

Contents

Part I Amorphous Semiconductors

1	Fundamentals of Amorphous Semiconductors	3
1.1	Definitions	3
1.2	Glass Transition	4
1.2.1	Phenomenology of Glass Transition	4
1.2.2	Glass-Formation Criteria	5
1.2.3	Reversible Amorphous-to-Crystal Transition	7
1.3	Atomic Structure	11
1.3.1	Long-Range Order	11
1.3.2	Short-Range Order	12
1.3.3	Medium-Range Order	14
1.3.4	Melting of Semiconductors	14
1.4	Structure of Prototypical Chalcogenides	15
1.4.1	Elemental Chalcogens	15
1.4.2	Chalcogenide Glasses	17
1.4.3	Phase-Change Materials	18
1.5	Defects	19
1.5.1	Ideal Glass and the “8–N” Rule	19
1.5.2	Topological Defects	20
1.5.3	Soft Configurations	23
1.6	Electronic Structure	24
1.6.1	Origin of the Bandgap	24
1.6.2	Anderson Localisation	25
1.6.3	Percolation	27
1.7	Fabrication of Amorphous Semiconductors	27
1.7.1	Melt Quenching	27
1.7.2	Vapour Deposition	28
1.7.3	Spin Coating	31
1.7.4	Ion Implantation	32
	References	32

2	Properties of Amorphous Chalcogenides	35
2.1	Electrical Properties	35
2.1.1	Pinning of the Fermi Level	35
2.1.2	P-Type Conductivity	35
2.1.3	Hall Effect Anomaly	36
2.1.4	Phase-Change Materials	36
2.1.5	Chalcogenides as Topological Insulators	38
2.1.6	Liquid Chalcogenides	39
2.2	Optical Absorption	40
2.2.1	Interband Absorption	40
2.2.2	Absorption Edge (the Urbach Rule)	41
2.2.3	Phase-Change Materials	42
2.3	Photoexcitation and Recombination	43
2.3.1	Photoluminescence	43
2.3.2	Photo-Induced Metastability	45
	References	46
3	Methods of Structure Analysis	49
3.1	Experimental Methods for Investigating Atomic Structure	49
3.1.1	Bragg Diffraction and Its Limitations	49
3.1.2	Pair-Distribution-Function Analysis	51
3.1.3	X-Ray Absorption Fine Structure Spectroscopy	52
3.1.4	Nanobeam Electron Diffraction	55
3.2	Electronic Structure	56
3.2.1	Band Structure	56
3.2.2	Defect Spectroscopy	58
3.3	Structural Modelling	60
3.3.1	Reverse Monte Carlo Modelling	60
3.3.2	Ring Statistics	61
3.3.3	Ab-Initio Density-Functional Theory Simulations	61
	References	62

Part II Chalcogenide Glasses

4	Reversible Photostructural Changes	67
4.1	Photodarkening	67
4.1.1	Reversible and Irreversible Photodarkening	67
4.1.2	Recovery of Initial Parameters	71
4.2	Reversible Structural Changes	72
4.2.1	Manifestations of Structural Changes	72
4.2.2	Phenomenological Description: Configuration-Coordinate Model	74

4.2.3	Microscopic Nature of Photostructural Changes	78
4.2.4	In Situ Studies of Reversible Photostructural Changes	81
4.2.5	Why Photostructural Changes are Restricted to Vitreous Chalcogenide Semiconductors	84
4.3	Photo-Induced Defect Creation and Modification	86
4.3.1	Photo-Induced Electron Spin Resonance	86
4.3.2	Photo-Induced Midgap Absorption	91
4.3.3	Photoluminescence Fatigue	91
4.3.4	Photo-Induced Change in AC-Conductivity	91
4.4	Relationship between Photo-Induced ESR and Reversible Photostructural Change (Photodarkening)	92
4.5	Photo-Induced Phenomena in Liquid Chalcogens	95
4.5.1	Liquid Sulphur	95
4.5.2	Liquid Selenium	98
4.6	Photo-Induced Site-Selective Oxidation	99
	References	99
5	Photo-Induced Anisotropy	103
5.1	Optical Linear Dichroism and Birefringence	103
5.1.1	Photo-Induced Optical Anisotropy	103
5.1.2	Optical Reversibility of Induced Anisotropy	103
5.1.3	Dependence of Photo-Induced Anisotropy on Exposure Parameters	104
5.1.4	Anisotropy Versus Photodarkening	107
5.1.5	Anisotropy Induced by Non-Polarised and Circularly Polarised Light	108
5.2	Photo-Induced Anisotropy of Other Properties	111
5.2.1	Anisotropic Photoluminescence	111
5.2.2	Anisotropy of Photoconductivity	111
5.2.3	Polarised Photodoping	111
5.2.4	Anisotropic Optomechanical Effect	111
5.2.5	Anisotropic Mass Flow	112
5.2.6	Macroscopic Anisotropic Deformations	112
5.2.7	Anisotropic Photocrystallisation	112
5.3	Structural Studies	114
5.4	Models of Photoanisotropy	116
	References	120
6	Photo-Induced Change of the Phase State	123
6.1	Photocrystallisation	123
6.1.1	Photocrystallisation of Selenium	123
6.1.2	Crystallisation of Phase-Change Materials Through the Use of Coherent Phonons	124

