

# Contents

## 1. Introduction

*William S. Rees, Jr.*

1.1	Organization of the Book . . . . .	2
1.1.1	Scope of the Book . . . . .	2
1.1.2	Potential Audience . . . . .	3
1.1.3	Selection of Chapter Topics . . . . .	3
1.1.4	Chapter Organization . . . . .	3
1.1.4.1	Cross-References Between Chapters . . . . .	3
1.1.4.2	Where to Find a Topic . . . . .	3
1.2	Uses of Materials . . . . .	3
1.2.1	Electronic Applications . . . . .	4
1.2.1.1	Band Gap Classifications . . . . .	4
1.2.2	Optical Applications . . . . .	4
1.2.3	Structural Applications . . . . .	4
1.3	Comparison of Deposition Techniques . . . . .	5
1.3.1	Comparison of Chemical Vapor Deposition Sub-Techniques . . . . .	5
1.3.1.1	Organometallic Vapor Phase Epitaxy (OMVPE) . . . . .	6
1.3.1.2	Plasma CVD . . . . .	6
1.3.1.3	Photo CVD . . . . .	7
1.3.1.4	Pressure Modifications in CVD . . . . .	8
1.3.1.5	Spray Pyrolysis Modifications . . . . .	8
1.3.2	Comparison of Non-Chemical Vapor Deposition Technologies . . . . .	9
1.3.2.1	Molecular Beam Epitaxy (MBE) . . . . .	9
1.3.2.2	Other Physical Vapor Deposition Techniques . . . . .	10
1.4	General Comments on CVD . . . . .	10
1.4.1	Reactor Types . . . . .	10
1.4.2	Important Reaction Locations in CVD Reactors . . . . .	11
1.5	Experimental Design . . . . .	12
1.5.1	System Configuration . . . . .	12
1.5.1.1	System Reactant Input . . . . .	12
1.5.1.2	Reaction Zones . . . . .	17
1.5.1.3	Reaction Co-Product Removal System . . . . .	19
1.5.2	Handling of Precursors . . . . .	20
1.5.3	Methods of Energy Input . . . . .	21
1.5.3.1	Thermal CVD . . . . .	21
1.5.3.2	Alternate Modes . . . . .	22
1.5.4	Vapor Analysis in CVD . . . . .	23
1.6	Reaction Kinetics in CVD . . . . .	23
1.6.1	General Comments . . . . .	23

1.6.2	Vapor Phase Reactions . . . . .	24
1.6.3	Vapor–Solid Phase Reactions . . . . .	24
1.6.4	Solid Phase Reactions . . . . .	26
1.6.5	Control of Reaction Location. . . . .	26
1.6.6	Rate-Determining Steps in CVD . . . . .	26
1.6.7	Temperature and Growth Rate Effects. . . . .	29
1.7	Thermodynamics in CVD . . . . .	29
1.8	General Comments on Precursors. . . . .	30
1.8.1	Design Considerations . . . . .	30
1.8.2	Structural Motifs . . . . .	32
1.8.3	Mechanistic Insights. . . . .	35
1.9	References . . . . .	35

