of GaN from solutions in gallium on GaN substrates	195
6.6.2	Seeded growth of GaN from solutions in gallium on GaN/sapphire substrates	197
6.7	Applications of pressure-grown bulk GaN substrates	201
6.8	Summary and conclusions	203
	References	205
<b>7</b>	<b>Bulk Growth of Cadmium Mercury Telluride (CMT)</b>	<b>209</b>
	<i>P. Capper</i>	
7.1	Introduction	209
7.2	Phase equilibria	210
7.3	Crystal growth	211
7.3.1	SSR	212
7.3.2	THM	217
7.3.3	Bridgman	222
7.4	Conclusions	238
	References	238
<b>8</b>	<b>Bulk Growth of CdZnTe/CdTe Crystals</b>	<b>241</b>
	<i>R. Hirano and H. Kurita</i>	
8.1	Introduction	241
8.2	High-purity Cd and Te	242
8.2.1	Cadmium	242
8.2.2	Tellurium	243
8.3	Crystal growth	243
8.3.1	Polycrystal growth	243
8.3.2	VGF single-crystal growth	244
8.4	Wafer processing	260
8.4.1	Process flow	261
8.4.2	Characteristics	264
8.5	Summary	266
	Acknowledgements	266
	References	266
<b>9</b>	<b>Bulk Crystal Growth of Wide-Bandgap II-VI Materials</b>	<b>269</b>
	<i>M. Isshiki, J.F. Wang</i>	
9.1	Introduction	269
9.2	Physical and chemical properties	270
9.3	Phase diagrams	270

9.4	Crystal-growth methods	270
9.4.1	Growth from vapor phase	272
9.4.2	Growth from liquid phase	276
9.4.3	Crystal growth from solid phase	280
9.5	Crystal growth of wide-bandgap compounds	280
9.5.1	ZnS	280
9.5.2	ZnO	282
9.5.3	ZnSe	284
9.5.4	ZnTe	291
9.6	Conclusions	294
	References	294
<b>10</b>	<b>Sapphire Crystal Growth and Applications</b>	<b>299</b>
	<i>V.A. Tatarchenko</i>	
10.1	Introduction	300
10.2	Sapphire structure	301
10.3	Sapphire crystal growth	302
10.3.1	Verneuil's technique (VT)	302
10.3.2	Floating-zone technique (FZT)	308
10.3.3	Czochralski technique (CzT)	310
10.3.4	Kyropulos technique (KT)	312
10.3.5	Horizontal Bridgman technique (HBT)	313
10.3.6	Heat-exchange method (HEM)	313
10.3.7	Techniques of pulling from shaper (TPS)	314
10.3.8	Flux technique (FT)	318
10.3.9	Hydrothermal technique (HTT)	319
10.3.10	Gas-phase technique (GPT)	319
10.4	Corundum crystal defects	319
10.4.1	Inclusions	319
10.4.2	Dislocations, low-angle grain boundaries, internal stresses	323
10.4.3	Twins	326
10.4.4	Faceting, inhomogeneities of impurity	326
10.4.5	Growth direction	327
10.5	Applications	327
10.5.1	Special windows	327
10.5.2	Domes	328
10.5.3	Substrates	329
10.5.4	Construction material	329
10.6	Brief crystal-growth technique characterization	329
10.6.1	VT	329
10.6.2	FZT	330
10.6.3	CzT	330
10.6.4	KT	330
10.6.5	HBT	330
10.6.6	HEM	330
10.6.7	TPS	330
10.6.8	FT, HTT, GPT	331

