ANALYSIS AND PERFORMANCE OF ELECTROCHEMICALLY SYNTHESIZED BARIUM TITANATE FILMS AND ELECTROLYTIC CAPACITORS

By

SRIDHAR VENIGALLA

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1995

UNIVERSITY OF FLORIDA LIBRARIES
Dedicated to:

my wife
Pramila Rani

and son
Srimanth

in appreciation of their patience, support and encouragement
ACKNOWLEDGMENTS

I would like to thank a number of people for their support, suggestions and contributions towards this study. First, I would like to express the utmost and most sincere thanks to my advisor and committee chair, Dr. James H. Adair, for his support, guidance, and constructive criticism in performing this study. I would also like to thank Drs. Ellis D. Verink, Jr., John R. Ambrose, Rajiv K. Singh, all of the Department of Materials Science and Engineering, and Dr. Daniel R. Talham of the Department of Chemistry, for useful comments, encouragement, advice, and assistance. Special thanks to Dr. Stephen A. Costantino, Cabot Performance Materials, Boyertown, PA, for his suggestions and guidance in the processing and characterization of electrolytic capacitors.

I would like to thank all of my present and former colleagues in Dr. Adair's research group for their collaboration and team participation in learning experimental techniques and performing research. Special thanks to Rob Chodelka, Jeff Opalko, and Takayuki Tsukada for research assistance. I am grateful to Richard Linhart and Henrik Krarup for their insights into computer calculations and analyzing thermodynamic data. I sincerely acknowledge the help from Jooho Moon and Jeff Kerchner in gathering information for the preparation of this manuscript. I also thank Dr. Augusto Morrone, Eric Lambers, Richard Crockett, and Wayne Acree, the staff of the Major Analytical Instrumentation Center at the University of Florida, for their technical help and analytical support in the characterization of specimens. I take this opportunity to thank Pam Howell for her administrative support and assistance all along my research.

Finally, I would like to thank my parents, my wife, Rani, and son, Srimanth, and my brother, Srinivas, and other relatives and friends for their constant support, encouragement, and belief in me.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xvii</td>
</tr>
<tr>
<td>CHAPTERS</td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2. LITERATURE REVIEW</td>
<td>6</td>
</tr>
<tr>
<td>2.1. Introduction</td>
<td>6</td>
</tr>
<tr>
<td>2.2. Dielectric Polarization and Ferroelectricity</td>
<td>6</td>
</tr>
<tr>
<td>2.2.1. Theory of Charge Storage and Capacitance</td>
<td>6</td>
</tr>
<tr>
<td>2.2.2. Mechanisms of Dielectric Polarization</td>
<td>9</td>
</tr>
<tr>
<td>2.2.3. Ferroelectricity</td>
<td>13</td>
</tr>
<tr>
<td>2.2.4. Ferroelectric Materials</td>
<td>22</td>
</tr>
<tr>
<td>2.2.5 Thin Film Ferroelectrics and Their Applications</td>
<td>23</td>
</tr>
<tr>
<td>2.3. Methods for Synthesizing BaTiO₃ Thin Films</td>
<td>23</td>
</tr>
<tr>
<td>2.3.1. Vapor Deposition Methods</td>
<td>27</td>
</tr>
<tr>
<td>2.3.2. Sol-Gel Synthesis</td>
<td>29</td>
</tr>
<tr>
<td>2.3.3. Hydrothermal and Electrochemical Synthesis</td>
<td>31</td>
</tr>
<tr>
<td>2.4. Characterization of Thin Films</td>
<td>34</td>
</tr>
<tr>
<td>2.4.1. Structural Characterization</td>
<td>34</td>
</tr>
<tr>
<td>2.4.2. Chemical Characterization</td>
<td>37</td>
</tr>
<tr>
<td>2.4.3. Dielectric Characterization</td>
<td>45</td>
</tr>
<tr>
<td>2.5. Dielectric Properties of BaTiO₃ Thin Films</td>
<td>48</td>
</tr>
<tr>
<td>2.5.1. Dielectric Constant and Dissipation Factor</td>
<td>48</td>
</tr>
<tr>
<td>2.5.2. Hysteresis Behavior</td>
<td>50</td>
</tr>
<tr>
<td>2.5.3. Resistivity and Leakage Current</td>
<td>51</td>
</tr>
<tr>
<td>2.6. Capacitors as Charge Storage Devices</td>
<td>52</td>
</tr>
<tr>
<td>2.6.1. Capacitor Characteristics</td>
<td>52</td>
</tr>
<tr>
<td>2.6.1.1. Volumetric Efficiency</td>
<td>52</td>
</tr>
<tr>
<td>2.6.1.2. Equivalent Series and Parallel Resistance</td>
<td>53</td>
</tr>
<tr>
<td>2.6.1.3. Dielectric Strength</td>
<td>54</td>
</tr>
<tr>
<td>2.7. Types of Capacitors</td>
<td>54</td>
</tr>
<tr>
<td>2.7.1. Non-Ceramic Capacitors</td>
<td>57</td>
</tr>
<tr>
<td>2.7.1.1. Polymer Film Capacitors</td>
<td>57</td>
</tr>
<tr>
<td>2.7.1.2. Mica Capacitors</td>
<td>57</td>
</tr>
<tr>
<td>2.7.2. Electrolytic Capacitors</td>
<td>58</td>
</tr>
<tr>
<td>2.7.2.1. Aluminum Foil Electrolytic Capacitors</td>
<td>58</td>
</tr>
<tr>
<td>2.7.2.2. Tantalum Electrolytic Capacitors</td>
<td>59</td>
</tr>
</tbody>
</table>
4.3.3. Effect of Heat Treatment on Crystal Structure .......................... 123
  4.3.3.1. Crystal Structure of BaTiO$_3$ ................................. 123
  4.3.3.2. Phase Transition After Heat Treatment .......................... 124
4.3.4. Dielectric Properties of BaTiO$_3$ Films .............................. 124
  4.3.4.1. Structural Dependence of Dielectric Properties ............... 124
  4.3.4.2. As-Prepared Films ........................................ 126
  4.3.4.3. Heat Treated Films ........................................ 126
  4.3.4.4. Ferroelectric Hysteresis .................................. 129
4.4 Conclusions ........................................................................ 129

5 PREPARATION AND CHARACTERIZATION OF BaTiO$_3$
ELECTROLYTIC CAPACITORS FROM POROUS Ti BODIES ......................... 130

5.1. Introduction .................................................................... 130
5.2. Materials and Methods .................................................. 131
  5.2.1. Preparation of Sintered Porous Ti Anodes ....................... 131
  5.2.2. Electrochemical Deposition of BaTiO$_3$ ......................... 135
    5.2.2.1. Vacuum Impregnation of the Electrolyte Solution .......... 135
    5.2.2.2. Electrolysis ................................................ 139
  5.2.3. Microstructural Characterization .................................. 139
  5.2.4. Fabrication of BaTiO$_3$ Electrolytic Capacitors ............... 140
  5.2.5. Dielectric Characterization ...................................... 140
5.3. Results and Discussion .................................................. 141
  5.3.1. Early Attempts .................................................. 141
  5.3.2. Sintered Porous Ti Anodes from Mixtures of Ti and Polystyrene
         ................................................................. 144
  5.3.3. Electrochemical Formation of BaTiO$_3$ .......................... 147
    5.3.3.1. Effect of Electrolyte Salt and Synthesis Temperature .... 147
    5.3.3.2. Effect Applied Cell Voltage ................................ 152
    5.3.3.3. Effect of Treatment Time .................................. 158
  5.3.4. Capacitor Fabrication and Dielectric Properties ............... 158
    5.3.4.1. First Generation Capacitors ................................ 160
    5.3.4.2. New Generation BaTiO$_3$ Electrolytic Capacitors ....... 160
    5.3.4.3. Effect of Purity of Ti Powder ................................ 160
    5.3.4.4. Effect of Heat Treatment .................................. 163
    5.3.4.5. Volumetric Efficiency ..................................... 164
    5.3.4.6. Penetration of Colloidal Carbon ............................ 166
5.4. Conclusions .................................................................... 166

6 THEORETICAL MODELING AND EXPERIMENTAL VERIFICATION
OF ELECTROCHEMICAL EQUILIBRIA IN Ba-Ti-C-H$_2$O SYSTEM ............. 169

6.1. Introduction .................................................................... 169
6.2. Thermodynamic Data ...................................................... 170
  6.2.1. Sources of Thermodynamic Data .................................. 171
  6.2.2. Reference States .................................................. 171
  6.2.3. Estimation at Elevated Temperatures ............................ 172
  6.2.4. Aqueous Ions ..................................................... 172
6.3. Construction of $E_h$-$pH$ Diagrams .................................... 175
  6.3.1. Types of Reactions Involved .................................... 175
    6.3.1.1. Reactions Involving the Transfer of Electrons Only .... 175

vi
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3.1.2. Reactions Involving the Transfer of H⁺ Ions Only</td>
<td>176</td>
</tr>
<tr>
<td>6.3.1.3 Reactions Involving the Transfer of Both Electrons and H⁺ Ions</td>
<td>177</td>
</tr>
<tr>
<td>6.3.2. Stability of Water</td>
<td>177</td>
</tr>
<tr>
<td>6.3.3. Representation of Equilibria</td>
<td>178</td>
</tr>
<tr>
<td>6.3.4. HSC Chemistry for Windows 2.0®</td>
<td>179</td>
</tr>
<tr>
<td>6.4. Limitations of Eh-pH Diagrams</td>
<td>180</td>
</tr>
<tr>
<td>6.4.1. Thermodynamic Data</td>
<td>180</td>
</tr>
<tr>
<td>6.4.2. Species Not Considered</td>
<td>180</td>
</tr>
<tr>
<td>6.4.3. Thermodynamics versus Kinetics</td>
<td>181</td>
</tr>
<tr>
<td>6.4.4. Activities versus Concentrations</td>
<td>181</td>
</tr>
<tr>
<td>6.5. Discussion on Electrochemical Equilibria</td>
<td>182</td>
</tr>
<tr>
<td>6.5.1. Ba-H₂O System</td>
<td>182</td>
</tr>
<tr>
<td>6.5.2. Ti-H₂O System</td>
<td>187</td>
</tr>
<tr>
<td>6.5.3. Ba-Ti-H₂O System</td>
<td>195</td>
</tr>
<tr>
<td>6.5.4. Ba-Ti-C-H₂O System</td>
<td>198</td>
</tr>
<tr>
<td>6.6. Experimental Verification</td>
<td>201</td>
</tr>
<tr>
<td>6.6.1. Synthesis of BaTiO₃ at Low Temperatures</td>
<td>201</td>
</tr>
<tr>
<td>6.6.2. Effect of pH and Ba²⁺ Concentration</td>
<td>203</td>
</tr>
<tr>
<td>6.6.3. Effect of Applied Potential</td>
<td>204</td>
</tr>
<tr>
<td>6.6.4. Effect of Carbon Contamination</td>
<td>205</td>
</tr>
<tr>
<td>6.7. Conclusions</td>
<td>206</td>
</tr>
</tbody>
</table>

**APPENDICES**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A REACTIONS AND EQUILIBRIUM FORMULAE FOR THE Ba-H₂O SYSTEM AT 25, 55, AND 100°C AND 1 ATMOSPHERE PRESSURE</td>
<td>207</td>
</tr>
<tr>
<td>B REACTIONS AND EQUILIBRIUM FORMULAE FOR THE Ti-H₂O SYSTEM AT 25, 55, AND 100°C AND 1 ATMOSPHERE PRESSURE</td>
<td>209</td>
</tr>
<tr>
<td>C REACTIONS AND EQUILIBRIUM FORMULAE FOR THE Ba-Ti-H₂O SYSTEM AT 25, 55, AND 100°C AND 1 ATMOSPHERE PRESSURE</td>
<td>212</td>
</tr>
<tr>
<td>D REACTIONS AND EQUILIBRIUM FORMULAE FOR THE Ba-Ti-C-H₂O SYSTEM AT 25, 55, AND 100°C AND 1 ATMOSPHERE PRESSURE</td>
<td>215</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>220</td>
</tr>
<tr>
<td>BIOGRAPHICAL SKETCH</td>
<td>229</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1.</td>
<td>Dielectric properties of ceramics and glasses</td>
<td>14</td>
</tr>
<tr>
<td>2-2.</td>
<td>Properties and applications of ferroelectric thin film materials</td>
<td>24</td>
</tr>
<tr>
<td>2-3.</td>
<td>Thin film deposition techniques</td>
<td>26</td>
</tr>
<tr>
<td>2-4.</td>
<td>Typical values of the volumetric efficiency for various types of capacitors</td>
<td>55</td>
</tr>
<tr>
<td>2-5.</td>
<td>Dielectric properties of ceramic dielectric materials</td>
<td>67</td>
</tr>
<tr>
<td>3-1.</td>
<td>Electrochemical synthesis conditions and characterization data for selected BaTiO3 thin films</td>
<td>81</td>
</tr>
<tr>
<td>3-2.</td>
<td>Diffraction data calculated from the electron diffraction pattern obtained in the TEM analysis of the BaTiO3 film (Sample BT-55-24), compared with standard JCPDS data</td>
<td>96</td>
</tr>
<tr>
<td>4-1.</td>
<td>Electrochemical synthesis conditions and characterization data for BaTiO3 films</td>
<td>109</td>
</tr>
<tr>
<td>4-2.</td>
<td>Electrolysis time-dependent characteristics of BaTiO3 Films</td>
<td>110</td>
</tr>
<tr>
<td>5-1.</td>
<td>Chemical and physical characteristics of SM Ti and JM Ti powders</td>
<td>134</td>
</tr>
<tr>
<td>5-2.</td>
<td>Electrochemical processing conditions for depositing BaTiO3 on various sintered porous Ti anodes</td>
<td>142</td>
</tr>
<tr>
<td>6-1.</td>
<td>Free energy of formation data for the solid species in Ba-Ti-C-H2O system at 25, 55, and 100°C and 1 atmosphere pressure</td>
<td>173</td>
</tr>
<tr>
<td>6-2.</td>
<td>Free energy of formation data for the dissolved species in Ba-Ti-C-H2O system at 25, 55, and 100°C and 1 atmosphere pressure</td>
<td>174</td>
</tr>
<tr>
<td>6-3.</td>
<td>Experimental conditions and synthesis products described in the published literature on hydrothermal/electrochemical synthesis of BaTiO3 thin films and powders</td>
<td>202</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2-1</td>
<td>Charge storage between two parallel plate conductors: (a) in free space, (b) with a dielectric material</td>
<td>7</td>
</tr>
<tr>
<td>2-2</td>
<td>Schematic illustration of dielectric constant (k) and dielectric loss (tan δ) as a function of applied frequency in a hypothetical material</td>
<td>11</td>
</tr>
<tr>
<td>2-3</td>
<td>Schematic description of various mechanisms of dielectric polarization: (a) electronic, (b) atomic or ionic, (c) high-frequency oscillatory dipole, (d) low frequency orientation dipole, (e) interfacial space charge, and (f) interfacial polarization at heterogeneities</td>
<td>12</td>
</tr>
<tr>
<td>2-4</td>
<td>Octahedral coordination of Ti⁴⁺ ion in the perovskite unit cell of BaTiO₃</td>
<td>16</td>
</tr>
<tr>
<td>2-5</td>
<td>Crystallographic transformations in BaTiO₃</td>
<td>18</td>
</tr>
<tr>
<td>2-6</td>
<td>Phase transformation-induced temperature dependence of polarization characteristics in BaTiO₃: (a) changes in unit cell dimensions, and (b) variation of dielectric constant along crystallographic axes</td>
<td>19</td>
</tr>
<tr>
<td>2-7</td>
<td>Typical polarization hysteresis loop of a ferroelectric material</td>
<td>21</td>
</tr>
<tr>
<td>2-8</td>
<td>Applications of ferroelectric thin films in micro-electronic devices</td>
<td>25</td>
</tr>
<tr>
<td>2-9</td>
<td>Schematic diagram of the apparatus for hydrothermal-electrochemical synthesis of perovskite titanate thin films on Ti substrates</td>
<td>33</td>
</tr>
<tr>
<td>2-10</td>
<td>Effect of Ba²⁺ concentration in the electrolyte on formation of BaTiO₃ on Ti substrate under hydrothermal/electrochemical conditions</td>
<td>35</td>
</tr>
<tr>
<td>2-11</td>
<td>Seeman-Bohlin grazing angle X-ray diffraction geometry for the analysis of thin films</td>
<td>38</td>
</tr>
<tr>
<td>2-12</td>
<td>Schematic of electron energy transitions: (a) initial state, (b) incident X-ray or electron ejects K shell electron, (c) X-ray emission when 2s electron fills vacancy, and (d) KLL Auger electron emission</td>
<td>40</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2-13.</td>
<td>Schematic illustration of a combined AES and XPS instrumentation</td>
<td>42</td>
</tr>
<tr>
<td>2-14.</td>
<td>Typical AES compositional depth profile analysis of a BaTiO₃ thin film on Si substrate</td>
<td>43</td>
</tr>
<tr>
<td>2-15.</td>
<td>Schematic circuit diagrams for dielectric characterization of ferroelectric thin films: (a) auto-balancing bridge for impedance analysis, and (b) modified Sawyer-Tower bridge in virtual ground mode for ferroelectric hysteresis measurement</td>
<td>46</td>
</tr>
<tr>
<td>2-16.</td>
<td>Dependence of dielectric constant and dissipation factor on film thickness for sol-gel derived BaTiO₃ films</td>
<td>49</td>
</tr>
<tr>
<td>2-17.</td>
<td>Frequency and capacitance ranges for applications of various types of capacitors</td>
<td>56</td>
</tr>
<tr>
<td>2-18.</td>
<td>Schematic cross section of a solid tantalum porous sintered anode electrolytic capacitor</td>
<td>60</td>
</tr>
<tr>
<td>2-19.</td>
<td>Variation of (a) dissipation factor and (b) capacitance with frequency for typical solid tantalum porous sintered anode electrolytic capacitors</td>
<td>62</td>
</tr>
<tr>
<td>2-20.</td>
<td>Typical impedance Vs frequency characteristics of solid Ta electrolytic capacitors</td>
<td>63</td>
</tr>
<tr>
<td>2-21.</td>
<td>Most common types of ceramic capacitors: (a) ceramic chip capacitor, (b) ceramic tube capacitor, and (c) ceramic multilayer capacitor</td>
<td>65</td>
</tr>
<tr>
<td>2-22.</td>
<td>Schematic process diagram of the 'wet' and 'dry' fabrication routes for ceramic multilayer capacitors</td>
<td>68</td>
</tr>
<tr>
<td>2-23.</td>
<td>Variation of (a) capacitance and (b) dissipation factor with frequency for capacitors made from various classes of dielectric ceramics</td>
<td>71</td>
</tr>
<tr>
<td>3-1.</td>
<td>Calculated phase stability diagram for Ba-Ti system at 25°C in a sealed vessel containing 20 v/o atmospheric air</td>
<td>77</td>
</tr>
<tr>
<td>3-2.</td>
<td>Schematic diagram of the electrochemical apparatus for the low temperature synthesis of BaTiO₃ thin films in open vessels</td>
<td>79</td>
</tr>
<tr>
<td>3-3.</td>
<td>Auger spectroscopy data for the thin films synthesized at (A) 100°C (Sample BT-100-24), (B) 55°C and low current density (Sample BT-55-24) and (C) 56°C and high current density (Sample BT-56-24) showing variation in film thickness as a function of temperature and current density</td>
<td>83</td>
</tr>
</tbody>
</table>
Figure 3-4. Comparison of X-ray diffraction data for the thin films synthesized at (A) 55°C (Sample BT-55-24), and (B) 100°C (Sample BT-100-24) ........................................ 86

Figure 3-5. X-ray diffraction data for the thin film (Sample BT-98-48) synthesized at pH 12.25. Titanium oxides are the predominant phases .................................................. 87

Figure 3-6. Scanning electron micrographs of the surfaces of the thin films synthesized at (A) 100°C (Sample BT-100-4) and (B) 55°C (Sample BT-55-24). Additional details for the synthesis are provided in Table 3-1 ........................................... 90

Figure 3-7. SEM photomicrograph of Sample BT-29-24 prepared at 29°C showing large, discrete particles ................................................................. 92

Figure 3-8. Transmission electron microscopy data of the BaTiO₃ thin film prepared at 55°C (Sample BT-55-24): (A) Bright field image showing the fine crystallites of BaTiO₃ embedded in a poorly crystalline TiO₂ film and surrounded by the fully grown BaTiO₃ grains seen as large, dark areas, and (B) selected area diffraction pattern collected from the center region of the above image. Indexing information for the SAD pattern is provided in Table 3-2 ........................................ 95

Figure 3-9. Cell voltage as a function of time for samples prepared at (A) 100°C (Sample BT-100-24), (B) 55°C (Sample BT-55-24), and (C) 29°C (Sample BT-29-24). Electrothermal conditions for all samples were similar other than the temperature ........................................ 98

Figure 3-10. SEM photomicrographs of large deposits on Sample BT-29-24 prepared at 29°C: (A) before argon milling and (B) after argon milling showing the texture in the hemispherical deposits ........................................ 100

Figure 4-1. Schematic diagram illustrating the experimental apparatus for electrochemical deposition of BaTiO₃ under constant applied voltage conditions ........................................ 105

Figure 4-2. Scanning electron micrographs of electrochemically prepared BaTiO₃ films on as-received Ti foils, showing the development of microstructure with reaction time: (A) Sample BT-55-4-3 - treated for 4 hours, (B) Sample BT-56-8-3 - treated for 8 hours, (C) Sample BT-57-16-3 - treated for 16 hours, and (D) Sample BT-55-24-3 - treated for 24 hours ........................................ 113
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-3.</td>
<td>Scanning electron micrographs of electrochemically prepared BaTiO3 films on polished Ti coupons, showing the microstructure at short reaction times: (A) Sample BT-56-2-3 - treated for 2 hours and (B) Sample BT-56-4-3 - treated for 4 hours</td>
<td>114</td>
</tr>
<tr>
<td>4-4.</td>
<td>Auger electron spectroscopy data for BaTiO3 film formed on as-received Ti foil (Sample BT-55-24-3). Top: Compositional survey on as-prepared film surface showing no presence of carbon, and Bottom: Compositional depth profile obtained by Ar ion sputtering (500Å/min)</td>
<td>115</td>
</tr>
<tr>
<td>4-5.</td>
<td>Scanning electron micrographs of BaTiO3 film (Sample BT-55-24-3) showing a thickness of 2-3 µm as revealed by a scratch</td>
<td>117</td>
</tr>
<tr>
<td>4-6.</td>
<td>X-ray diffraction data for BaTiO3 films formed on as-received Ti foils showing the peak intensities as a function of reaction time: 8 hours (Sample BT-56-8-3), 16 hours (Sample BT-57-16-3), and 24 hours (Sample BT-55-24-3)</td>
<td>118</td>
</tr>
<tr>
<td>4-7.</td>
<td>Relation between calculated film thickness and X-ray diffraction peak intensity and the total electric charge passed through the electrolytic cell for BaTiO3 films prepared at various reaction times</td>
<td>119</td>
</tr>
<tr>
<td>4-8.</td>
<td>Comparison between calculated film thickness, film thickness estimated from AES depth profile analysis, and the total electric charge passed through the electrolytic cell for BaTiO3 films prepared at various reaction times</td>
<td>120</td>
</tr>
<tr>
<td>4-9.</td>
<td>Typical strip chart data recorded during the electrochemical synthesis of BaTiO3 films: Ag/AgCl reference electrode potential (top) and electrolysis current (bottom) for a 24 h reaction (Sample BT-54-24-3)</td>
<td>122</td>
</tr>
<tr>
<td>4-10.</td>
<td>X-ray diffraction data of as-prepared and heat treated BaTiO3 film (Sample BT-55-24-3) showing the peak shifts toward tetragonal structure after heat treatment</td>
<td>125</td>
</tr>
<tr>
<td>4-11.</td>
<td>Dependence of relative dielectric constant and dissipation factor on applied frequency for the as-prepared and heat treated BaTiO3 films prepared with TEAOH containing electrolyte (Sample BT-55-24-3) and NaOH containing electrolyte (Sample BT-55-24-NH)</td>
<td>127</td>
</tr>
<tr>
<td>4-12.</td>
<td>Polarization hysteresis data for the BaTiO3 thin film (Sample BT-55-24-3) in (a) as-prepared and (b) heat treated conditions</td>
<td>128</td>
</tr>
<tr>
<td>5-1.</td>
<td>Schematic cross section of the proposed BaTiO3 electrolytic capacitor</td>
<td>132</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>5-2.</td>
<td>Processing diagram for the preparation of sintered porous Ti anodes</td>
<td>133</td>
</tr>
<tr>
<td>5-3.</td>
<td>Schematic cross section of the modified die assembly for uniaxial pressing of Ti and polystyrene powder mixtures with solid Ti wire embedded in the compact</td>
<td>136</td>
</tr>
<tr>
<td>5-4.</td>
<td>Processing scheme for the preparation and characterization of BaTiO₃ electrolytic capacitors from sintered porous Ti anodes</td>
<td>137</td>
</tr>
<tr>
<td>5-5.</td>
<td>Schematic illustration of the electrochemical apparatus for depositing BaTiO₃ on the surface of sintered porous Ti anode</td>
<td>138</td>
</tr>
<tr>
<td>5-6.</td>
<td>Scanning electron micrographs of the cross section of JM-NH-BA-99-12, taken from different regions revealing only a partial infiltration of the electrolyte. (A) Low magnification image showing most of the cross section of the Ti anode, (B) high magnification image from the region close to the surface, showing the presence of BaCO₃, (C) high magnification image from the region about 200 μm away from surface, showing the presence of BaTiO₃ coating on Ti particles, and (D) high magnification image from a deeper region showing no presence of coating on Ti surfaces</td>
<td>143</td>
</tr>
<tr>
<td>5-8.</td>
<td>Scanning electron micrographs of green and sintered Ti bodies made from mixtures of polystyrene and two different grades of Ti. A: green body, 20 v/o polystyrene, JM Ti, B: sintered body, 800°C, JM Ti, C: green body, 40 v/o polystyrene, SM Ti, D: sintered body, 900°C, SM Ti</td>
<td>146</td>
</tr>
<tr>
<td>5-9.</td>
<td>Scanning electron micrograph of the cross section of a sintered porous Ti anode showing the presence of Ti wire electrode that was embedded during pressing</td>
<td>148</td>
</tr>
<tr>
<td>5-10.</td>
<td>Scanning electron micrographs of the cross section of an electrochemically treated sintered Ti anode (SM-TH-BH-97-8): (A) at low magnification, revealing complete infiltration of the electrolyte, and (B) at high magnification, showing the presence of a uniform, dense layer of BaTiO₃</td>
<td>149</td>
</tr>
</tbody>
</table>
Figure 5-11. Scanning electron micrographs of the cross sections of electrochemically treated sintered Ti anodes showing the formation of BaTiO₃ in various electrolytes at about 55°C and 100°C: A: barium acetate at 56°C, JM-TH-BA-56-4, (B) barium acetate at 98°C, JM-TH-BA-98-4, (C) barium nitrate at 55°C, JM-TH-BN-55-4, (D) barium nitrate at 97°C, JM-TH-BN-97-4, (E) barium hydroxide at 55°C, JM-TH-BH-55-4, and (F) barium hydroxide at 95°C, JM-TH-BH-95-4.

5-12. X-ray diffraction data for the electrochemically treated sintered Ti anode (JM-TH-BH-95-4) shown with JCPDS standard reference patterns for cubic BaTiO₃ and Ti.

5-13. Low magnification scanning electron micrographs of the cross sections of electrochemically treated sintered Ti anodes, revealing the extent of contamination formed on the surfaces of Ti particles with various electrolyte solutions: (A) barium acetate, JM-TH-BA-98-4, (B) barium nitrate, JM-TH-BN-97-4, and (C) barium hydroxide, JM-TH-BH-95-4.

5-14. Scanning electron micrographs of the cross sections of electrochemically treated sintered Ti anodes showing the formation of BaTiO₃ as a function of applied cell voltage: (A) 3V, SM-TH-BH-96-12, (B) 6V, SM-TH-BH-99-12, (C) 9V, SM-TH-BH-97-12, and (D) 12V, SM-TH-BH-95-12.

5-15. Scanning electron micrographs of the BaTiO₃ film formed on Ti at 12V cell voltage (SM-TH-BH-95-12), showing (A) film detachment due to cracking, and (B) the rough film surface and cracks formed during dielectric breakdown.

5-16. Scanning electron micrographs of the cross sections of electrochemically treated sintered Ti anodes showing the formation of BaTiO₃ as a function of treatment time: (A) 2h, SM-TH-BH-97-2, (B) 4h, SM-TH-BH-96-4, (C) 8h, SM-TH-BH-97-8, and (D) 12h, SM-TH-BH-99-12.

5-17. Capacitance as a function of frequency for BaTiO₃ electrolytic capacitors compared with oxidized Ti anodes.

5-18. Dissipation factor (tan δ) as a function of frequency for BaTiO₃ electrolytic capacitors compared with oxidized Ti anodes.

5-19. Impedance Vs. frequency characteristics of the BaTiO₃ electrolytic capacitors.
Figure 5-20. Scanning electron micrographs of the cross section of the BaTiO₃ electrolytic capacitor (SM-TH-BH-96-8) showing (A) the depth of colloidal carbon (external electrode) penetration into the anode, and (B) the saturation of porosity with colloidal carbon near to the anode surface.

6-1(a). $E_h$-$pH$ diagram for Ba-H₂O system at 25°C and 1 atmosphere pressure, considering the formation of BaH₂. Total activity of dissolved Ba species is varied from 1 m to $10^{-3}$ m. See Appendix A for more information on reactions and equilibrium formulae.

6-1(b). $E_h$-$pH$ diagram for Ba-H₂O system at 25°C, 55°C ($\Delta$), and 100°C ($\Theta$), and 1 atmosphere pressure, considering the formation of BaH₂. Total activity of dissolved Ba species is kept constant at 1 m. See Appendix A for more information on reactions and equilibrium formulae.

6-2(a). $E_h$-$pH$ diagram for Ba-H₂O system at 25°C and 1 atmosphere pressure, not considering the formation of BaH₂. Total activity of dissolved Ba species is varied from 1 m to $10^{-3}$ m. See Appendix A for more information on reactions and equilibrium formulae.

6-2(b). $E_h$-$pH$ diagram for Ba-H₂O system at 25°C, 55°C ($\Delta$), and 100°C ($\Theta$), and 1 atmosphere pressure, not considering the formation of BaH₂. Total activity of dissolved Ba species is kept constant at 1 m. See Appendix A for more information on reactions and equilibrium formulae.

6-3(a). $E_h$-$pH$ diagram for Ti-H₂O system at 25°C and 1 atmosphere pressure, considering the formation of TiH₂. Total activity of dissolved Ti species is varied from 1 m to $10^{-3}$ m. See Appendix B for more information on reactions and equilibrium formulae.

6-3(b). $E_h$-$pH$ diagram for Ti-H₂O system at 25°C, 55°C ($\Delta$), and 100°C ($\Theta$), and 1 atmosphere pressure, considering the formation of TiH₂. Total activity of dissolved Ti species is kept constant at 1 m. See Appendix B for more information on reactions and equilibrium formulae.

6-4(a). $E_h$-$pH$ diagram for Ti-H₂O system at 25°C and 1 atmosphere pressure, not considering the formation of TiH₂. Total activity of dissolved Ti species is varied from 1 m to $10^{-3}$ m. See Appendix B for more information on reactions and equilibrium formulae.
6-4(b). Eh-pH diagram for Ti-H₂O system at 25 (●), 55 (△), and 100°C (●), and 1 atmosphere pressure, not considering the formation of TiH₂. Total activity of dissolved Ti species is kept constant at 1 m. See Appendix B for more information on reactions and equilibrium formulae.

6-5(a). Eh-pH diagram for Ti-H₂O system at 25°C and 1 atmosphere pressure, for extended range of pH, not considering the formation of TiH₂. Total activity of dissolved Ti species is varied from 1 m to 10⁻³ m. See Appendix B for more information on reactions and equilibrium formulae.

6-5(b). Eh-pH diagram for Ti-H₂O system at 25 (●), 55 (△), and 100°C (●), and 1 atmosphere pressure, for extended range of pH, not considering the formation of TiH₂. Total activity of dissolved Ti species is kept constant at 1 m. See Appendix B for more information on reactions and equilibrium formulae.

6-6(a). Eh-pH diagram for Ba-Ti-H₂O system at 25°C and 1 atmosphere pressure. Total activities of dissolved species are independently varied for Ba and Ti, in the range 1 m to 10⁻³ m. See Appendix C for more information on reactions and equilibrium formulae.