## 2. Superconducting Materials

*Douglas L. Schulz and Tobin J. Marks*

2.1	Introduction . . . . .	39
2.2	Overview of Superconductivity. . . . .	40
2.2.1	Physical Properties of Superconductors . . . . .	40
2.2.2	Low Temperature Superconducting Materials . . . . .	43
2.2.2.1	Crystal Structures of LTS Materials . . . . .	43
2.2.3	High Temperature Superconducting Materials . . . . .	44
2.2.3.1	Crystal Structure of HTS Materials . . . . .	44
2.2.4	Applications of Superconductors . . . . .	48
2.2.4.1	Large-Scale Applications of Superconducting Magnets . . . . .	48
2.2.4.2	Low-Field Applications of Superconductors . . . . .	49
2.2.4.3	Superconducting Electronics Applications. . . . .	50
2.3	CVD of LTS Materials . . . . .	52
2.3.1	Nb <sub>3</sub> Sn CVD Film Growth . . . . .	52
2.3.1.1	Nb <sub>3</sub> Sn CVD Precursors and Reaction Schemes . . . . .	53
2.3.1.2	Nb <sub>3</sub> Sn CVD Reactor Design . . . . .	53
2.3.1.3	Substrates for Nb <sub>3</sub> Sn CVD . . . . .	54
2.3.1.4	Physical Properties of CVD-Derived Nb <sub>3</sub> Sn Films . . . . .	55
2.3.2	Nb <sub>3</sub> Ge CVD Film Growth. . . . .	56
2.3.2.1	Nb <sub>3</sub> Ge CVD Precursors and Reaction Schemes . . . . .	56
2.3.2.2	Nb <sub>3</sub> Ge CVD Reactor Design . . . . .	57
2.3.2.3	Physical Properties of CVD-Derived Nb <sub>3</sub> Ge Films . . . . .	57
2.3.2.4	Effects of Chemical Doping Upon Physical Properties of CVD-Derived Nb <sub>3</sub> Ge Films . . . . .	58
2.3.3	NbC <sub>1-y</sub> N <sub>y</sub> CVD Film Growth . . . . .	59
2.3.3.1	NbC <sub>1-y</sub> N <sub>y</sub> CVD Precursors and Reaction Schemes . . . . .	60
2.3.3.2	Reactor Design for CVD of NbC <sub>1-y</sub> N <sub>y</sub> on Carbon Fiber. . . . .	61
2.3.3.3	Physical Properties of CVD-Derived NbC <sub>1-y</sub> N <sub>y</sub> Films . . . . .	62
2.3.4	NbN CVD Film Growth . . . . .	62
2.3.4.1	NbN CVD Precursors and Reaction Schemes . . . . .	63

2.3.4.2	Physical Properties of CVD-Derived NbN Films . . . . .	63
2.3.5	CVD of Other LTS Materials . . . . .	64
2.3.5.1	Nb <sub>3</sub> Si CVD Film Growth . . . . .	64
2.3.5.2	V <sub>3</sub> Si CVD Film Growth . . . . .	64
2.3.5.3	V <sub>3</sub> Ge CVD Film Growth . . . . .	65
2.3.5.4	Nb <sub>3</sub> Ga CVD Film Growth . . . . .	65
2.3.5.5	TiC <sub>1-y</sub> N <sub>y</sub> CVD Film Growth . . . . .	65
2.3.5.6	W <sub>1-y</sub> Ge <sub>y</sub> CVD Film Growth . . . . .	66
2.3.5.7	Ta CVD Film Growth . . . . .	66
2.3.5.8	LTS Film Growth by CVD of Hydrides and Organometallics on Hot Wires . . . . .	66
2.3.6	Thermodynamic Analysis of LTS CVD . . . . .	67
2.4	CVD of HTS Materials . . . . .	67
2.4.1	CVD Precursor Design Strategies for HTS Materials . . . . .	68
2.4.1.1	Metal β-Diketonate Complexes for HTS CVD . . . . .	69
2.4.1.2	Limitations of Alkaline Earth β-Diketonate Complexes for HTS CVD . . . . .	71
2.4.1.3	New Barium Precursors for CVD of HTS Materials . . . . .	71
2.4.2	CVD of YBCO . . . . .	74
2.4.2.1	Compositional Analysis of CVD-Derived YBCO Films . . . . .	74
2.4.2.2	Structural Orientations of YBCO Films by CVD . . . . .	78
2.4.2.3	Low Temperature CVD of YBCO Using N <sub>2</sub> O as a Reactant Gas . . . . .	83
2.4.2.4	Plasma-Enhanced CVD of YBCO . . . . .	84
2.4.2.5	CVD of YBCO Films Using Other Precursors . . . . .	85
2.4.2.6	Alternative Precursor Delivery Systems . . . . .	87
2.4.2.7	CVD Processing of Technologically Related YBCO Films . . . . .	90
2.4.2.8	CVD of YBa <sub>2</sub> Cu <sub>4</sub> O <sub>8</sub> . . . . .	91
2.4.2.9	Thermodynamic Analysis of YBCO CVD . . . . .	92
2.4.3	CVD of BSCCO . . . . .	111
2.4.3.1	In Situ CVD Growth of BSCCO . . . . .	112
2.4.3.2	BSCCO Films by CVD Using Fluorinated Metal-Organic Precursors . . . . .	115
2.4.3.3	Doping Studies in the CVD of BSCCO Thin Films . . . . .	116
2.4.3.4	CVD of BSCCO on Novel Substrates . . . . .	117
2.4.3.5	Novel BSCCO Film Orientations . . . . .	117
2.4.3.6	Novel CVD Routes to BSCCO Thin Films . . . . .	118
2.3.4.7	Halide CVD of BSCCO Thin Films . . . . .	119
2.4.3.8	Thermodynamic Analysis of BSCCO CVD . . . . .	120
2.4.4	CVD of TBCCO . . . . .	121
2.4.4.1	CVD of TBCCO Thin Films on Single Crystal Substrates . . . . .	121
2.4.4.2	CVD of TBCCO Thin Films on Metallic Substrates . . . . .	128
2.4.4.3	Doping Studies for CVD of TBCCO Thin Films . . . . .	129
2.4.4.4	Mist Microwave-Plasma CVD of (Tl, Pb)-Sr-Ca-Cu-O Films . . . . .	129
2.4.4.5	Thermodynamic Analysis of TBCCO CVD . . . . .	129
2.5	CVD of HTS Lattice-Matched Metal Oxides . . . . .	132
2.6	Conclusions . . . . .	136
	References . . . . .	137

