

Contents

Preface	xiii
Acknowledgments.....	xv
Introduction.....	xvii
CHAPTER 1 Integration and devices.....	1
1.1 Introduction	2
1.2 Structure of film devices	2
1.3 Obstacles to integration.....	7
1.3.1 Thermal.....	7
1.3.2 Thermo-chemical.....	8
1.3.3 Thermo-chemo-mechanical	9
1.3.4 Size really does matter	10
1.4 Overcoming challenges.....	11
1.4.1 Reducing temperature.....	11
1.4.2 Separating reactants.....	15
1.4.3 Decrease differential strain.....	16
1.4.4 Make it thinner	17
1.4.5 Increase in strength.....	19
1.5 Overview of functional devices	20
1.5.1 Introduction.....	20
1.5.2 Piezoelectric devices	21
1.5.2.1 Actuators, speakers, and pumps.....	22
1.5.2.2 Sound and acoustic emission sensors	22
1.5.2.3 Ultrasound transducers.....	23
1.5.2.4 Acceleration sensors	25
1.5.2.5 Pressure and chemical sensors.....	26
1.5.2.6 Transformers	27
1.5.2.7 Energy transmitters	27
1.5.2.8 Energy harvesters	28
1.5.3 Pyroelectric devices.....	28
1.5.3.1 Pyroelectric sensors.....	28
1.5.3.2 Pyroelectric energy harvester.....	29
1.5.4 Other functional devices.....	29
1.5.4.1 Solid oxide fuel cells	29
1.5.4.2 Electrochemical gas sensor	30
1.5.4.3 Resistive gas sensor	30
1.5.4.4 Thermoelectric generator	31
1.5.4.5 Micro hotplate	31

CHAPTER 2	Routes to thick films	35
2.1	Introduction	36
2.2	Routes to achieve non-thick-thick films.....	36
2.2.1	Vapor deposition	36
2.2.2	Liquid deposition	37
2.3	Thick-film powder-based routes	39
2.3.1	Processing	39
2.3.2	Sintering.....	40
2.3.3	Constrained sintering.....	42
2.3.4	Sintering aids	44
2.3.5	Sol infiltration	45
2.4	Modified powder routes	46
2.4.1	Composite sol-gel	46
2.4.1.1	Drying.....	47
2.4.1.2	Pyrolysis	48
2.4.1.3	Crystallization	48
2.4.2	Enhancement of composite sol-gel systems.....	50
2.4.2.1	Infiltrated composite sol-gel films	50
2.4.2.2	Sintering aid in composite sol-gel films	52
2.4.3	Kinetic deposition.....	52
2.4.4	Polymer composite films.....	53
2.4.5	Machining	53
2.5	Powder manufacturing routes	53
2.5.1	Solid state	54
2.5.2	Molten salt	54
2.5.3	Mechanochemical synthesis	56
2.5.4	Sol-gel	56
2.5.5	Precipitation.....	57
2.5.6	Hydrothermal synthesis	58
2.6	Milling	58
2.6.1	Roll mill.....	58
2.6.2	Jet mill	58
2.6.3	Ball mill	59
2.6.4	Vibrator and attrition mills.....	60
CHAPTER 3	Thick-film deposition techniques	63
3.1	Introduction	64
3.2	Creating stable inks.....	65
3.2.1	Dispersion	65
3.2.1.1	Electrostatic stabilization	67
3.2.1.2	Steric stabilization.....	68
3.2.1.3	Electrosteric stabilization.....	69
3.2.2	Rheology	70

3.3	Components of inks.....	73
3.3.1	Solvent	73
3.3.2	Dispersants.....	74
3.3.3	Binders and plasticizers	75
3.4	Directed coating techniques	75
3.4.1	Spray coating	75
3.4.2	Mist coating	76
3.4.3	Aerosol deposition.....	76
3.5	Spreading coating techniques	77
3.5.1	Screen printing.....	77
3.5.2	Spin coating	78
3.5.3	Doctor blade/tape casting	79
3.6	Immersion coating techniques	79
3.6.1	Dip coating	79
3.6.2	Electrophoretic deposition.....	80
3.6.3	Sedimentation	81
3.6.4	Interfacial polymerization	81
3.6.5	Texturing.....	82
3.7	Post-production poling	82
3.8	Help! It has all gone wrong	83
CHAPTER 4	Microstructure–property relationships.....	85
4.1	Introduction	86
4.2	Material properties	86
4.3	Why are film properties not the same as bulk properties?.....	87
4.4	Microstructural variations	88
4.4.1	Grain size and grain-boundary effects	91
4.4.2	Second phases.....	92
4.4.3	Porosity	93
4.4.4	Interfaces and surface zones	94
4.4.5	Graded structures.....	95
4.4.6	Preferential orientation and texturing	96
4.5	Functional properties.....	98
4.5.1	Relationship between ferroelectric, pyroelectric, piezoelectric, and dielectric materials	98
4.5.2	Ferroelectric (piezoelectric and pyroelectric) properties.....	99
4.5.3	Relative permittivity	102
4.5.3.1	Grain size effects in ferroelectrics.....	104
4.5.3.2	Additional porosity and second-phase effects in dielectrics	104
4.5.4	Dielectric loss	104
4.5.5	Electrical breakdown strength.....	105
4.5.6	Electrical conductivity.....	107

