

Table of Contents

Preface	xiii
Emmanuel DEFAÝ	
Chapter 1. The Thermodynamic Approach	1
Emmanuel DEFAÝ	
1.1. Background	1
1.2. The functions of state	2
1.3. Linear equations, piezoelectricity	6
1.4. Nonlinear equations, electrostriction	8
1.5. Thermodynamic modeling of the ferroelectric–paraelectric phase transition	9
1.5.1. Assumption on the elastic Gibbs energy	9
1.5.2. Second-order transition	12
1.5.3. Effect of stress	18
1.5.4. First-order transition	20
1.6. Conclusion	24
1.7. Bibliography	25
Chapter 2. Stress Effect on Thin Films	27
Pierre-Eymeric JANOLIN	
2.1. Introduction	27
2.2. Modeling the system under consideration	27
2.3. Temperature–misfit strain phase diagrams for monodomain films	28
2.3.1. Phase diagram construction from the Landau–Ginzburg–Devonshire theory	29
2.3.2. Calculations limitations	34
2.4. Domain stability map	35
2.4.1. Presentation and description of the framework of study	36

2.4.2. Main contributions to the total energy of a film	36
2.4.3. Influence of thickness	39
2.4.4. Macroscopic elastic energy for each type of tetragonal domain	39
2.4.5. Indirect interaction energy	40
2.4.6. Domain structures at equilibrium	42
2.4.7. Domain stability map	43
2.5. Temperature–misfit strain phase diagram for polydomain films.	48
2.6. Discussion of the nature of the “misfit strain”	50
2.6.1. Mechanical misfit strain	50
2.6.2. Thermodynamic misfit strain	51
2.6.3. As an illustration	51
2.7. Conclusion	52
2.8. Experimental validation of phase diagrams: state of the art	52
2.9. Case study	53
2.10. Results	53
2.10.1. Evolution of the lattice parameters	53
2.10.2. Associated stresses and strains	56
2.11. Comparison between the experimental data and the temperature–misfit strain phase diagrams.	60
2.11.1. Thin film of PZT	60
2.11.2. Thin layer of PbTiO ₃	63
2.12. Conclusion	65
2.13. Bibliography	66
Chapter 3. Deposition and Patterning Technologies	71
Chrystel DEGUET, Gwenaël LE RHUN, Bertrand VILQUIN and Emmanuel DEFAÝ	
3.1. Deposition method	71
3.1.1. Cathodic sputtering	71
3.1.2. Ion beam sputtering	74
3.1.3. Pulsed laser deposition	75
3.1.4. The sol–gel process	77
3.1.5. The MOCVD	79
3.1.6. Molecular beam epitaxy	81
3.2. Etching	86
3.2.1. Wet etching	86
3.2.2. Dry etching	86
3.3. Contamination	86
3.4. Monocrystalline thin-film transfer	87
3.4.1. Smart Cut™ technology	88
3.4.2. Bonding/thinning	89

3.4.3. Interest in the material in a thin layer	91
3.4.4. State of the art of the domain/applications	91
3.4.5. An exemplary implementation	94
3.5. Design of experiments	96
3.5.1. The assumptions	97
3.5.2. Reproducibility	99
3.5.3. How can we reduce the number of experiments?	100
3.5.4. A DOE example: PZT RF magnetron sputtering deposition.	102
3.6. Conclusion	107
3.7. Bibliography	108
Chapter 4. Analysis Through X-ray Diffraction of Polycrystalline Thin Films	111
Patrice GERGAUD	
4.1. Introduction	111
4.2. Some reminders of x-ray diffraction and crystallography.	112
4.2.1. Nature of X-rays	112
4.2.2. X-ray scattering and diffraction	113
4.3. Application to powder or polycrystalline thin-films	122
4.4. Phase analysis by X-ray diffraction.	126
4.4.1. Grazing incidence diffraction.	128
4.4.2. De-texturing	131
4.4.3. Quantitative analysis	131
4.5. Identification of coherent domain sizes of diffraction and micro-strains	132
4.5.1. Analysis methodologies	134
4.6. Identification of crystallographic textures by X-ray diffraction	139
4.6.1. Texture analysis by a symmetric diffractogram	140
4.6.2. Pole figures and orientations distribution function	143
4.6.3. Measurement principle.	143
4.6.4. Orientations distribution function	144
4.7. Determination of strains/stresses by X-ray diffraction	146
4.7.1. X-ray diffraction and strain	146
4.7.2. Determination of stresses from strains	148
4.7.3. Specificity of the X-ray diffraction in stress analysis.	151
4.7.4. Equipment	153
4.7.5. Example of stress identification by the $\sin^2\psi$ method	154
4.7.6. Precaution in the case of thin films	154
4.7.7. Application example for a $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ film	155
4.8. Bibliography	156

