

**FABRICATION AND STUDY
OF BST-BASED FUNCTIONAL
MATERIALS**

Dionizy E. Czekaj

**FABRICATION AND STUDY
OF BST-BASED FUNCTIONAL
MATERIALS**



UNIVERSITY OF SILESIA



GNOME PUBLISHING HOUSE

K A T O W I C E 2 0 1 0

Reviewed by
Marta Radecka

Publikacja sfinansowana ze środków
UNIWERSYTETU ŚLĄSKIEGO

Set in Times and Arial
ISBN 978-83-87819-00-2

GNOME – Wydawnictwa Naukowe i Artystyczne
Katowice, ul. Drzymały 18/6, wydawnictwognome@gmail.com

INTRODUCTION	7
LIST OF SYMBOLS	9
1. FUNCTIONAL MATERIALS	11
2. BST SOLID SOLUTION	14
2.1. MATERIAL OF INVESTIGATION.....	16
2.2. FABRICATION OF BST CERAMICS	20
2.2.1. <i>Mixed oxide method</i>	20
2.2.2. <i>Sol-gel method</i>	20
2.3. CHARACTERIZATION METHODS	23
2.4. THERMAL ANALYSIS OF BST DRIED GEL	23
2.5. CRYSTAL STRUCTURE	28
2.6. GRAIN-SIZE ANALYSIS OF BST CERAMIC POWDER	32
2.7. MICROSTRUCTURE OF BST CERAMICS.....	35
2.8. DIELECTRIC PROPERTIES OF BST CERAMICS	36
3. OXIDE THIN FILMS OF BST	39
3.1. TECHNIQUES FOR OXIDE FILM GROWTH.....	39
3.1.1. <i>Reactive evaporation</i>	41
3.1.2. <i>Molecular beam epitaxy</i>	42
3.1.3. <i>Sputtering</i>	43
3.1.4. <i>Pulsed laser deposition</i>	44
3.2. A BRIEF REVIEW ON SOME PROPERTIES OF BST THIN FILMS.....	46
3.3. BST THIN FILM TECHNOLOGY.....	52
3.3.1. <i>Substrate preparation and characterization</i>	52
3.3.2. <i>BST thin film fabrication</i>	55
4. CHARACTERIZATION OF BST-BASED FERROELECTRIC THIN FILMS	59
4.1. CRYSTALLINE STRUCTURE AND PHASE COMPOSITION OF BST THIN FILMS	59
4.1.1. <i>Study of $Ba_{0.6}Sr_{0.4}TiO_3$ thin films</i>	59
4.1.2. <i>Study of MgO – doped BST6040 thin films</i>	61
4.1.3. <i>Study of compositionally graded BST thin films</i>	63
4.2. MICROSTRUCTURE.....	66
4.2.1. <i>Sol-gel derived BST6040 thin films</i>	66
4.2.2. <i>MgO-doped BST6040 thin films</i>	67

4.2.3. Compositionally graded BST thin films	69
4.3. RAMAN SPECTROSCOPY OF BST THIN FILMS	73
4.3.1. Raman scattering method.....	73
4.3.2. Characterization of MgO-doped $Ba_{0.6}Sr_{0.4}TiO_3$ thin films	74
4.4. NANOSCALE STUDIES OF BST THIN FILMS	80
4.4.1. Nanoindentation.....	80
4.4.2. Nanomechanical properties of BST thin films	82
4.4.3. PFM – piezoresponse force microscopy.....	84
4.4.4. Piezoresponse of BST thin films	86
4.5. DIELECTRIC PROPERTIES.....	91
4.5.1. Impedance spectroscopy.....	91
4.5.2. Method of the thin film characterization by IS.....	91
4.5.3. Dynamic properties of BST thin films.....	95
4.5.4. Leakage current.....	104
4.5.5. Dielectric hysteresis loop and C-U characteristics.....	105
4.5.6. Tunability	109
5. APPLICATION OF BST-TYPE FUNCTIONAL MATERIALS	112
5.1. MEMORY DEVICES	112
5.2. PYROELECTRIC DEVICES	113
5.3. VOLTAGE TUNABLE MICROWAVE DEVICES.....	113
REFERENCES.....	117

The objective of the monograph *Fabrication and Study of BST-based Functional Materials* is to review the results of theoretical approaches and original experimental investigations carried out by the author and related to the synthesis, structure and properties of barium strontium titanate thin films grown by sol-gel technique on stainless steel substrates.