6-6(b). Eh-pH diagram for Ba-Ti-H₂O system at 25 (●), 55 (△), and 100°C (●), and 1 atmosphere pressure. Total activities of dissolved species of Ba and Ti are kept constant at 1 m each. See Appendix C for more information on reactions and equilibrium formulae.

6-7(a). Eh-pH diagram for Ba-Ti-C-H₂O system at 25°C and 1 atmosphere pressure. Total activities of dissolved species are independently varied for Ba, Ti and C, in the range 1 m to 10⁻⁶ m. See Appendix D for more information on reactions and equilibrium formulae.

6-7(b). Eh-pH diagram for Ba-Ti-C-H₂O system at 25 (●), 55 (△), and 100°C (●), and 1 atmosphere pressure. Total activities of dissolved species of Ba, Ti, and C are kept constant at 1 m each. See Appendix D for more information on reactions and equilibrium formulae.
Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

ANALYSIS AND PERFORMANCE OF ELECTROCHEMICALLY SYNTHESIZED BARIUM TITANATE FILMS AND ELECTROLYTIC CAPACITORS

By

SRIDHAR VENIGALLA

December 1995

Chairperson: Dr. James H. Adair
Major Department: Materials Science and Engineering

Polycrystalline BaTiO$_3$ thin films of approximately 1 μm thickness have been synthesized on Ti substrates by an electrochemical process, at temperatures as low as 55°C. The effect of various processing parameters, such as solution chemistry, atmosphere, quality of substrate surface, applied voltage, current density, temperature and reaction time have been discussed. Formation of BaTiO$_3$ is found to be favored only in highly alkaline (pH~14) solutions. Film thickness and uniformity increase with reaction time up to 24 hours. The quantity of total electric charge passed through the electrolytic cell is found to govern the film thickness and uniformity. Use of tetraethylammonium hydroxide, a non-alkali base reagent to adjust solution pH, has resulted in films having improved dielectric properties as opposed to the films prepared with alkali metal bases such as NaOH. Heat treatment at 200°C further improved the dielectric properties through a phase transition to the thermodynamically stable, ferroelectric tetragonal BaTiO$_3$.

Current work also involves the fabrication and characterization of BaTiO$_3$ electrolytic capacitors. Effects of electrochemical processing parameters on the formation of BaTiO$_3$ on the surface of sintered porous Ti anode are described. Influence of the purity of Ti powder, porosity of the sintered anode, and post-deposition heat treatment on the dielectric properties of the fabricated capacitors are discussed. Complete penetration of the
electrolyte solution and an uniform coating of BaTiO₃ was achieved over the entire surface of Ti using high porosity (35-40% theoretical density) sintered Ti anodes. Samples treated for 8h in 0.5M Ba(OH)₂·8H₂O electrolyte solutions at 100°C with 12V applied cell voltage showed the formation of dense, uniform BaTiO₃ coating on the surface of Ti anode. Higher purity (Sumitomo, 99.96% Ti), chloride free Ti powder provided smaller dissipation factors at low frequencies. Heat treatment at 400°C has significantly increased the capacitance at all frequencies, while it lowered the dissipation factors at low frequencies. Calculated volumetric efficiencies are comparable to those typically obtained for Ta solid electrolytic capacitors. Penetration of colloidal carbon (external) electrode was found to be limited to a depth of 300μm, which might have limited the volumetric efficiencies.

Finally, the electrochemical equilibria in Ba-H₂O, Ti-H₂O, Ba-Ti-H₂O and Ba-Ti-C-H₂O systems are represented in the form of Eh-pH diagrams. The diagrams are constructed based on the most recent thermochemical data available, at temperatures of 25, 55, and 100°C. The effect of total activities of dissolved species of Ba, Ti, and C on thermodynamic equilibria has been represented in the diagrams. BaTiO₃ is found to be the stable phase at high pH and moderate potentials. The presence of even small amounts of carbon, usually in the form of dissolved atmospheric CO₂, significantly restricts the stability of BaTiO₃. The validity Eh-pH equilibrium diagrams obtained for Ba-Ti-H₂O and Ba-Ti-H₂O systems is verified using the data published in the literature for the hydrothermal and electrochemical synthesis of BaTiO₃.

xviii
CHAPTER 1
INTRODUCTION

Barium titanate (BaTiO₃) is an important engineering material for electronic applications due to its high dielectric permittivity and ferroelectric properties. It is widely used in multilayer ceramic capacitors, ceramic chip capacitors, pyroelectric sensors, and the piezoelectric devices [1-4]. In the world of miniaturization, BaTiO₃ thin films are promising for the future development of hybrid microelectronic devices such as high charge storage capacitors (used as Dynamic Random Access Memories) and nonvolatile ferroelectric memories [5, 6]. Many techniques have been investigated for preparing barium titanate thin films. The physical vapor deposition (PVD) techniques are vacuum intensive and require high temperatures (above 500°C) to deposit crystalline films. The amorphous films prepared at low temperatures require a post-deposition annealing, which may result in selective evaporation of chemical constituents or undesirable reactions with atmosphere and substrate. Chemical methods such as sol-gel, metal-organic decomposition, and chemical vapor deposition (CVD) also require either a post-deposition annealing or a high temperature substrate to prepare phase-pure, crystalline BaTiO₃ [7]. Use of high temperatures to deposit or heat treat the films not only causes compatibility problems with integrated silicon technology, but also induces thermal stresses in the films. Therefore, an inexpensive process to directly prepare crystalline BaTiO₃ films at low temperatures is highly desirable.

Electrochemical methods have potential for the near room temperature production of simple and complex oxide thin films on metallic substrates. Deposition or growth of sparingly soluble single component oxides on metal surfaces is neither novel nor difficult to accomplish [8-11]. The process of anodization is achieved by anodic polarization of the
metal surface to form the resistive metal oxide coating. Composition of the coating depends upon the composition of the metal and the solution in which the anodization is performed, with cationic and anionic species incorporated into the structure of the oxide. It is critical to ensure that the polarization induced reactions proceed with sufficient singularity to assure that the desired reaction product is formed and that parallel or side reactions that result in formation of alternative compositions are avoided.

Several investigations were recently reported on the synthesis of perovskite (ABO₃) complex oxides such as BaTiO₃, SrTiO₃, and CaTiO₃ and their solid solutions on Ti substrates using hydrothermal-electrochemical methods. This process involves the anodization of a Ti substrate in an electrolyte containing A ion (Ba²⁺, Sr²⁺, and Ca²⁺) at elevated temperatures (150-800°C) and pressures [12-22]. The thickness, microstructural uniformity, and crystallinity of these films depend on various processing parameters such as temperature, reaction time, electrolyte chemistry, atmosphere, applied potential and current density. To fully exploit the advantages of electrochemical methods and make them commercially viable, it is critical to lower the synthesis temperatures to below the boiling point of water, thereby avoiding the use of sealed reaction vessels that are capital intensive, low in productivity and industrial safety. By understanding the fundamentals of BaTiO₃ phase stability and the mechanisms of electrochemical corrosion and anodization of metals in aqueous solutions, the early part of this dissertation attempts to synthesize BaTiO₃ thin films on Ti substrates at low temperatures, employing open reaction vessels. Several processing conditions such as electrolyte chemistry and pH, atmosphere, cell voltage, current density, reaction temperature and time were studied to optimize the film thickness and microstructure. Several techniques (scanning electron microscopy, transmission electron microscopy, Auger electron spectroscopy, and X-ray diffraction) were utilized to characterize the physical and chemical properties of the films. Dielectric characterization was also performed on selected samples in as-prepared and heat treated conditions.
Electrolytic capacitors are very popular in applications where a large capacitance (charge storage ability) is required [2]. Typical applications include motor starters, photo flash equipment and charge blockage devices. Electrolytic capacitors provide a large capacitance per unit volume of the device (volumetric efficiency), owing to the large surface area of the dielectric. The dielectric material in an electrolytic capacitor consists of an anodically formed oxide of the anode material, which serves as the positive electrode of the capacitor. The metals most employed are aluminum and tantalum, and the anodic oxides are $\gamma$-$\text{Al}_2\text{O}_3$ and $\text{Ta}_2\text{O}_5$ respectively [23]. The effective dielectric constant of pure $\gamma$-$\text{Al}_2\text{O}_3$ is 8.4 and that of tantalum oxide is 28. In certain commercial grade capacitors, the dielectric constant can be slightly lower for aluminum oxide and appreciably lower for tantalum oxide due to the presence of impurities and the amorphous nature of the as-formed film [24]. Most commonly used among the several kinds of electrolytic capacitors is the 'porous sintered anode solid tantalum' electrolytic capacitor. They are fabricated from lightly sintered porous (about 60 percent density) Ta anodes that contain internally attached solid Ta wire (which acts as the internal electrode). The anodes are electrochemically treated in a bath containing borates or phosphates to form $\text{Ta}_2\text{O}_5$ coating on the entire surface of tantalum. The porous nature of the anode and the fine particle size of Ta powder used to prepare the anode provide a large surface area of the dielectric per unit volume. Subsequent electroding and cathode encasement provide a capacitor with a very large capacitance [24-26].

Development of $\text{BaTiO}_3$ electrolytic capacitors, utilizing the electrochemical process developed for the synthesis of $\text{BaTiO}_3$ thin films on Ti substrates and the technology described above for the solid tantalum electrolytic capacitors will have significant impact on the applicability of these capacitors. Higher dielectric constant of $\text{BaTiO}_3$ (~3000 for single crystal, and about 300 for polycrystalline thin films) will tremendously improve the volumetric efficiency of these capacitors and open a wide range of new applications, where very large capacitances are required at low operating voltages. Recent advances in methods
to electrochemically synthesize BaTiO$_3$ thin films on Ti substrates at low temperatures make it feasible to economically prepare BaTiO$_3$ electrolytic capacitors. The later part of investigation in this dissertation focuses on the optimization of electrochemical processing parameters to prepare BaTiO$_3$ electrolytic capacitors from porous, sintered Ti anodes. Dielectric characterization to evaluate the electrical properties of these capacitors has also been performed and comparisons are made with the conventional Ta solid electrolytics.

Understanding phase stability relationships is critical to succeed in synthesizing novel materials, controlling their properties and predicting their environmental stability. Chemical synthesis methods for the preparation of structural and electronic ceramic materials has seen significant advances in recent years. However, very few studies were performed to construct phase stability diagrams in the relevant systems [27, 28]. The advent of electrochemical methods to prepare perovskite titanate thin films on Ti substrates further warrants the construction of phase equilibria in aqueous electrolytes. Therefore, representation of electrochemical equilibria in Ba-Ti-C-H$_2$O system in the form of $E_h$-pH diagrams (where $E_h$ is the equilibrium electrode potential versus the standard hydrogen electrode) will be beneficial to optimize the processing conditions in the electrochemical synthesis of BaTiO$_3$. The final segment of this dissertation involves the construction of $E_h$-pH diagrams for Ba-H$_2$O, Ti-H$_2$O, Ba-Ti-H$_2$O, and Ba-Ti-C-H$_2$O systems, utilizing the most recent thermodynamic data available for various species in each system. The diagrams were constructed at 25, 55, and 100°C, and at various activities of the dissolved species to study the phase equilibria under various conditions. The resulting phase equilibria are verified with the synthesis data obtained in the current work as well as the data reported in the literature.

The dissertation is divided into five major chapters. Chapter 2 provides a detailed review of literature on phenomena of dielectric polarization, charge storage and ferroelectricity, ferroelectric materials, synthesis of ferroelectric thin films with emphasis on BaTiO$_3$, electrochemical synthesis of BaTiO$_3$ thin films. In the later part of the chapter,
the various kinds of capacitors, their fabrication methods, device characteristics and applications are discussed, with a special emphasis on Ta solid electrolytic capacitors. Chapters 3 and 4 present the study on low temperature electrochemical synthesis of BaTiO$_3$ thin films on Ti substrates, under galvanostatic and constant voltage conditions, respectively. Film formation mechanisms under electrochemical conditions are discussed in Chapter 3, while the use of non-alkali electrolyte solutions to improve dielectric properties of the prepared films is the focus of Chapter 4. Preparation of BaTiO$_3$ electrolytic capacitors from lightly sintered porous Ti bodies is described in Chapter 5, including the dielectric characterization data. $E_h$-$pH$ diagrams describing the electrochemical equilibria in the Ba-Ti-C-H$_2$O system are presented in Chapter 6. Experimental verification of these diagrams is provided, based on the available literature as well as the data obtained in the present study.
CHAPTER 2
LITERATURE REVIEW

2.1. Introduction

Barium titanate, the first ceramic material in which ferroelectric behavior was observed, is extremely popular in electrical and electronic applications, where its ferroelectric and piezoelectric properties are exploited. Used in various forms ranging from single crystals to thin films, BaTiO$_3$ is frequently chosen to fabricate a wide variety of devices, such as high frequency capacitors, transducers, memory devices and pyroelectric sensors. Since ferroelectricity is the single most important characteristic behind the prominence of BaTiO$_3$, the early part of this chapter provides a detailed description on the theory of dielectric polarization and ferroelectricity, ferroelectric materials and their properties. In the later sections, a review of literature on methods to fabricate BaTiO$_3$ thin films is provided. To emphasize the importance of high dielectric constant for capacitor applications, a summary on various types of capacitors, their characteristics, and fabrication methods is also provided. This chapter concludes with a discussion on the feasibility of developing BaTiO$_3$ electrolytic capacitors, based on the concept of solid Ta electrolytic capacitors and the electrochemical methods to prepare BaTiO$_3$ thin films on Ti substrates.

2.2. Dielectric Polarization and Ferroelectricity

2.2.1. Theory of Charge Storage and Capacitance

When an electric field is applied to an ideal dielectric material there is no long-range transport of charge, but only a limited rearrangement such that the dielectric acquires a dipole moment and is said to be polarized. Polarization in a material causes charge storage (capacitance) on the electrodes as shown schematically in Figure 2-1. Electrically,
Figure 2-1. Charge storage between two parallel plate conductors: (a) in free space, (b) with a dielectric material [1].
capacitance is present between any two adjacent conductors that are separated by non-conducting medium. A conventional capacitor consists of two parallel metal plates (termed electrodes) separated by a dielectric material. When a voltage is applied across the plates, the capacitor will become charged, and the amount of charge primarily depends on the source voltage and the polarizability of the dielectric material. The capacitance ($C$) of a capacitor is defined as the ratio of the charge ($Q$) acquired to the applied voltage ($V$):

$$C(\text{farads}) = \frac{Q(\text{coulombs})}{V(\text{volts})} \quad [2.1]$$

A capacitor is said to possess 1 farad of capacitance if its potential is raised 1 volt when it receives a charge of 1 Coulomb. This unit of capacitance is inconveniently large and in practice only submultiples like $mF$ ($10^{-3} F$), $\mu F$ ($10^{-6} F$), $nF$ ($10^{-9} F$), and $pF$ ($10^{-12} F$) are used to specify the capacitances of most commercial capacitors.

Capacitance, as defined above, determines the amount of charge that can be stored by a capacitor at any given applied voltage. Therefore, capacitance is a device characteristic that depends on geometry of the capacitor and permittivity of the dielectric, as described by the following relation for a parallel plate capacitor:

$$C = \frac{\varepsilon A}{d} \quad [2.2]$$

where $\varepsilon$ is the dielectric permittivity, $A$ is the area of one plate in square meters, and $d$ is the distance between the plates in meters. The higher the permittivity of the dielectric between the plates, the higher the capacitance. Dielectric polarizability of a material is often represented by the relative dielectric constant ($k$), defined as the ratio of permittivity ($\varepsilon$) of the material to the permittivity of free space ($\varepsilon_0 = 8.854 \times 10^{-12} F / m$).

$$k = \frac{\varepsilon}{\varepsilon_0} \quad [2.3]$$

Therefore, the capacitance of a parallel plate capacitor can be written as

$$C = \frac{k\varepsilon_0 A}{d} \quad [2.4]$$
Dissipation factor is a measure of loss in a capacitor. In an ideal capacitor, the alternating current will lead the voltage by $90^\circ$. In practice, the current leads the voltage by some lesser phase angle $\phi$ owing to the series resistance $R$, the complement of this angle ($90 - \phi$) is called the loss angle $\delta$. The dissipation factor (also called loss tangent) is given by $\tan \delta$. Variation of dissipation factor with frequency of applied alternating voltage implies the presence of polarization mechanism in the dielectric material. Molecular interferences in the material limit the frequency at which the alignment (polarization) can occur. If the applied frequency is less than the limiting frequency, full alignment can occur, then the capacitance is high and the dissipation factor is low. If the applied frequency is comparable to the limiting frequency, the losses become high. However, as explained in the following sections, there can be more than one polarization mechanism in a dielectric material and each mechanism can exhibit a frequency dispersion, owing to variations in microstructure and chemical homogeneity. As a result, most dielectrics show a frequency dependence of dielectric constant and dissipation factors. In addition, ionic migration can cause space charge polarization at low frequencies, resulting high capacitances, but also high loss factors.

2.2.2. Mechanisms of Dielectric Polarization

Dielectric processes in materials are very important for their applications in electronic and electrical components. These processes determine the suitability of a material either as a capacitive device (high dielectric polarization) or as an insulating device (low dielectric polarization). There are several ways in which a dielectric material responds to neutralize the external applied electric field, which are called dielectric polarization mechanisms, as described below:

There are four major polarization mechanisms in dielectric materials, involving a short range motion of charge in each case, contributing to the total polarization in the material. The polarization mechanisms are: electronic polarization ($P_e$), atomic polarization ($P_a$), dipole polarization ($P_d$), and interfacial polarization ($P_i$). Each of these mechanisms
have a frequency limit below which they can follow an applied alternating electric field. Above the limiting frequency, the structural features in the material restrict the ability of the charge centers to align with the applied field (dielectric relaxation) and the polarization is lost. Therefore, when a material has more than one polarization mechanism, the contribution from all mechanisms is present at low frequencies, and as the frequency is increased, each mechanism loses its contribution at the relaxation frequency, until all the polarization is lost at extremely high (> $10^{15}$ Hz) frequencies. Figure 2-2 schematically illustrates the frequency dependence of the polarization mechanisms in dielectric materials. The dielectric losses (represented as dielectric loss factor, tan δ) that occur due to the resonance between the relaxation frequency and the applied frequency are also shown in Figure 2-2.

The schematic description of the four major kinds of polarization mechanisms is provided in Figure 2-3. Electronic polarization ($P_e$) arises from the shift of the negatively charged valence electron cloud of the ions within the material with respect to the positively charged nucleus. This very short range charge displacement occurs in the optical regime ($10^{15}$ Hz) of the electromagnetic spectrum and contributes to the refractive index of the material. At lower frequencies, in the infrared range ($10^{12} - 10^{13}$ Hz), atomic or ionic polarization occurs ($P_a$) by the displacement of oppositely charged ions with respect to each other. The exact frequency at which the relaxation occurs is characteristic of the bond strength between the ions. In the sub-infrared range of frequency, dipole polarization occurs, which involves the perturbation of the thermal motion of ionic and molecular dipoles producing a net dipolar orientation in the direction of applied field. There are two general types of dipolar polarization. First, the molecules containing a permanent dipole moment rotate against an elastic restoring force and align in the direction of applied field ($P_{d2}$). This mechanism of dipolar polarization is important for liquids, gases, and polar solids such as ice and many organic plastic insulators. Since the dipoles are oscillated around their equilibrium position, the frequency of relaxation for this mechanism is very
Figure 2-2. Schematic illustration of dielectric constant (k) and dielectric loss (tan δ) as a function of applied frequency in a hypothetical material [1].
Figure 2-3. Schematic description of various mechanisms of dielectric polarization: (a) electronic, (b) atomic or ionic, (c) high-frequency oscillatory dipole, (d) low frequency orientation dipole, (e) interfacial space charge, and (f) interfacial polarization at heterogeneities [1].
high, in the range of $10^{11}$ Hz. In the second type of dipolar polarization, the molecules rotate between two equivalent equilibrium positions ($P_{eq}$). It is the spontaneous alignment of dipoles in one of the equilibrium positions which gives rise to the large, nonlinear polarization in ferroelectric materials, as described later. Since an appreciable distance of charge migration is involved between the equilibrium positions, the relaxation occurs at a frequency range of $10^3 - 10^6$ Hz.

The last mechanism of polarization is the interfacial or space charge polarization ($P_{n}$), which occurs when mobile charge carriers are impeded by a physical barrier that restricts charge migration. The charges accumulate at the barriers producing a localized polarization in the material. Since the charge migration is relatively long ranged, this occurs only at a sufficiently low frequency ($<1$ Hz). However, if the barriers are an internal structural feature, or the density of charges contributing to the interfacial polarization is sufficiently large, the frequency range may extend to $10^3$ Hz range ($P_{n}$). Table 2-1 lists the frequencies and dielectric constants for several ceramics and glasses.

2.2.3. Ferroelectricity

Ferroelectricity is special characteristic of a group of dielectric materials (termed as non-linear dielectrics or ferroelectrics) leading to the presence of spontaneous polarization (polarization without the external applied electric field), and the ability to switch the direction of the internal polarization with an externally applied electric field. The spontaneous alignment of dipoles which occurs at the onset of ferroelectricity is often associated with a crystallographic phase change from a centrosymmetric, non-polar lattice to a non-centro symmetric polar lattice. Of the 32 crystal classes or point groups, 11 are centrosymmetric and therefore can not possess polar properties or spontaneous polarization [1]. One of the remaining 21 noncentrosymmetric point groups (cubic 432) has symmetry elements that prevent polar characteristics. However, the other 20 point groups have one or more polar axes and thus can exhibit several polar effects such as piezoelectricity, pyroelectricity and ferroelectricity.
Table 2-1. Dielectric properties of ceramics and glasses.

<table>
<thead>
<tr>
<th>Dielectric Material</th>
<th>Frequency (Hz)</th>
<th>Dielectric Constant</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>$10^2$-$10^{10}$</td>
<td>3.78</td>
<td>1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>dc</td>
<td>8.60</td>
<td>1</td>
</tr>
<tr>
<td>Pyrex</td>
<td>$10^2$-$10^6$</td>
<td>5.02 - 4.84</td>
<td>1</td>
</tr>
<tr>
<td>Diamond</td>
<td>dc</td>
<td>6.6</td>
<td>1</td>
</tr>
<tr>
<td>α-SiC</td>
<td>dc</td>
<td>9.7</td>
<td>1</td>
</tr>
<tr>
<td>LiF</td>
<td>dc</td>
<td>9.0</td>
<td>1</td>
</tr>
<tr>
<td>KBr</td>
<td>dc</td>
<td>4.9</td>
<td>1</td>
</tr>
<tr>
<td>MgO</td>
<td>dc</td>
<td>9.6</td>
<td>1</td>
</tr>
<tr>
<td>Mg₂SiO₄</td>
<td>dc</td>
<td>6.2</td>
<td>1</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>$10^2$-$10^{10}$</td>
<td>1400</td>
<td>2</td>
</tr>
<tr>
<td>PbTiO₃</td>
<td>$10^2$-$10^{10}$</td>
<td>210</td>
<td>2</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>$10^2$-$10^{10}$</td>
<td>320</td>
<td>6</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>$10^2$-$10^{10}$</td>
<td>68</td>
<td>2</td>
</tr>
<tr>
<td>PZT</td>
<td>$10^2$-$10^{10}$</td>
<td>1800</td>
<td>6</td>
</tr>
</tbody>
</table>

Note: 'dc' refers to frequency independent behavior, which indicates that electronic polarization is the only dielectric mechanism in the material.
Piezoelectricity is the property of a crystal to exhibit electric polarity when subjected to a stress, and conversely, if an electric field is applied, a piezoelectric material will expand or compress depending on the orientation of the applied field. Of the 20 piezoelectric classes, 10 have unique polar axis, an axis which shows properties at one end different than the other. Crystals in these classes are called polar crystals because they are spontaneously polarized and exhibit ferroelectricity. Spontaneous polarization is a function of temperature, and therefore, if a change in temperature is imposed on a polar crystal, electric charge is induced on the opposite faces. This effect is called pyroelectricity. Ferroelectric crystals are also pyroelectric. However, ferroelectric crystals are only those crystals for which the spontaneous polarization can be reversed by applying an electric field.

Barium titanate (BaTiO$_3$) is an excellent example to illustrate the structural changes that occur when a crystal changes from nonferroelectric (paraelectric) to a ferroelectric state. The Ti$^{4+}$ ions of BaTiO$_3$ are surrounded by six oxygen ions in an octahedral configuration, as shown in Figure 2-4. Since a regular TiO$_6$ octahedron has a center of symmetry, the six Ti-O dipole moments cancel each other in antiparallel pairs. A net permanent dipole moment of the octahedron can result only by a unilateral displacement of the positively charged Ti$^{4+}$ ion against its negatively charged O$^{2-}$ surroundings. Ferroelectricity requires the coupling of such displacements and the dipole moments associated with the displacements. In the ABO$_3$ or BaTiO$_3$ (perovskite-like) structure, named after the CaTiO$_3$ perovskite mineral, each oxygen has to be coupled to only two Ti ions. As a result, the TiO$_6$ octahedra in BaTiO$_3$ can be placed in identical orientations, joined at their corners, and fixed in position by Ba ions. Thus, in BaTiO$_3$, the Ba and O ions form a fcc lattice, with Ti ions fitting into octahedral (body center) interstices. The characteristic feature of the Ba, Pb, and Sr titanates is that the large size of the Ba, Pb, and Sr ions increases the size of the cell of the fcc AO$_3$ structure so that the Ti atom is at the lower edge of the stability in the octahedral interstices. Consequently, there are equivalent minimum
Figure 2-4. Octahedral coordination of Ti$^{4+}$ ion in the perovskite unit cell of BaTiO$_3$ [2].
energy positions for the Ti atom which are off-center and can therefore give rise to permanent electric dipoles.

At a temperature higher than $T_c$ (curie temperature) the thermal energy is sufficient to allow the Ti atoms to move randomly from one position to another, so there is no fixed asymmetry. The open octahedral site still allows the Ti atom to develop a large dipole moment when an external field is applied, but there is no spontaneous polarization. The material is called paraelectric in this symmetric configuration. When temperature is lowered below $T_c$, the position of the Ti ion and the octahedral site changes from cubic to tetragonal symmetry, with the Ti ion in an off-centered position corresponding to a permanent dipole. Those dipoles are ordered, giving a domain structure with a net spontaneous polarization within the domains. The cubic to tetragonal phase transition in BaTiO$_3$ occurs around 120°C. It also undergoes two other phase transitions (Figure 2-5) at lower temperatures: a tetragonal to orthorhombic transition at 5°C, and an orthorhombic to rhombohedral transition at -90°C [1]. The crystallographic dimensions of the BaTiO$_3$ lattice change with temperature, and at the phase transitions, as shown in Figure 2-6 (a), mainly due to the distortion in the TiO$_6$ octahedra as the temperature is lowered from the high temperature cubic phase. Because the distorted octahedra are coupled together, there is a very large spontaneous polarization, giving rise to a large dielectric constant ($\sim$3000 at 25°C), and a strong dependence of dielectric constant on temperature [2], as shown in Figure 2-6 (b). In regard to capacitors, it is extremely important that the dielectric constant is high over a wide range of temperature. The presence of the two lower ferroelectric transitions ensures that the dielectric constant remains high below the Curie temperature. As seen in Figure 2-6 (b), the dielectric constant along the $a$ axis is larger than that along the polar $c$ axis. This is attributed to the instability of the structure that makes it easy to tilt the spontaneous polarization vector with a transverse electric field [3]. However, the dielectric constant in rhombohedral state is incorrectly represented as a function of crystallographic axes $a$ and $c$ in Figure 2-6(b), while there is only one crystallographic axis ($a$) in rhombohedral
Figure 2-5. Crystallographic transformations in BaTiO$_3$ [1].
Figure 2-6. Phase transformation-induced temperature dependence of polarization characteristics in BaTiO$_3$: (a) changes in unit cell dimensions, and (b) variation of dielectric constant along crystallographic axes [2].
structure (Figure 2-6(a)). Even though this mistake has been realized for a long time, no attempts were made to obtain corrected data due to several problems associated with low temperature (-90°C) dielectric measurements while applying mechanical load to prevent twinning [29].

An essential consequence of the presence of spontaneous polarization in the ferroelectric materials is their hysteresis behavior. The hysteresis loop (Figure 2-7) is due to the presence of crystallographic domains within which there is complete alignment of electric dipoles. At low field strengths in unpolarized (also called virgin) ferroelectric material, the polarization \( P, \mu C/cm^2 \) is initially reversible and is nearly linear with the applied field \( E, V/cm \). At higher field strengths, the polarization increases considerably as a result of the switching of the ferroelectric domains. The polarization switches so as to align with the applied field by means of domain boundaries moving through the crystal. At high enough field strengths, the change in polarization is small due to polarization saturation \( P_{sat} \), i.e., all the domains of like orientation are aligned with the field. Extrapolation of the saturation curve back to zero field gives \( P_s \), the saturation polarization, corresponding to the spontaneous polarization with all the dipoles aligned in parallel, with no applied field. When the applied field continues to increase beyond the value required for saturation polarization, the polarization also continues to increase, albeit slowly and linearly with the field. Even though all the domains are aligned parallel to each other, the individual TiO\(_6\) polarizable units can continue to be distorted increasing the unit polarization. This is an important contrast to ferromagnetic materials, where application of magnetic field greater than required for saturation magnetization \( M_s \) does not increase the net magnetic moment of the material. When the applied field is withdrawn, a finite polarization remains in the material, called remnant polarization, \( P_r \). This is due to the oriented domains being not able to go to the random state without an additional energy input, by an oppositely directed field [4]. The strength of field required for bringing polarization to zero is called coercive field, \( E_c \). The value of coercive field is a significant
Figure 2-7. Typical polarization hysteresis loop of a ferroelectric material [4].
characteristic of a ferroelectric material, as it determines the ability of the material to switch polarization direction.

2.2.4. Ferroelectric Materials

Ferroelectric materials include titanates, zirconates, and niobates with oxygen octahedral structure types. Some of the prominent materials are perovskite compounds BaTiO₃, PbTiO₃, PbZrO₃, Pb(Mg,Nb)O₃ (PMN), KNbO₃, and their solid solutions, tungsten-bronze compounds such as (Sr,Ba)Nb₂O₆, and the ilmenite compound LiNbO₃. Among the solid solutions of perovskites, perhaps the most important thin film material for memory applications is Pb(Zr,Ti)O₃ (PZT), the solid solution of PbTiO₃ and PbZrO₃. PbTiO₃ and PZT are suitable for pyroelectric sensing applications due to their large pyroelectric coefficients, whereas BaTiO₃ and PMN are considered for capacitor applications due to their high dielectric constants [5].

Since barium titanate is by far the most popular ferroelectric material, used as the dielectric in multilayer ceramic capacitors, there have been many studies of its solid solutions [3-7, 30, 31]. Substitutions for Ba²⁺ or Ti⁴⁺ are used to raise the permittivity, decrease the temperature dependence of dielectric constant, and lower the dielectric losses. Substituting a divalent cation for barium in BaTiO₃ modifies the transition temperatures. The three most commonly used "Curie point shifters" are Pb²⁺, Sr²⁺, and Ca²⁺. Modest amounts of Pb²⁺ raise Tᶜ, and Ca²⁺ has little effect. Divalent Pb is one of the very few additions which increases the transition temperature. This is because the tetragonal pyramidal coordination favored by Pb²⁺ stabilizes the tetragonal phase with respect to the adjacent cubic and orthorhombic phases. All three curie point shifters destabilize the orthorhombic and rhombohedral phases of BaTiO₃ as the lower two transition temperatures drop when increasing amounts of Pb²⁺, Sr²⁺, or Ca²⁺ are added. The opposite effect is achieved by replacing titanium with larger tetravalent ions, for example, Zr.

A number of niobates having a tetragonal or related orthorhombic tungsten-bronze structure are also receiving attention because of their potential in applications in
electrooptic, nonlinear optic, photorefractive, pyroelectric, bulkwave, and surface acoustic wave (SAW) devices [5]. These niobates include Ba$_2$NaNb$_5$O$_{15}$ (BNN), (Sr,Ba)Nb$_2$O$_6$ (SBN), (Pa,Ba) Nb$_2$O$_6$ (PBN), K$_3$Li$_2$Nb$_5$O$_{15}$ (KLN), and Pb$_2$KNb$_5$O$_{15}$ (PKN).