Chapter 5. Physicochemical and Electrical Characterization	159
Gwenaël LE RHUN, Brahim DKHIL and Pascale GEMEINER	
5.1. Introduction	159
5.2. Useful characterization techniques	159
5.2.1. Electron microscopy	160
5.2.2. Spectroscopy analysis	162
5.3. Ferroelectric measurement	170
5.3.1. Sawyer–Tower assembly	171
5.3.2. “Virtual ground” assembly	173
5.4. Dielectric measurement	177
5.5. Bibliography	180
Chapter 6. Radio-Frequency Characterization	183
Thierry LACREVAZ	
6.1. Introduction	183
6.2. Notions and basic concepts associated with HF	184
6.2.1. Introduction to the phenomena associated with HF signals	184
6.2.2. Lumped or distributed behavior of an electric circuit	186
6.2.3. Notion of quadripoles: two-port circuits or four-terminal network [MÉS 85]	187
6.2.4. Basic theoretical elements of transmission lines:	
HF electric model	191
6.2.5. HF electric model of a parallel MIM capacitor	195
6.2.6. Signal flow graph [BOR 93]	197
6.2.7. Scattering waves	198
6.2.8. Scattering parameters: S-parameters	199
6.2.9. Vector network analyzer (VNA)	202
6.3. Frequency analysis: HF characterization of materials	204
6.3.1. Objectives	204
6.3.2. Issues of HF measurements through a VNA	204
6.3.3. Calibration of the measuring system	206
6.3.4. Extraction of the propagation exponent of the transmission line: de-embedding associated with the TRL calibration	208
6.3.5. Extraction results of the complex permittivity of materials SrTiO ₃ and PbZrTiO ₃	210
6.4. Bibliography	211
Chapter 7. Leakage Currents in PZT Capacitors	213
Emilien BOUYSOU	
7.1. Introduction	213
7.2. Leakage current in metal/insulator/metal structures	215

7.2.1. Metal/insulator contact: definitions	215
7.2.2. Conduction mechanisms limited by the interfaces	219
7.2.3. Conduction mechanisms limited by the bulk of film	222
7.3. Problem of leakage current measurement	225
7.3.1. Relaxation current and true leakage current	226
7.3.2. Drift of true leakage current.	230
7.3.3. Discussion	232
7.4. Characterization of the relaxation current	233
7.4.1. Origin of the relaxation current.	233
7.4.2. Modeling of relaxation currents	234
7.4.3. Conclusion	237
7.5. Literature review of true leakage current in PZT	237
7.6. Dynamic characterization of true leakage current: $I(t, T)$	239
7.6.1. Study of the resistance degradation	241
7.6.2. Study of the resistance restoration phenomenon.	256
7.6.3. Conclusion	262
7.7. Static characterization of the true leakage current: $I(V, T)$	263
7.7.1. Space-charge influenced-injection model.	263
7.7.2. Quantitative description of the model	264
7.7.3. Static modeling $J_{min}(V)$ and $J_{max}(V)$	267
7.8. Conclusion	273
7.9. Bibliography	275
Chapter 8. Integrated Capacitors	281
Emmanuel DEFAÝ	
8.1. Introduction	281
8.2. Potentiality of perovskites for RF devices: permittivity and losses	283
8.2.1. RF MIM capacitors of STO and PZT	284
8.2.2. Coplanar line waveguides on PZT	288
8.2.3. How to perform a good integrated capacitor at RF frequencies?	292
8.3. Bi-dielectric capacitors with high linearity	294
8.3.1. Introduction	294
8.3.2. Design	295
8.3.3. Technology	296
8.3.4. Results	296
8.4. STO capacitors integrated on CMOS substrate by AIC technology.	298
8.4.1. Introduction	298
8.4.2. Technology	298
8.4.3. Electrical tests	301
8.4.4. Conclusion	303
8.5. Bibliography	303