6.2	Photo-Induced Loss of Long-Range Order	126
6.2.1	Athermal Photoamorphisation	126
6.2.2	Photo-induced Viscosity/Fluidity	128
6.2.3	Photomelting of Selenium	129
	References	130
7	Photo-Induced Phenomena in Chalcogenide-Metal Structures . . .	133
7.1	Photodoping.	133
7.1.1	Photodissolution	133
7.1.2	Lateral Diffusion	134
7.1.3	Diffusion Mechanism	136
7.1.4	Reaction Products and Their Properties.	138
7.2	Photodeposition of Silver.	139
7.2.1	Light Intensity, Photon Energy and Temperature Dependencies	140
7.2.2	Reversibility	141
7.2.3	Mechanism of Photosurface Deposition.	141
7.2.4	Programmable Metallisation Cell	143
	References	144
 Part III Phase-Change Materials		
8	Structure of the Crystalline Phase.	149
8.1	Structure of the Stable Phase	149
8.1.1	Binary GeTe	149
8.1.2	Ge ₂ Sb ₂ Te ₅ and Related Materials.	152
8.2	Structure of the Metastable Phase.	155
8.2.1	Long-Range Order (Global Structure)	155
8.2.2	Short-Range Order (Local Structure).	162
8.2.3	Resonance Bonding	164
8.2.4	Point Defects, Vacancies and Distortions.	168
8.3	Engineered Structures	172
8.3.1	GeTe–Sb ₂ Te ₃ Layered Structures	172
8.3.2	Epitaxial Growth of Phase-Change Materials	173
	References	177
9	Structure of the Amorphous Phase	181
9.1	Experimental Studies	182
9.1.1	Binary GeTe	182
9.1.2	Quasibinary GeTe–Sb ₂ Te ₃ Alloys	183
9.1.3	Differently Prepared Amorphous Phases: Polymorphism	189

9.2	Computer Simulations	192
9.2.1	Around the Umbrella-Flip Model	192
9.2.2	Melt-Quenched Amorphous Phase	195
9.2.3	Ab Initio XANES Studies	203
9.2.4	Ag-In-Sb-Te Alloys	208
9.3	Liquid Phase	209
9.3.1	Experimental Studies	209
9.3.2	Computer Simulations	211
	References	213
10	Pressure-Induced Transformations	217
10.1	Ge-Sb-Te Alloys	217
10.1.1	Pressure-Induced Amorphisation	217
10.1.2	High-Pressure BCC Phase and Initial Structure Memory	221
10.2	Pressure-Induced Changes in Ge-Free Phase-Change Alloys.	225
10.2.1	Binary Sb ₂ Te	225
10.2.2	Ag-In-Sb-Te Alloy	225
10.3	Ab Initio Studies of Pressure-Induced Changes	226
10.3.1	Pressure-Induced Amorphisation	226
10.3.2	High-Pressure BCC Phase	229
10.3.3	Amorphisation Upon Decompression	229
	References	230
11	Mechanism of the Phase-Change Process	231
11.1	Microscopic Models of Phase Change	231
11.1.1	Umbrella-Flip of Ge Atoms	231
11.1.2	Four-Membered Rings Rearrangement	232
11.1.3	Resonance Bonding	232
11.1.4	Photo-Assisted Amorphisation of Ge ₂ Sb ₂ Te ₅	236
11.2	Pressure-Induced Amorphisation	239
11.2.1	Amorphisation Upon Compression	239
11.2.2	Amorphisation Upon Decompression	241
11.3	Amorphisation of Ag-In-Sb-Te: Bond-Interchange Model	241
11.4	Origin of Optical and Electrical Contrast	242
11.4.1	Coordination Change	242
11.4.2	Resonant Bonding	243
	References	246

Part IV Applications

12 Memory Devices 251

 12.1 Optical Memories 251

 12.1.1 Compact Disc and Digital Versatile Disc Families . . . 252

 12.1.2 Recordable Discs (CD-R and DVD-R) 256

 12.1.3 Erasable Discs (CD-RW, DVD-RW
 and DVD-RAM). 257

 12.1.4 Super-RENS Discs 259

 12.2 Non-Volatile Electronic Memories 265

 12.2.1 Phase-Change Random Access Memory 265

 12.2.2 Phase-Change Memory for the Future 268

 References 274

Index 277