10.7 Conclusion	331
References	331
Appendix: sapphire physical properties	334
<b>11 Crystal Growth of Fluorides</b>	<b>339</b>
<i>P.P. Fedorov, V.V. Osiko</i>	
11.1 Introduction	339
11.2 Polymorphism and crystal growth	340
11.3 Solid solutions: decomposition and ordering	342
11.4 Type of compound melting: congruent/incongruent	347
11.5 Phases that are not in equilibrium with melt	347
11.6 Dopant segregation coefficients	348
11.7 Morphological stability	348
11.8 Hydrolysis and melt fluoride growth	350
Acknowledgments	352
References	352
<b>12 Scintillators: Crystal Growth and Scintillator Performance</b>	<b>357</b>
<i>A. Gektin</i>	
12.1 Introduction	357
12.2 Scintillator applications	358
12.2.1 High-energy physics	359
12.2.2 Medical imaging	361
12.3 Scintillation-material efficiency estimation	361
12.4 Halide scintillator growth	364
12.5 Activator distribution in scintillation single crystals	374
12.6 Oxide scintillation crystal growth	376
12.7 Influence of single-crystal perfection on scintillation characteristics	378
12.8 New scintillation crystals	381
12.9 Conclusion	382
List of definitions and abbreviations	383
References	383
<b>13 Growth of Quartz Crystals</b>	<b>387</b>
<i>K. Byrappa</i>	
13.1 Introduction	387
13.2 History of quartz crystal growth	388
13.3 Physical chemistry of the growth of quartz	391
13.4 Solubility	392
13.5 Apparatus	396
13.6 Crystal growth	396
13.7 Growth of high-quality (and dislocation-free) quartz crystals	398
13.7.1 Growth rate	399
13.7.2 Seed effect	400
13.7.3 Nutrient effect	400
13.8 Defects observed in synthetic $\alpha$ -quartz single crystals	401

13.9 Processing of $\alpha$ -quartz for high-frequency devices	402
13.10 Conclusions	404
References	404
<b>14 Crystal Growth of Diamond</b>	<b>407</b>
<i>Hisao Kanda</i>	
14.1 Introduction	407
14.2 Diamond synthesis	408
14.2.1 Phase diagram of carbon	408
14.2.2 Direct transformation	408
14.2.3 Agents for diamond formation	409
14.2.4 Carbon source	411
14.2.5 High-pressure apparatus	412
14.2.6 Diamond growth methods	412
14.3 Properties of diamond single crystals made with high-pressure methods	417
14.3.1 Morphology	417
14.3.2 Surface morphology	419
14.3.3 Inclusions	421
14.3.4 Atomic impurities, color and luminescence	422
14.3.5 Color control	423
14.4 Summary	428
References	428
<b>15 Growth of Silicon Carbide</b>	<b>433</b>
<i>T.S. Sudarshan, D. Cherednichenko, and R. Yakimova</i>	
15.1 Introduction	433
15.2 Historical development	434
15.3 Industrial production of SiC wafers	435
15.3.1 Growth along the conventional <i>c</i> - or [0001] direction	435
15.3.2 Bulk SiC growth along alternate orientations	436
15.3.3 Bulk growth of semi-insulating SiC	436
15.3.4 Bulk-crystal doping	437
15.4 Essentials of the bulk growth process and thermal-stress-generation mechanisms	437
15.4.1 Basics of the bulk growth process	437
15.4.2 Thermal-stress-generation mechanisms	443
15.5 Growth-related defects	444
15.6 Outlook	447
Acknowledgements	447
References	447
<b>16 Photovoltaic Silicon Crystal Growth</b>	<b>451</b>
<i>T.F. Ciszek</i>	
16.1 Introduction	451
16.2 Traditional silicon growth methods applied to PV	452
16.2.1 Czochralski growth	452

16.2.2	FZ growth	455
16.2.3	Comparisons between CZ and FZ growth for PV	456
16.3	Multicrystalline ingot growth methods for PV	459
16.3.1	Casting and directional solidification	459
16.3.2	Semicontinuous electromagnetic casting	461
16.4	Ribbon or sheet growth methods for PV	463
16.4.1	Small-area solid/liquid interface growth methods	463
16.4.2	Large-area solid/liquid interface growth methods	468
16.5	Thin-layer growth on substrates for PV	472
16.6	Comparison of growth methods	473
	References	475
<b>17</b>	<b>Bulk Crystal Growth Under Microgravity Conditions</b>	<b>477</b>
	<i>Thierry Duffar</i>	
17.1	Introduction	477
17.2	Experimental and technological environment	502
17.2.1	Technical limitations: time, size, power and space management	502
17.2.2	Environmental limitations: the gravity level	504
17.3	Scientific achievements	505
17.3.1	Segregation studies in Bridgman configuration	505
17.3.2	Experiments of crystal growth from a molten zone or molten drop	508
17.3.3	Sample–crucible interactions and structural aspects	510
17.3.4	Growth from solutions	514
17.3.5	Growth from the vapor phase	515
17.4	Conclusion and future directions	516
17.4.1	Summary of major breakthroughs	516
17.4.2	Problems still to be investigated and perspectives	517
	References	517
<b>Index</b>		<b>525</b>