2.2.5 Thin Film Ferroelectrics and Their Applications

The quest for miniaturization and high performance in the electronic device manufacturing, and the necessity to integrate the bulky, discrete electronic components has led to the development of thin film materials for many applications. Thin films have the added advantages of small volume, large geometrical flexibility, and convenient integration with semiconductor or optical integrated circuits. Prominent among them are the ferroelectric thin films, owing to the wide variety of properties and high charge storage capacities. Although there are many applications for ferroelectric thin films such as in dielectric barrier layers, ultrasonic transducers, and electrooptic modulators/switches, the most significant application is in the case of computer and microprocessor memories where more capacitance is required for reliability as the density of the dynamic random access memory (DRAM) increases beyond several megabits, and a permanent memory is desirable to prevent loss of information during power failure. Nonvolatile memories also have other potential advantages such as high access speed, high density, radiation hardness, and low operating voltage. Table 2-2 summarizes the properties and applications of several thin film ferroelectric materials [5]. The schematic illustrations of various device applications for ferroelectric thin films are presented in Figure 2-8.

2.3. Methods for Synthesizing BaTiO$_3$ Thin Films

The various techniques available to prepare ferroelectric thin films are listed in Table 2-3. In general, there are two major categories of deposition techniques for thin films, i.e., (1) vapor deposition and (2) chemical processes. Vapor deposition techniques require a vacuum in order to obtain a sufficient flux of atoms or ions capable of depositing on to a substrate, whereas the chemical processes do not require vacuum. Thus, one can roughly
Table 2-2. Properties and applications of ferroelectric thin film materials [5].

<table>
<thead>
<tr>
<th>Thin Film Material</th>
<th>Phenomena</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perovskite Titanates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>Dielectric</td>
<td>Capacitors, sensors, phase shifters</td>
</tr>
<tr>
<td>(Ba,Sr)TiO$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>Pyroelectric</td>
<td>Pyrodetectors</td>
</tr>
<tr>
<td></td>
<td>PTCR</td>
<td>Thermistors</td>
</tr>
<tr>
<td>PbTiO$_3$ (PT)</td>
<td>Pyroelectric</td>
<td>Pyrodetectors</td>
</tr>
<tr>
<td></td>
<td>Piezoelectric</td>
<td>Acoustic transducer</td>
</tr>
<tr>
<td>Pb(Zr,Ti)O$_3$ (PZT)</td>
<td>Dielectric</td>
<td>Nonvolatile memory</td>
</tr>
<tr>
<td></td>
<td>Pyroelectric</td>
<td>Pyrodetectors</td>
</tr>
<tr>
<td></td>
<td>Piezoelectric</td>
<td>Waveguide devices</td>
</tr>
<tr>
<td></td>
<td>Electroptic</td>
<td>SAW substrates</td>
</tr>
<tr>
<td>(Pb,La)(Zr,Ti)O$_3$ (PLZT)</td>
<td>Pyroelectric</td>
<td>Pyrodetectors</td>
</tr>
<tr>
<td>Niobates</td>
<td>Electroptic</td>
<td>Wave guide devices, optical memory, displays, SHG</td>
</tr>
<tr>
<td>Pb(Mg$<em>{1/3}$, Nb$</em>{2/3}$)O$_3$ (PMN)</td>
<td>Dielectric</td>
<td>Capacitors, memory</td>
</tr>
<tr>
<td>PMN/PT</td>
<td>Electroptic</td>
<td>Waveguide devices</td>
</tr>
<tr>
<td>LiNbO$_3$ (LN)</td>
<td>Piezoelectric</td>
<td>Pyrodetectors</td>
</tr>
<tr>
<td>LiTaO$_3$ (LT)</td>
<td>Electroptic</td>
<td>Waveguide devices, optical modulators, SAW, SHG</td>
</tr>
<tr>
<td>KNbO$_3$ (KN)</td>
<td>Electrooptic</td>
<td>Wave guide devices, frequency doubler, holographic storage</td>
</tr>
<tr>
<td>K(Ta,Nb)O$_3$ (KTN)</td>
<td>Pyroelectric</td>
<td>Pyrodetectors</td>
</tr>
<tr>
<td>Tungsten-bronze (Sr,Ba)Nb$_2$O$_6$ (SBN)</td>
<td>Dielectric</td>
<td>Memory</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 2-8. Applications of ferroelectric thin films in micro-electronic devices [7].
Table 2-3. Thin film deposition techniques [31].

<table>
<thead>
<tr>
<th>Physical vapor deposition (PVD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering (dc, ion beam, rf magnetron)</td>
</tr>
<tr>
<td>Evaporation (e-beam, resistance, molecular beam epitaxy (MBE))</td>
</tr>
<tr>
<td>Laser ablation</td>
</tr>
<tr>
<td>Chemical vapor deposition (CVD)</td>
</tr>
<tr>
<td>Metalorganic (MOCVD)</td>
</tr>
<tr>
<td>Plasma enhanced (PECVD)</td>
</tr>
<tr>
<td>Low pressure (LPCVD)</td>
</tr>
<tr>
<td>Chemical solvent deposition</td>
</tr>
<tr>
<td>Sol-gel (solution-gelation)</td>
</tr>
<tr>
<td>Metalo-organic decomposition (MOD)</td>
</tr>
<tr>
<td>Melt solution deposition</td>
</tr>
<tr>
<td>Liquid phase epitaxy (LPE)</td>
</tr>
<tr>
<td>Hydrothermal/electrochemical methods</td>
</tr>
<tr>
<td>Hydrothermal oxidation</td>
</tr>
<tr>
<td>Anodic oxidation</td>
</tr>
</tbody>
</table>
identify these two categories as vacuum and nonvacuum techniques, respectively. In both these cases, the fabricated films are most commonly polycrystalline. However, in some cases, it is desirable to produce epitaxial growth on a substrate of the proper crystalline orientation and lattice matching. Recent reports show that epitaxial film growth is more readily achieved with vacuum techniques, whereas chemical deposition methods have proved to be most successful in regard to their ease of preparation and low equipment costs [7]. Some of these methods are discussed in more detail in the following sections.

2.3.1. Vapor Deposition Methods

Vacuum deposition processes to synthesize solid, thin films are mainly divided into two types: physical vapor deposition (PVD) and chemical vapor deposition (CVD) processes. In PVD, solid precursors (targets) to the desired film material are vaporized and deposited on a substrate by a variety of sputtering techniques such as radio-frequency (rf) magnetron, ion beam, laser ablation and electron beam evaporation. Sputtering has been one of the most common deposition methods and has the advantage of producing thin films of very high quality [32-40]. Radio-frequency sputtering has been the most widely used technique for the deposition of BaTiO$_3$ thin films on silicon substrates. Substrate temperatures for depositing crystalline films varied between 100-800°C, and deposition rates of upto 20 Å/min were achieved [32-34]. Films deposited at lower substrate temperatures were amorphous in nature and required a post deposition annealing between 400-500°C to crystallize. Amorphous BaTiO$_3$ films, however, possess interesting dielectric properties such as large charge storage capacity, and have been studied in detail [35, 36]. Ion beam assisted evaporation and ion beam sputtering are continuing to become more popular in order to increase film uniformity and deposition rates, and have been used to deposit several ferroelectric compositions including BaTiO$_3$, PbTiO$_3$, PZT, PLZT, and KNbO$_3$ [35-38]. Laser ablation is another recent technique used to deposit thin BaTiO$_3$ films on substrates such as silicon and quartz. Substrate temperatures are typically between 400-600°C and deposition rates of 10-15 Å/pulse can be obtained. Substrate temperature,
oxygen partial pressure, and laser energy density are the typical processing parameters that effect the composition and microstructure of the deposited films [39, 40]. Molecular beam epitaxy (MBE) technique has been used to grow epitaxial BaTiO_3 on Si substrates, with BaO as the intermediate layer to facilitate lattice matching [41]. Physical vapor deposition techniques described above offer a wide choice of parameters to control film composition, quality, deposition rate and crystallinity. However, PVD processes have several shortcomings: deposition rates are slow, high energy atoms and particles can damage the substrate, and the stoichiometry of the films formed can vary from that of the source. An additional limitation of sputtering is that it requires expensive and complicated equipment.

In chemical vapor deposition (CVD), volatile chemical precursors are vaporized and transported to a reaction chamber and deposited on heated substrates. Reactions occur at the substrate to form the desired thin-film material. Advantages include high deposition rates, superior microstructure (pin-hole free), and good stoichiometry control. Metalorganic chemical vapor deposition (MOCVD) has been the most widely used CVD technique to prepare BaTiO_3 thin films [42-44]. The potential advantages of MOCVD include the ability to deposit high quality, ultrathin layers on three dimensional complex geometries and the amenability to large scale processing. MOCVD is typically carried out at low pressures (4-5 Torr) in a horizontal quartz reactor with a cylindrical configuration and equipped with a gas inlet, substrate mounting, and a gas outlet, all are mounted coaxial with the walls of the reactor. The substrate is held facing down, and the metalorganic precursors are introduced through separate manifolds and allowed to react at the heated substrate before they escape through the outlet. Precursor manifolds and reactor walls are heated to avoid condensation of the reacting gases. BaTiO_3 films are grown on Si, SrTiO_3, NdGaO_3, and La AIO_3 substrates at temperatures ranging from 600-1000°C. The success of any MOCVD process critically depends on volatility and stability of individual precursors, as well as the reactivity among them. Titanium tetraisopropoxide [Ti(OC_3H_7)_4] is almost universally used as the Ti precursor, whereas the selection of a Ba
precursor is less obvious. Ba(hfa)$_2$(tetraglyme), Ba(fod)$_2$ and Ba(dpm)$_2$ are some of the examples. The precursors are transported to the reaction zone by an argon carrier gas. Growth rates of 100-150 Å/min are typically achieved. By carefully controlling the substrate surface quality, deposition rate, and substrate temperature, it has been demonstrated that epitaxial BaTiO$_3$ films can be grown using MOCVD process. Chemical vapor deposition methods have excellent potential as a production method for device quality ferroelectric thin films, especially when MOCVD is used. The CVD process can be extremely reproducible once conditions are established to produce a film with a particular composition and crystal structure. An additional advantage is that scale-up of a CVD process from the laboratory to production is typically not as difficult as it is for PVD (sputtering). Unfortunately, the CVD processes require high temperatures, which is a limitation when device integration and metallization with non-refractory electrode materials such as doped aluminum or tungsten are required. The CVD deposition temperatures have significantly decreased in recent years, through the use of plasma enhanced CVD (PECVD) methods [45].

2.3.2. Sol-Gel Synthesis

Sol-gel processing is currently one of the most actively studied processing techniques for metal oxide based ferroelectric materials [7]. In its simplest form, the sol-gel process first involves the preparation of a homogeneous solution containing the precursors, usually as metal alkoxides. The deposition of a thin film on the substrate is performed while simultaneous hydrolysis and polycondensation occur, thus producing an amorphous thin film. The final step involves heating (500-800°C) of this amorphous thin film, until it crystallizes to give the ferroelectric crystalline thin film. The sol-gel process is similar to the MOCVD process explained above, in the sense that both processes use metalorganic precursors. However, the difference lies in the way the precursors are reacted: a high temperature condensaton of crystalline oxides in the case of MOCVD, and a
room temperature hydrolysis and condensation to produce an amorphous film in sol-gel process. In addition, sol-gel doesn't employ vacuum and therefore low in capital costs.

Metal alkoxides have a general formula: $M(OC_nH_{2n+1})_x$ where $M$ is a metal, $n$ is an integer, and $x$ is the valence state of the metal. All metals form alkoxides, and by varying the alkyl group, liquids or solids, soluble or insoluble, volatile or non-volatile materials can be obtained. It is convenient for sol-gel process to choose liquid materials that are soluble in organic solvents and volatile and therefore readily purified by distillation. Most metal alkoxides are readily hydrolyzed to the corresponding oxide or hydroxide [46]:

$$M(OR)_x + xH_2 \leftrightarrow M(OH)_x + xROH \quad [2.5]$$
$$2M(OH)_x \leftrightarrow M_2O_x + xH_2O \quad [2.6]$$

where $R$ represents $C_nH_{2n+1}$.

Sol-gel methods begin with the preparation of liquid precursors. The starting materials can be metalorganics such as alkoxides described above, acetates, acetyl acetonates, or inorganics such as metal hydroxide or nitrates. Recently, much attention has been directed towards the effect of the correlation between the solution structure and the final crystal structure of the sol-gel derived systems. It was found that a close resemblance of the local atomic arrangement of the alkoxide complexes in the solution can play a critical role during the crystallization processes [47]. The 'sol' is prepared by dispersing the starting materials in an organic solvent (usually alcohols). Water and catalysts are added to the sol solution to initiate a series of hydrolysis and polycondensation reactions which produces a viscoelastic oxide gel network. The conditions of partial hydrolysis (i.e., alkoxide concentration, relative amount of water, additive) have important effect on the deposition characteristics, quality of final microstructure, and the microstructure development in the layer after heat treatment. The partially hydrolysed sols give rise to precursor solutions with suitable viscosity for dip-coating or spin coating onto a substrate. the dried 'gel' film is then densified by a heat treatment. Sol-gel techniques are widely
used to prepare many ferroelectric materials including BaTiO₃, PZT, PLZT, and LiNbO₃ [7].

Preparation of BaTiO₃ films using sol-gel techniques have been reported [46, 48-51]. Titanium isopropoxide is generally used as the Ti precursor, and several variations of Ba metalorganics such as barium isopropoxide [Ba(OC₃H₇)₂], barium 2-ethyl hexanoate [Ba(C₇H₁₅COO)₂], and barium neodecanoate [Ba(C₉H₁₉COO)₂] are used as the precursors. Sol-gel films can be deposited on arbitrary surfaces, as in the case for BaTiO₃: stainless steel, fused silica, platinum, and platinized silicon. Usually, the films are prepared directly on electrode surfaces to facilitate characterization or device fabrication. Annealing (densification, crystallization) temperatures for sol-gel thin films of BaTiO₃ typically varied between 700-800°C. Sol-gel processing is a relatively new method for the fabrication of ferroelectric thin films and is one of the most promising techniques. The advantages of sol-gel processing are good homogeneity, ease of composition control, low sintering temperature, large area thin films, possibility of epitaxy and lower capital cost than other techniques. Main disadvantages of this technique include high cost of precursor materials, difficulty of handling atmosphere-sensitive alkoxides, and lack of control in the crystallization of thicker films.

An alternative chemical process, called metal organic decomposition (MOD), is similar to sol-gel processing, except that no hydrolysis step is performed prior to annealing. MOD methods often use carboxylate precursors with large organic groups, such as barium neodecanoate [Ba(C₉H₁₉COO)₂] and titanium dimethoxy dineodecanoate [(CH₃O)₂Ti(C₉H₁₉COO)₂] to yield viscous precursor solutions, to facilitate formation of thick precursor films after spin coating [52]. Cracking can be a problem because of the high organic content of the films.

2.3.3. Hydrothermal and Electrochemical Synthesis

In recent years, a novel technique has been developed to synthesize polycrystalline thin films of perovskite type ABO₃ compounds (CaTiO₃, SrTiO₃, BaTiO₃, and BaZrO₃)
and their solid solutions [such as (Ba,Sr)TiO$_3$] on substrates of $B$ metal [12-22]. The process involves a hydrothermal treatment of polished metal (Ti or Zr) substrates in aqueous solutions containing $A$ cation. The film growth is accelerated by combining electrochemical treatment with hydrothermal treatment. Anodization of the metallic substrate by applying an external dc voltage enhances the dissolution (corrosion) of metallic species into solution which react with $A$ type ($Ba^{2+}$, $Sr^{2+}$, and$Ca^{2+}$) cations and form the complex oxide $ABO_3$. The process has several advantages over the conventional deposition techniques. Low synthesis temperature and no necessity for a crystallization treatment eliminate the substrate-film interactions, and facilitate device integration. Deposition on complex geometries and large area substrates is another advantage of this solution deposition technique. Less toxicity of inorganic precursors and aqueous solutions help keep the capital and processing costs low.

A schematic diagram describing the hydrothermal-electrochemical apparatus to deposit BaTiO$_3$ thin film on Ti substrate is shown in Figure 2-9. A mechanically polished and degreased Ti substrate was coupled to the positive terminal of an external galvanostat and a platinum foil was placed opposite to the Ti anode and connected to the negative terminal. Platinum wires were used as the electrical leads. The electrode assembly was immersed in a Teflon beaker containing the aqueous solution of $Ba(OH)_2.8H_2O$, which in turn is placed in an electrolytic autoclave. Sufficient amount of redistilled water is placed around the beaker, to avoid the over heating of the Teflon vessel, and also to control the pressure inside the autoclave. The autoclave was equipped with a stirrer and pressure tight electrical feedthroughs for the electrode leads. Early investigations in this technique involved the use of high temperatures (400-600°C) under supercritical conditions of aqueous solutions, to deposit tetragonal BaTiO$_3$ films with preferred crystallographic orientation [16]. In the later efforts, a better understanding of the effects of solution chemistry has resulted in a gradual decrease in synthesis temperature, to about 150-200°C. The effect of $Ba^{2+}$ concentration in the electrolyte on the formation of BaTiO$_3$ is shown in
Figure 2-9. Schematic diagram of the apparatus for hydrothermal/electrochemical synthesis of perovskite titanate thin films on Ti substrates [5].
Figure 2-10 [5]. With increasing concentration of Ba$^{2+}$, formation of BaTiO$_3$ is favored at lower temperatures. Similar attempts have been successfully made to synthesize CaTiO$_3$ and SrTiO$_3$ thin films on Ti substrates. Formation of titanate films on Ti substrates under purely hydrothermal conditions has also been reported [17-19, 21], verifying that the anodization of the Ti substrate is not necessary to form the titanate film, but only accelerates the reaction through enhanced corrosion of Ti. The process also has been adopted to deposit high quality titanate films on arbitrary surfaces by sputtering Ti on to glass, silicon, and polymer films. Major limitations of the technique include slow deposition rates, contamination from carbonates, difficulties in growing thick films, and microstructural defects caused by the electrode reactions (gas evolution) and electrolytic breakdown of the films.

2.4. Characterization of Thin Films

With the explosive growth of thin film utilization in microelectronics and the interdisciplinary nature of applications, there is a compelling urge for film characterization and intrinsic property measurements. As a result, several techniques are employed to evaluate structural, chemical and dielectric characteristics of thin films. Some of these techniques provide unprecedented structural resolution and chemical analysis capabilities over small lateral and depth dimensions. Some techniques only sense and provide information on the first few atomic layers of the surface. These diverse, yet complimentary characterization techniques are described in the following sections.

2.4.1. Structural Characterization

Structural features such as grain size, film thickness, uniformity, surface topography, morphology of film constituents, voids and other defects are of significant interest in the characterization of thin films. These features control the ultimate properties of the film and provide useful information about the deposition process variables. Scanning electron microscopy (SEM) is generally employed to reveal the above features.
Figure 2-10. Effect of $\text{Ba}^{2+}$ concentration in the electrolyte on formation of $\text{BaTiO}_3$ on Ti substrate under hydrothermal/electrochemical conditions [5].
The most common imaging mode in SEM is the secondary electron imaging, where low energy electron emitted from the sample surface by the interaction of the electron beam are detected. Sloping surfaces produce a greater secondary electron yield because the portion of the interaction volume projected on the emission region is larger than on a flat surface. Similarly, edges will appear even brighter. Compositional information in SEM can be obtained using backscattered imaging mode. Backscattered electrons are the high energy electrons that are elastically scattered and essentially possess the same energy as the incident electrons. The probability of backscattering increases with the atomic number $Z$ of the sample material. Useful contrast can develop between regions of the specimen that differ widely in $Z$.

Transmission electron microscopy (TEM) is used to obtain internal structural information from specimens that are thin enough to transmit electrons. Thin films are, therefore, ideal for study, but they must be removed from electron-impenetrable substrates prior to insertion in the TEM. This problem is usually solved by making a cross sectional sample, from a thin slice cut from the sample. Electrons thermionically emitted from the gun are accelerated by a high voltage bias (100 kV- 800 kV) and first projected on to the specimen by means of a condenser lens system. The scattering processes experienced by electrons during their passage through the specimen determine the kind of information obtained. Elastic scattering, involving no energy loss when electrons interact with the potential field of the ion cores, gives rise to diffraction patterns. Inelastic interactions between beam and matrix electrons at heterogeneities such as grain boundaries, dislocations, second phase particles, defects, density variations, etc., cause complex absorption and scattering effects, leading to a spatial variation in the intensity of the transmitted beam. This effect is used to image the internal microstructure of the specimen.

X-ray diffraction (XRD), based on Bragg's law, has long been used to address all issues related to the crystal structure of bulk solids, including lattice constants and geometry, identification of unknown materials, orientation of single crystals, and preferred
orientation of polycrystals, defects, stresses, etc. Extension of X-ray diffraction methods to thin film analysis poses a limitation: the great penetrating power of X-rays means that with typical incident angles, their path length through films is too short to produce diffracted beams of sufficient intensity. Under such conditions, the substrate, rather than the film, dominates the scattered X-ray signal. To overcome this problem, Seeman-Bohlin diffraction geometry (Figure 2-11) is employed [53]. This is done by using a grazing angle of incidence \( \gamma \), which increases the effective thickness of the film by several times. The focal point of the X-ray source, film specimen, and detector slit are all located on the circumference of one great circle. Each of the diffracted peaks are sequentially swept through as the X-ray detector moves along the circumference.

2.4.2. Chemical Characterization

Several spectroscopic techniques are employed to characterize the chemistry of thin films. Most popular among these are X-ray energy dispersive spectroscopy (EDS), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), and Rutherford backscattering (RBS). Principle of detection and the specific applications of each of these techniques are briefly described here.

Most EDS systems are interfaced with an SEM, where the electron beam serves to excite characteristic X-rays from the area of the specimen being probed. A Si(Li) detector is aimed to efficiently intercept emitted X-rays. An incoming X-ray generates a photoelectron in Li doped Si, that eventually dissipates its energy by creating electron-hole pairs. The incident photon energy is linearly proportional to the number of pairs produced or equivalently proportional to the amplitude of the voltage pulse they generate when separated. The pulses are amplified and then sorted according to voltage amplitude by a multichannel analyzer, which also counts and stores the number of pulses within given increments of voltage (X-ray energy) range. The result is the characteristic X-ray spectrum from the specimen area being probed. Identification of the elements present in the specimen with their relative X-ray intensities can be performed by comparing the peak
Figure 2-11. Seeman-Bohlin grazing angle X-ray diffraction geometry for the analysis of thin films [53].
energies in the EDS spectrum with the characteristic X-ray energies for all the elements in the periodic table. Si(Li) detectors typically have a resolution of about 150 eV, so overlap of peaks occurs when they are not separated in energy by more than this amount. Overlap usually occurs in multicomponent samples or when neighboring elements in the periodic table are present. A variation of EDS is the wavelength-dispersive spectroscopy (WDS), where wavelength rather than energy is dispersed, a factor of 20 or so improvement in X-ray line width resolution is possible. In this case, emitted X-rays, rather than entering a Si(Li) detector, are diffracted from single crystals with known interplanar spacings. From Bragg's law, each characteristic wavelength reflects constructively at different corresponding angles, which can be measured with very high precision. The electron microprobe (EMP) is an instrument specially designed to perform WDS analysis.

The Auger process (Figure 2-12), which is the basis of AES, first involves an electron transition from an outer level (e.g., $L_1$) to a hole in the inner shell ($K$). The resulting excess energy is not channeled into the creation of a photon but is expended in ejecting an electron from yet a third level (e.g., $L_2$). The atom finally contains two electron holes after starting with a single hole created by the incident electron beam. The electron that leaves the atom by the Auger process is known as an Auger electron, and it possesses an energy given by [53]:

$$E_{KLL} = E_K - E_{L_1} - E_{L_2} = E_K - E_{L_2} - E_{L_1}$$

[2.7]

The last equality indicates $KL_L_2$ and $KL_2L_1$ transitions are indistinguishable in terms of energy and consequently denoted by $KLL$. Similarly, other transitions observed are denoted by $LMM$ and $MNN$. Since the $K$, $L$, and $M$ energy levels in a given atom are unique, the Auger spectral lines are characteristic of the element in question. Therefore, by measuring the energy of the Auger electrons emitted by the sample, it is possible to identify its chemical composition. Since light elements (low Z) have a higher probability of Auger transition, AES is especially suited for their detection. However, due to the fact that Auger process requires presence of at least three electron energy levels, detection of hydrogen and
Figure 2-12. Schematic of electron energy transitions: (a) initial state, (b) incident X-ray or electron ejects K shell electron, (c) X-ray emission when 2s electron fills vacancy, and (d) KLL Auger electron emission [53].
helium is not possible by AES technique. The extremely low energy of Auger electrons limits the analysis depth to the top few atomic layers of the sample, making AES a true surface analytical technique.

A typical AES spectrometer schematically shown in Figure 2-13, is housed within a ultrahigh vacuum chamber maintained at \( \approx \times 10^{-10} \) torr. This level of cleanliness is required to prevent surface coverage by contaminants (e.g., C, O) in the system. Two very useful capabilities of AES for thin film analysis are depth profiling and lateral scanning. The first is accomplished with incorporated ion guns that enable the specimen surface to be continuously sputtered away while Auger electrons are detected. Multielement composition depth profiles can thus be determined over total film thicknesses of several thousand angstroms by sequentially sampling and analyzing arbitrarily thin layers. Although depth resolution is extremely high, the frequently unknown sputter rates for various materials makes precise depth determinations difficult. A typical AES depth profile analysis for a BaTiO\(_3\) thin film is shown in Figure 2-14. Through raster or line scanning the electron beam, the AES is converted into an SEM and images of the surface topography can be obtained. By modulating the imaging beam with the Auger electron signal, a lateral composition mapping of the surface can be obtained.

The basis for XPS lies in the same atomic core electron scheme that is considered for X-ray and Auger electron emission. Rather than incident electrons in the case of EDS and AES, relatively low-energy X-rays (Mg or Al \( K\alpha \)) impinge on the specimen in this technique. The absorption of the photon results in the ejection of electrons via photoelectric effect. Energetics of this process are governed by the equation [53]:

\[
E_{KE} = h\nu - E_B
\]  
[2.8]

where \( E_{KE} \), \( h\nu \), and \( E_B \) are the energies of the ejected electron, incident photon, and the involved bound electron state. Since values of the binding energy are element-specific, atomic identification is possible through measurement of photoelectron energies. Aside from chemical bonding information, XPS has an important advantage relative to AES. X-
Figure 2-13. Schematic illustration of a combined AES and XPS instrumentation [53].
Figure 2-14. Typical AES compositional depth profile analysis of a BaTiO$_3$ thin film on Si Substrate [42].
rays are less prone to damage surfaces than are electrons. For example, electron beams can reduce hydrocarbon contaminants to carbon, destroying the sought-after evidence. For this reason, XPS tends to be preferred in assessing the cleanliness of semiconductor films.

RBS is a popular thin film characterization technique which relies on the use of very high energy (MeV) beams of low mass (usually $^4\text{He}^+$) ions. These ions can penetrate thousands of angstroms or even microns deep into films or film-substrate combinations. However, the high energy ions cause negligible sputtering of the surface atoms. Instead, they lose their energy through electronic excitation and ionization of target atoms. These ‘electronic collisions’ are so numerous that the energy loss can be considered to be continuous with depth. Sometimes the fast moving light ions penetrate the electron cloud and undergo elastic collisions with the nuclei of the much heavier stationary target atoms. The resulting scattering from the Coulomb repulsion between ion and nucleus is known as Rutherford backscattering. Energy of the backscattered ion precisely depends on the mass of the target atom, and the incident energy of the He ion at the point of collision. Since the incident energy of the He ion is a function of the distance traveled into the film, it is possible to estimate the depth of collision and the mass of the colliding target atom from the measured energy of the backscattered ion. Thus, by measuring the number and energy of backscattered He ions, information on the nature of the elements present, their concentration, and depth distribution can all be simultaneously determined without appreciably damaging the specimen. All elements and their isotopes including Li and those above it in the periodic table are, in principle, detectable with $^4\text{He}^+$ ions. It may be difficult to resolve neighboring elements, and the limit depends on the resolution of the detector. High-Z elements produce a stronger backscattered signal than low-Z elements. Consideration of these factors suggests that specimens for RBS analysis should ideally contain elements of widely different atomic weight stacked with the heavy atoms near the surface and the lighter atoms beneath them. In a bilayer film structures it is desirable for the high-Z film to be at the outer surface. In general, RBS can detect concentration levels
of about 1 at%. The technique is unmatched in determining the stoichiometry of thin film binary compounds.

A critical need to measure thermally diffused and ion-implanted depth profiles of dopants in semiconductor devices spurred the development of SIMS. In typical devices, peak dopant levels are about $10^{20}/cm^3$, while background levels are $10^{15}/cm^3$. These correspond to atomic concentrations in Si of 0.2% to $2 \cdot 10^{-6}$%, respectively [53]. None of the analytical techniques considered thus far has the capability of detecting such low concentration levels. In SIMS, a source of ions bombards the surface and sputters neutral atoms, for the most part, but also positive and negative ions from the outer most film layers. Once in the gas phase, the ions are mass analyzed in order to identify the species present as well as determine their abundance. The primary ions most frequently employed are Ar⁺, O₂⁻, and Cs⁺, and these are focused into a beam ranging from 2 to 15 keV in energy. One of the unique features of SIMS is the mass discrimination, which allows to distinguish the isotopes.

2.4.3. Dielectric Characterization

Dielectric properties of ferroelectric thin films that are frequently determined include dielectric constant and dissipation factor (capacitive characteristics), $ac / dc$ resistivities and leakage current (impedance characteristics), and ferroelectric polarization hysteresis behavior.

Since dielectric polarization response of a material depends on the frequency regime of the applied field and the measurement temperature, the capacitive and impedance characteristics are usually determined as a function of frequency and temperature. An LCR meter or an impedance analyzer equipped with an auto-balancing bridge is employed to measure these properties [54, 55]. The material is stimulated with an ac source and the actual voltage across the sample is monitored between the high (H) and low (L) terminals (Figure 2-15 (a)). The low terminal is 0 V by a virtual ground of the operational amplifier. The output voltage is proportional to the current through the material. Material test
Figure 2-15. Schematic circuit diagrams for dielectric characterization of ferroelectric thin films: (a) auto-balancing bridge for impedance analysis [55], and (b) modified Sawer-Tower bridge in virtual ground mode for ferroelectric hysteresis measurement [57].
parameters are derived by knowing the dimensions of the material and by measuring its capacitance and dissipation factor. The auto-balancing bridge technique provides highly accurate capacitance and dissipation factor measurements between 5 Hz and 40 MHz.

A ferroelectric hysteresis loop (also termed $P-E$ loop, where $P$ stands for polarization and $E$ is the applied electric field) is the most important criterion for verifying the existence of ferroelectricity in materials. A $P-E$ loop is usually measured by a modified Sawer-Tower bridge [56, 57], shown schematically in Figure 2-15 (b). Although earlier methods utilized a dynamic (60 Hz) measurement with an oscilloscope readout, the more recent techniques essentially involve a dc ($\sim 1/10$ Hz) measurement using an X-Y plotter or computerized calculations [30]. Hysteresis loops are usually run on virgin (thermally depoled), electroded samples, by varying the electric field $E$ across the sample while monitoring the charge collected on a large (approximately 1000 times larger in capacitance than the sample), low-loss capacitor (also called sensing capacitor) in series with the sample. This charge (actually measured as voltage, which relates to charge by the familiar $Q = CV$) on the low-loss capacitor is proportional to the charge on the sample, and thus one obtains a continuous plot of polarization as a function of the electric field. In a strict sense, dielectric displacement rather than polarization is being measured, however, in the case of high dielectric constant materials such as ferroelectrics, the two quantities are very nearly equal and the term ‘polarization’ is usually preferred. For some particular cases, $P-E$ loop may be observed in non-ferroelectric materials, especially if the specimen has a high electrical conductivity while the compensation of signal phase in Sawer-Tower bridge is not suitable. However, this kind of loop should be distinguishable from a ‘real’ ferroelectric loop. When the applied field increases to a sufficiently high value, the value of the polarization increases continuously in the ‘false’ loop, but nearly saturates in a ‘real’ loop, owing to the total alignment of ferroelectric domains [7].
2.5. Dielectric Properties of BaTiO₃ Thin Films

The dielectric and ferroelectric properties of BaTiO₃ thin films vary significantly from those of bulk BaTiO₃ single crystal or polycrystalline ceramic, and the extent of deviation is dependent on film thickness, thermal history, microstructure and synthesis technique. In the following sections, these irregularities are discussed in more detail.