The subject is varied, covering many important, sophisticated, and practical areas, which are built upon the same foundation. I have attempted to present this complex subject matter by emphasizing the scientific and technological ideas in order to give an understanding of the physical phenomena, thin film processing and practical areas of thin film application.

The stages of investigation devoted to the improvement of the technology of BST thin film fabrication by means of sol-gel method are given. Investigation into their structure, microstructure, and basic dielectric, ferroelectric, and optical properties as well as the application of the grown BST thin films in the construction of voltage tunable microwave devices are presented in the monograph. Due to the material used as the thin film substrates (i.e., stainless steel) and the specificity of the “substrate-thin film” system, the suitable technological conditions of the thin film growth have been worked out, specific experimental attachments necessary to provide adequate technological conditions have been designed and new methods of measurement and experimental measuring systems have been developed.

Results of investigations on BST thin films and the analysis presented in the current monograph include research in the field of material science, structural analysis, spectroscopy and mathematical modelling. The developed technology of BST thin film synthesis by sol-gel method afford possibilities for application of synthesized thin films for construction of ferroelectric tunable devices.

The main subjects covered in the present monograph are organised as follows:

Chapter 1 describes functional materials and discusses the problem of materials smartness.

Chapter 2 considers structure, compositional modifications and properties of $BaTiO_3$ and $BaTiO_3$ - $SrTiO_3$ solid solution on the basis of the current theoretical and experimental data.

Chapter 3 discusses the state-of-the-art in the field of the thin film technology including the reasons for increasing importance of ferroelectric thin films, and presents a brief description of various deposition techniques applied to produce ferroelectric films.

Chapter 4 presents original results obtained by the author on developing the BST thin film technology. The methods of investigation into the physical properties of the BST thin films are presented and the main experimental results on: thermal analysis, crystal structure, phase composition, microstructure, as well as optical, nano-mechanical, piezoelectric and dielectric properties of the grown BST thin films are brought together.

Chapter 5 covers the subject of the application of BST-based thin films. An emphasis is laid on the application in microwave electronics.

References are given in the order of appearance in the main text.

Acknowledgement

In writing this book I have constantly appreciated the huge amount of help that I have had from so many people. To all of you, who have helped in large and small ways, I would like to say thank you very much.

This book could not possibly have been completed without the immense help of my Wife Dr Agata Lisińska-Czekaj of the University of Silesia, Katowice, Poland who helped a great deal on many important and difficult points. She also kept me going when I needed encouragement. I also wish to thank her for her patience during the writing of this book.

Much of the work described here was accomplished with the help of a number of outstanding scientists and persons and I would like to acknowledge their co-operation by giving their names: Prof. Dr M.J.M.Gomes, Prof. Dr M.Vasilevskiy, Dr A.G.Rolo, of the University of Minho, Braga, Portugal; Prof. Dr N.Sobolev, of the University of Aveiro, Aveiro Portugal, Dr hab. inż. J.Plewa, of the Muenster University of Applied Sciences, Steinfurt, Germany, Dr D.Kozodayev of the NT-MDT Europe BV, Eindhoven, The Netherlands, Dr hab. inż. M.Bučko, and Prof. Dr hab. M. Radecka of the AGH Technical University, Kraków, Poland, Dr K.Osińska, Dr. B.Wodecka-Duś, Dr M.Adamczyk-Habrajska, and Dr L.Kozielski of the University of Silesia, Katowice, Poland. I am very grateful to these people for the help that they have given me.

And last but not least, I have to mention the great help and technical assistance provided by my PhD students Dr J.Orkisz, Dr T.Orkisz, mgr G.Smalarz, mgr J.Dzik, and mgr H.Bernard.

The use of facilities in the Faculty of Physics and Department of Materials Science at the University of Silesia, Department of Physics at the University of Minho, Braga, Portugal, Department of Inorganic Chemistry, Faculty of Materials Science and Ceramics, AGH University of Technology, Krakow as well as NT-MDT Europe BV, The Netherlands is gratefully acknowledged.

And I would be remiss if I did not acknowledge those who have financially supported my work through the past five years: the Polish Ministry of Education and Science (grant No. N507 098 31/2319), THIOX (research fellowship), University of Silesia, Poland (grants No. BS/KM/317/2006, BW/KM/317/2006 and BS-08-0500-008-07).