Chapter 9. Reliability of PZT Capacitors	305
Emilien BOUYSSOU	
9.1. Introduction	305
9.2. Accelerated aging of metal/insulator/metal structures	307
9.2.1. The electrical stresses	307
9.2.2. The breakdown	310
9.2.3. Statistical treatment of breakdown	312
9.3. Accelerated aging of PZT capacitors through CVS tests	316
9.3.1. Literature review	316
9.3.2. Statistical study of time-to-breakdown data	318
9.3.3. Discussion: characterization strategy	320
9.4. Lifetime extrapolation of PZT capacitors	325
9.4.1. Determination of the temperature acceleration factor	325
9.4.2. Determination of voltage acceleration	327
9.5. Conclusion	335
9.6. Bibliography	336
Chapter 10. Ferroelectric Tunable Capacitors	341
Benoit GUIGUES	
10.1. Introduction	341
10.2. Overview of the tunable capacitors	342
10.2.1. Applications requiring a tunable element	342
10.2.2. The tunable capacitors	343
10.2.3. Which material to choose?	350
10.3. Types of actual tunable capacitors	355
10.3.1. MIM capacitor	355
10.3.2. Planar capacity	363
10.3.3. Anisotropy effects	364
10.4. Toward new tunable capacitors	366
10.4.1. Composite ferroelectric materials	366
10.4.2. Hybrid tunable capacitor	372
10.5. Bibliography	375
Chapter 11. FRAM Ferroelectric Memories: Basic Operations, Limitations, Innovations and Applications	379
Christophe MULLER	
11.1. Taxonomy of non-volatile memories	379
11.1.1. Present and future solutions	379
11.1.2. Difficult penetration of a highly competitive market	381
11.2. FRAM memories: basic operations and limitations	383
11.2.1. Charge storage in a ferroelectric capacitor	383
11.2.2. Ferroelectric materials	384

11.3. Technologies available in 2011	387
11.4. Technological innovations	388
11.4.1. 3D ferroelectric capacitors.	389
11.4.2. Ferroelectric field effect transistors	391
11.4.3. What about ferroelectric polymers?	393
11.5. Some application areas of FRAM technology.	394
11.5.1. An alternative to EEPROM memories	394
11.5.2. Ferroelectric devices for RFID systems	395
11.6. Conclusion	396
11.7. Bibliography	397
Chapter 12. Integration of Multiferroic BiFeO₃ Thin Films into Modern Microelectronics	403
Xiaohong ZHU	
12.1. Introduction	403
12.2. Preparation methods	407
12.2.1. Pulsed laser deposition	408
12.2.2. Chemical solution deposition	411
12.2.3. RF magnetron sputtering.	414
12.3. Ferroelectricity and magnetism	416
12.3.1. Ferroelectricity.	416
12.3.2. Magnetism	422
12.3.3. Magnetolectric coupling	424
12.4. Device applications	427
12.4.1. Non-volatile ferroelectric memories	427
12.4.2. Spintronics	428
12.4.3. Terahertz radiation	432
12.4.4. Switchable ferroelectric diodes and photovoltaic devices	433
12.5. Bibliography	436
List of Authors	443
Index	445