2.5.1. Dielectric Constant and Dissipation Factor

BaTiO₃ films prepared by e-beam evaporation technique showed a strong dependency of dielectric behavior on film thickness [58]. Films having thicknesses in the range of 0.1 μm were cubic at room temperature and possessed very small dielectric constants with no dielectric anomaly in the neighborhood of Curie temperature for BaTiO₃ (near 125°C). Thicker films (about 1.0 μm), however, showed essentially bulk dielectric constant at room temperature, and dielectric anomaly as T_c is approached. In a separate study [59], the sputtered BaTiO₃ films showed a sharp, well defined dielectric anomalies near 120°C, down to film thicknesses of about 0.023 μm. At a film thickness of about 0.01 μm, this anomaly disappeared, even though the films exhibited the anomaly associated with the tetragonal to orthorhombic transition at 0°C. These discrepancies are mainly attributed to the variation of the defect structures in the BaTiO₃ films prepared by various techniques. Evaporation of ternary compounds such as BaTiO₃ are complicated by the different volatilities of the constituents, so that the defect structure in the film depends on several processing parameters. BaTiO₃ thin films deposited by MOD technique showed room temperature spontaneous polarization of 3.1 μC/cm² and bias field and frequency dependence of dielectric constant (k~1000 at 20kV/cm field, and 1kHz frequency) at a grain size up of 0.2 μm, which are similar to those obtained for bulk BaTiO₃ [52]. The spontaneous polarization decreased with decreasing grain size, and films with an average grain size of 34 nm were not ferroelectric. Figure 2-16 shows the dependence of dielectric constant and dissipation factor on the film thickness [7]. In another investigation, a 0.5 μm thick BaTiO₃ film deposited by MOCVD process showed a dielectric constant of 100 and a
Figure 2-16. Dependence of dielectric constant and dissipation factor on film thickness for sol-gel derived BaTiO$_3$ films [7].
remnant polarization of 0.65 μC/cm², indicating the presence of ferroelectricity [42]. The room temperature dielectric constant reached a high value of 1300, with a low dissipation factor of 0.03, beyond a film thickness of about 0.3 μm. The dielectric properties of sol-gel derived BaTiO₃ films were also reported to be dependent on film thickness, substrate material, and relative humidity of the ambient atmosphere [51]. Films deposited on stainless steel substrates showed increasing dielectric constant with increasing film thickness. This was attributed to the presence of a electrode barrier capacitance. Ni and Fe present in stainless steel might have diffused into BaTiO₃, increasing the film resistance (barrier layer) in the vicinity of the electrode. The effect of barrier layer capacitance on the measured dielectric constant diminishes with increasing film thickness. Dielectric losses in these films were very high at room temperature and showed a substantial decrease at higher temperatures. In addition, dielectric losses measured in ambient air were higher than those obtained in dry air. These observations were attributed to the presence of porosity as well as uncondensed hydroxyl groups in the sol-gel derived films, which makes them susceptible to surface conduction due to adsorbed moisture. It has also been reported that the electrical properties of BaTiO₃ can be affected by moisture and this property has been related to the microstructure of the material and that samples having smaller grain size were more affected by moisture [19, 51]. BaTiO₃ thin films prepared on Ti substrates using electrochemical methods exhibited similar dependence of dielectric properties on relative humidity. Capacitance and dielectric loss factor measured at 70% relative humidity were extremely large at low frequencies, owing to surface conduction. Dielectric constants reported for these films range between 100-200. This ‘size effect,’ i.e., the anomalous change in electrical properties associated with film thickness, is also complicated by the additional influences of compositional and structural disorders and residual stresses [7].

2.5.2. Hysteresis Behavior

One possible explanation for the discrepancy between film and bulk properties, as explained for the films deposited by MOD process [52], is that the polarization reversal is
inhibited by an inhomogeneous distribution of stresses and electric fields resulting from the elastic clamping of the material near the grain boundaries by the neighboring grains. A near total clamping effect was observed in a film with 34 nm grain size, as evidenced by an extremely narrow hysteresis loop, similar to that of a paraelectric material. With increasing grain size, the hysteresis loop gradually exhibited ferroelectric behavior with a remnant polarization of about 3.1 \( \mu \text{C/cm}^2 \) for a 0.2 \( \mu \text{m} \) grain size film. Another characteristic behavior of ferroelectric thin films is the presence of a nested, non-saturating hysteresis loop, as reported for BaTiO_3 thin films deposited by MOCVD process [42]. While the contamination of the film material was one of the proposed reasons for this behavior, a strong domain fixing effect of the intermediate layer between the film and substrate was reported to be the reason in high purity films.

2.5.3. Resistivity and Leakage Current

The electrical resistivity and associated leakage currents in BaTiO_3 thin films were found to depend on dielectric constant, temperature, and frequency [37, 42, 51, 60]. Films with lower dielectric constants exhibited higher resistivities and smaller leakage currents. In the films that possessed higher dielectric constants, the leakage current increased substantially when the Curie temperature for tetragonal to cubic transformation was approached [60]. For BaTiO_3 films deposited by rf magnetron sputtering, the dielectric constant was increased from 16 to 330 as the substrate temperature during deposition was raised from room temperature to 700\(^\circ\)C. The corresponding \( dc \) resistivity decreased from \( 1.2 \times 10^{10} \) to \( 3.7 \times 10^4 \) \( \Omega \).cm. This was attributed to the amorphous and polycrystalline natures of the deposited films formed at low temperatures and high temperatures, respectively. A sandwich of amorphous/polycrystal structure was found to give a combination of high dielectric constant (\( k=210 \)) and high electrical resistivity (\( 10^{10} \Omega \).cm). BaTiO_3 film synthesized on Si (1 0 0) substrate using MOCVD process exhibited a ohmic resistivity of \( 10^{13} \Omega \).cm and a breakdown strength of 12 MV/m [42]. High electrical resistivity and breakdown strengths are desirable for capacitor applications, particularly in
high power circuits. In a separate study, BaTiO$_3$ films deposited by sol-gel method showed a room temperature $dc$ resistivity of about $10^{15}$ $\Omega$.cm, and breakdown strength of 20 MV/m [51].

2.6. Capacitors as Charge Storage Devices

Capacitors can perform several functions in electrical circuits including blocking, coupling and decoupling, $ac-dc$ separation, filtering and energy storage. They can block direct currents but pass alternating currents, and therefore can couple alternating currents from one part of a circuit to another while decoupling $dc$ voltages. A capacitor, when suitably designed can separate direct from alternating currents and also discriminate between different frequencies. The charge storage capability of capacitors is more commonly exploited in the electronic devices, for example, the photoflash unit of a camera. The device characteristics of a capacitor, and the several kinds of capacitors and their applications are discussed in the following sections.

2.6.1. Capacitor Characteristics

2.6.1.1. Volumetric Efficiency. Volumetric efficiency is a measure of the capacitance that can be accommodated in a given size of capacitor. In the case of a parallel plate capacitor of area $A$ and electrode separation $d$, the volume efficiency can be written as:

$$\frac{C}{V} = \frac{k\varepsilon_0}{d^2}$$

[2.9]

where $C$ is the capacitance and $V$ is the volume of the capacitor. It is clear from this relation that the volumetric efficiency is directly proportional to dielectric constant and inversely proportional to the square of the dielectric thickness. However, for a given working voltage $U_w$, the dielectric thickness can not be decreased indefinitely, as the field developed in the capacitor may exceed the breakdown strength $E_b$ of the dielectric. In fact, to ensure acceptable reliability, the working voltage should not exceed a level set by the following relation:
\[ \eta U_w = E_p d \]  

[2.10]

where \( \eta \) is the limiting factor. The maximum permissible energy density in a capacitor can be calculated from the above two relations:

\[ \frac{CU_w^2}{2V} = \frac{kE_p^2 E_p^2}{2\eta^2} \]  

[2.11]

The term \( KE_p^2 \) is a figure of merit for a dielectric that is to be considered for use in high field strengths. However, from a practical standpoint, a useful figure of merit is the product of volumetric efficiency and the maximum recommended working voltage \( \frac{CU_w}{V} \), which represents the charge storage efficiency of the capacitor, but often quoted as the volumetric efficiency.

2.6.1.2. Equivalent Series and Parallel Resistance. When an \( ac \) voltage is applied to an ideal capacitor, no energy is dissipated, since there is no current flowing through the capacitor. However, a real capacitor dissipates energy due to the lead and electrode resistance, \( dc \) leakage current, and more importantly, the dielectric losses. As explained earlier, the dielectric losses contribute to the dissipation factor, or loss tangent, \( \tan \delta \). For the purpose of characterizing the losses in capacitors, it is convenient to consider a real capacitor as an ideal capacitor shunted with a parallel resistance \( R_p \) or and series with a resistance \( R_s \). All dielectric materials used in manufacture of capacitors will allow certain amounts of \( dc \) flow. This current, known as \( dc \) leakage current, resulting from an applied voltage, can be expressed in terms of resistance in capacitor at a specified measurement voltage and temperature. Also termed ‘insulation resistance’, it is measured across the terminals of a capacitor and consists primarily of the parallel resistance \( R_p \). As capacitance values increase and hence the area of dielectric increases or thickness of the dielectric decreases, the insulation resistance decreases proportionately, and hence it is often specified as ohmfarads or megohmfarads. Insulation resistance is inversely proportional to temperature and is usually specified over the capacitor design temperature.
range. In the case of electrolytic capacitors, where the $R_p$ is low owing to the very high capacitance and thin dielectric, dc leakage current is normally specified rather than resistance.

2.6.1.3. Dielectric Strength. The ability of a capacitor dielectric to withstand an applied dc voltage without breakdown is called dielectric strength and is normally specified as volts per meter at a specified temperature. Breakdown in a capacitor results in the replacement of a reactive insulating component by either a low-resistance short circuit or an open circuit, usually with disastrous consequences as far as the overall circuit function is concerned. Certain types of capacitors, e.g. metallized polyester film and electrolytic capacitors have self-healing properties, as described later, such that a breakdown cases a brief short circuit followed by a rapid restoration of normal reactive behavior. So far, no method of making a ceramic unit self healing has been devised, and therefore recommended working voltages are usually about a factor of 5 below the minimum breakdown voltage.

2.7. Types of Capacitors

Capacitors are classified into different categories, primarily based on the type of dielectric material used to construct them. Since the polarization characteristics of dielectric materials strongly depend on field strength, frequency, and temperature, an understanding of the interrelationship between the design and construction of the capacitors with their nominal characteristics is generally required for proper selection. Depending on the type of dielectric material used and the design of construction, capacitors offer a wide range of volumetric efficiencies, as listed in Table 2-4. Figure 2-17 shows the frequency ranges for the application of various capacitor types, and their ranges of capacitance. Capacitors can be divided into two major kinds: non-ceramic and ceramic. Capacitors constructed from polymer films (polymer, paper, or both), electrolytic capacitors, and capacitors using mica as the dielectric are classified as non-ceramic types. Ceramic capacitors are made from various classes of dielectric ceramic materials, giving a wide range of permittivities, loss
Table 2-4. Typical values of the volumetric efficiency for various types of capacitors [2].

<table>
<thead>
<tr>
<th>Capacitor Type</th>
<th>$\frac{C}{V} \ (pF \cdot mm^{-3})$</th>
<th>$\frac{C}{V} \cdot U_w \ (pC \cdot mm^{-3})$</th>
<th>Maximum Permissible Energy Density $\ (nJ \cdot mm^{-3})$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrolytics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet aluminum</td>
<td>7000</td>
<td>$4 \cdot 10^5$</td>
<td>10000</td>
</tr>
<tr>
<td>Wet tantalum</td>
<td>15000</td>
<td>$4 \cdot 10^6$</td>
<td>33000</td>
</tr>
<tr>
<td>Solid tantalum</td>
<td>35000</td>
<td>$1.3 \cdot 10^6$</td>
<td>24000</td>
</tr>
<tr>
<td><strong>Polymer film</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paper foil/metal foil</td>
<td>10</td>
<td>5000</td>
<td>1300</td>
</tr>
<tr>
<td>Paper foil/metallized</td>
<td>40</td>
<td>15000</td>
<td>2800</td>
</tr>
<tr>
<td>Polystyrene/metal foil</td>
<td>6</td>
<td>2000</td>
<td>300</td>
</tr>
<tr>
<td>Polyester/metallized</td>
<td>30</td>
<td>11000</td>
<td>2000</td>
</tr>
<tr>
<td>Polymer chip</td>
<td>1000</td>
<td>50000</td>
<td>1300</td>
</tr>
<tr>
<td><strong>Single crystal</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mica</td>
<td>5</td>
<td>2000</td>
<td>400</td>
</tr>
<tr>
<td><strong>Single-plate ceramic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPO</td>
<td>0.5</td>
<td>500</td>
<td>250</td>
</tr>
<tr>
<td>Z5U</td>
<td>5</td>
<td>5000</td>
<td>2500</td>
</tr>
<tr>
<td>Barrier layer</td>
<td>700</td>
<td>2000</td>
<td>3</td>
</tr>
<tr>
<td><strong>Ceramic multilayer chip</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPO</td>
<td>500</td>
<td>15000</td>
<td>230</td>
</tr>
<tr>
<td>X7R</td>
<td>10000</td>
<td>$3.5 \cdot 10^5$</td>
<td>6000</td>
</tr>
<tr>
<td>Z5U</td>
<td>30000</td>
<td>$1 \cdot 10^6$</td>
<td>17000</td>
</tr>
</tbody>
</table>

$C$ = capacitance, $V$ = volume, $U_w$ = working voltage, $pF =$ pieco farad, $pC =$ pieco Coulomb, $nJ =$ nano joule

NPO, X7R, and Z5U are the Electronics Industries Association (EIA) codes for Class II dielectrics possessing specific temperature range and capacitance variation [2].
Figure 2-17. Frequency and capacitance ranges for applications of various types of capacitors [2].
factors, and operational voltages. In the following sections, each of these capacitor types are described in more detail, with regard to their construction, properties and applications.

2.7.1. Non-Ceramic Capacitors

2.7.1.1. Polymer Film Capacitors. Polymer film capacitors essentially comprise dielectric films (polymer or paper or both together) interleaved with aluminum electrodes. The electrodes can be either an aluminum foil or more commonly, in the form of a layer evaporated directly on the dielectric, and rolled together. They are sealed in an aluminum can or in epoxy resin. Because the dielectric films and the electrode layers can be as thin as 0.025 μm, the volumetric efficiencies can be high, despite the low dielectric constants of this class of materials. The dielectric films are typically polystyrene, polypropylene, polyester, polycarbonate or paper. Paper dielectrics are always impregnated with an insulating liquid. Polystyrene capacitors have exceptionally low dissipation factors (less than 10⁻³), making them well suited in frequency selective circuits in telecommunications. Other polymer and paper units are widely used in power-factor correction circuits for fluorescent lighting units, start/run circuitry for medium type electric motors, and filter circuits to suppress radio frequencies transmitted along main leads.

2.7.1.2. Mica Capacitors. Mica used in the construction of capacitors is obtained from mineral muscovite (KAl₂(Si₃Al)O₁₀(OH)₂) which can be cleaved into single crystal plates between 0.25 and 50 μm thick. Capacitors are constructed from mica plates carrying fired-on silver electrodes stacked and clamped together to form a set of capacitors connected in parallel. The assembly is encapsulated in a thermosetting resin to provide protection against the moisture. Special features of mica capacitors are long-term stability, low temperature coefficient of capacitance, and a low dissipation factor.

Owing to their unique design, construction and properties, electrolytic capacitors command a significant share in the capacitor market and are used in many electronic circuits. For this reason, even though they are classified as non-ceramic capacitors, electrolytic capacitors are discussed in a separate section below.
2.7.2. Electrolytic Capacitors

Electrolytic capacitors are the first to be considered when large blocks of capacitance are needed in electrical circuits. No other capacitors offer such large capacitance per unit volume at a low cost. Electrolytic capacitors are deservedly popular in by-pass, blocking, and power supply filter applications and for motor starting purposes. The dielectric material in an electrolytic capacitor consists of an anodically formed oxide of the anode material, which serves as the positive electrode of the capacitor. The metals most employed are aluminum and tantalum, and the anodic oxides are γ-Al₂O₃ and Ta₂O₅ respectively [23]. The effective dielectric constant of pure γ-Al₂O₃ is 8.4 and that of tantalum oxide is 28. In certain commercial grade capacitors, the dielectric constant can be slightly lower for aluminum oxide and appreciably lower for tantalum oxide due to the impurities.

2.7.2.1. Aluminum Foil Electrolytic Capacitors. Electrolytic capacitors are produced in two basic styles. The sintered anode or pellet style with either wet or dry electrolyte is used only for tantalum electrolytic capacitors [24-26]. The foil style, which is primarily used for aluminum electrolytics, employs a wet, dry, or paste electrolyte. The aluminum electrolytic capacitor comprises two high-purity (99.99% Al) aluminum foil electrodes, approximately 50 μm thick, interleaved with porous paper and wound into the form of a cylinder [2]. One electrode - the anode - carries an anodically formed alumina layer approximately 0.1 μm thick. The completed winding is placed into an aluminum can where the porous paper is vacuum impregnated with an electrolyte (adipic acid or ammonium penta borate). The formed aluminum foil is the anode, the Al₂O₃ layer is the dielectric and the electrolyte together with the unformed Al foil is the cathode. After the capacitors have been sealed in the can, they are reformed by subjecting them to a dc potential sufficient to heal any possible damage to the oxide layer caused during the fabrication. Both aluminum foils are etched to increase their effective areas (by a factor of 20) and this, together with the very thin dielectric, leads to high volumetric efficiencies.
Aluminum electrolytic capacitors are exploited in a range of applications and their relatively low cost makes them attractive for printed circuits for car radios, stereo equipment, pocket calculators, digital clocks etc. Also the very high value capacitors are used in large photo-flash equipment and for voltage smoothing.

2.7.2.2. Tantalum Electrolytic Capacitors. There are two types of tantalum electrolytic capacitors: 'wet' and 'solid'. Both varieties consist of a porous anode made by sintering tantalum powder at 1800°C in vacuum. In the wet type, the porous structure is impregnated with sulfuric acid, anodized to form a thin layer of $\text{Ta}_2\text{O}_5$ and encapsulated in a tantalum container that also serves as the cathode. The use of sulfuric acid gives a lower resistance and increases the temperature range of operation. The sintered anode tantalum electrolytic capacitor is fundamentally different from any other electrolytic in that it contains no liquids, but it consists solely of stable, inorganic, non-volatile materials. This results in important advantages, including small volume, absence of the necessity for an hermetic seal, flexibility as to shape, superior temperature characteristics, relatively low dielectric loss factor (0.1-0.5), and indefinitely long shelf-life. However, the main disadvantage of this kind of electrolytic capacitors is their low maximum recommended dc operating potential (5-100 V) and poor high frequency performance. This limitation, however, has not proved serious in most applications, especially in transistor circuits where the principal consumption of electrolytic capacitors is [24].

A schematic cross section of a sintered anode solid Ta electrolytic capacitor is shown in Figure 2-18. Fabrication of these capacitors involves attaching a dense tantalum wire to the porous tantalum body (about 60 percent density) either by embedding it in the porous block during pressing or by subsequent welding. A layer of dielectric tantalum oxide is formed on the tantalum surfaces electrochemically by making the tantalum the anode in an electrolytic bath containing phosphates or borates. After the formation of an oxide layer of desired thickness, a layer of semiconductor is deposited over all of the dielectric surface. Manganese dioxide, formed by the pyrolysis of manganous nitrate is
Figure 2-18. Schematic cross section of a solid tantalum porous sintered anode electrolytic capacitor [24].
used for this purpose and is applied in the following way. The pellet is saturated with an aqueous solution of manganous nitrate of 50 percent or greater concentration [24]. It is then placed in a furnace until the water evaporates and the decomposition of manganous nitrate is complete as evidenced by cessation of evolution of nitrogen oxides. Several coats of MnO₂ are applied this way. The unit is then coated with a layer of carbon from a graphite dispersion. This coating makes intimate electrical contact with the MnO₂ and guards against excessive thermal and mechanical shock of the underlying layers in subsequent operations. At this point, the unit is ready for application of a metallic cathode encasement. Because solid tantalum capacitors are very stable with respect to temperature and time and have high reliability, they are widely used, particularly in large main-frame computers, military systems and telecommunications. Currently they command approximately 30% of the capacitor market [2]. Dielectric properties of sintered anode solid Ta electrolytic capacitors depend on the formation voltage and the capacitance range. Variation of dissipation factor with applied frequency for typical Ta solid electrolytics is shown in Figure 2-19 (a). Change in capacitance with applied frequency is seen Figure 2-19 (b). The high dissipation factors of Ta electrolytic capacitors make them unsatisfactory for most high frequency applications such as tuning circuits and also generally limit the use in ac circuits, bypass, coupling, and filter applications. Typical impedance versus frequency characteristics for several solid Ta electrolytics of varying capacitance are shown in Figure 2-20. High capacitance is generally associated with a low impedance value and also a flatter frequency dependance compared to the ones with lower capacitance. High dissipation factors possessed by the high capacitance electrolytics make the impedance relatively insensitive to applied frequency. As the applied frequency increases, the capacitor eventually passes through a self-resonance and becomes inductive with gradually increasing impedance. Capacitors with small capacitance and dissipation factors show a sharp decline in impedance with applied frequency and a clear resonant frequency, a behavior more similar to that of an insulator. The self-healing characteristic of the solid Ta
Figure 2-19. Variation of (a) dissipation factor and (b) capacitance with frequency for typical solid tantalum porous sintered anode electrolytic capacitors [23].
Figure 2-20. Typical impedance Vs. frequency characteristics of solid Ta electrolytic capacitors [23].
electrolytic capacitor is particularly interesting. The positive electrode of a solid Ta electrolytic capacitor consists only of tantalum metal core, and therefore does not present any complications. However the cathode is a complex structure of heterogeneous materials. As a result, heavy charge or discharge currents could produce localized hot spots, rapidly raising small sites to temperatures far above ambient. Normally amorphous Ta2O5 will crystallize at high temperatures, losing much of the dielectric strength. A severely heated site in the dielectric could then fail catastrophically under an electric field well below the rated value, exposing bare Ta metal. However, reduction of semiconducting manganese dioxide can provide a counter action (by re-forming Ta2O5 to heal the hot spot) to isolate the fault and prevent catastrophic failure.

2.7.3. Ceramic Capacitors

Ceramic materials used for capacitor applications are broadly divided into three categories [2]. Class I dielectrics, usually include low and medium permittivity ceramics, with dissipation factors less than 0.003. Medium permittivity covers a dielectric constant range of 15-500 with stable temperature coefficients. Class II dielectrics consist of high-permittivity ferroelectric materials, with dielectric constant ranging between 2000-20000 and properties that are more dependent on temperature, field strength, and frequency than Class I dielectrics. Dissipation factors for Class II ceramics are generally below 0.03 but may exceed this level in some temperature ranges and in many cases become much higher when high ac fields are applied. The main advantage of Class II ceramics is their high volumetric efficiency. Class III dielectrics contain a conductive phase that relatively reduces the thickness of the dielectric in capacitors by at least an order of magnitude. Properties are generally similar to those of Class II, but their working voltages are only between 2 and 25V. Advantage of Class III ceramics is that the simple structures, such as small discs and tubes with two parallel electrodes can give large capacitances, over 1 μF. Figure 2-21 shows the most common types of ceramic capacitors commercially used in
Figure 2-21. Most common types of ceramic capacitors: (a) ceramic chip capacitor, (b) ceramic tube capacitor, and (c) ceramic multilayer capacitor [2].
electrical and electronic devices. Dielectric properties of some of the ceramic dielectrics are presented in Table 2-5.

2.7.3.1. Ceramic Disc and Tube Capacitors. Discs can be formed by dry pressing calcined and milled powders, typically containing some organic binder (5-10 vol %). Alternatively, they can be cut from an extruded ribbon or a cast-tape. The pieces are fired in small stacks and when suitably formulated, do not adhere strongly to one another during sintering. After firing, silver paint is applied to the major surfaces and the discs are briefly refired in a single layer at 600-800°C. Tubes are formed by extrusion. They have the advantage of being less fragile than flat pieces and are more suitable in some types of circuit assembly. After sintering, the tubes are completely coated with silver. Silver from one end-face is removed by automatic grinding machines, and a ring of silver from the outer surface of the other end is cut (Figure 2-21(b)). The leads are looped around each end and soldered in place by immersing in molten solder. Disc and tubular shapes are used for all classes of dielectric since they are lowest in cost. Using Class I dielectrics they cover 0.1-1000 pF capacitance range, with Class II they cover 1-100 nF, and with Class III dielectrics they cover 0.1-2.0 µF. Except for Class III, the safe working voltages are usually at least 100V although in electronic circuits they are not likely to encounter voltages more than 10V. Thicknesses of dielectric layers vary in the range 50 µm to 2 mm, thicker units designed to withstand higher voltages, such as mains supply.

2.7.3.2. Multilayer Ceramic Capacitors. Multilayer ceramic capacitors usually made from Class II ferroelectric materials (mostly BaTiO₃) provide large volumetric efficiencies. The multilayer structure enables the maximum capacitance available from a thin dielectric to be packed into the minimum space in mechanically robust form. The interelectrode distance is typically about 20 µm, and the overall dimensions range from 1pF to 2 µF. Much larger multilayer capacitors have recently become available with capacitance values upto 300 µF. A schematic process diagram illustrating the steps involved in the manufacture of multilayer capacitors is shown in Figure 2-22. Broadly speaking, there are
Table 2-5. Dielectric properties of ceramic dielectric materials.

<table>
<thead>
<tr>
<th>Dielectric Material</th>
<th>Dielectric Constant (at 25°C)</th>
<th>tan δ (10^{-4}) (at 1 MHz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Class I dielectrics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10</td>
<td>0.5-2.0</td>
<td>1, 2</td>
</tr>
<tr>
<td>MgO</td>
<td>10</td>
<td>1-2</td>
<td>1</td>
</tr>
<tr>
<td>MgTiO₃</td>
<td>16</td>
<td>1-3</td>
<td>2</td>
</tr>
<tr>
<td>BaTi₄O₉</td>
<td>38</td>
<td>1-3</td>
<td>2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>110</td>
<td>2-4</td>
<td>2</td>
</tr>
<tr>
<td>CaTiO₃</td>
<td>130</td>
<td>10-20</td>
<td>2</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>285</td>
<td>10-20</td>
<td>2, 6</td>
</tr>
<tr>
<td><strong>Class II dielectrics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>1740</td>
<td>70-100</td>
<td>2, 30</td>
</tr>
<tr>
<td>PbTiO₃</td>
<td>203</td>
<td>220-250</td>
<td>2, 30</td>
</tr>
<tr>
<td>PZT</td>
<td>1200</td>
<td>30-50</td>
<td>2, 30</td>
</tr>
<tr>
<td><strong>Class III dielectrics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrTiO₃-based</td>
<td>10000-20000</td>
<td>2500-3200</td>
<td>2, 23</td>
</tr>
<tr>
<td>BaTiO₃-based</td>
<td>20000-50000</td>
<td>3000-4000</td>
<td>2, 23</td>
</tr>
</tbody>
</table>
Figure 2-22. Schematic process diagram of the 'wet' and 'dry' fabrication routes for ceramic multilayer capacitors [2].
two kinds of fabrication schemes. In the dry process, the dielectric powder is formed into a slip with organic solvents and a polymeric binder, and is tape cast to form a continuous strip. The cast tape is cut into sheets, typically 15 cm square, on to which the electrode pattern is printed. The electroded sheets are stacked, and consolidated under pressure at about 70°C. The consolidated stack is diced along lines in such a fashion that the electrodes of successive layers are exposed at the opposite end-faces of the stack. The polymer binder, which may comprise up to 35 v/o of the green body, is next removed by heating in air without any disruption of the multilayer structure. Following removal of the polymer, the chips are fired to the full sintering temperature (1200-1300°C) during which process the electrodes must remain solid and in place. The ink used for screen printing the electrodes contains Ag-Pd alloy as submicron particles. Palladium (m.p. 1550°C), and silver (m.p. 960°C) form solid solutions with melting points in proportion to the content of the end members. The sintered chips are then 'terminated', which involves coating the end faces with a paint typically made of Ag-Pd powder, glass frit, and an organic carrier. The terminations are fired at about 800°C. The terminations make contact with the alternating electrodes that are exposed on that end face, connecting up the stack of plate capacitors in parallel.

In the 'wet' process, a slip carrying the ceramic powder is laid down, usually by screen printing, on to a suitable temporary carrier, such as a glass substrate. The process can be repeated to build up the required thickness of the dielectric, on to which the electrodes are screen printed. The next dielectric layer is then laid down and the process is repeated. The multilayer structure is then diced for subsequent stages of fabrication as described for 'dry' process.

2.7.3.3. Barrier Layer Capacitors. Most titanate based Class II dielectrics, whether as a single phase or in combination with other oxides, become conductive on firing in reducing atmospheres. The ease of reduction is strongly affected by the other ions present: acceptor ions tend to inhibit reduction and donor ions tend to enhance it. In most cases, high resistivity can be restored by annealing in air or oxygen. Barrier layer
capacitors are based on the limited reoxidation of a reduced composition. This results, in the simplest case, a surface layer of high resistivity and a central portion of conductive material (Class III dielectrics), so that the effective dielectric thickness is twice the thickness $d_b$ of a single reoxidized layer and there is an apparent gain in permittivity over that of a fully oxidized unit by a factor of $d/2d_b$, where $d$ is the overall dielectric thickness. Alternatively, each conductive grain may be surrounded by an insulating barrier layer so that the dielectric property is dispersed throughout the ceramic.

Barrier layer capacitors depending on a reoxidized surface layer are generally made by firing BaTiO$_3$ or SrTiO$_3$ discs, approximately 0.5 mm thick, under reducing conditions. A silver electrode paint is applied to the surfaces of the disc and fired on at about 800°C. the silver paint typically contains a PbO-Bi$_2$O$_3$-B$_2$O$_3$ glass frit to which is added a small amount (~1%) of acceptor ions, e.g. Cu. This leads to the formation of a thin (~10 μm) insulating layer separating the electrodes from the semiconducting titanate and to an associated very high capacitance. Because the major part of the applied voltage is dropped across the two thin dielectric layers, the working voltage is low, typically about 10 V. Barrier layer capacitors based on SrTiO$_3$ are more stable with respect to field and temperature than those based on BaTiO$_3$. Their capacitance is only reduced by 5% at the maximum $dc$ field and their variation with temperature can be kept within ±20% over a -20 to +85°C range. Their effective dielectric constant is 10000-20000. BaTiO$_3$ units have effective permittivities of upto 50000. Barrier layer capacitors are less expensive to manufacture than multilayer units and compete in the low-voltage applications.

Dielectric characteristics of ceramic capacitors significantly depend on the type (Class) of ceramic used as the dielectric. Figure 2-23 (a) shows the variation of capacitance with frequency for ceramic capacitors made from various types of ceramics and the dependence of dissipation factor on frequency is shown in Figure 2-23 (b).
Figure 2-23. Variation of (a) capacitance and (b) dissipation factor with frequency for capacitors made from various classes of dielectric ceramics [23].
2.8. Feasibility of BaTiO$_3$ Electrolytic Capacitors

Tantalum solid electrolytic capacitors, as described earlier in this chapter, offer a variety of advantages such as large volumetric efficiency, high operating voltages, long shelf life, temperature stability, and high reliability. However, the reliability and volumetric efficiency of solid Ta anode electrolytic capacitors are best for those designed for use at high operating voltages. For low voltage, high capacitance applications, a thin dielectric film is desired to obtain the maximum volumetric efficiency. It is possible to tailor the dielectric thickness in solid Ta electrolytic capacitors, since the thickness of dielectric film (anodically formed Ta$_2$O$_5$) depends on the forming voltage. However, thin Ta$_2$O$_5$ films formed at low voltages (below 10V) tend to be defective, possess high dissipation factors, crystallize at the hot spots developed during charging and fail prematurely during service [23-26]. The typical maximum safe operating (rated) voltage for a Ta solid electrolytic capacitor is about a third of its forming voltage. However, the anodes for low voltage applications are formed at considerably higher (5-10 times the rated value) voltages, to avoid the operational and reliability limitations imposed by the thinner films. As a result, the volumetric efficiencies for low rated voltage Ta solid electrolytics are significantly lower than their high voltage counterparts. The low dielectric constant of Ta$_2$O$_5$, further sacrifices the volumetric efficiency, particularly at low operating voltages. Therefore, use of an alternative dielectric system that possesses a higher dielectric constant and can perform satisfactorily at small operating voltages employing thin dielectric layers is highly desirable. Attempts to utilize other anodic oxides such as TiO$_2$ on Ti, were not successful, for lack of acceptable structural and electrical properties in such films [61]. However, the advent of electrochemical methods to prepare BaTiO$_3$ thin films on Ti substrates provides an opportunity to conceive and develop BaTiO$_3$ electrolytic capacitors from porous Ti anodes. Synthesis of uniform, dense, electrically insulating BaTiO$_3$ films at relatively low cell voltages has been achieved in recent investigations [18-21]. High
dielectric constant of BaTiO₃ (~1400 for polycrystalline ceramic, and ~300 for thin films) is advantageous for achieving high volumetric efficiencies.