Contents

4.5.7	Ionic conductivity	108
4.5.8	Thermal conductivity and heat capacity	109
4.6	Mechanical properties	109
4.6.1	Stiffness	109
4.6.2	Strength and toughness.....	110
4.7	Cracking	111
4.8	Interrelationship between property–microstructure relationships	111
CHAPTER 5	Patterning	113
5.1	Introduction	114
5.2	Subtractive patterning	114
5.2.1	Masking	115
5.2.2	Isotropic and anisotropic etching	116
5.2.3	Physical etching.....	117
5.2.3.1	Types of physical etching	117
5.2.3.2	Precision machining.....	118
5.2.3.3	Powder blasting.....	118
5.2.4	Chemical etching.....	120
5.2.4.1	Wet chemical etching.....	120
5.2.4.2	Reactive and deep reactive ion etching.....	123
5.2.4.3	Directed energy-based etching.....	123
5.3	Additive Patterning.....	124
5.3.1	Molding.....	124
5.3.2	Placement based	127
5.3.2.1	Types of placement-based additive patterning	127
5.3.2.2	Inkjet printing.....	128
5.3.2.3	Electrohydrodynamic atomization	129
5.3.2.4	Challenges associated with droplet deposition techniques.....	130
5.3.2.5	Screen printing	132
5.3.2.6	Pad printing	133
5.3.2.7	Pen lithography	135
5.4	Capabilities and limitations of patterning.....	135
5.4.1	Feature size.....	136
5.4.1.1	Subtractive.....	136
5.4.1.2	Molding	139
5.4.1.3	Placement	139
5.4.2	Aspect ratio.....	139
5.4.2.1	Subtractive.....	139
5.4.2.2	Molding	139
5.4.2.3	Placement	139
5.4.3	Resolution	140

5.4.3.1	Subtractive.....	140
5.4.3.2	Molding	140
5.4.3.3	Placement	140
5.4.4	Accuracy and precision	140
5.4.4.1	Subtractive.....	140
5.4.4.2	Molding	141
5.4.4.3	Placement	141
5.4.5	Comparison of capabilities.....	141
CHAPTER 6	Houston, we have a problem	145
6.1	Introduction	146
6.2	Integration.....	147
6.2.1	Issue: Poor-quality electrode under PZT films	147
6.2.1.1	Circumstances	147
6.2.1.2	Investigation	147
6.2.1.3	Solution	149
6.2.2	Issue: Catastrophic loss of film and substrate.....	149
6.2.2.1	Circumstances	149
6.2.2.2	Investigation	149
6.2.2.3	Solution	150
6.3	Cracking and surface finish.....	151
6.3.1	Issue: Cracking of thick film.....	151
6.3.1.1	Circumstances	151
6.3.1.2	Investigation	151
6.3.1.3	Solution	152
6.3.2	Issue: Uneven surface finish on dip-coated porous lanthanum strontium manganite (LSMO) films.....	152
6.3.2.1	Circumstances	152
6.3.2.2	Investigation	152
6.3.2.3	Solution	153
6.3.3	Issue: Uneven surface finish on a screen-printed film.....	153
6.3.3.1	Circumstances	153
6.3.3.2	Investigation	153
6.3.3.3	Solution	154
6.3.4	Issue: Overly porous spray-deposited PZT film	154
6.3.4.1	Circumstances	154
6.3.4.2	Investigation	154
6.3.4.3	Solution	155
6.4	Poor properties	155
6.4.1	Issue: Poor electrical connections.....	155
6.4.1.1	Circumstances	155
6.4.1.2	Investigation	155
6.4.1.3	Solution	156