**3. Chemical Vapor Deposition of Conducting Materials***Tobias Gerfin and Klaus-Hermann Dahmen*

3.1	Introduction . . . . .	152
3.2	Deposition Techniques . . . . .	153
3.3	Nontransparent Conducting Films . . . . .	155
3.3.1	Titanium Nitride . . . . .	155
3.3.1.1	Introduction . . . . .	155
3.3.1.2	Precursors . . . . .	156
3.3.1.3	Properties . . . . .	168
3.3.2	Other Nitrides . . . . .	170
3.3.2.1	Film Deposition Using Halides . . . . .	170
3.3.2.2	Film Deposition Using Metal-Organic Precursors . . . . .	171
3.3.3	Conclusions . . . . .	171
3.4	Transparent Conducting Films . . . . .	172
3.4.1	Introduction . . . . .	172
3.4.2	Indium Oxide Systems . . . . .	172
3.4.2.1	Precursors and Preparation . . . . .	172
3.4.2.2	Properties and Applications . . . . .	174
3.4.3	Tin Oxide Systems . . . . .	176
3.4.3.1	Preparation and Precursors . . . . .	176
3.4.3.2	Properties and Applications . . . . .	178
3.4.4	Zinc Oxide Systems . . . . .	180
3.4.4.1	Precursors and Preparation . . . . .	180
3.4.4.2	Properties and Applications . . . . .	183
3.4.5	Conclusion . . . . .	184
	References . . . . .	185

**4. Semiconducting Materials***Gary S. Tompa*

4.1	Introduction to Semiconductors and Formation Technology . . . . .	194
4.2	The Growth Technology . . . . .	197
4.2.1	Competing Technologies . . . . .	197
4.2.1.1	Liquid Phase Epitaxy (LPE) . . . . .	197
4.2.1.2	Implantation . . . . .	198
4.2.1.3	Molecular Beam Epitaxy (MBE) . . . . .	199
4.2.1.4	Vapor Phase Epitaxy (VPE) . . . . .	202
4.2.1.5	Others . . . . .	203
4.2.2	Organometallic Vapor Phase Epitaxy (OMVPE) . . . . .	204
4.2.2.3	Organometallic Vapor Phase Epitaxy (OMVPE) System Technology . . . . .	208
4.2.3.1	Reactor History . . . . .	211
4.2.3.2	Modeling . . . . .	216
4.2.3.3	Control Systems . . . . .	218
4.2.3.4	Safety . . . . .	221
4.2.3.5	Assisted Techniques . . . . .	222

4.2.3.6 The Deposition Equipment Manufacturers . . . . .	223
4.2.3.7 Cost of Ownership . . . . .	224
4.2.3.8 Choice of Process . . . . .	225
4.3 The Substrates . . . . .	225
4.4 The Reactants . . . . .	227
4.4.1 The Gases . . . . .	228
4.4.2 The Metal-Organics . . . . .	228
4.4.3 Organometallic Source Vessels . . . . .	230
4.4.4 Reactant Efficiencies . . . . .	233
4.5 The Materials . . . . .	234
4.5.1 Group II-VI Materials . . . . .	234
4.5.2 Group III-V Materials . . . . .	235
4.5.3 Group III-V Nitrides . . . . .	237
4.5.4 Group IV-IV Materials Silicon, Silicon germanium . . . . .	239
4.5.5 Carbides (Including and Diamond) . . . . .	240
4.5.6 Oxides . . . . .	241
4.5.7 Organic Materials . . . . .	242
4.5.8 Characterization . . . . .	243
4.6 The Device Applications . . . . .	243
4.6.1 Field Effect Transistors (FETs) . . . . .	243
4.6.2 Heterojunction Bipolar Transistors (HBTs) . . . . .	244
4.6.3 High Electron Mobility Transistors (Modulation Deped Field Effect Transistors [(HEMTs (MODFETs)] . . . . .	245
4.6.4 LEDs . . . . .	246
4.6.5 Lasers . . . . .	248
4.6.6 Photodiode Detectors . . . . .	250
4.6.7 Solar Cells . . . . .	251
4.6.8 High Temperature Devices . . . . .	253
4.6.9 III-V Integrated circuits, Opto Electronic Integrated Circuits (OEICs) . . . . .	253
4.7 The Future Prospects . . . . .	254
4.7.1 Selective Area Epitaxy . . . . .	254
4.7.2 Atomic Layer Epitaxy (ALE) . . . . .	254
4.7.3 Real-Time In-Situ Process Monitoring . . . . .	256
4.7.4 Alternative Sources . . . . .	256
4.7.5 Large Area Production Technology . . . . .	257
4.7.6 Insights . . . . .	257
4.8 Conclusion . . . . .	257
References . . . . .	258