2.9. Summary

Barium titanate exhibits spontaneous polarization below the Curie temperature (T_c ~125°C), in its ferroelectric, tetragonal state. Polarization is induced by the asymmetric alignment of Ti⁴⁺ ion in the TiO₆ octahedral coordination of the perovskite unit cell of BaTiO₃, resulting in a large dipole moment. As a result, it possesses a large dielectric constant (k ~ 3000 for a single crystal and ~ 1400 for a polycrystalline ceramic), and exhibits non-linear ferroelectric, piezoelectric, and pyroelectric properties. Most popular among the family of ferroelectric ceramics, BaTiO₃ finds a variety of applications in electrical, electronic, and sensing devices. Used in various forms ranging from single crystal to thin films, BaTiO₃ is used to fabricate multilayer capacitors, transducers, pyroelectric sensors, and microelectronic devices.

Several methods are available to synthesize BaTiO₃ thin films. Most conventional methods such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) involve high temperature (above 500°C) processing (a heated substrate during deposition, or a post-deposition annealing) to obtain crystalline films. While providing advantages such as uniform, dense microstructure, high deposition rates and chemical purity, vapor deposition methods are capital intensive and not suitable for device integration in Si-based microelectronics. Sol-gel methods promise a low-cost alternative and flexibility in substrate size and nature, combined with high deposition rates. However, these techniques also require a high temperature processing step to either crystallize or pyrolyze the precursor film. Recently developed electrochemical methods to prepare perovskite type titanate film on Ti substrates offer an unique opportunity to directly prepare crystalline BaTiO₃ thin films at very low temperatures. Even though current methods involve use of sealed pressure vessels and reaction temperatures above 150°C, aqueous electrochemical nature of
the process makes it feasible to lower the synthesis temperature by understanding the phase stability of BaTiO₃ and mechanisms of electrochemical processes.

Electrochemical method to prepare BaTiO₃ films on Ti substrates also offers an opportunity to develop BaTiO₃ electrolytic capacitors. Solid tantalum sintered anode electrolytic capacitors, possess a large capacitance per unit volume (volumetric efficiency), owing to the porous nature of the Ta anode, which provides a large surface area of the dielectric, Ta₂O₅, electrochemically formed on the surface of tantalum. Ta₂O₅, however has a very small dielectric constant (k ~ 20) and thus limits the maximum volumetric efficiency that can be achieved in solid Ta electrolytics. The use of an alternative dielectric system, such as BaTiO₃/Ti has potential to improve the volumetric efficiency of electrolytic capacitors, due to the large dielectric constant of BaTiO₃. Based on the electrochemical process to synthesize BaTiO₃ films on Ti substrates, electrolytic capacitors can be fabricated by anodizing porous, lightly sintered Ti bodies, in a Ba²⁺ containing electrolyte, to form a layer of BaTiO₃ on the entire surface of Ti. The proposed BaTiO₃ electrolytics have potential applications in high capacitance, low voltage circuits.
CHAPTER 3
LOW TEMPERATURE ELECTROCHEMICAL SYNTHESIS OF BaTiO$_3$ THIN FILMS ON Ti SUBSTRATES UNDER GALVANOSTATIC CONDITIONS

3.1. Introduction

Based on the recent investigations reported on the electrochemical synthesis of perovskite titanate thin films such as CaTiO$_3$, SrTiO$_3$ and BaTiO$_3$ on titanium substrates [12-16], the present work primarily focuses on lowering the synthesis temperature of this novel, inexpensive route to fabricate thin films of complex oxides. To achieve this objective, with specific emphasis on synthesis of BaTiO$_3$ on Ti substrates, the investigation reported in this chapter involves understanding the basic concepts of electrochemical corrosion and anodic oxidation of metals in aqueous solutions [8-11] and the theoretical phase stability of BaTiO$_3$ at low temperatures [27, 28].

Preliminary experiments in the current work confirm the electrochemical synthesis of BaTiO$_3$. More significantly, BaTiO$_3$ thin films have been synthesized in aqueous solutions at temperatures as low as 55°C, thus eliminating the use of pressurized vessels. Attempts to form BaTiO$_3$ near 25°C have produced isolated deposits of an unknown material. In this chapter, the conditions and procedures required to achieve approximately 1μm thick films at 55°C are presented followed by an experimentally verifiable hypothesis for the formation mechanism.

3.2. Background and Approach

The general approach has been to develop methods that promote the synthesis of BaTiO$_3$ films at temperatures less than 100°C. Sealed pressure vessels are ordinarily required in hydrothermal synthesis for reaction temperatures at 100°C or greater to prevent
boiling of the solution. Continuous processing is more efficient with open vessels at lower temperatures. Thus, lower synthesis temperatures make the overall process more feasible.

Theoretical phase stability for BaTiO$_3$ reported in the literature provides the fundamental understanding of the solution chemistry of the Ba-Ti-CO$_2$-H$_2$O system to develop procedures to produce BaCO$_3$-free BaTiO$_3$ thin films at low temperatures [27, 28]. As shown in the phase stability diagram in Figure 3-1 for this system, BaTiO$_3$ is predicted to be the stable phase only under highly alkaline conditions (pH above 13) even with a small amount of CO$_2$ present. With increased CO$_2$ concentration, BaCO$_3$ becomes stable over the entire range of practical pH values. Therefore care must be exercised to exclude CO$_2$ if the low temperature synthesis of BaTiO$_3$ is to be achieved as predicted.

Experimental work on hydrothermal synthesis and dissolution studies in solution verify that the phase stability theoretically predicted for BaTiO$_3$ at 25°C is valid [63-75]. The phase stability of a material in a particular solution is best determined by both precipitation and dissolution of the relevant material because reaction kinetics may be slow particularly for the former phenomenon. Several studies have demonstrated that the dissolution behavior of BaTiO$_3$ at 25°C is consistent with the phase stability diagram in Figure 3-1. BaTiO$_3$ measurably decomposes in aqueous solutions below pH 11 to either BaCO$_3$ or Ba$^{2+}$ and a TiO$_2$-rich layer depending on the CO$_2$ concentration in solution [27, 28, 63-65]. In contrast, BaTiO$_3$ particles have been synthesized in aqueous solutions at temperatures as low as 60°C [68, 73]. The reaction rates, however, were sluggish for the hydrothermal synthesis of BaTiO$_3$ at low temperatures and only nanometer size particles are produced. In general, it has been demonstrated that BaTiO$_3$ can be synthesized over a large range of temperatures with reaction rate increasing with increasing temperature [64-75].

It is likely that the formation of BaTiO$_3$ from solution follows classical concepts of nucleation and growth from solution [76-78] such that a sufficient degree of supersaturation as well as heterogeneous nucleation sites are necessary. Dissolution
Figure 3-1. Calculated phase stability diagram for Ba-Ti system at 25°C in a sealed vessel containing 20 v/o atmospheric air [28].
studies support the theoretical prediction that BaTiO$_3$ is the stable phase in alkaline aqueous solution at 25°C [27]. The sluggish reaction rates and the inability to form particles from aqueous solution at temperatures below 60°C supports the contention that the required levels of supersaturation of cationic species, particularly Ti$^{4+}$, are not achieved in conventional precipitation. Thus, a key feature of the electrochemical process is that a heterogeneous surface with a high local chemical potential of the cationic species is provided for the formation of BaTiO$_3$. This observation may have implications in the formation of electrothermal films in other systems as well.

3.3. Materials and Methods

3.3.1. Electrochemical Apparatus

A schematic diagram of the experimental setup is shown in Figure 3-2. Preliminary experiments were performed in a borosilicate vessel, but the highly alkaline solution pH values required for BaTiO$_3$ formation lead to etching of the glass. Therefore, a one liter teflon vessel was used in all reported experiments. All surfaces in contact with the electrolyte solution were either teflon or platinum except the anode. The cathode and anode were a platinum plate and a titanium corrosion coupon, respectively. The titanium corrosion coupons* (1.5 cm x 1.5 cm x 0.1 cm) were mechanically polished with alumina to 0.05 μm and degreased in ethanol# prior to anodic deposition. The electrodes were suspended from platinum wires and placed in a teflon beaker containing the electrolyte. All experiments were performed under galvanostatic conditions (i.e., constant current) with the current density varied from 0 to 2.5 mA·cm$^{-2}$ with a commercial power source®. Changes in potential as a function of reaction time were collected on a strip chart recorder for selected experiments. Since all experiments were conducted under galvanostatic conditions, it was not necessary to include a reference electrode in the apparatus. The

---

*Electronic grade, Johnson Matthey, Ward Hill, MA.
#All chemicals are reagent grade unless otherwise indicated. Fisher Scientific, Fair Lawn, NJ.
®Potentiostat Model 173, Princeton Applied Research, Princeton, NJ.
Figure 3-2. Schematic diagram of the electrochemical apparatus for the low temperature synthesis of BaTiO$_3$ thin films in open vessels.
atmosphere in the vessel was controlled by purging the solution with suitable gas (O₂ or N₂) using a gas dispersion tube made of teflon. The flow rate for the gas through the solution was maintained between 1 and 10 cm³·min⁻¹ for all experiments.

3.3.2. Electrochemical Treatment

Details for each of the experiments are outlined in Table 3-1. Preliminary experiments indicated that the formation of BaTiO₃ required solution pH values greater than pH 12.5. Ba²⁺ in 0.5 M concentration as either Ba(OH)₂·8H₂O or Ba(CH₃COO)₂, the acetate salt, were used to assess the effect of the source of the electrolyte on the formation of BaTiO₃ films. NaOH as a 2 M solution was used to achieve the desired pH. Atmospheres of ambient air, N₂, and O₂ were also evaluated. Electrolyte solutions were prepared by preheating the sodium hydroxide to remove dissolved CO₂ and then adding the Ba²⁺ salt. Prior to anodic deposition, electrolyte solutions were purged for 24 hours with the desired atmosphere.

After each experiment, the coupons were washed in water adjusted to pH 9-10 with NH₄OH, rinsed in isopropanol or ethanol, and air dried prior to characterization. Samples were stored in covered containers in a desiccator prior to characterization. Care was taken to expose the samples to the ambient environment for as short a time as possible during handling to minimize BaCO₃ formation.

3.3.3. Characterization

X-ray diffraction (XRD)⁵, scanning electron microscopy (SEM)⁶, transmission electron microscopy (TEM)† and Auger electron spectroscopy (AES)⁷ were used to characterize the structural, compositional and topographical features of the BaTiO₃ thin films. XRD was performed on the washed and dried samples using Cu-Kα radiation and a scanning rate of 2.4 degrees per minute from 10 to 70 degrees two-theta. SEM

⁵X-Ray Diffractometer APD3720, Cu-Kα, Fine Tube, 40kV - 20mA, Philips Electronics, Mahwah, NJ.
⁶Scanning Electron Microscope JSM6400, JEOL, Boston, MA.
†Transmission Electron Microscope JEOL200CX, JEOL, Boston, MA.
⁷Auger Electron Spectrometer PHI660, Perkin-Elmer Corp., Eden Prairie, MN.
<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Temp. (°C)</th>
<th>Time (hours)</th>
<th>pH</th>
<th>Current (mA/cm²)</th>
<th>Solution</th>
<th>Atmosphere</th>
<th>Phases</th>
<th>Grain Size (μm)</th>
<th>Thickness (μm)</th>
<th>AES Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT-101-53</td>
<td>101</td>
<td>53</td>
<td>13.75</td>
<td>0.5</td>
<td>BaCl₂·2H₂O</td>
<td>Air</td>
<td>BaTiO₃</td>
<td>0.2-0.5</td>
<td>0.4</td>
<td>Na</td>
</tr>
<tr>
<td>BT-98-48</td>
<td>98</td>
<td>48</td>
<td>12.25</td>
<td>0.5</td>
<td>0.5M Ba(OH)₂·8H₂O</td>
<td>N₂</td>
<td>Na</td>
<td>BaTiO₃, TiO₂</td>
<td>0.2-0.5</td>
<td>BA</td>
</tr>
<tr>
<td>BT-99-30</td>
<td>99</td>
<td>30</td>
<td>13.25</td>
<td>0.5</td>
<td>0.5M Ba(OH)₂·8H₂O</td>
<td>O₂</td>
<td>BaTiO₃</td>
<td>0.2-0.5</td>
<td>0.4</td>
<td>BA</td>
</tr>
<tr>
<td>BT-100-4</td>
<td>100</td>
<td>4</td>
<td>13.5</td>
<td>0.5</td>
<td>0.5M BaCl₂·CO₂·2H₂O</td>
<td>O₂</td>
<td>BaTiO₃</td>
<td>0.2-0.5</td>
<td>0.4</td>
<td>BA</td>
</tr>
<tr>
<td>BT-98-4</td>
<td>98</td>
<td>4</td>
<td>13.75</td>
<td>0.0</td>
<td>0.5M BaCl₂·CO₂·2H₂O</td>
<td>O₂</td>
<td>BaTiO₃</td>
<td>0.2-0.5</td>
<td>0.4</td>
<td>BA</td>
</tr>
<tr>
<td>BT-100-24</td>
<td>100</td>
<td>24</td>
<td>13.75</td>
<td>1.25</td>
<td>0.5M BaCl₂·CO₂·2H₂O</td>
<td>O₂</td>
<td>BaTiO₃</td>
<td>0.2-0.5</td>
<td>0.4</td>
<td>BA</td>
</tr>
<tr>
<td>BT-55-24</td>
<td>55</td>
<td>24</td>
<td>13.75</td>
<td>1.25</td>
<td>0.5M BaCl₂·CO₂·2H₂O</td>
<td>O₂</td>
<td>BaTiO₃</td>
<td>0.2-0.5</td>
<td>0.4</td>
<td>BA</td>
</tr>
<tr>
<td>BT-29-24</td>
<td>29</td>
<td>24</td>
<td>13.75</td>
<td>1.25</td>
<td>0.5M BaCl₂·CO₂·2H₂O</td>
<td>O₂</td>
<td>BaTiO₃</td>
<td>0.2-0.5</td>
<td>0.4</td>
<td>BA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XRD Analysis</th>
<th>SEM</th>
<th>Electrochemical History</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT-101-53</td>
<td>101</td>
<td>13.75 0.5 BaCl₂·2H₂O Air BaTiO₃</td>
</tr>
<tr>
<td>BT-98-48</td>
<td>98</td>
<td>12.25 0.5 0.5M Ba(OH)₂·8H₂O N₂ BaTiO₃</td>
</tr>
<tr>
<td>BT-99-30</td>
<td>99</td>
<td>13.25 0.5 0.5M Ba(OH)₂·8H₂O O₂ BaTiO₃</td>
</tr>
<tr>
<td>BT-100-4</td>
<td>100</td>
<td>13.5 0.5 0.5M BaCl₂·CO₂·2H₂O O₂ BaTiO₃</td>
</tr>
<tr>
<td>BT-98-4</td>
<td>98</td>
<td>13.75 0.0 0.5M BaCl₂·CO₂·2H₂O O₂ BaTiO₃</td>
</tr>
<tr>
<td>BT-100-24</td>
<td>100</td>
<td>13.75 1.25 0.5M BaCl₂·CO₂·2H₂O O₂ BaTiO₃</td>
</tr>
<tr>
<td>BT-55-24</td>
<td>55</td>
<td>13.75 1.25 0.5M BaCl₂·CO₂·2H₂O O₂ BaTiO₃</td>
</tr>
<tr>
<td>BT-29-24</td>
<td>29</td>
<td>13.75 1.25 0.5M BaCl₂·CO₂·2H₂O O₂ BaTiO₃</td>
</tr>
</tbody>
</table>

* Dominant phases. Ti was found in all XRD patterns.
† AES analysis showed the presence of a very thin layer of BaCO₃ on surface, probably formed during the post-synthesis handling of the films.
photomicrographs were obtained on uncoated samples. During SEM analysis, energy dispersive analysis for X-rays was performed with an ultra-thin window for light elements (UTW)\(^9\) to verify the presence of Ba, Ti, and O in each of the samples. Samples for TEM analysis were prepared by mechanically polishing the treated coupons on one side to about 75 micron thickness and subsequently cut into 3 mm diameter discs using an ultrasonic disc cutter. The disc samples were then dimpled on the polished side to obtain a central thickness of about 15 microns, and finally, back-thinned employing Ar-ion milling at room temperature to remove Ti substrate at the center of the sample. The milled samples were coated with carbon to improve conductivity. Bright field imaging and selected area diffraction (SAD) studies were performed on the central thin regions of the samples using a 200 kV accelerating voltage (electron beam wave length \(\lambda=0.0251\text{Å}\)) and 820 mm camera length (L). The SAD patterns were indexed by measuring the distance (R) between individual spots and rings using a magnifier lens with an accuracy of \(\pm 0.1\) mm. The d-spacings for various sets of crystallographic planes were calculated using the formula \(R_d_{hkl} = L\lambda\).

AES was performed using a 10 kV electron beam to determine the near surface composition of the films. Argon ions accelerated at 3 kV on a 3 mm by 3 mm area were used to remove layers of material to obtain a compositional profile of the film as a function of depth into the film. The sputter rate was estimated to be 10 nm per minute. The films were incrementally sputtered at 30 second intervals (~5 nm depths) and AES performed until the titanium substrate was reached to obtain composition as a function of depth through the film. All films in which BaTiO\(_3\) is present also have an underlying layer of TiO\(_2\) or TiO indicated by XRD and AES analyses. Therefore, BaTiO\(_3\) film thickness was defined as the midpoint between the sputter times at which Ba and Ti crossover and Ti and O crossover. For example, in Figure 3-3(C), the Ba and Ti crossover in the compositional profile at ~38 minutes corresponding to about 380 nm and Ti and O intersect at ~68 minutes.

\(^9\)Tracer Northern, Dallas, TX.
Figure 3-3. Auger spectroscopy data for the thin films synthesized at (A) 100°C (Sample BT-100-24), (B) 55°C and low current density (Sample BT-55-24) and (C) 56°C and high current density (Sample BT-56-24) showing variation in film thickness as a function of temperature and current density.
corresponding to 680 nm. The BaTiO$_3$ film thickness is taken as the midpoint between these two values at 53 minutes or about 530 nm. The relatively small contribution in overall thickness produced by any BaCO$_3$ on the surfaces of the films was ignored in the calculation of BaTiO$_3$ film thickness.

Whether the films were continuous or contained pores and fissures was determined by electrical resistivity measurements in conjunction with SEM photomicrographs of the microstructure. Films were electroded by placing a mask with a regular array of holes over the film and sputter coating a Au/Pd film or painting on silver electrodes. The silver electrodes could be subsequently washed from the film with a suitable solvent such as acetone and the films were used for further analysis. The relative electrical resistivity of each film was determined with a standard electrometer and electrical probes.

### 3.4. Results and Discussion

The formation of polycrystalline BaTiO$_3$ thin films on titanium substrates has been observed under a variety of electrothermal conditions. Table 3-1 gives the experimental conditions and some of the relevant physical characteristics of selected films. Visual examination of the thinner films indicates the presence of multiple interference patterns of yellow, blue and purple, as previously reported [15, 16]. The films with thicknesses of about 0.2 μm are typically reflective and transparent whereas thicker films are dark gray and optically opaque. The characteristics of the synthesized BaTiO$_3$ thin films are dependent on the processing conditions as discussed below.

#### 3.4.1. Phase Stability of the BaTiO$_3$ Films

The phases present in the films were evaluated as a function of the starting electrolyte, atmosphere, solution pH, and temperature. BaTiO$_3$ thin films were initially synthesized in 0.5M Ba(OH)$_2$·8H$_2$O at 100°C, for periods up to 53 hours as reported in previous studies [12-16]. These conditions produce a dark grey BaTiO$_3$ films contaminated with BaCO$_3$ (Sample BT-101-53). Reagent grade Ba(OH)$_2$·8H$_2$O is
inherently contaminated with BaCO₃ (~2 wt%). A CO₃²⁻-free Ba²⁺ solution solution was
more easily achieved with Ba(CH₃COO)₂ as the electrolyte. Representative XRD traces are
given in Figure 3-4 for Samples BT-100-24 and BT-55-24 synthesized at 100°C and 55°C,
respectively. BaCO₃ in samples was confined to the surface as determined by AES
compositional profile analysis as shown in Figure 3-3(B) for Sample BT-55-24. BaCO₃ in
samples BT-99-30 and BT-100-4 was attributed to the reaction of atmospheric CO₂ with
the aqueous, alkaline electrolyte film covering the sample surface at the time of removal
from vessel. The surface contamination by BaCO₃ was minimized in Samples BT-98-4
through 9BT-29-24 (Table 3-1) by careful washing with CO₂-free, ammoniated water at
~pH 9 followed by a rinse with isopropanol or ethanol.

The atmosphere also has a strong effect on the phase purity of the film. Electrothermal syntheses in an ambient atmosphere produced a mixture of BaTiO₃ and
BaCO₃. Both the atmosphere and pH were varied in the preparation of Sample BT-98-48.
Nitrogen was evaluated as an atmosphere to minimize the formation of the carbonate salt.
The pH was also decreased to determine if BaTiO₃ would form or TiO₂ as predicted in
Figure 3-1. Both TiO₂ and possibly a poorly crystallized form of BaTiO₃ are present in
Sample BT-98-48 as shown in Figure 3-5. However, the basis for the presence of BaTiO₃
is only the poorly crystallized (100) peak at 22 degrees two-theta. Furthermore, the
combination of the N₂ atmosphere and lower pH also leads to a reduced form of Ti(II) as
TiO. Therefore, samples in subsequent experiments were produced using an O₂
atmosphere and at elevated pH values.

The role of oxygen in the process of thin film formation is not fully understood. However, the presence of O₂ facilitates the formation of BaTiO₃ at low temperatures. It is
possible that O₂ either is physically adsorbed at the metal/electrolyte interface to promote
oxide formation or provides an oxidizing medium, itself getting reduced at the
oxide/electrolyte interface to generate an excess of OH⁻ ions or H₂O₂ resulting in a change
in local pH and ionic equilibria. If the local environment is changed because of OH⁻ or
Figure 3-4. Comparison of X-ray diffraction data for the thin films synthesized at (A) 55°C (Sample BT-55-24), and (B) 100°C (Sample BT-100-24).
Figure 3-5. X-ray diffraction data for the thin film (Sample BT-98-48) synthesized at pH 12.25. Titanium oxides are the predominant phases.
H$_2$O$_2$ generation, then the efficiency of dissolution-reprecipitation reactions will govern the product of anodization. Oxygen can react to form H$_2$O$_2$ under the conditions in which all experiments have been performed in the current work via reactions such as [79]:

$$O_2(g) + 2H^+(aq) + 2e^- \leftrightarrow H_2O_2(aq) \quad E^\circ = +0.68V$$

[3.1]

The electrochemical conditions leading to Ti (IV), a valence state suitable for BaTiO$_3$ formation, may be promoted by complex ion formation with H$_2$O$_2$. The formation of Ti-H$_2$O$_2$ complexes elevate the solubility of Ti (IV) [80] and, thus, may provide a greater driving force for the deposition of BaTiO$_3$. Alternatively, the peroxide may promote the formation of BaO$_2$ at lower temperatures. The implications of this latter effect are discussed below. A calculation of ionic equilibria that incorporates all of these various electrochemical scenarios is beyond the scope of the current work, but will be addressed in future studies.

Solution pH also has a strong role in controlling the formation of phase pure BaTiO$_3$. As shown in Figure 3-1, BaTiO$_3$ is the stable phase only at solution pH values greater than ~ pH 12. The theoretical phase stability is verified by the XRD pattern in Figure 3-5 for the film formed under N$_2$ atmosphere at pH 12.25 (Sample BT-98-48) which shows only a poorly crystalline BaTiO$_3$ associated with TiO and TiO$_2$ as the predominant phases, whereas the most phase pure BaTiO$_3$ films have been formed in solutions with pH values greater than 13 and with an O$_2$ reflux. This data supports, but not conclusively, the hypothesis that under highly alkaline conditions, the presence of Ba$^{2+}$ in solution promotes the formation of crystalline BaTiO$_3(s)$ as the most stable phase with an amorphous titanium oxide acting as the intermediate phase. This observation is consistent with Prusi and Arsov [62], who recently reported the formation of X-ray amorphous titanium oxide on titanium surfaces in highly alkaline solutions under open circuit conditions.

There is a minimum temperature at which continuous BaTiO$_3$ films will form within 24 hours. BaTiO$_3$ films have been synthesized within 4 hours at 100°C (e.g., Samples
BT-100-4 and BT-98-4). BaTiO\textsubscript{3} films are formed within 24 hours at 55°C. Shorter synthesis times at 55°C have not yet been evaluated. However, continuous BaTiO\textsubscript{3} films are not formed within 24 hours at 29°C based on the characteristics of Sample BT-29-24. No BaTiO\textsubscript{3} has been detected by XRD even with slow scans across the major XRD peaks for sample BT-29-24. Thus, at least for 24 hour reaction times, there is a minimum temperature between 55°C and 29°C at which BaTiO\textsubscript{3} will form. Regardless, the conditions promoting the formation of BaTiO\textsubscript{3} films at 55°C indicate validity of the theoretical stability approach to guide the development of the low temperature synthesis of BaTiO\textsubscript{3}. The short reaction times relative to those required for the homogeneous formation of BaTiO\textsubscript{3} particles [68, 73] at similar temperatures also support the thesis that a heterogeneous surface is required to synthesize BaTiO\textsubscript{3} at low temperatures in aqueous solutions.

3.4.2. Thickness, Grain Size, and Porosity of The BaTiO\textsubscript{3} Films

Microstructural characteristics of the phase-pure BaTiO\textsubscript{3} films, particularly Samples BT-98-4 through BT-56-24, are strongly influenced by the current density and temperature at which a particular film is synthesized. In general, the current density has less influence on film thickness at 100°C than 55°C. For example, Sample BT-98-4 prepared at 100°C without an applied current had a BaTiO\textsubscript{3} film thickness of about 0.1 \(\mu m\) while Sample BT-100-24 prepared at 100°C with 1.25mA-cm\(^{-2}\) current density had only a modest increase in thickness to 0.2 \(\mu m\). However, it is obvious from the AES compositional profile data for Samples BT-100-24, BT-55-24, and BT-56-24 summarized in Figure 3-4 that lower temperatures and not current density have the most profound effect on film thickness. Film thicknesses approaching 1 \(\mu m\) were obtained at 55°C (Samples BT-55-24 and BT-56-24) in contrast to films in the range of 0.2 \(\mu m\) synthesized at 100°C.

Thickness of the films corresponds to the size of grains observed in SEM photomicrographs shown in Figure 3-6. Estimates of the thickness of films based on SEM analysis of either grain size or cross-sectional views are erroneous because of the
Figure 3-6. Scanning electron micrographs of the surfaces of the thin films synthesized at (A) 100°C (Sample BT-100-4) and (B) 55°C (Sample BT-55-24). Additional details for the synthesis are provided in Table 3-1.
underlying TiO$_2$ film leading to an overestimate of the actual BaTiO$_3$ film thickness. Compositional profile analysis by AES or X-ray photon spectroscopy provide more accurate estimates of the ferroelectric film thickness. The diameter of the uniform grains in Sample BT-100-4 synthesized at 100°C are approximately 0.2 μm while the grain diameter in Sample BT-55-24 synthesized at 55°C range from 0.2 μm to greater than 1 μm. The large grains in Sample BT-29-24 synthesized at 29°C are similar to those present in Sample BT-55-24 as shown in Figure 3-7. However, there are no fine grains obvious in the microstructure of Sample BT-29-24. The bimodal grain size distribution indicates that there are two pathways for grain formation as discussed below.

The degree of porosity indicated by the electrical resistivity of the films is also dependent on synthesis temperature. All films, except those prepared at 55°C with the bimodal grain sizes had pores and fissures which provided electrically conductive pathways and very low resistivities. In contrast, Samples BT-55-24 and BT-56-24 prepared at 55°C are electrically resistive. Capacitance and the dielectric loss factor will be reported at a later time, but it is expected that a static dielectric constant as low as 300, similar to that of other electrothermally synthesized films will be found because of the relatively fine grain size [18, 21].

3.4.3. Discussion of Film Formation Mechanisms

The kinetic studies necessary to determine the rate limiting step(s) specific to the formation of BaTiO$_3$ films have not yet been performed. However, based on a knowledge of the corrosion behavior of titanium, the hydrothermal synthesis of BaTiO$_3$, and the current work, a film formation mechanism is proposed that accommodates both the literature and the data developed from the current study. The microstructural and AES compositional profile data suggest two distinct mechanisms based on the synthesis temperature that control film formation.

It is proposed that the formation of BaTiO$_3$ films is controlled by three distinct, but interrelated processes:
Figure 3-7. SEM photomicrograph of Sample BT-29-24 prepared at 29°C showing large, discrete particles.
1. The rapid formation of either a Ti oxide or Ti hydrous oxide film, whose crystallinity and composition depend on the solution chemistry, atmosphere, and reaction temperature as discussed earlier;

2. Nucleation of fine barium titanate crystallites on the surface of the amorphous, metastable Ti oxide film (formed under highly alkaline conditions), and their further growth to constitute an insulating, polycrystalline film of barium titanate,

3. Concurrent with 1 and 2 is the dielectric breakdown of the films if the voltage exceeds a critical value or range of values.

Titanium belongs to an important group of metals known as "valve metals" which have a large driving force to react with water to form metal oxides or hydrous oxides [11]. AES compositional profiles on the as-polished titanium coupons indicate a TiO₂ layer 10-20 nm thick. Thicker oxide layers form when an anodic current is passed across these metals. As shown in Figure 3-6, a TiO₂ layer approximately 0.1 μm to 0.2 μm is present in the anodized films. These results are consistent with a recent report by Prusi and Arsov on the growth kinetics of films formed on Ti under alkaline conditions [62]. Based on kinetic analyses of film formation in alkaline solutions under open circuit conditions and in-situ ellipsometry measurements as a function of time, Prusi and Arsov showed that Ti hydrous oxide films formed at 25°C within 100 minutes after an initial dissolution of the native TiO₂ layer. The initial dissolution period ranged from less than one minute in 10 M KOH to ~20 minutes in 1 M KOH. In the conditions most closely approximating the present study, the Ti hydrous oxide film grew to a thickness of approximately 60 nm. In correspondence with Pourbaix's analysis [79], Prusi and Arsov maintained that metastable Ti(OH)₃ was formed initially, but transformed electrochemically to TiO₂·H₂O with time. This secondary oxidation from Ti³⁺ to Ti⁴⁺ has not been observed in the current studies with the anodic polarization on the Ti coupon. Furthermore, the elevated temperatures used to prepare some of the samples (at 55°C and 100°C) promote the formation of the rutile, anhydrous phase of TiO₂ under hydrothermal conditions [81]. The elevated temperatures
used in the current study, if consistent with the aqueous phase equilibria of TiO$_2$ deduced from hydrothermal work, promote the formation of the anhydrous, crystalline material. Thus, based on the work of Prusi and Arsov and the current study, a relatively thick Ti hydrous oxide or hydroxide film forms rather rapidly on the Ti surface within the first 100 minutes.

Hertl [75] has shown that it is likely that diffusion of Ba$^{2+}$ into precursor TiO$_2$ particles is the rate limiting step in the synthesis of BaTiO$_3$ particles. However, the low synthesis temperature of the crystalline BaTiO$_3$ films (55°C) formed in aqueous solutions and the relatively short times (as low as 4 hours) compared to the much longer times (i.e., greater than 48 hours) required for the synthesis of particles under similar conditions [68, 73, 75] suggest that the crystallization of BaTiO$_3$ is augmented by a faster growth mechanism in the electrochemical process. Also, the diffusion of Ba$^{2+}$ into the Ti oxide or Ti hydroxide under electrochemical conditions seems less likely since the transport process would have to overcome the repulsion of the electric field on the anode.

In contrast, nucleation and growth of BaTiO$_3$ particulates in the electrochemical process is strongly supported by both microstructural data and the relatively rapid formation of the barium titanate films on the Ti substrates. The bright field transmission electron image and the selected area diffraction (SAD) pattern (taken from the region close to the substrate) of the film prepared at 55°C (Sample BT-55-24) shown in Figure 3-8 indicate the presence of very fine BaTiO$_3$ crystallites embedded in a poorly crystalline TiO$_2$ film. These crystallites continue to grow into large BaTiO$_3$ grains seen as large, dark areas in the micrograph. This is supported by the presence of various BaTiO$_3$ spots and diffuse rings belonging to TiO$_2$ in the SAD pattern, as analyzed in Table 3-2. Ion milling conditions employed during the TEM sample preparation might have promoted partial crystallization of the originally amorphous Ti oxide film on the substrate. Based on this analysis, it is believed that the formation of BaTiO$_3$ involves heterogeneous nucleation in a
Figure 3-8. Transmission electron microscopy data of the BaTiO$_3$ thin film prepared at 55°C (Sample BT-55-24): (A) Bright field image showing the fine crystallites of BaTiO$_3$ embedded in a poorly crystalline TiO$_2$ film and surrounded by the fully grown BaTiO$_3$ grains seen as large, dark areas, and (B) selected area diffraction pattern collected from the center region of the above image. Indexing information for the SAD pattern is provided in Table 3-2.
Table 3-2. Diffraction data calculated from the electron diffraction pattern obtained in the TEM analysis of the BaTiO$_3$ film (Sample BT-55-24), compared with standard JCPDS data.