Contents

6.4.2 Issue: Electrical shorting on insulating thick film	156
6.4.2.1 Circumstances	156
6.4.2.2 Investigation	156
6.4.2.3 Solution	157
6.4.3 Issue: Poor piezoelectric properties	158
6.4.3.1 Circumstances	158
6.4.3.2 Investigation	158
6.4.3.3 Solution	159
6.5 Patterning	159
6.5.1 Issue: Poor-quality micro-molded thick-film features	159
6.5.1.1 Circumstances	159
6.5.1.2 Investigation	159
6.5.1.3 Solution	160
6.5.2 Issue: Poor-quality inkjet-printed features	161
6.5.2.1 Circumstances	161
6.5.2.2 Investigation	161
6.5.2.3 Solution	162
6.5.3 Issue: Poor quality of edge on cantilever device	162
6.5.3.1 Circumstances	162
6.5.3.2 Investigation	162
6.5.3.3 Solution	163
6.5.4 Issue: Unsmooth edges on etched features	163
6.5.4.1 Circumstances	163
6.5.4.2 Investigation	164
6.5.4.3 Solution	164
6.5.5 Issue: Excess material attached to edges of micro-molded features.....	165
6.5.5.1 Circumstances	165
6.5.5.2 Investigation	165
6.5.5.3 Solution	165
 CHAPTER 7 Recipes	167
7.1 Powders	169
7.1.1 Lanthanum strontium manganate powder (sol-gel derived)	169
7.1.1.1 Ingredients	169
7.1.1.2 Instructions	169
7.1.2 PZT powder (molten salt)	170
7.1.2.1 Ingredients	170
7.1.2.2 Instructions	170
7.1.3 KNN powder (mixed oxide).....	170
7.1.3.1 Ingredients	170
7.1.3.2 Instructions	171

7.1.4	PZT powder (for spray pyrolysis).....	171
7.1.4.1	Ingredients.....	171
7.1.4.2	Instructions.....	171
7.2	Sols.....	172
7.2.1	YSZ sol (propanol solvent).....	172
7.2.1.1	Ingredients.....	172
7.2.1.2	Instructions.....	172
7.2.2	YSZ sol (butanol solvent).....	172
7.2.2.1	Ingredients.....	172
7.2.2.2	Instructions.....	172
7.2.3	PZT sol (2ME solvent).....	172
7.2.3.1	Ingredients.....	172
7.2.3.2	Instructions.....	173
7.3	Films and inks.....	173
7.3.1	Screen-printing inks – Alumina ink.....	173
7.3.1.1	Ingredients.....	173
7.3.2	Screen-printing inks – YSZ ink.....	173
7.3.2.1	Ingredients.....	173
7.3.2.2	Instructions (for all inks).....	173
7.3.3	EHDA spray deposition – YSZ spray ink.....	174
7.3.3.1	Ingredients.....	174
7.3.4	EHDA spray deposition – PZT spray ink.....	174
7.3.4.1	Ingredients.....	174
7.3.4.2	Instructions.....	174
7.3.5	Dip coating.....	174
7.3.6	Spin coating PZT composite film.....	174
7.3.6.1	Ingredients.....	174
7.3.6.2	Instructions.....	175
7.4	Processing, poling, and useful stuff!.....	175
7.4.1	Contact poling (PZT).....	175
7.4.1.1	Instructions.....	175
7.4.1.2	Notes.....	175
7.4.2	Corona poling (PZT).....	176
7.4.2.1	Instructions.....	176
7.4.2.2	Notes.....	176
7.4.3	PZT etching.....	176
7.4.3.1	Ingredients.....	176
7.4.3.2	Instructions.....	176
7.4.3.3	Notes.....	177
7.4.4	Chilli con carne.....	177
7.4.4.1	Ingredients.....	177
7.4.4.2	Instructions.....	177
7.4.5	How to make an EHDA spray head.....	177
7.4.5.1	Ingredients.....	177

Contents

7.4.5.2 Instructions	178
7.4.6 Wafer cleaning – Piranha etch	178
7.4.6.1 Ingredients	178
7.4.6.2 Instructions	178
7.4.7 ZrO ₂ diffusion barrier layer	178
7.4.7.1 Ingredients	178
7.4.7.2 Instructions	179
7.4.8 Volume fraction of second phase	179
7.4.8.1 Instructions	179
7.4.9 Grain-size analysis.....	180
7.4.9.1 Instructions	180
7.4.10 Ball milling.....	181
7.4.10.1 Instructions	181
Bibliography	183
Index	187