## 5. CVD of Insulating Materials

*Andrew R. Barron*

5.1 Introduction . . . . .	262
5.2 Applications for Electrically Insulating Materials . . . . .	262
5.2.1 Device Isolation and Gate Insulation . . . . .	263

5.2.2	Passivation . . . . .	265
5.2.3	Planarization . . . . .	266
5.3	General Considerations . . . . .	267
5.3.1	Deposition Methods. . . . .	267
5.3.2	Deposition Variables . . . . .	268
5.3.3	Precursor Considerations . . . . .	269
5.4	Oxides . . . . .	269
5.4.1	Silicon Oxides. . . . .	270
5.4.1.1	Silica ( $\text{SiO}_2$ ) . . . . .	270
5.4.1.2	Silicate Glasses . . . . .	278
5.4.2	Aluminium Oxides . . . . .	282
5.4.2.1	Alumina ( $\text{Al}_2\text{O}_3$ ) . . . . .	283
5.4.2.2	Aluminum Silicates . . . . .	288
5.4.3	Transition Metal Oxides . . . . .	290
5.4.3.1	Tantalum and Niobium Oxide . . . . .	290
5.4.3.2	Titanium, Zirconium and Hafnium Oxide. . . . .	292
5.4.4	Superconducting Metal Oxide (SMO) Lattice-Matched Insulators . . . . .	294
5.5	Nitrides . . . . .	295
5.5.1	Silicon Nitride and Oxynitride . . . . .	296
5.5.2	Aluminum Nitride . . . . .	300
5.5.3	Transition Metal Nitrides . . . . .	307
5.6	Sulfides . . . . .	308
5.6.1	Gallium Sulfide . . . . .	309
5.6.2	Indium Sulfide . . . . .	311
5.7	Fluorides . . . . .	312
5.8	Concluding Remarks . . . . .	313
	References . . . . .	313

## 6. Structural Ceramic Coatings and Composites

*W. Jack Lackey*

6.1	Introduction . . . . .	321
6.2	Fibers . . . . .	322
6.2.1	Current Status . . . . .	322
6.2.2	Reactor Designs . . . . .	324
6.2.3	Stress in Coated Fibers . . . . .	329
6.2.4	Processing . . . . .	331
6.2.5	Economic Analysis . . . . .	339
6.3	Interface Coatings . . . . .	341
6.3.1	Types of Interface Coatings . . . . .	342
6.3.2	Layered Oxide Structures as Interfaces . . . . .	342
6.3.3	CVD of Oxides. . . . .	344
6.3.3.1	Textured CVD Coatings . . . . .	345
6.3.3.2	CVD of Alumina . . . . .	347
6.3.3.3	Porous Interface Coatings . . . . .	348

6.3.3.4	Coatings of $\beta''$ -Alumina . . . . .	348
6.4	Composite Consolidation . . . . .	349
6.4.1	Chemical Vapor Infiltration of Carbon . . . . .	350
6.4.2	Chemical Vapor Infiltration of Silicon Carbide . . . . .	360
6.4.3	Chemical Vapor Infiltration of Alumina . . . . .	361
6.4.4	Chemical Vapor Infiltration of Zirconium Oxide <sub>2</sub> . . . . .	361
	References . . . . .	361