<table>
<thead>
<tr>
<th>Calculated $d_{hkl}$</th>
<th>Reference data $d_{hkl}$</th>
<th>Intensity</th>
<th>$h$ $k$ $l$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spots</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.84±0.04</td>
<td>2.850</td>
<td>100</td>
<td>1 1 0</td>
</tr>
<tr>
<td>2.32±0.03</td>
<td>2.328</td>
<td>30</td>
<td>1 1 1</td>
</tr>
<tr>
<td>1.99±0.02</td>
<td>2.016</td>
<td>35</td>
<td>2 0 0</td>
</tr>
<tr>
<td>1.65±0.02</td>
<td>1.6445</td>
<td>25</td>
<td>2 1 1</td>
</tr>
<tr>
<td><strong>Rings</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.05±0.05</td>
<td>3.11</td>
<td>90</td>
<td>0 0 2</td>
</tr>
<tr>
<td>2.06±0.02</td>
<td>2.073</td>
<td>70</td>
<td>0 0 3</td>
</tr>
</tbody>
</table>
local environment provided by the electrochemical process in which the activity of Ti$^{4+}$ or related Ti-hydroxide complex ions is high enough to react with Ba$^{2+}$ in solution.

As the insulating oxide film grows at the anode, there is a steady increase in the voltage to accommodate the increase in resistance under galvanostatic conditions (i.e., constant current) across the growing film. As the film becomes thicker, further passage of anodic current can result in dielectric breakdown of the film resulting in metal dissolution, oxygen evolution, or oxidation of species in the electrolyte. This behavior is consistent with the voltage oscillations as a function of reaction time shown in Figure 3-9.

The voltage required to breakdown the TiO$_2$ and BaTiO$_3$ films in the current work indicates that dielectric breakdown is a factor in dictating the nature of the film. The dielectric breakdown strength for TiO$_2$ ranges from 2×10$^4$ V·cm$^{-1}$ to 1.2×10$^5$ V·cm$^{-1}$ depending on the crystallographic direction of the applied voltage [82]. The breakdown strength for polycrystalline barium titanate [82] is approximately 1.17×10$^5$ V·cm$^{-1}$. For either a TiO$_2$ or BaTiO$_3$ film thickness of 0.2 μm, these dielectric breakdown strengths correspond to applied voltages ranging from 0.4 to 2.4 V. The voltages as a function of time for selected samples summarized in Figure 3-9 are consistent with the range of voltage expected for dielectric breakdown. However, temperature influences the range of voltages as well as the frequency of the breakdown with a greater oscillation in voltage present in the 100°C samples (from 1.5 V to 3.5 V) than the 55°C (from 1V to 2.5 V) or 29°C (1.75V to 2.5V) samples. Furthermore, the cell voltages were relatively constant for the samples prepared at the latter two temperatures after about 10 hours while the sample at 100°C required 20 hours to achieve a stable voltage. At present, it is uncertain how the microstructure changed with time during the deposition.

The BaTiO$_3$ films fabricated by the "electrothermal" process at 100°C appear to be continuous and compact in the scanning electron micrographs. However, the high electrical conductance indicates the films synthesized at 100°C contain "shorts" or porosity.
Figure 3-9. Cell voltage as a function of time for samples prepared at (A) 100°C (Sample BT-100-24), (B) 55°C (Sample BT-55-24), and (C) 29°C (Sample BT-29-24). Electrothermal conditions for all samples were similar other than the temperature.
During the formation of the anodic oxide, stresses are produced at a metal/oxide interface which result in dielectric breakdown and induce fissures through the insulating layer. The evaluation of the physical nature, size, and distribution of these "shorts" can be analyzed more rigorously by using voltage contrast method in the SEM [83].

The major microstructural difference between the films formed at 100°C and those formed at 55°C are the large grains present in the latter samples. It is currently believed that the large grains form at fissures created by the dielectric breakdown of the films. The hemispherical deposits physically fill the fissure thereby preventing electrical current to flow. This contention is supported by the hemispherical deposits formed at 29°C where BaTiO₃ is not found. The native oxide layer is still subject to dielectric breakdown as shown in Figure 3-9 although the magnitude of the oscillations in voltage is significantly smaller than that present in the 55°C or 100°C samples. Furthermore, the oscillations in voltage indicating the cycle of deposition and breakdown is continuing are still experienced in the 100°C sample for times as long as 20 hours while the oscillations have basically ceased within 10 hours for the 55°C and 29°C samples.

The precise nature of the large grains in samples prepared at 55°C and 29°C is unknown. Energy dispersive analysis for X-rays performed with an ultra-thin window for light elements indicates the deposits in Sample BT-29-24 prepared at 29°C contains oxygen, barium and titanium. However, at least some of the latter element is from the underlying TiO₂ and Ti layers. Argon sputtering on the surface of Sample BT-29-24 shown in the SEM photomicrographs in Figure 3-10 resolves some of the ultrastructure of the hemispherical deposits. The sputtered sample reveals that the hemispherical deposits are composed of elongated structures that may be related to the crystallographic orientation in the deposit. It is unlikely that the elongated structures in the argon milled hemispherical structures are due to a phenomenon similar to that which leads to sputter-induced cone formation observed in ion milled polycrystalline metal surfaces [84]. Energy dispersive analysis with an ultra thin window for light element detection indicates that the ion-milled
Figure 3-10. SEM photomicrographs of large deposits on sample BT-29-24 prepared at 29°C: (A) before argon milling and (B) after argon milling showing the texture in the hemispherical deposits.
deposits are still composed of Ba, O, and Ti although again the latter may be due primarily to the substrate. Thus, it is believed that the milling reveals the crystallographic orientation or texture in the large deposits.

It is possible that the X-ray amorphous, hemispherical deposits are a barium-titanium hydrous oxide, or alternatively, barium oxide or barium peroxide if the Ti indicated by the microanalysis is due to the underlying substrate. In any case, the validity of the following formation scheme can be more rigorously tested in future experiments:
1. The Ti oxide layer forms rapidly upon introduction of the Ti coupon into solution. The thickness of this layer is dictated to some extent by the current density on the Ti anode.
2. The nucleation and growth of the BaTiO₃ layer is dictated by the nature of the Ti oxide layer, solution chemistry and the atmosphere.

The formation rate of the BaTiO₃ particles under hydrothermal conditions follow a parabolic rate law as developed by Hertl [75]. This scheme is also consistent with the well-established mechanistic models for the diffusion controlled growth of the anodic films [85]. The growth rates for the electrochemically prepared BaTiO₃ films can be evaluated against these models, particularly those associated with the anion diffusion and point defects [85], to elucidate different stages of the film formation. It is currently believed that one of these reaction mechanisms leads to the formation of the 0.2 μm grains and small pores observed in the films synthesized at 100°C.

3.5. Conclusions

Electrically insulating, polycrystalline thin films of BaTiO₃ have been electrochemically deposited on titanium substrates at temperatures as low as 55°C. Formation of BaTiO₃ is found to be favored only in highly alkaline solutions. This is consistent with the phase stability predicted for the Ba-Ti-CO₂-H₂O system at 25°C.

Lower processing temperatures (55°C) favor the formation of thick, electrically resistive and well-crystallized BaTiO₃ films, apparently due to increased oxygen solubility
in the electrolyte solution. Films produced at 100°C are much thinner and are electrically conductive due to fissures and pores in their microstructure.

Auger spectroscopic analyses with depth profiling indicate that a titanium oxide layer whose thickness is governed by current density acts as a precursor to BaTiO₃.

Transmission electron microscopy study revealed the precipitation of BaTiO₃ microcrystals in the TiO₂ intermediate layer. Initial studies on the effect of current density indicate the formation of thinner and porous films with thicker titanium oxide intermediate layers.
CHAPTER 4
ELECTROCHEMICAL PREPARATION AND DIELECTRIC CHARACTERIZATION
OF BaTiO₃ FILMS ON Ti SUBSTRATES UNDER CONSTANT VOLTAGE
CONDITIONS USING NON-ALKALI ELECTROLYTES

4.1. Introduction

Recent investigations by many researchers worldwide have indicated the feasibility of electrochemically synthesizing BaTiO₃ films on Ti substrates by anodic oxidation of Ti in Ba²⁺ containing electrolytes at temperatures above 80°C [13-19]. In earlier work [86, 87], the electrochemical preparation of BaTiO₃ films at temperatures as low as 55°C in open vessels was reported. Electrochemical conditions such as solution alkalinity, ambient atmosphere, current density, cell potential, and temperature were identified as key processing parameters to control the chemical composition, crystallinity, thickness and microstructure of the deposited films. Formation of BaTiO₃ at low temperature requires highly alkaline solutions (pH=14), consistent with the phase stability diagram for the Ba-Ti-H₂O system [27, 28]. The presence of an oxygen atmosphere promotes the formation of thicker BaTiO₃ films at lower temperatures. Transmission electron microscopy and Auger electron spectroscopy analyses show that the formation of BaTiO₃ is preceded by the anodic oxidation of Ti to form titanium hydrous oxide complexes which act as precursors to precipitate BaTiO₃. Highly alkaline conditions require large concentrations of the alkali reagents (2M NaOH) in the conventional process, which leads to the incorporation of alkali ions in the synthesized films. The presence of even parts per million levels of alkali ions in dielectric materials is highly undesirable, as they increase dielectric loss factors and degrade the polarization characteristics. In the present investigation, we synthesized BaTiO₃ films on Ti substrates using tetraethyl-ammoniumhydroxide (TEAOH) as the base reagent. Effects of various processing parameters on the phase stability, film thickness and
uniformity have been studied. The mechanism of film formation is discussed, based upon the electrochemical data. Reaction time-dependent characteristics of the films such as total electric charge passed through the electrolytic cell, weight gain of the substrate after the electrochemical treatment, and X-ray peak intensity of the films have been compared and related. Finally, dielectric properties of the as-prepared and heat treated films are determined and compared to those prepared with NaOH as the base reagent.

4.2. Materials and Methods

4.2.1. Electrochemical Synthesis

A schematic diagram illustrating the electrochemical apparatus to synthesize BaTiO$_3$ films on Ti substrates is shown in Figure 4-1. The general synthesis procedure has been discussed in Section 3.3.

4.2.1.1. Materials. Certified reagent grade chemicals and deionized water with a specific resistivity greater than 10 MΩ·cm were used in all experiments. The deionized water was boiled with dry nitrogen purging to minimize dissolved CO$_2$(g). Barium acetate* (Ba(CH$_3$COO)$_2$) was used as the Ba$^{2+}$ source. Electrolyte pH was adjusted to highly alkaline conditions (~14) using TEAOH (tetraethylammonium hydroxide, 35 w/o in water)#. As-received 50 µm thick Ti foil® was used as the substrate in most experiments. Mechanically polished Ti coupons® of approximately 1 mm thickness were also used in some experiments to study the effect of surface quality on film deposition. All substrates were cut to 20 mm x 20 mm size for using as the anode in the electrochemical cell.

4.2.1.2. Electrolysis Method. The electrochemical apparatus consisted of a Pt counter electrode coupled to the working electrode (Ti substrate) through a constant voltage power supply™. Pt wires (0.5mm diameter) were used to provide electrical contacts. The

---

*Fisher Scientific, Pittsburgh, PA.
#Aldrich Chemical Company, Milwaukee, WI.
®Goodfellow Corporation, Malvern, PA.
®Johnson Matthey, Ward Hill, MA.
™KEPCO Model HB 8A (M), 0-325 V and 0-800 mA, Kepco, Inc. Flushing, NY.
Figure 4-1. Schematic diagram illustrating the experimental apparatus for electrochemical deposition of BaTiO$_3$ under constant applied voltage conditions.
separation distance between the electrodes was kept constant at 25 mm. Electrolysis was performed at a constant temperature (usually 55°C) within a fluctuation of ± 2°C. A 100 ml Teflon® beaker was used as the reaction vessel to minimize contamination. A 70 ml, 0.5M Ba²⁺ electrolyte solution was prepared by dissolving 9.0 g of barium acetate in 40 ml hot CO₂-free deionized water followed by the addition of approximately 30 ml TEAOH solution to attain pH 13.75. In experiments to study the effect of solution pH, the relative amounts of deionized water and TEAOH solution were carefully adjusted to keep the Ba²⁺ concentration at 0.5M. Purified oxygen gas was used to continuously purge the electrolyte solution to provide an oxidizing atmosphere, except in one experiment where nitrogen was used to study the effect of atmosphere. A single junction, high temperature Ag/AgCl reference electrode was placed in the electrolyte and coupled to the anode through an electrometer to measure the potential on the Ti substrate. Electrolysis current and reference electrode potential were recorded as functions of reaction time on strip chart recorders. Total electric charge (in coulombs) passed through the cell in each experiment was determined by measuring the area under the current vs time curve.

At the end of each experiment, the Ti anode was removed from the electrode assembly and washed in ammoniated water (pH~11) to avoid contamination from BaCO₃, and subsequently cleaned in deionized water using an ultrasonic cleaner for 1min. The samples were then air-dried at 110°C for 12 hours. Some of the films were heat treated at 200°C in air for 12 hours to study the effect of heat treatment on the crystal structure of BaTiO₃. All samples were weighed using an analytical balance prior to and after the electrochemical treatment and the difference in weights was recorded as the weight change due to the formation of barium titanate.

4.2.1.3. Film Thickness Calculation. Assuming that there was no loss of Ti⁴⁺ into the electrolyte, and the weight gain was entirely due to the formation of BaTiO₃ by the

₄M KCl saturated with AgCl, -5° to +110°C, 0 to 14 pH range, porous ceramic junction, 8mL/h flow rate, Model 13-620-53, Fisher Scientific, Pittsburgh, PA.

Keithley Model 614, Keithley Instruments, Cleveland, OH.

0.1 mg readability, ±0.1 mg accuracy, Model A-250, Fisher Scientific, Pittsburgh, PA.
incorporation of Ba\textsuperscript{2+} and O\textsuperscript{2-} ions into the substrate, the thickness of the BaTiO\textsubscript{3} film was calculated from the weight change using the following formula:

\[ t = \frac{w \cdot M_1}{\rho \cdot M_2 \cdot A} \]  

where \( t \) = calculated film thickness (cm)  
\( w \) = weight change (g)  
\( M_1 \) = molecular weight of BaTiO\textsubscript{3} (233.21 g/mole)  
\( \rho \) = specific gravity of BaTiO\textsubscript{3} (6.02 g/cm\textsuperscript{3})  
\( M_2 \) = molecular weight of BaO\textsubscript{3} (185.33 g/mole)  
\( A \) = combined surface area of both sides of the substrate (cm\textsuperscript{2})

4.2.2. Characterization

4.2.2.1. Phase, Chemistry, and Microstructure. Chemical and microstructural characterization of the as-prepared and heat treated BaTiO\textsubscript{3} films were performed using powder X-ray diffraction (XRD), Auger electron spectroscopy (AES), and scanning electron microscopy (SEM). X-ray samples were prepared by cutting a 15 mm x 15 mm size piece from the center region of the treated substrate and mounting it in the same area of the analysis slide for accurate comparison of the peak intensities of various samples. Some of the films were scratched with a diamond tipped scribing pen and viewed under SEM with a 45° tilt angle to roughly estimate the film thickness.

4.2.2.2. Dielectric Properties. Dielectric characterization of the as-prepared and heat treated films was performed at room temperature, using an impedance analyzer. The silver electrical contacts for dielectric characterization were prepared by dc sputtering, using a 1 cm diameter circular mask on one side of the sample. The synthesized film on the

1Cu-K\textsubscript{α}, 40kV - 20mA, scan rate 2.4°/min., PHILIPS APD3720, Philips Electronics, Mahwah, NJ.  
210 keV, 50 nA beam current, 30° angle of incidence, 500 Å/min. Ar sputtering rate for depth profile analysis, PHI660, Perkin-Elmer, Eden Prairie, MN.  
315 keV, JSM6400, Jeol, Boston, MA.  
45Hz-13MHz, HP4192A, Hewlett Packard Co., San Francisco, CA.  
510 nm/min. sputtering rate, 9 kV, Ar, 100 mT, 10 min. sputtering time, Hummer I, Anatech Ltd., Alexandria, VA.
other side of the Ti substrate was carefully removed by mechanical polishing, exposing the bare Ti metal, which acted as the other electrode. Since the impedance analyzer measures the capacitance of the sample, the calculated dielectric constant depends on the assigned value of film thickness, according to the following relation:

\[ C = \frac{k \cdot \varepsilon_0 \cdot A}{d} \]  

where  
\( C \) = sample capacitance (F)  
\( k \) = dielectric constant  
\( \varepsilon_0 \) = permittivity of vacuum = 8.854 x 10^{-12} (F/m)  
\( A \) = sample area (m^2)  
\( d \) = film thickness (m)

To minimize the error in the calculation of dielectric constant, BaTiO_3 films of nearly same thickness (as determined from X-ray peak intensity) were selected for dielectric characterization. Film thickness value calculated from the weight gain after electrochemical treatment was used in the above formula to calculate dielectric constant. Polarization hysteresis measurements were performed on selected samples using a standardized ferroelectric test system employing a modified Sawer-Tower bridge, in a virtual ground mode. Field strengths of up to 30 kV/cm have been applied to reach the saturation polarization.

4.3. Results and Discussion

Table 4-1 summarizes the various experimental conditions and characterization data for the BaTiO_3 films prepared in the present study. Reaction time-dependent characteristics of selected films are listed in Table 4-2.
Table 4-1. Electrochemical synthesis conditions and characterization data for BaTiO₃ films.

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Electrochemical Conditions</th>
<th>Color</th>
<th>Crystallinity* (XRD)</th>
<th>Microstructure (SEM)</th>
<th>Chemistry* (AES)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C) t (h) pH (V) V (V) Atm.</td>
<td></td>
<td>Major Phases</td>
<td>Grain Size (µm)</td>
<td>Film Structure</td>
</tr>
<tr>
<td>BT-53-24-3</td>
<td>54 24 13.00 3.0 O₂ Yellow</td>
<td>TiO₂</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>BT-57-24-3</td>
<td>57 24 13.25 3.0 O₂ Silver</td>
<td>Unknown</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>BT-56-24-3</td>
<td>56 24 13.50 3.0 O₂ Gray</td>
<td>BaTiO₃</td>
<td>0.2-0.5</td>
<td>Discontinuous</td>
<td>Ba, Ti, O</td>
</tr>
<tr>
<td>BT-55-24-3</td>
<td>55 24 13.75 3.0 O₂ Gray</td>
<td>BaTiO₃</td>
<td>0.5-1.5</td>
<td>Dense, Uniform</td>
<td>Ba, Ti, O</td>
</tr>
<tr>
<td>BT-45-24-3</td>
<td>45 24 13.75 3.0 O₂ Brown</td>
<td>Unknown</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>BT-57-24-4</td>
<td>57 24 13.75 4.0 O₂ White</td>
<td>BaCO₃</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>BT-56-24-2</td>
<td>56 24 13.75 2.5 O₂ Silver</td>
<td>Unknown</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>BT-54-2-3</td>
<td>54 2 13.75 3.0 O₂ Yellow</td>
<td>None</td>
<td>None</td>
<td>Rough</td>
<td>Ba, Ti, O, C</td>
</tr>
<tr>
<td>BT-55-4-3</td>
<td>55 4 13.75 3.0 O₂ Yellow</td>
<td>None</td>
<td>Fine</td>
<td>Rough</td>
<td>Ba, Ti, O, C</td>
</tr>
<tr>
<td>BT-56-8-3</td>
<td>56 8 13.75 3.0 O₂ Gray</td>
<td>BaTiO₃</td>
<td>0.2-0.5</td>
<td>Discontinuous</td>
<td>Ba, Ti, O, Si</td>
</tr>
<tr>
<td>BT-55-12-3</td>
<td>55 12 13.75 3.0 O₂ Gray</td>
<td>BaTiO₃</td>
<td>0.2-1.0</td>
<td>Discontinuous</td>
<td>Ba, Ti, O</td>
</tr>
<tr>
<td>BT-57-16-3</td>
<td>57 16 13.75 3.0 O₂ Blue</td>
<td>BaTiO₃</td>
<td>0.2-1.0</td>
<td>Granular</td>
<td>Ba, Ti, O</td>
</tr>
<tr>
<td>BT-56-2-3</td>
<td>56 2 13.75 3.0 O₂ Gray</td>
<td>BaTiO₃</td>
<td>0.1-0.2</td>
<td>Thin Layer</td>
<td>Ba, Ti, O</td>
</tr>
<tr>
<td>BT-56-4-3</td>
<td>56 4 13.75 3.0 O₂ Gray</td>
<td>BaTiO₃</td>
<td>0.2-0.5</td>
<td>Thin Layer</td>
<td>Ba, Ti, O</td>
</tr>
<tr>
<td>BT-54-24-3</td>
<td>54 24 13.75 3.0 N₂ Gray</td>
<td>BaTiO₃</td>
<td>0.2-1.5</td>
<td>Dense, Uniform</td>
<td>Ba, Ti, O, C</td>
</tr>
<tr>
<td>BT-55-24-NH</td>
<td>55 24 13.75 * O₂ Gray</td>
<td>BaTiO₃</td>
<td>0.5-1.5</td>
<td>Dense, Uniform</td>
<td>Ba, Ti, O</td>
</tr>
</tbody>
</table>

T = Temperature, t = Time, V = Applied Voltage, Atm. = Atmosphere, NA = Not Analyzed

* Substrate Ti peaks were observed in all samples. Only other crystalline phases are reported in this column.

$ Presence of carbon observed in some samples was restricted to the top few atomic layers of the surface

* Prepared under galvanostatic conditions (current density = 7.5 mA/cm²) using NaOH for pH adjustment
Table 4-2. Electrolysis time-dependent characteristics of BaTiO$_3$ Films.

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Time (h)</th>
<th>Weight Change (mg)</th>
<th>Surface Area (cm$^2$)</th>
<th>Calculated Thickness (μm)</th>
<th>SEM Thickness (μm)</th>
<th>AES Thickness (μm)</th>
<th>XRD Peak Intensity (a.u)</th>
<th>Total Charge (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT-56-2-3*</td>
<td>2</td>
<td>0.1</td>
<td>4.5</td>
<td>0.06</td>
<td>NM</td>
<td>0.04</td>
<td>90</td>
<td>210</td>
</tr>
<tr>
<td>BT-56-4-3*</td>
<td>4</td>
<td>0.2</td>
<td>4.5</td>
<td>0.10</td>
<td>NM</td>
<td>0.08</td>
<td>135</td>
<td>370</td>
</tr>
<tr>
<td>BT-56-8-3</td>
<td>8</td>
<td>0.2</td>
<td>8.0</td>
<td>0.06</td>
<td>NM</td>
<td>0.08</td>
<td>200</td>
<td>415</td>
</tr>
<tr>
<td>BT-55-12-3</td>
<td>12</td>
<td>0.3</td>
<td>8.0</td>
<td>0.10</td>
<td>&lt;1</td>
<td>0.12</td>
<td>350</td>
<td>575</td>
</tr>
<tr>
<td>BT-57-16-3</td>
<td>16</td>
<td>0.5</td>
<td>8.0</td>
<td>0.16</td>
<td>~1</td>
<td>0.20</td>
<td>375</td>
<td>620</td>
</tr>
<tr>
<td>BT-54-24-3</td>
<td>24</td>
<td>1.4</td>
<td>8.0</td>
<td>0.45</td>
<td>1-2</td>
<td>0.50</td>
<td>775</td>
<td>1840</td>
</tr>
</tbody>
</table>

* mechanically polished Ti surface
4.3.1. Effect of Processing Parameters on Synthesis of BaTiO$_3$ Films

Polycrystalline BaTiO$_3$ films of varying thickness, grain size and microstructural uniformity have been prepared using TEAOH as the base reagent. The phase stability, film uniformity, thickness and microstructure are dependent on various processing parameters such as solution pH, temperature, applied voltage, atmosphere, reaction time, and the quality of substrate surface.

4.3.1.1. Electrolyte pH. Extremely alkaline conditions (pH above 13.5) are required to synthesize phase pure BaTiO$_3$ films. Initial experiments conducted at lower pH values (Samples BT-53-24-3 and BT-57-24-3) resulted in the formation of either crystalline TiO$_2$ or unknown phases. This observation is consistent with the phase stability of BaTiO$_3$ discussed earlier and the previously reported electrochemical synthesis of BaTiO$_3$ films under galvanostatic conditions [87].

4.3.1.2. Synthesis Temperature. The lowest temperature at which BaTiO$_3$ could be synthesized in the present study was 55°C. One sample treated at a lower temperature (45°C, Sample BT-45-24-3) contained small amount of an unknown phase. Also, precipitation of Ba(OH)$_2$ has been observed at the bottom of the reaction vessel, indicating a very low solubility of Ba$^{2+}$ at this temperature. Extremely low concentrations of Ba$^{2+}$ in the electrolyte might have lowered the supersaturation for BaTiO$_3$ well below the level required for precipitation. This argument follows from the contention that electrochemical formation of BaTiO$_3$ is by a classical precipitation mechanism in the local environment of the anolyte, where chemical potentials of Ba$^{2+}$ and Ti$^{4+}$ are high enough to raise the supersaturation level for BaTiO$_3$.

4.3.1.3. Applied Voltage. BaTiO$_3$ films were synthesized at an applied voltage of 3 V between the working and counter electrodes, which corresponds to a potential of 1.6 V vs the Ag/AgCl reference electrode. A lower applied voltage (2.5 V, Sample BT-56-24-2) has resulted in an unknown phase, whereas a higher applied voltage (4 V, Sample BT-57-24-3) has resulted in the formation of BaCO$_3$, most likely due to electrolytic breakdown of
barium acetate. Use of other barium salts such as Ba(OH)$_2$·8H$_2$O is required if higher voltages are to be used.

4.3.1.4. Atmosphere. In contrast to the results seen in Chapter 3, oxygen atmosphere has no obvious effect in promoting the formation of BaTiO$_3$ as seen in Samples BT-55-24-3 and BT-54-24-3, prepared with oxygen and nitrogen atmospheres, respectively. An oxygen atmosphere resulted only in a slightly thicker film as indicated by the respective X-ray peak intensities shown in Table 4-2.

4.3.1.5. Reaction Time. Reaction time has a strong influence on the film uniformity, microstructure, and overall thickness, as seen in Figure 4-2. Barium titanate nucleates and forms discrete deposits on top of the native oxide layer of the as-received Ti foil, at reaction times up to 8 h. Film growth continues with time and full coverage is obtained after about 24 h. Simultaneously, the underlying native oxide layer also transforms to fine grained BaTiO$_3$ film as seen in Sample BT-55-24-3. The spherical, fine grain structure of the underlying layer suggests a dissolution-precipitation mechanism for the electrochemical conversion of native TiO$_2$ layer to BaTiO$_3$. The large, scattered grains seen in the top-most layer at longer reaction times are probably formed by the dissolution-recrystallization of BaTiO$_3$ itself. This observation supports the earlier proposed precipitation mechanism for the formation of BaTiO$_3$ under electrochemical conditions [87].

4.3.1.6. Substrate Surface Quality. Reaction kinetics were significantly improved by the use of polished Ti substrates, as shown in Figure 4-3. A thin, fine grained BaTiO$_3$ film was obtained at a 2 h reaction time (Sample BT-56-2-3), and a slightly thicker and uniform film was obtained at 4 h (Sample BT-56-4-3). The absence of thick, native oxide film (as in the case of as-received Ti foils) is believed to be the reason for the enhanced reaction kinetics and shorter reaction times for the formation of BaTiO$_3$.

4.3.1.7. Film Chemistry. AES compositional survey (Figure 4-4) on the surface of the as-prepared film showed only Ba, Ti, and O peaks, and no contamination. Some of
Figure 4-2. Scanning electron micrographs of electrochemically prepared BaTiO$_3$ films on as-received Ti foils, showing the development of microstructure with reaction time: (A) Sample BT-55-4-3 - treated for 4 hours, (B) Sample BT-56-8-3 - treated for 8 hours, (C) Sample BT-57-16-3 - treated for 16 hours, and (D) Sample BT-55-24-3 - treated for 24 hours.
Figure 4-3. Scanning electron micrographs of electrochemically prepared BaTiO$_3$ films on polished Ti coupons, showing the microstructure at short reaction times: (A) Sample BT-56-2-3 - treated for 2 hours and (B) Sample BT-56-4-3 - treated for 4 hours.
Figure 4-4. Auger electron spectroscopy data for BaTiO$_3$ film formed on as-received Ti foil (Sample BT-55-24-3). Top: Compositional survey on as-prepared film surface showing no presence of carbon, and Bottom: Compositional depth profile obtained by Ar ion sputtering (500Å/min).
the samples contained a small amount of carbon contamination (Table 4-1), which was limited to the surface. It was most likely due to the formation of BaCO$_3$ from the electrolyte solution exposed to the ambient atmosphere after the sample was removed from the cell at the end of the electrochemical treatment. A compositional depth profile obtained by Ar sputtering at a rate of 500 Å/min. is also shown in Figure 4-4, indicating a film thickness of about 0.5 μm.

4.3.1.8. Film Thickness. Figure 4-5 shows the maximum film thickness of approximately 1 μm obtained at 24 h reaction time (Sample BT-55-24-3). Change in X-ray peak intensity of the films with reaction time is illustrated in Figure 4-6. Film thickness calculated from weight change shows a linear relationship with X-ray peak intensity as shown in Figure 4-7. Comparison between calculated film thickness and the film thickness estimated from AES depth profile analysis is shown in Figure 4-8. While there is an excellent agreement between the two thicknesses, the film thickness shows a non-linear relationship with reaction time. This trend, at first was difficult to understand and warranted a more rigorous electrochemical analysis of the process. Figure 4-7 shows a linear relation between calculated film thickness and total electric charge passed through the cell. This indicates that the total electric charge is the determining factor for film thickness. A non-linear relationship between the total electric charge and the reaction time shown in Figure 4-8 explains the similar relationship between film thickness and the reaction time. Since independent experiments were conducted for each reaction time, variations in electrolyte conductivity and/or the contact resistance between the electrodes and the Pt wires are suspected to cause the non-linear variation of electric charge with reaction time.

Calculated film thickness as well as AES film thickness (~0.5μm) are considerably lower than the film thickness observed in SEM micrographs (~1μm) of Sample BT-55-24-3 shown in Figure 4-5. Surface roughness and the uneven microstructure of the films affect the sputtering rate and average Auger electron signal obtained over the sputtered area of the sample, leading to an incorrect estimation of the film thickness in AES analysis. However,
Figure 4-5. Scanning electron micrographs of BaTiO$_3$ film (Sample BT-55-24-3) showing a thickness of 2-3 μm as revealed by a scratch.
Figure 4-6. X-ray diffraction data for BaTiO₃ films formed on as-received Ti foils showing the peak intensities as a function of reaction time: 8 hours (Sample BT-56-8-3), 16 hours (Sample BT-57-16-3), and 24 hours (Sample BT-55-24-3).
Figure 4-7. Relation between calculated film thickness and X-ray diffraction peak intensity and the total electric charge passed through the electrolytic cell for BaTiO$_3$ films prepared at various reaction times.
Figure 4-8. Comparison between calculated film thickness, film thickness estimated from AES depth profile analysis, and the total electric charge passed through the electrolytic cell for BaTiO$_3$ films prepared at various reaction times.
the agreement between the calculated and AES thicknesses is difficult to explain. Corrosive loss of some Ti$^{4+}$ into the electrolyte and the presence of a native oxide layer on the Ti substrate might have caused an under estimation in calculated thickness as well.

4.3.2. Electrochemical Nature of Film Formation

4.3.2.1. Electrochemistry of Titanium. Ti belongs to a group of metals called the "valve metals" which have a large driving force to react with water to form metal oxides. The result of passing anodic current is to increase the thickness of the oxide film on the surface of the metal. As the passivating oxide film grows, there is a steady increase in the voltage across the film and further passage of anodic current can result in the breakdown of the film. At this stage, further anodic polarization can result in metal dissolution, oxygen evolution or oxidation of species in the electrolyte. It is possible that during breakdown, some dissolution of the TiO$_2$ film takes place which creates an excess of Ti$^{4+}$ ions at the oxide/electrolyte interface. In an alkaline medium, these Ti$^{4+}$ ions may be associated with OH$^-$ ions at the interface along with Ba$^{2+}$ ions. Pourbaix [79] mentions the possibility of formation of peroxide TiO$_3$.2H$_2$O at high anodic potentials, which dissolves in alkaline medium with the formation of titanate HTiO$_3^-$ and/or pertitanate HTiCV$^-$ ions.

4.3.2.2. Mechanism of BaTiO$_3$ Film Formation. Figure 4-9 shows the anodic potential (on Ti substrate vs Ag/AgCl reference electrode) and the electrolysis current recorded with reaction time for Sample BT-54-24-3. At a constant applied voltage of 3 V, the reference electrode potential gradually increased from about 1.6 V at the start of the electrolysis to about 1.8 V at the end of 24 h reaction period. Electrolysis current, however, showed a more complicated variation with reaction time. The initial value of electrolysis current was small, about 15 mA. However, it gradually increased with time to a maximum of about 28 mA and then continuously decreased to about 18 mA at the end of the 24 h reaction period. It is currently believed that a gradual dissolution of native TiO$_2$ layer (under the highly alkaline conditions of the electrolyte) and/or the corrosion of Ti occur until the current reaches the maximum, where the soluble corrosion products provide
Figure 4-9. Typical strip chart data recorded during the electrochemical synthesis of BaTiO$_3$ films: Ag/AgCl reference electrode potential (top) and electrolysis current (bottom) for a 24 h reaction (Sample BT-54-24-3).
supersaturation levels sufficient for the nucleation of BaTiO$_3$. Subsequent growth of a resistive BaTiO$_3$ film is consistent with the gradual decrease in the electrolysis current. This is also evident in the gradual increase of the reference electrode potential, indicating the formation of a resistive film on the anode.

4.3.3. Effect of Heat Treatment on Crystal Structure

4.3.3.1. Crystal Structure of BaTiO$_3$. BaTiO$_3$ exhibits various crystallographic forms, with a tetragonal ferroelectric form possessing a high dielectric constant at temperatures between 0 and 130°C, above which the unit cell converts to a paraelectric cubic structure [2]. Tetragonal BaTiO$_3$ is the desirable phase for electronic applications since it is ferroelectric and has a large dielectric constant. However, room temperature crystal structure of as-prepared BaTiO$_3$ depends on grain size and synthesis temperature [88]. Low temperature (80-200°C) synthesis techniques such as hydrothermal and sol-gel generally yield sub-micron (~0.1μm) BaTiO$_3$ powders with metastable cubic, paraelectric form [89]. These powders are compacted and sintered at high temperatures (1100-1300°C) to produce bulk ceramic components possessing tetragonal crystal structure at room temperature [90, 91]. Grain growth and densification occur during sintering, leading to the formation of tetragonal BaTiO$_3$ after cooling to room temperature. However, it has been reported that hydrothermally prepared sub-micron (0.1 μm) powders can be densified with small grain size and high dielectric properties [92]. Also, the preparation of tetragonal BaTiO$_3$ powders of 0.2-0.3 μm grain size at 240°C, using a modified hydrothermal technique is recently reported [93]. BaTiO$_3$ thin films prepared at low temperatures by electrochemical, hydrothermal, and electrochemical-hydrothermal techniques were also reported to be cubic in crystal structure [12,15, 18, 19, 86, 87].

4.3.3.2. Phase Transition After Heat Treatment. In agreement with the literature discussed above, X-ray diffraction analysis of as-prepared BaTiO$_3$ films in the current work shown in Figure 4-6 indicates cubic crystal structure. However, a low temperature heat treatment of these films (200°C, air, 12 h) resulted in a phase transition from the as-
prepared pseudo-cubic structure to the stable tetragonal structure, as seen in Figure 4-10. The peaks obtained at 41° and 53° 2θ are from the Ti substrate. The (200), (210), and (211) BaTiO₃ peaks exhibit splitting and a shift in peak positions toward the tetragonal structure after heat treatment. SEM observation of the heat treated film surfaces did not indicate any significant morphological changes. Even though the mechanism of phase transition is not clear at this point, cooling through the Curie point (130°C, cubic to tetragonal phase transition temperature) might have triggered the formation of tetragonal phase. This idea is consistent with the published literature on preparation of sintered tetragonal BaTiO₃ ceramics with very fine grain size from hydrothermally prepared cubic sub-micron powders [93, 94].

4.3.4. Dielectric Properties of BaTiO₃ Films

4.3.4.1. Structural Dependence of Dielectric Properties. Tetragonal BaTiO₃ is ferroelectric and in bulk ceramic form, it exhibits a room temperature dielectric constant in the range 1500-6000, depending on grain size [93, 94]. Dielectric constant gradually decreases with decreasing grain size, down to a point where the material loses ferroelectricity below a grain size of approximately 0.05 μm [52, 94]. Polycrystalline BaTiO₃ thin films also show a similar dependence of dielectric constant on grain size. Moreover, for a given grain size, thin films possess a lower dielectric constant compared to bulk BaTiO₃. As reported in the literature [52], chemically-synthesized tetragonal BaTiO₃ thin films with 0.2 μm or larger grain size typically possess a room temperature dielectric constant (k) in the range 1000-1500. On the other hand, films with finer grain size (0.1 μm or lower) typically have a k value in the range 200-500.
Figure 4-10. X-ray diffraction data of as-prepared and heat treated BaTiO$_3$ film (Sample BT-55-24-3) showing the peak shifts toward tetragonal structure after heat treatment.
4.3.4.2. As-Prepared Films. Figure 4-11 shows the variation of relative dielectric constant and dissipation factor ($\tan \delta$) with frequency for the BaTiO$_3$ films prepared with TEAOH and NaOH base reagents. BaTiO$_3$ prepared with NaOH (Sample BT-55-24-NH) showed relatively high dielectric constant and dissipation factor at low frequencies, indicating space charge polarization and conductive losses, possibly due to Na$^+$ ion incorporation. The AES analysis of the films prepared with NaOH, however, showed no presence of Na. It is currently believed that the concentration of Na in the films is too low to be detected using this technique. Due to a high Auger electron energy (990 eV) and a high sensitivity factor (low resolution), it is possible that the signal is buried in the background noise.

4.3.4.3. Heat Treated Films. Heat treated films exhibited a significant decrease in dielectric constant at low frequencies and an increase at high frequencies (Figure 4-11). This can be attributed to the removal of moisture and other volatile species as well as the phase transition to tetragonal BaTiO$_3$. The corresponding dissipation factors are lower and relatively independent of frequency. The heat treated TEAOH film (Sample BT-55-24-3) showed the maximum dielectric constant (~150) and the minimum dissipation factor (~0.5) at high frequencies. However, dielectric constant is still lower than expected for a tetragonal, ferroelectric BaTiO$_3$ film. This is probably due to fine-grained nature of the films. Even though the microstructure of the film formed at 24h reaction time (Sample BT-55-24-3) consists of larger grains (0.5-1.0 $\mu$m) in the top layer, the underlying film is much finer in grain size (0.1-0.2 $\mu$m). It is likely that the top, coarse grained layer forms by dissolution-reprecipitation of the primary, fine-grained BaTiO$_3$ formed by the electrochemical process. After the heat treatment, only the top layer might have transformed to tetragonal structure while the rest of the film still remained as cubic or amorphous BaTiO$_3$, resulting in a lower dielectric constant.

4.3.4.4. Ferroelectric Hysteresis. Figure 4-12 shows the polarization hysteresis data for Sample BT-55-24-3, in as-prepared and heat treated conditions. In as-prepared
Figure 4-11. Dependence of relative dielectric constant and dissipation factor on applied frequency for the as-prepared and heat treated BaTiO$_3$ films prepared with TEAOH containing electrolyte (Sample BT-55-24-3) and NaOH containing electrolyte (Sample BT-55-24-NH).
Figure 4-12. Polarization hysteresis data for the BaTiO$_3$ thin film (Sample BT-55-24-3) in (a) as-prepared and (b) heat treated conditions.
condition (Figure 4-12(a)), the sample behaved in a manner similar to a paraelectric material, with a small, linear polarization with increasing field strength. On the other hand, the heat treated sample (Figure 4-12(b)) possessed significantly larger polarization at similar field strengths, and exhibited non-linear polarization characteristics, with a remanant polarization of about 0.03 μC/cm². The remanant polarization is about two orders of magnitude less than the typical values reported for polycrystalline BaTiO₃ ceramics (2-4 μC/cm²). The hysteresis behavior is consistent with the low dielectric constant values (100-300) obtained earlier for the same sample. Small polarization (charge storage) value directly corresponds to the small dielectric constant. However, the switch to a non-linear polarization behavior verifies the cubic to tetragonal phase transition after heat treatment.

4.4. Conclusions

Phase pure, polycrystalline barium titanate films of approximately 1 μm thickness have been electrochemically prepared on Ti substrates using alkali-free electrolytes at temperatures as low as 55°C.

Phase stability, film uniformity, microstructure and thickness depend on several electrochemical parameters such as electrolyte pH, applied voltage, temperature, and reaction time. The total electric charge passed through the electrolytic cell determines the amount of barium titanate formed on the substrate and therefore the film thickness.

Use of tetraethylammonium hydroxide as the base reagent improved the dielectric properties significantly, compared to the films prepared with NaOH. Heat treatment at 200°C in air has resulted in a phase transition to the stable tetragonal BaTiO₃ phase, and further improved the dielectric properties.
CHAPTER 5
PREPARATION AND CHARACTERIZATION OF BaTiO₃ ELECTROLYTIC CAPACITORS FROM POROUS Ti BODIES

5.1. Introduction

Electrochemical synthesis of BaTiO₃ thin films on Ti substrates at temperatures as low as 55°C using open reaction vessels has been described in Chapters 3 and 4, and also reported in literature [87, 95]. Using highly alkaline electrolyte solutions (pH greater than 14) is identified as the key to synthesize BaTiO₃ at low temperatures. To minimize dielectric losses in the films, use of a non-alkali electrolyte (tetraethyl ammonium hydroxide) is recommended [95]. A low temperature (200°C) heat treatment of the synthesized films is reported to have increased the dielectric constant through a phase transition to ferroelectric tetragonal BaTiO₃ [95].

As mentioned in Chapter 2, electrolytic capacitors are widely used in applications where extremely large charge storage capacities are required, due to their high volumetric efficiency [23]. Conventional electrolytic capacitors are fabricated from porous, lightly sintered, Ta anodes that are subsequently treated in an electrolytic bath to form Ta₂O₅ dielectric layer on the entire surface [24-26]. The large surface area of the dielectric, resulting from the porous nature of the anode, gives a high charge storage per unit volume of the capacitor. However, pure Ta₂O₅ has a dielectric constant of only 28, and often due to several impurities present in the electrolytic thin films, the dielectric constant usually obtained are much lower [24]. This indicates the possibility of achieving even higher volumetric efficiencies, by replacing Ta₂O₅ / Ta system by the one that provides a higher dielectric constant, such as BaTiO₃ / Ti. This idea has motivated the investigation reported in this chapter. Based on the state of the art for synthesizing BaTiO₃ by anodic
oxidation of Ti substrates in Ba$^{2+}$ containing electrolytes and the technology developed for the fabrication of the solid Ta electrolytic capacitors, the current work attempts to develop BaTiO$_3$ electrolytic capacitors as schematically illustrated in Figure 5-1. This work also includes characterization of the microstructure and dielectric properties of the developed BaTiO$_3$ electrolytic capacitors.

5.2. Materials and Methods

5.2.1. Preparation of Sintered Porous Ti Anodes

The processing steps involved in the preparation of sintered porous titanium anodes are described in Figure 5-2. Two grades of Ti powder were used in this study to evaluate the effect of their chemical purity on dielectric properties of the BaTiO$_3$ electrolytic capacitors. A 99.4% pure, -100 mesh titanium powder was obtained from Johnson Matthey$^1$ and sieved to obtain a narrow size distribution (-200+270 mesh, 50$\mu$m average particle size). A higher grade (99.6% pure, <150 $\mu$m particle dia.) spherical Ti powder was obtained from Sumitomo$^2$ and used as received. Ti powder obtained from Johnson Matthey (JM) is relatively inexpensive, but it is manufactured from TiCl$_4$, and therefore contains substantial quantities of chlorides (~1400 ppm) and other contaminants. Besides, the particles are very irregular in shape and size. Higher grade Sumitomo (SM) Ti powder on the other hand, is manufactured from liquid Ti by melt spinning technique and the particles possess near spherical shape and narrow size distribution. Table 5-1 lists the chemical and physical characteristics of both grades of Ti powder. To enhance porosity and green strength, the Ti powders were mixed with varying amounts of polystyrene spheres$^3$ (50 $\mu$m average dia.) and pressed at various pressures using an uniaxial hydraulic press. After several attempts, it has been determined that 20v/o polystyrene spheres is sufficient for Johnson Matthey Ti to provide

$^1$AESAR/Johnson Matthey, Ward Hill, MA.
$^2$Tilop-150, Lot#IAP327, Sumitomo Corporation of America, San Francisco, CA.
$^3$Eastman Fine Chemicals, Eastman Kodak Company, Rochester, NY.
Figure 5-1. Schematic cross section of the proposed BaTiO$_3$ electrolytic capacitor.
Figure 5-2. Processing diagram for the preparation of sintered porous Ti anodes.
Table 5-1. Chemical and physical characteristics of SM Ti and JM Ti powders.

<table>
<thead>
<tr>
<th>Chemical and Physical Characteristics</th>
<th>Sumitomo Ti (SM Ti) Tilop-150, Lot # IAP327</th>
<th>Johnson Matthey Ti (JM Ti) Stock # 10383, Lot # C09E31</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assay, Ti (%)</td>
<td>99.6 (Min.)</td>
<td>99.4</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Oxygen (%)</td>
<td>0.20 (Max.)</td>
<td>0.13</td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>Iron (%)</td>
<td>0.25 (Max.)</td>
<td>0.04</td>
</tr>
<tr>
<td>Chlorides (%)</td>
<td>-</td>
<td>0.14</td>
</tr>
<tr>
<td>Silicon (%)</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>Manganese (%)</td>
<td>0.005</td>
<td>-</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>0.015</td>
<td>-</td>
</tr>
<tr>
<td>Average Particle Size (µm)</td>
<td>150</td>
<td>50</td>
</tr>
<tr>
<td>Specific Surface Area (cm²/g)</td>
<td>504</td>
<td>1105</td>
</tr>
</tbody>
</table>
durable green strength at a reasonable pressure (9000 psi). Due to spherical shape and larger particle size, 40 v/o polystyrene and 15000 psi were required for Sumitomo Ti powder, to achieve comparable green strength. A 0.8mm dia., 50mm long solid Ti wire was embedded into the green pellet while pressing, by a suitable modification of the die. A schematic illustration of the modified die assembly is shown in Figure 5-3. The green Ti anodes (12.75mm diameter and 2.5mm thick) were subsequently sintered at 800°C (JM Ti) and 900°C (SM Ti) in high purity argon atmosphere for 2 hours to improve the mechanical strength while retaining most of the porosity. Thermal gravimetric analysis was performed on the polystyrene spheres between 25°C and 1000°C in Ar at a heating rate of 10°C/min to evaluate the decomposition characteristics.

5.2.2. Electrochemical Deposition of BaTiO$_3$

Figure 5-4 shows the various processing steps involved in the preparation of BaTiO$_3$ electrolytic capacitors from the sintered porous Ti anodes. After degreased in methanol by ultrasonic cleaning for 15 min., the Ti anodes were lightly etched in 2 wt% HF solution for 15 seconds. The Ti anode was then dried in a vacuum oven at 90°C and subsequently mounted in the electrochemical apparatus, as shown Figure 5-5. A Pt foil is placed parallel to the bottom circular face of the anode at 5 mm distance, and attached to a Pt wire to act as the counter electrode.

5.2.2.1. Vacuum Impregnation of the Electrolyte Solution. A 100 ml Teflon® beaker was used as the reaction vessel to eliminate container interactions under the highly alkaline conditions of the electrolyte. The electrolyte solution usually contained 0.5M barium hydroxide$^5$ [Ba(OH)$_2$·8H$_2$O] with sufficient amount of tetraethylammonium hydroxide$^6$ (TEAOH) to achieve a pH of 14 or higher, required for the formation of BaTiO$_3$. To evaluate the effect of electrolyte salt on the formation of BaTiO$_3$, other electrolytes such as barium acetate$^7$ [Ba(CH$_3$CO$_2$)$_2$] and barium nitrate$^6$ [Ba(NO$_3$)$_2$]

---

$^4$TG/DTA 320, Seiko Instruments Inc., Torrance, CA.
$^5$Fluka Chemical corp., Ronkonkoma, NY.
$^6$Aldrich Chemical Company, Milwaukee, WI.
$^7$Fisher Scientific, Pittsburgh, PA.
Figure 5-3. Schematic cross section of the modified die assembly for uniaxial pressing of Ti and polystyrene powder mixtures with solid Ti wire embedded in the compact.
Sintered Porous Ti Anode
Degreased in Methanol
and Elched in 2\%o HF

Prepare Electrolyte Solution with Hot CO\textsubscript{2}-free Water
0.5 M Ba\textsuperscript{2+}, pH adjusted to >14.0 with TEAOH

Vacuum Impregnation of Porous Ti Anode w/ Electrolyte Solution
at 25mm Hg, 90°C

Electrochemical Treatment
55 - 100°C, up to 12 h, Constant Voltage (3-12V), O\textsubscript{2} Purging

Washed in Ammoniated Hot Water
Dried @ 80°C in Air

Characterization
XRD and SEM

Heat Treatment @ 400°C in Air
10°C/min, 2 hr Soak, Furnace Cooled

Electroding with Colloidal Carbon
Attach External Al Electrode
Polymer Encapsulation

Dielectric Characterization
Capacitance, Loss factor

Figure 5-4. Processing scheme for the preparation and characterization of BaTiO\textsubscript{3} electrolytic capacitors from sintered porous Ti anodes.
Figure 5-5. Schematic illustration of the electrochemical apparatus for depositing BaTiO$_3$ on the surface of sintered porous Ti anode.
were also used in some experiments. Hot CO₂-free deionized water, prepared by boiling under Ar purging, was used to prepare the solutions. After experiencing the lack of electrolyte penetration in the initial treatments of the Ti anodes, as explained in the later sections, it was decided to use vacuum to impregnate the anode with the electrolyte solution. A Teflon® lid housing the electrode assembly was placed on top of the vessel containing the electrolyte solution. The entire assemblage was kept in a vacuum oven at 90°C and a vacuum of 25 in-Hg was applied for 10 min.

5.2.2.2. Electrolysis. The electrochemical apparatus was then connected to a constant voltage power supply⁸ and placed in a sand bath for uniform heating. A water cooled condenser tube was attached to reaction vessel to minimize solution loss, particularly for treatments performed in boiling electrolyte solutions (near 100°C). Deposition of BaTiO₃ was also attempted at lower temperatures (close to 55°C). High purity oxygen was continuously purged through the electrolyte solution, to minimize the carbon contamination from atmospheric air, while keeping the solution gently stirred. Electrochemical treatments were performed at a constant applied cell voltage, in the range of 3-12V. The treatment time varied between 2-12h, even though most samples were treated for 4 or 8h. The electrolysis current passing through the cell was recorded as a function of time on a strip chart recorder. The Ti anode was removed from the cell at the end of treatment and immediately washed in hot ammoniated water to avoid BaCO₃ contamination from the residual electrolyte.

5.2.3. Microstructural Characterization

Scanning electron microscopy (SEM)⁹ was used to characterize the microstructure of the green and sintered porous Ti anodes as well as the BaTiO₃ formation on the electrochemically treated anodes. Porosity, particle size and shape, film uniformity, grain size and thickness, and the presence of contaminants such as BaCO₃ are some of the parameters investigated. SEM analysis was also performed to determine the extent of contamination from the residual electrolyte.

---

⁸Kepco Model HB 8A (M), 0-325 V and 0-800 mA, Kepco, Inc., Flushing, NY.
⁹JEOL JSM6400 Scanning Electron Microscope, JEOL, Boston, MA.
penetration of the colloidal carbon electrode. Ti wire electrodes were removed from the anodes and the porous cylindrical pellets were fractured into two equal halves. One of the pieces was mounted vertically on an aluminum mount and the SEM analysis was performed on the fractured cross section. X-ray diffraction analysis (XRD)\textsuperscript{10} was used to verify the formation of BaTiO\textsubscript{3} on Ti anodes. Samples for XRD analysis were obtained by removing the Ti wire electrode from the Ti anode after electrochemical treatment, and the pellet was mounted on a glass slide with the circular face (that was facing the Pt cathode during electrolysis) up and exposed to the X-ray source.

5.2.4. Fabrication of BaTiO\textsubscript{3} Electrolytic Capacitors

A schematic diagram of the BaTiO\textsubscript{3} electrolytic capacitor is shown in Figure 5-1. The titanium wire attached to the sintered porous titanium anode serves as the internal electrode whereas an aluminum disc of equal diameter attached to the opposite face of the anode serves as the external electrode. An aluminum wire was soldered to the disc to provide the electrical contact. The rest of the porous body is penetrated with repeated coatings of colloidal carbon to achieve the maximum contact area of the external electrode with the BaTiO\textsubscript{3} dielectric film. After electroding, all capacitors were hermetically sealed in a hard polymer\textsuperscript{11} envelope and characterized for dielectric properties.

5.2.5. Dielectric Characterization

Dielectric characterization of the BaTiO\textsubscript{3} electrolytic capacitors was performed using an ac impedance analyzer\textsuperscript{12} at frequencies ranging from 100Hz to 1MHz. Capacitance, dielectric loss factor (tan \(\delta\)), and impedance were recorded at various frequencies for the electrolytic capacitors prepared with JM Ti and SM Ti powders in both as received and heat treated conditions. For comparison, sintered Ti anodes, one each made from JM Ti and SM Ti (without electrochemical treatment) were oxidized at

\textsuperscript{10}PHILIPS APD3720 X-ray Diffractometer, Cu-Ka radiation, 40kV, 20mA, 2.4°/min 2Θ continuous scan rate, 10-70° 2Θ scan range. Philips Electronics, Mahwah, NJ.

\textsuperscript{11}Plastidip, PDI Inc., Circle Pines, MN.

\textsuperscript{12}HP4192A ac LF Impedance Analyser, 5Hz-13MHz, Hewlett Packard Co., San Francisco, CA.
600°C in air for 2h and electroded with colloidal carbon and characterized for dielectric properties.

5.3. Results and Discussion

Table 5-2 lists the electrochemical processing parameters and characterization data for several Ti anodes. BaTiO₃ electrolytic capacitors were fabricated from some of the anodes and characterized for dielectric properties. For the ease of reference, sample identification for each anode consists of some of the important processing information such as type of the Ti powder (JM or SM), base reagent used to adjust electrolyte pH (NH for NaOH or TH for tetraethyl ammonium hydroxide), type of electrolyte salt (BA for barium acetate, BH for barium hydroxide, and BN for barium nitrate), treatment temperature in °C, and the treatment time in hours.

5.3.1. Early Attempts

Figure 5-6 shows the cross section of one of the initial porous Ti anodes (JM-NH-BA-99-12) that was electrochemically treated to form BaTiO₃ on surface. As can be seen in the low magnification micrograph (Figure 5-6(A)) of the cross section, the depth penetration of the electrolyte solution was limited to only a few hundred microns from the surface. High magnification micrographs taken from different regions of the cross section reveal the nature of the deposits formed on Ti surface. In the regions close to the surface of the anode (Figure 5-6(B)), formation of BaCO₃ is evident from the accicular morphology of the deposit, whereas BaTiO₃ apparently formed in the regions just below the surface (Figure 5-6(C)), and to a depth to which the electrolyte could penetrate. The inner regions of the Ti anode remain entirely free of any deposition (Figure 5-6(D)). Lack of interconnected porosity in the sintered Ti anode (~60% theoretical density) is believed to have limited the penetration of the electrolyte. The initial anodes were prepared from Ti powder only, without any polystyrene filler. Surface contamination of BaCO₃ had most likely occurred by the reaction of the electrolyte solution migrating to
Table 5-2. Electrochemical processing conditions for depositing BaTiO$_3$ on various sintered porous Ti anodes.

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Voltage (V)</th>
<th>pH</th>
<th>Temp. (°C)</th>
<th>Electrolyte Composition</th>
<th>Time (h)</th>
<th>Analysis</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>JM-NH-BA-99-12</td>
<td>5</td>
<td>14.2</td>
<td>99</td>
<td>0.5M Ba(CH$_3$CO$_2$)$_2$ + 2M NaOH</td>
<td>12</td>
<td>SEM</td>
<td>No polymer in Ti</td>
</tr>
<tr>
<td>JM-NH-BA-98-12</td>
<td>5</td>
<td>14.2</td>
<td>98</td>
<td>0.5M Ba(CH$_3$CO$_2$)$_2$ + 2M NaOH</td>
<td>12</td>
<td>Dielectric Properties</td>
<td>No polymer in Ti</td>
</tr>
<tr>
<td>JM-TH-BA-56-4</td>
<td>3</td>
<td>14.2</td>
<td>56</td>
<td>0.5M Ba(CH$_3$CO$_2$)$_2$ + 20w/o TEAOH</td>
<td>4</td>
<td>SEM, XRD</td>
<td>X-ray amorphous</td>
</tr>
<tr>
<td>JM-TH-BA-98-4</td>
<td>3</td>
<td>14.1</td>
<td>98</td>
<td>0.5M Ba(CH$_3$CO$_2$)$_2$ + 20w/o TEAOH</td>
<td>4</td>
<td>SEM, XRD</td>
<td>X-ray amorphous</td>
</tr>
<tr>
<td>JM-TH-BN-55-4</td>
<td>3</td>
<td>14.3</td>
<td>55</td>
<td>0.5M Ba(NO$_3$)$_2$ + 35w/o TEAOH</td>
<td>4</td>
<td>SEM, XRD</td>
<td>X-ray amorphous</td>
</tr>
<tr>
<td>JM-TH-BN-97-4</td>
<td>3</td>
<td>14.2</td>
<td>97</td>
<td>0.5M Ba(NO$_3$)$_2$ + 35w/o TEAOH</td>
<td>4</td>
<td>SEM, XRD</td>
<td>X-ray amorphous</td>
</tr>
<tr>
<td>JM-TH-BH-54-4</td>
<td>3</td>
<td>14.0</td>
<td>54</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>4</td>
<td>SEM, XRD</td>
<td>X-ray amorphous</td>
</tr>
<tr>
<td>JM-TH-BH-95-4</td>
<td>3</td>
<td>14.2</td>
<td>95</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>4</td>
<td>SEM, XRD</td>
<td>BaTiO$_3$ in XRD</td>
</tr>
<tr>
<td>SM-TH-BH-96-12</td>
<td>3</td>
<td>14.3</td>
<td>96</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>12</td>
<td>SEM</td>
<td>Fine grained film</td>
</tr>
<tr>
<td>SM-TH-BH-99-12</td>
<td>6</td>
<td>14.2</td>
<td>99</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>12</td>
<td>SEM</td>
<td>Dense &amp; grainy film</td>
</tr>
<tr>
<td>SM-TH-BH-97-12</td>
<td>9</td>
<td>14.2</td>
<td>97</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>12</td>
<td>SEM</td>
<td>Rough surface</td>
</tr>
<tr>
<td>SM-TH-BH-95-12</td>
<td>12</td>
<td>14.1</td>
<td>95</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>12</td>
<td>SEM</td>
<td>Cracks in the film</td>
</tr>
<tr>
<td>SM-TH-BH-97-2</td>
<td>6</td>
<td>14.2</td>
<td>97</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>2</td>
<td>SEM</td>
<td>Fine grained, uniform</td>
</tr>
<tr>
<td>SM-TH-BH-96-4</td>
<td>6</td>
<td>14.3</td>
<td>96</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>4</td>
<td>SEM</td>
<td>Fine grained, uniform</td>
</tr>
<tr>
<td>SM-TH-BH-97-8</td>
<td>6</td>
<td>14.1</td>
<td>97</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>8</td>
<td>SEM</td>
<td>Dense and uniform</td>
</tr>
<tr>
<td>SM-TH-BH-96-8</td>
<td>6</td>
<td>14.2</td>
<td>96</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>8</td>
<td>SEM</td>
<td>Dense and uniform</td>
</tr>
<tr>
<td>JM-TH-BH-95-8</td>
<td>6</td>
<td>14.1</td>
<td>95</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>8</td>
<td>Dielectric Properties</td>
<td>As Prepared</td>
</tr>
<tr>
<td>JM-TH-BH-94-8</td>
<td>6</td>
<td>14.1</td>
<td>94</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>8</td>
<td>Dielectric Properties</td>
<td>Heat Treated, 400°C</td>
</tr>
<tr>
<td>SM-TH-BH-95-8</td>
<td>6</td>
<td>14.2</td>
<td>95</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>8</td>
<td>Dielectric Properties</td>
<td>As Prepared</td>
</tr>
<tr>
<td>SM-TH-BH-98-8</td>
<td>6</td>
<td>14.3</td>
<td>98</td>
<td>0.5M Ba(OH)$_2$·8H$_2$O+10w/o TEAOH</td>
<td>8</td>
<td>Dielectric Properties</td>
<td>Heat treated, 400°C</td>
</tr>
</tbody>
</table>
Figure 5-6. Scanning electron micrographs of the cross section of JM-NH-BA-99-12, taken from different regions revealing only a partial infiltration of the electrolyte: (A) Low magnification image showing most of the cross section of the Ti anode, (B) high magnification image from the region close to the surface, showing the presence of BaCO₃, (C) high magnification image from the region about 200 μm away from surface, showing the presence of BaTiO₃ coating on Ti particles, and (D) high magnification image from a deeper region showing no presence of coating on Ti surfaces.
the surface during drying of the treated anode. The lack of a complete, uniform BaTiO₃ layer on surface of Ti has resulted in unsatisfactory dielectric properties as discussed later in a separate section. To alleviate the problem of electrolyte penetration, it has been decided to use a polymeric filler, in the form of polystyrene spheres, mixed with Ti powder during pressing, thereby improving the interconnected porosity. Electrolyte penetration was further assisted by applying vacuum on the electrochemical apparatus during the initial stage of the treatment. In order to improve the dielectric properties, a superior grade Ti powder (SM Ti) has been used in some of the later experiments. To reduce dielectric loss factors, sodium hydroxide was replaced by TEAOH as the base reagent to adjust electrolyte pH. Different electrolyte salts were also evaluated to obtain dense, crystalline films of BaTiO₃ on Ti surface. The impact of these modifications to the initial processing scheme on microstructure and dielectric properties of later generation BaTiO₃ electrolytic capacitors have been discussed in the following sections.

5.3.2. Sintered Porous Ti Anodes from Mixtures of Ti and Polystyrene

Addition of polystyrene spheres to Ti powders has increased the compressibility and green strength of the compacts. This allowed the use of significantly lower pressures to prepare green Ti pellets, thereby improving the interconnected porosity in the sintered Ti anodes. As evident from the thermal analysis data shown in Figure 5-7, Polystyrene completely decomposes to gaseous products at around 400°C in argon atmosphere, leaving behind a clean, porous sintered Ti anode. Scanning electron micrographs of the fractured cross sections of green and sintered anodes made from both JM Ti and SM Ti are shown in Figure 5-8. Polystyrene spheres appear as bright circular patches in the microstructures of the green bodies (Figures 5-8(A) and 5-8(C)), due to the static electrical charging effect of insulators under the electron beam. Ti anodes prepared from JM Ti possess a relatively tortuous porosity (Figure 5-8(B)), primarily due to the irregular shape and size of the Ti particles. The presence of a very narrow neck on each Ti particle (particularly visible in Figure 5-8(D), for SM Ti) indicates the mechanically durable,
Figure 5-7. Thermal analysis of polystyrene spheres heated at 10°/min, in Ar atmosphere. TG: Thermal Gravimetry, DTA: Differential Thermal Analysis, and DTG: Differential Thermal Gravimetry.
Figure 5-8. Scanning electron micrographs of green and sintered Ti bodies made from mixtures of polystyrene and two different grades of Ti: (A) green body, 20 v/o polystyrene, JM Ti, (B) sintered body, 800°C, JM Ti, (C) green body, 40 v/o polystyrene, SM Ti, and (D) sintered body, 900°C, SM Ti.
interconnected structure of the anode. Figure 5-9 shows a low magnification scanning electron micrograph of the fractured cross section of a sintered Ti anode, with the Ti wire electrode embedded. The sintered Ti anodes possessed 35-40% theoretical density and were mechanically strong.