## 7. Other Materials

*Gertrud E. Kräuter and William S. Rees, Jr.*

7.1	Halides . . . . .	369
7.1.1	Fluorides . . . . .	369
7.1.1.1	Group 1 Fluorides . . . . .	369
7.1.1.2	Group 2 Fluorides . . . . .	369
7.1.1.3	Transition Element Fluorides . . . . .	370
7.1.2	Metal Iodides . . . . .	370
7.2	Metal Oxides . . . . .	370
7.2.1	Transition Element Oxides . . . . .	372
7.2.1.1	Titanium, Zirconium and Hafnium Oxides . . . . .	372
7.2.1.2	Vanadium, Niobium and Tantalum Oxides . . . . .	373
7.2.1.3	Chromium, Molybdenum and Tungsten Oxides . . . . .	373
7.2.1.4	Iron and Ruthenium Oxides . . . . .	374
7.2.1.5	Cobalt Oxide . . . . .	375
7.2.1.6	Nickel Oxide . . . . .	375
7.2.1.7	Zinc Oxide . . . . .	375
7.2.2	Main Group Element Oxides . . . . .	376
7.2.2.1	Antimony Oxide . . . . .	376
7.2.2.2	Indium Oxide . . . . .	376
7.2.2.3	Thallium Oxide . . . . .	376
7.2.3	Rare Earth Element Oxides . . . . .	377
7.3	Metal Sulfides . . . . .	377
7.3.1	Transition Element Sulfides . . . . .	377
7.3.1.1	Titanium Sulfide . . . . .	377
7.3.1.2	Molybdenum and Tungsten Sulfides . . . . .	378
7.3.2	Main Group Element Sulfides . . . . .	378
7.3.2.1	Group 2 Element Sulfides . . . . .	378
7.3.2.2	Group 14 Element Sulfides . . . . .	378
7.3.2.3	Arsenic Sulfide . . . . .	379
7.4	Metal Selenides and Tellurides . . . . .	379
7.4.1	Indium Selenide . . . . .	379
7.4.2	Germanium Selenide . . . . .	380
7.4.3	Tin Selenide . . . . .	380
7.4.4	Arsenic Selenide . . . . .	380
7.4.5	Antimony and Bismuth Tellurides . . . . .	380

7.5	Metal Nitrides . . . . .	381
7.5.1	Transition Element Nitrides . . . . .	381
7.5.1.1	Titanium, Zirconium and Hafnium Nitrides . . . . .	381
7.5.1.2	Vanadium, Niobium and Tantalum Nitrides. . . . .	382
7.5.1.3	Tungsten Nitride . . . . .	382
7.5.2	Main Group Element Nitrides . . . . .	383
7.5.2.1	Magnesium Nitride . . . . .	383
7.5.2.2	Carbon Nitride . . . . .	383
7.5.2.3	Germanium Nitride . . . . .	383
7.5.2.4	Phosphorus Nitride . . . . .	383
7.6	Metal Carbides . . . . .	383
7.6.1	Transition Element Carbides . . . . .	384
7.6.1.1	Titanium, Zirconium and Hafnium Carbides . . . . .	384
7.6.1.2	Vanadium, Niobium and Tantalum Carbides . . . . .	384
7.6.1.3	Chromium, Molybdenum and Tungsten Carbides . . . . .	385
7.6.2	Main Group Element Carbides. . . . .	386
7.6.2.1	Boron Carbide . . . . .	386
7.7	Elemental Boron and Metal Borides . . . . .	386
7.7.1	Elemental Boron. . . . .	386
7.7.2	Metal Borides. . . . .	387
7.7.2.1	Titanium, Zirconium and Hafnium Borides. . . . .	387
7.7.2.2	Niobium and Tantalum Borides . . . . .	388
7.7.2.3	Molybdenum and Tungsten Borides. . . . .	388
7.8	Complex Ceramic Materials. . . . .	389
7.8.1	Metal Carbonitrides . . . . .	389
7.8.1.1	Boron–Carbon–Nitrogen Compounds . . . . .	389
7.8.1.2	Titanium and Zirconium Carbonitrides . . . . .	389
7.8.1.3	Niobium Carbonitride . . . . .	390
7.8.1.4	Molybdenum Carbonitride . . . . .	390
7.8.2	Titanium Silicocarbide . . . . .	390
7.8.3	Spinels . . . . .	390
7.8.4	Garnets . . . . .	391
7.8.5	Other Magnetic Metal Oxides . . . . .	391
7.8.6	Other Compounds . . . . .	391
References . . . . .	392	
Glossary . . . . .	401	
Index . . . . .	415	