5.3.3. Electrochemical Formation of BaTiO₃

The sintered porous Ti anodes were electrochemically treated in Ba²⁺ containing electrolytes, to form BaTiO₃ on the surfaces of the Ti particles. The enhanced porosity and application of vacuum on the electrochemical apparatus have resulted in complete penetration of the electrolyte solution. As shown in Figure 5-10, this has led to the formation of a dense, uniform coating of BaTiO₃ over the entire surface of the porous Ti anode (Figure 5-10(A)). The dark, circular region seen in the high magnification image (Figure 5-10(B)) is the fractured neck between two adjacent Ti particles. Several of these necks can also be seen at low magnification. The uniform contrast and relatively rough topography of the Ti particles indicate the formation of BaTiO₃ coating throughout the cross section. However, the microstructure and crystallinity of the coating are found to depend on several processing variables as discussed below.

5.3.3.1. Effect of Electrolyte Salt and Synthesis Temperature. The microstructure of the coatings formed on the surfaces of Ti particles after electrochemical treatment of the sintered Ti anodes in the electrolytes containing different sources of barium are shown in Figure 5-11. The scanning electron micrographs for each sample were taken from the central regions of the fractured cross section. Electrochemical treatments were performed at low (near 55°C) and high (near 100°C) temperatures for each electrolyte salt. Samples treated in barium acetate electrolytes formed a very fine grained, discontinuous coating at low temperature (Figure 5-11(A)), and a thick, amorphous looking film covered with scattered, spherical grains at high temperature (Figure 5-11(B)). Even though the films formed uniformly over the entire surface of the anode, the film formed at high temperature had several deep, short cracks, apparently caused by the
Figure 5-9. Scanning electron micrograph of the cross section of a sintered porous Ti anode showing the presence of Ti wire electrode that was embedded during pressing.
Figure 5-10. Scanning electron micrographs of the cross section of an electrochemically treated sintered Ti anode (SM-TH-BH-97-8): (A) at low magnification, revealing complete infiltration of the electrolyte, and (B) at high magnification, showing the presence of a uniform, dense layer of BaTiO$_3$. 
Figure 5-11. Scanning electron micrographs of the cross sections of electrochemically treated sintered Ti anodes showing the formation of BaTiO$_3$ in various electrolytes at about 55°C and 100°C: (A) barium acetate at 56°C, JM-TH-BA-56-4, (B) barium acetate at 98°C, JM-TH-BA-98-4, (C) barium nitrate at 55°C, JM-TH-BN-55-4, (D) barium nitrate at 97°C, JM-TH-BN-97-4, (E) barium hydroxide at 55°C, JM-TH-BH-55-4, and (F) barium hydroxide at 95°C, JM-TH-BH-95-4.
dielectric breakdown. Another important characteristic of barium acetate electrolyte was the presence of large amounts of barium carbonate on the outer surface of the anode, and at the bottom of the container. This indicates the electrolytic breakdown of the acetate ion, leading to the formation of BaCO₃. Precipitation of barium carbonate drastically lowers the concentration of barium in solution, impeding the formation of BaTiO₃. Under such circumstances, the films formed on Ti were most likely the amorphous Ti oxide. The scattered grains on the surface of the film are likely to be BaTiO₃, but not confirmed in the X-ray diffraction analysis. The electrolytic breakdown of acetate at the low applied cell voltage (3V) was quite unexpected. Use of barium acetate electrolytes to synthesize carbonate-free BaTiO₃ thin films on planar Ti substrates at 3V applied voltage has been reported [95], and also discussed in Chapter 4. However, significantly large electrolysis currents (100-200 mA) in the treatment of Ti anodes compared to the planar substrates (5-25 mA), might have caused the breakdown.

The samples treated with barium nitrate containing electrolytes have yielded very peculiar films. Film formed near 55°C (Figure 5-11(C)) was discontinuous, with large, faceted grains of unknown material, surrounded by very fine, spherical grains. On the other hand, the film formed at 100°C (Figure 5-11(D)) was dense and uniform, but the film possessed a layered structure, with large, flowery grains. The grains also had a needle like substructure, very similar to that of BaCO₃. However, there was no visual evidence of BaCO₃ formation, and the X-ray diffraction data contained no crystalline phases other than Ti. Films formed on the samples treated in barium hydroxide (Ba(OH)₂·8H₂O) electrolytes looked similar to the BaTiO₃ thin films formed on planar Ti substrates reported in Chapter 4. At low temperature (Figure 5-11(E)), the coating was thin, dense, and fine grained, with several discontinuities, mainly in the form of pin holes. The film was found to be amorphous from the X-ray diffraction analysis. Ba(OH)₂·8H₂O was relatively insoluble at low temperatures, and as a result, a clear precipitate was formed at the bottom of the cell. However, the sample treated at high
temperature (Figure 5-11(F)) formed a crystalline, relatively uniform and coarse grained film. X-ray diffraction data shown in Figure 5-12 confirms the presence of BaTiO$_3$ on the surface of Ti particles. The relative intensities for BaTiO$_3$ peaks are very small, but closely match with the lines in the JCPDS standard reference pattern for cubic BaTiO$_3$. Small relative intensities are suspected to be a consequence of the porous and topographically rough nature of the Ti anode surface exposed to the X-ray source.

Figure 5-13 shows the low magnification scanning electron micrographs for the samples treated near 100°C in barium acetate (Figure 5-13(A)), barium nitrate (Figure 5-13(B)), and barium hydroxide (Figure 5-13(C)) electrolytes. The film formation appears to be uniform over the entire surface in all three cases. However, the extent of contamination on the film surface varied from one sample to the other. Film formed in the barium acetate electrolyte shows the presence of large BaCO$_3$ needles in isolated areas, whereas the film formed in barium hydroxide exhibits a finer grained and wide spread contamination. The sample treated in barium nitrate, however, showed no visible contamination on top of the film. More rigorous washing procedures were followed in the later experiments to minimize the extent of contamination.

From the above discussed results, it was decided that Ba(OH)$_2$·8H$_2$O is the suitable electrolyte salt for the electrochemical treatment of the sintered Ti anodes. Also, treatment temperatures near 100°C were found to be suitable for obtaining crystalline BaTiO$_3$ films.

5.3.3.2. Effect Applied Cell Voltage. To evaluate the effect of applied cell voltage on the formation of BaTiO$_3$ on the surface of the electrochemically treated sintered Ti anodes, samples were treated for 12h in barium hydroxide electrolytes at temperatures near 100°C, with 3, 6, 9, and 12 V. As shown in the scanning electron micrographs (Figure 5-14) taken from the fractured cross sections of these samples, applied cell voltage has significant effect on the microstructure, thickness, and topography of the films. Film thickness and uniformity seem to improve with increasing
Figure 5-12. X-ray diffraction data for the electrochemically treated sintered Ti anode (JM-TH-BH-95-4) shown with JCPDS standard reference patterns for cubic BaTiO$_3$ and Ti.
Figure 5-13. Low magnification scanning electron micrographs of the cross sections of electrochemically treated sintered Ti anodes, revealing the extent of contamination formed on the surfaces of Ti particles with various electrolyte solutions: (A) barium acetate, JM-TH-BA-98-4, (B) barium nitrate, JM-TH-BN-97-4, and (C) barium hydroxide, JM-TH-BH-95-4.
Figure 5-14. Scanning electron micrographs of the cross sections of electrochemically treated sintered Ti anodes showing the formation of as function of applied cell voltage: (A) 3V, SM-TH-BH-96-12, (B) 6V, SM-TH-BH-99-12, (C) 9V, SM-TH-BH-97-12, and (D) 12V, SM-TH-BH-95-12.
cell voltage, whereas the topography and quality of the film structure apparently deteriorate at high cell voltages. Film formed at 3V (Figure 5-14 (A)) possessed a thin, grainy and relatively discontinuous film structure. At 6V applied cell voltage, the film looks denser and uniform, with larger grain structure. Films formed at 6V (Figure 5-14(C)), and 12V (Figure 5-14(D)) showed rough, fine grained surfaces, although the thickness and uniformity of coverage appear to have increased. Especially, the film formed at 12V possessed several cracks and discontinuities and seem to have a layered structure. At high voltages it is likely that a combination of gas evolution (oxygen at the anode) and the dielectric breakdown caused the cracks and other discontinuities in the film.

Higher magnification scanning electron micrographs shown in Figure 5-15 reveal the nature of the cracks formed at 12V applied cell voltage. The coating seems to have two major types of cracks: fine, short hairline cracks, usually surrounding a pinhole, and wide, long cracks, often making fragments of the film detach (Figure 5-15(A)) from the Ti particle. The earlier kind are probably the cracks formed due to gas evolution. Very fine bubbles of oxygen might have burst through the film causing the pin holes and surrounding fine cracks. The long, wide cracks are more likely due to the dielectric breakdown of the film. As the film grows thicker, the dielectric strength of the material gradually decreases, and reaches a point where the field across the film exceeds the dielectric strength. Dielectric breakdown occurs at this stage, often associated with sparking caused by the high intensity electrical discharge. The energetic nature of the dielectric breakdown can cause the film to develop wide, long cracks seen in Figure 5-15(B). The films formed at high cell voltage are, however, very dense, and relatively thicker (0.25-0.50 μm) as seen from the free standing fragments of the film in Figure 5-15(A).
Figure 5-15. Scanning electron micrographs of the BaTiO₃ film formed on Ti at 12V cell voltage (SM-TH-BH-95-12), showing (A) film detachment due to cracking, and (B) the rough film surface and cracks formed during dielectric breakdown.
In order to obtain a uniform, defect-free BaTiO$_3$ coating, it has been decided, based on the results discussed above, to employ 6V applied cell voltage for the rest of the experiments.

**5.3.3.3. Effect of Treatment Time.** Sintered Ti anodes were electrochemically treated at 6V applied cell voltage in barium hydroxide containing electrolytes, for 2, 4, 8, and 12h of reaction time. Scanning electron micrographs of the coatings formed on the surfaces of Ti at the above reaction times are shown in Figure 5-16. As evident from these micrographs, treatment time has a significant effect on the microstructure of the films. At short reaction time (2h), the coating appears to be very thin and fine grained as shown in Figure 5-16(A). Increasing reaction time increases the grain size, thickness and the uniformity of the coating as observed in Figures 5-16(B) and 5-16(C) at 4h and 8h reaction times, respectively. The grain size distribution seems to widen, with finer grains filling the spaces between the large grains. At longer reaction time (12h), no further growth of the film was observed. Even though the surface of the film appears dense with large and uniform grain size, it was not continuous over the surface of Ti (Figure 5-16(D)). The film possessed several discontinuities in the form of fine cracks and wide patches with no apparent coating. It is possible that the film growth has become sluggish due to the lowering of Ba$^{2+}$ concentration and/or the change of pH in the electrolyte within the anode. Replenishment and homogenization of the internal electrolyte may be difficult due to mass transport limitations. As a consequence, only dissolution and recrystallization of the film occurs at longer reaction times, leading to the coarse, uniform grain structure. To obtain a continuous and uniform coating, a treatment time of 8h was selected for the rest of the experiments.

**5.3.4. Capacitor Fabrication and Dielectric Properties**

BaTiO$_3$ electrolytic capacitors were fabricated from the sintered porous Ti anodes after electrochemical treatment under the optimum processing conditions as described in the previous section. The dielectric properties (capacitance and dissipation factor) of the
Figure 5-16. Scanning electron micrographs of the cross sections of electrochemically treated sintered Ti anodes showing the formation of BaTiO₃ as a function of treatment time: (A) 2h, SM-TH-BH-97-2, (B) 4h, SM-TH-BH-96-4, (C) 8h, SM-TH-BH-97-8, and (D) 12h, SM-TH-BH-99-12.
as-prepared and heat treated capacitors are presented in Figures 5-17 and 5-18, along with
the data for the earlier capacitors fabricated from Ti anodes with less porosity and
incomplete penetration of the electrolyte during the treatment.

5.3.4.1. First Generation Capacitors. The variation of capacitance with frequency
for one of the early capacitors (JM-NH-BA-99-12) is shown in Figure 5-17. Capacitance
at low frequencies (<1kHz) was in the range of 10^-5 to 10^-6F range but it rapidly falls to
10^-9F level at high frequencies. The corresponding dissipation factors are shown in
Figure 5-18. The dielectric losses were very high (>5) at low frequencies and
considerably lower at (0.3-0.4) at high frequencies. The overall dielectric behavior of this
sample indicates a lack of dielectric polarization. Relatively high capacitances and loss
factors at low frequencies indicate the presence of lossy, charge migration processes,
probably contributed by the residual electrolyte contaminations and the electrodes. Rapid
decline of capacitance and loss factor to negligible levels at high frequencies clearly
indicate the absence of a dielectric material. This interpretation is consistent with the
microstructure of the capacitor shown in Figure 5-4, in which most of the Ti anode is free
of any electrolytic coating. Presence of BaTiO_3 was discrete and limited to few microns
of depth.

5.3.4.2. New Generation BaTiO_3 Electrolytic Capacitors. BaTiO_3 electrolytic
capacitors prepared with sintered Ti anodes with high porosity (35-40% theoretical
density) exhibited significantly higher capacitance both at low and high frequencies, as
shown in Figure 5-17. Dielectric loss behavior is also very different from the earlier
capacitors, as seen in Figure 5-18. Losses at low frequencies are substantially lower,
indicating better insulation characteristics of these capacitors, whereas the dissipation
factors are slightly higher at high frequencies, indicating a dielectric relaxation
phenomena.

5.3.4.3. Effect of Purity of Ti Powder. Capacitors prepared from two different
grades of Ti (JM and SM) showed very similar capacitance values at high frequencies.
Figure 5-17. Capacitance as a function of frequency for BaTiO₃ electrolytic capacitors compared with oxidized Ti anodes.
Figure 5-18. Dissipation factor (tan δ) as a function of frequency for BaTiO$_3$ electrolytic capacitors compared with oxidized Ti anodes.
But at low frequencies, the capacitors made from higher grade, chloride free SM Ti showed slightly less capacitance. Corresponding dielectric loss factors are also smaller. Even though the differences are not significant, it appears that the high capacitance and loss factors at low frequencies for JM Ti samples are due to charge migration processes caused by the Cl\(^-\) contamination. Usually referred to as interfacial or space charge polarization, it occurs when mobile charge carriers are impeded by a physical barrier (grain boundaries, interfaces, electrodes) that inhibits charge migration. The charges pile up at the barrier producing a localized polarization of the material, at sufficiently low frequencies (<1Hz), producing a very large capacitance [1]. If the barriers are an internal structural feature, or the density of charges contributing to the interfacial polarization is sufficiently large, the frequency response may extend to the kilocycle range.

5.3.4.4. Effect of Heat Treatment. Heat treatment of the BaTiO\(_3\) electrolytic capacitors at 400\(^\circ\)C has substantially improved the capacitance over the entire frequency range. Consistent with the data reported earlier Chapter 4 for the heat treated BaTiO\(_3\) thin films on Ti substrates, increase in capacitance is likely due to a phase transition from as-prepared cubic to a stable tetragonal phase, as cools through the curie temperature (~130\(^\circ\)C). The effective dielectric constant calculated from capacitance value (at 1kHz) and the surface area of the porous anodes range between 30-45 after heat treatment, with SM Ti showing smaller values than JM Ti. The corresponding dissipation factors (Figure 5-18) show a slight decrease at low frequencies, indicating the removal of moisture and other volatiles. However, the dissipation factors at high frequencies show a gradual increase, indicating the presence of a dielectric polarization mechanism. Minimum dissipation factors (tan \(\delta\) ~0.5) are obtained for SM-TH-BH-98-8 in the frequency range 10\(^3\) - 10\(^5\) Hz. On the other hand, as prepared BaTiO\(_3\) electrolytic capacitors exhibited significantly higher loss factors at low frequencies. The loss curves show an upward slope at low frequency, indicating surface conduction due to moisture and other contaminations.
The variation in impedance with frequency for as-prepared and heat treated BaTiO$_3$ electrolytic capacitors is shown in Figure 5-19. Capacitors made from as-prepared anodes showed higher impedance value at low frequencies that decreased very sharply with frequency. This behavior is consistent with their low capacitance values seen in Figure 5-17 and similar to the impedance Vs frequency behavior of low capacitance Ta electrolytics, as shown in Figure 2-20. For capacitors made from heat treated anodes, however, possessed much smaller impedance that is relatively flat with frequency. This behavior is similar to that of a high capacitance device with a high dissipation factor, which is consistent with their capacitance and loss data shown in Figures 5-17 and 5-18.

5.3.4.5. Volumetric Efficiency. Charge storage capacity of an electrolytic capacitor is usually expressed as the amount of charge stored per unit volume of the capacitor at the maximum operating voltage. The maximum operating (rated) voltage for a solid Ta electrolytic capacitor is usually two-thirds the cell voltage where the Ta$_2$O$_5$ dielectric is formed on the surface of Ta (forming voltage).

\[
\text{Volumetric Efficiency} = \frac{\text{Capacity (}\mu\text{F}) \times \text{Rated Voltage (V)}}{\text{Volume (in}^3\text{)}}
\]

Volumetric efficiencies for heat treated BaTiO$_3$ electrolytic capacitors (SM-TH-BH-98-8, and JM-TH-BH-94-8) are calculated using the above relation to compare with the values typically reported for Ta electrolytics. The values obtained for BaTiO$_3$ electrolytic capacitors range between 100,000-200,000 $\mu$F.V/in$^3$ at 1kHz frequency. These values fall in the higher end of the range (5,000-100,000 $\mu$F.V/in$^3$) reported for solid Ta electrolytic capacitors [23]. However, higher formation voltages (upto 100V) used to form Ta electrolytic capacitors significantly effect the volumetric efficiencies. At the formation voltages comparable to those used to treat Ti anodes (6V) in the present study, the volumetric efficiencies of the Ta electrolytic capacitors are in the range 10,000-50,000 $\mu$F.V/in$^3$. This indicates the possibility of achieving significant enhancement in
Figure 5-19. Impedance Vs. frequency characteristics of the BaTiO₃ electrolytic capacitors.
the charge storage capability at low operating voltages, using BaTiO$_3$ electrolytic capacitors. However, the rapid decrease in capacitance with frequency is of particular concern for high frequency applications. Corresponding volumetric frequencies are only in the range 1000-2000 $\mu$F/V/in$^3$ at $10^5$ Hz. Even though the sharp decline in capacitance with frequency is not clearly understood, incomplete penetration of the colloidal carbon electrode is suspected to have limited the capacitance at high frequencies.

5.3.4.6. Penetration of Colloidal Carbon. Scanning electron micrographs of the cross section of a BaTiO$_3$ electrolytic capacitor is shown in Figure 5-20, to estimate the depth of penetration of the colloidal carbon electrode. As seen at low magnification in Figure 5-20(A), the depth of carbon electrode from the surface of the capacitor is limited to about 300 $\mu$m, which is about 1/10 th of the total thickness of the anode. The colloidal carbon suspension (5 w/o solids) seems to have clogged the pores and repeated coatings have only saturated the voids within the depth of penetration, as seen in the high magnification image in figure 5-20(B). The space between the Ti particles was completely filled by carbon, particularly in the regions close to the outer surface. The incomplete electroding of the anode surface significantly affects the peak capacitance of the device, and complete coverage of the carbon electrode must be achieved to obtain the maximum capacitance. Colloidal carbon suspensions with lesser solids content and finer particle size can probably penetrate deeper without clogging the pores between Ti particles.

5.4. Conclusions

BaTiO$_3$ electrolytic capacitors were fabricated by electrochemically treating sintered porous Ti anodes in Ba$^{2+}$ containing electrolytes. Formation of BaTiO$_3$ coating on the surface of Ti anode depends on several processing parameters such as the type of electrolyte salt, applied cell voltage, treatment temperature and time.
Figure 5-20. Scanning electron micrographs of the cross section of the BaTiO$_3$ electrolytic capacitor (SM-TH-BH-96-8) showing (A) the depth of colloidal carbon (external electrode) penetration into the anode, and (B) the saturation of porosity with colloidal carbon near to the anode surface.
Complete impregnation of the electrolyte solution was achieved by using high porosity sintered Ti anodes (35-40% theoretical density). Green compacts made from mixtures of polystyrene (20-40%v/o) and Ti powder provided the desired porosity after sintering.

Dense, uniform BaTiO$_3$ coatings of 0.25-0.5μm thickness were formed on the entire surface of porous Ti anodes electrochemically treated for 8 hr in 0.5M Ba(OH)$_2$·8H$_2$O electrolytes at 100°C, with 12V applied cell voltage.

Heat treatment of the electrochemically treated Ti anodes at 400°C for 2h in air has increased the capacitance at all frequencies and decreased the dissipation factor at low frequencies. Slight, but gradual increase in dissipation factor with frequency in the case heat treated capacitors indicate the presence of a dielectric polarization mechanism.

Heat treated BaTiO$_3$ electrolytic capacitors possessed volumetric efficiencies that are comparable to those reported for solid Ta anode electrolytic capacitors at low frequencies (1kHz). However, the capacitance decreases with frequency rather rapidly, resulting in significantly low volumetric efficiencies at high frequencies.

BaTiO$_3$ electrolytic capacitors, produced from higher grade (99.6% Ti, Sumitomo) Ti powder possessed lower dissipation factors, compared to those fabricated from lower grade, TiCl$_4$ derived (99.4%, Johnson Matthey) Ti powder.

Scanning electron microscopy of a fractured cross section of a BaTiO$_3$ electrolytic capacitor revealed only a partial penetration of the colloidal carbon electrode into the Ti anode. Modified electroding techniques are required to achieve complete penetration and thereby improve the volumetric efficiency of the capacitors.
CHAPTER 6
THEORETICAL MODELING AND EXPERIMENTAL VERIFICATION OF
ELECTROCHEMICAL EQUILIBRIA IN Ba-Ti-C-H2O SYSTEM

6.1. Introduction

Recent years have witnessed significant advances in the chemical synthesis of advanced ceramic materials for a variety of applications, using techniques such as hydrothermal synthesis, co-precipitation, and sol-gel synthesis. These techniques involve chemical reactions among precursor materials in an aqueous environment. More recently, an electrochemical-hydrothermal technique has been developed to synthesize perovskite type titanate (BaTiO3, SrTiO3, and CaTiO3) thin films on titanium substrates [12-22, 86, 87, 95]. The success of these methods to produce the desired material with specific characteristics, depends to a large extent on process parameters such as pH, composition, electrode potential, and temperature. While several investigators are currently working worldwide, in developing and improving methods to synthesize advanced ceramic powders and thin films, very few focused on studying thermodynamic stability relationships in the relevant systems [27, 28]. Such data is crucial to understand the interactions between precursors and other reactants, which ultimately govern the characteristics of the produced material. In addition, understanding electrochemical equilibria in multicomponent systems is critical to evaluate the effect of processing conditions on the electrochemical synthesis of complex oxide thin films.

Electrochemical equilibria in systems containing various elements and their compounds, ionic and neutral species in aqueous environments are represented in the form of $E_{H}$-pH diagrams [96-98]. These diagrams are extensively used in predicting the stability of materials, usually metals, in aqueous solutions. When interpreted with an understanding of their advantages and limitations, $E_{H}$-pH diagrams can provide useful information about
the corrosion and passivation behavior of metals and solubility data for their compounds
and dissolved (ionic and neutral) species, as a function of solution pH and electrode
potential. Even though the Eₜ-pH diagrams are usually constructed for one element - water
systems, a few studies in the multielement - water systems have been performed to predict
stability relationships in the extraction of metals and beneficiation of ore minerals using
hydrometallurgical techniques [99]. Other areas of interest in the application of multi-
element Eₜ-pH diagrams included biochemistry and geochemistry [100]. The current work
involves developing Eₜ-pH diagrams to describe electrochemical equilibria in Ba-Ti-C-H₂O
system, and attempts to verify the theoretical predictions with experimental data published
in literature on synthesis of BaTiO₃ powders and thin films using hydrothermal and
electrochemical methods.

6.2. Thermodynamic Data

To construct Eₜ-pH diagrams, we require the values of standard Gibbs energies of
formation (ΔGᵢ° ) for all the species considered in the system. To obtain most accurate
information about the stability of various phases in the system, we need to consider as
many species as possible, restricted only by the availability of thermodynamic data. In
addition, it is desirable to obtain the values of ΔGᵢ° as a function of temperature, to
facilitate the construction of the equilibrium diagrams at various temperatures. Standard
Gibbs energy of formation for each species can be calculated as a function of temperature,
if the values of the heat of formation (ΔHᵢ°), and entropy Sᵢ° at a reference temperature
(usually 25°C) as well as the heat capacity (Cᵢ°) as a function of temperature (T) are
known. From this set of values, the ΔGᵢ° can be calculated using standard thermodynamic
relations [101]:

$$Hᵢ^\circ = ΔHᵢ^\circ_{298.15K} + \int_{298.15K}^{T} Cᵢ°(T)dT \tag{6.1}$$

$$Sᵢ^\circ = Sᵢ°_{298.15K} + \int_{298.15K}^{T} \frac{Cᵢ°(T)}{T}dT \tag{6.2}$$
where $H^o_T$ and $S^o_T$ are the enthalpy and entropy, respectively, at 1 atm pressure and temperature $T$. The above equations can also be used to calculate the enthalpy and entropy for the elements. The heat of formation and entropy of formation for compounds are subsequently calculated from the expressions:

$$
\Delta H^o_T = H^o_T(\text{compound}) - \Sigma H^o_T(\text{elements}) \quad [6.3]
$$

$$
\Delta S^o_T = S^o_T(\text{compound}) - \Sigma S^o_T(\text{elements}) \quad [6.4]
$$

Finally, the Gibbs free energy for compounds is calculated using the relation

$$
\Delta G^o_T = \Delta H^o_T - T\Delta S^o_T \quad [6.5]
$$

### 6.2.1. Sources of Thermodynamic Data

Thermodynamic data for several species in the Ba-Ti-C system has been recently compiled by Lencka and Riman [28]. For many species, the data is readily available in several existing compilations of thermochemical data [101-109]. Lenka and Riman have critically evaluated the consistency of these data by verifying the conformity of the relations between the experimental values to the general relations of thermodynamics. For species that are not available in the existing databases, Lenka and Riman [28] have used a computer program [110] that uses Helgeson-Kirkham-Flowers (HKF) estimation method to predict the standard thermodynamic data. The data for additional species that are not considered by Lenka and Riman is obtained from existing thermodynamic databases as well as the database included in HSC Chemistry for Windows [111], the computer program used to calculate and plot the $E_h$-$pH$ diagrams. However, thermodynamic data for some species, particularly Ti$^{2+}$, Ti$^{3+}$ and their hydrolyzed species are not available and therefore are not considered in the calculation of the diagrams.

### 6.2.2. Reference States

The reference state used in the thermodynamic databases is the most stable form of the pure elements at 298.15K and 1 atm. The enthalpy and entropy scales of the elements are established by:

$$
H^o_{\text{element}} = 0 \quad \text{at 298.15K and 1 atm.}
$$
\[ S_{\text{element}}^o = 0 \] at 0K and 1 atm.

For aqueous ions, the scales are fixed assuming the enthalpy and entropy values for hydrogen ion (H\(^+\)) to be zero in a hypothetical ideal 1 molal (mol/kg) solution at 298.15K and 1 atm. Therefore,
\[ \Delta H^o(H^+) = 0 \] at 298.15K and 1 atm,
\[ \Delta S^o(H^+) = 0 \] at 298.15K and 1 atm, and thus from relation [6.5],
\[ \Delta G^o_f(H^+) = 0 \] at 298.15K and 1 atm.

**6.2.3. Estimation at Elevated Temperatures**

To obtain the Gibbs energy of formation at elevated temperatures, the standard thermochemical data for each species is converted into the following data set:

Heat of formation (\( \Delta H^o_{298.15K} \))

Entropy (\( S^o_{298.15K} \))

Heat capacity (\( C_p^o \)) as an empirical function of temperature (\( T \)):
\[
C_p = A + B \times 10^{-3} \times T + C \times 10^5 \times T^{-2} + D \times 10^6 \times T^2
\]
[6.6]

where A, B, C, and D are coefficients estimated from experimental data.

**6.2.4. Aqueous Ions**

The thermodynamic properties of aqueous ions are traditionally given only at 25°C, which limits the use of calculations to low temperatures. Therefore, the heat capacity values of these ions are extrapolated to higher temperatures using the entropy correspondence principle developed by Criss and Coble [112]. Using this method, it is possible to extrapolate heat capacity values and estimate them up to 300°C. According to previous references in the literature [113-115], extrapolated values have been found to be quite consistent with the experimental data available.

Table 6-1 and Table 6-2 list the solid and dissolved species, respectively, that are considered and not considered along with the corresponding values of \( \Delta G^o_f \) at 25, 55, and 100°C. The source of thermochemical data for each species is also cited.
Table 6-1. Free energy of formation data for the solid species in Ba-Ti-C-H₂O system at 25, 55, and 100°C and 1 atmosphere pressure.

<table>
<thead>
<tr>
<th>Oxidation Number</th>
<th>(Z)</th>
<th>Not Considered</th>
<th>Considered</th>
<th>ΔG°ₚ (kJ / mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td></td>
<td></td>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>0</td>
<td>Ti</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>+2</td>
<td>TiO</td>
<td>-513.28</td>
<td>-510.32</td>
<td>-505.90</td>
</tr>
<tr>
<td>+2</td>
<td>Ti(OH)₂</td>
<td>-105.07</td>
<td>-101.09</td>
<td>-95.00</td>
</tr>
<tr>
<td>+3</td>
<td>Ti₂O₃</td>
<td>-1433.82</td>
<td>-1425.07</td>
<td>-1411.97</td>
</tr>
<tr>
<td>+3</td>
<td>Ti(OH)₃</td>
<td>-105.07</td>
<td>-101.09</td>
<td>-95.00</td>
</tr>
<tr>
<td>+3.33</td>
<td>Ti₃O₅</td>
<td>-2317.29</td>
<td>-2303.03</td>
<td>-2281.72</td>
</tr>
<tr>
<td>+3.5</td>
<td>Ti₄O₇</td>
<td>-3213.01</td>
<td>-3193.76</td>
<td>-3164.96</td>
</tr>
<tr>
<td>+4</td>
<td>TiO₂(R)</td>
<td>-890.67</td>
<td>-885.10</td>
<td>-876.77</td>
</tr>
<tr>
<td>+4</td>
<td>TiO₂(A)</td>
<td>-883.26</td>
<td>-877.69</td>
<td>-869.34</td>
</tr>
<tr>
<td>+4</td>
<td>TiO₂.H₂O</td>
<td>-883.26</td>
<td>-877.69</td>
<td>-869.34</td>
</tr>
<tr>
<td>+4</td>
<td>Ti(OH)₄</td>
<td>-883.26</td>
<td>-877.69</td>
<td>-869.34</td>
</tr>
<tr>
<td>+6</td>
<td>TiO₃</td>
<td>-883.26</td>
<td>-877.69</td>
<td>-869.34</td>
</tr>
</tbody>
</table>

| Ba               |     |                |            | 25°C            | 55°C            | 100°C          | Ref. |
| 0                | Ba₂O | -576.98        | -573.13    | -567.43         | 109             |
| +2               | BaH₂ | -151.29        | -147.37    | -141.44         | 105             |
| +2               | BaO  | -525.34        | -522.53    | -518.41         | 28              |
| +2               | Ba(OH)₂ | -855.10 | -846.44 | -833.55 | 28 |
| +2               | Ba(OH)₂·8H₂O | -2779.31 | -2723.42 | -2637.37 | 28 |
| +2               | BaCO₃ | -1166.06       | -1158.15   | -1146.33        | 28              |
| +4               | BaO₂ | -582.27        | -577.06    | -569.28         | 107             |
| +4               | Ba₂TiO₄ | -1572.44 | -1563.72 | -1550.86 | 28 |
| +4               | Ba₂TiO₄ | -2132.90 | -2121.84 | -2105.31 | 28 |

Table 6-2. Free energy of formation data for the dissolved species in Ba-Ti-C-H$_2$O system at 25, 55, and 100°C and 1 atmosphere pressure.

<table>
<thead>
<tr>
<th>Oxidation Number</th>
<th>(Z)</th>
<th>Not Considered</th>
<th>$\Delta G_f$ (kJ/mole)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Ba</td>
<td>Considered</td>
<td>25°C</td>
<td>55°C</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>Ti$^{2+}$</td>
<td>-354.18</td>
<td>-339.78</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>HTiO$_2^-$</td>
<td>-955.88</td>
<td>-959.58</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>Ti(OH)$_2^+$</td>
<td>-614.00</td>
<td>-607.78</td>
</tr>
<tr>
<td>+3</td>
<td></td>
<td>Ti$^{3+}$</td>
<td>-869.56</td>
<td>-867.98</td>
</tr>
<tr>
<td>+3</td>
<td></td>
<td>HTiO$_2$-$^-$</td>
<td>-1092.50</td>
<td>-1094.03</td>
</tr>
<tr>
<td>+4</td>
<td></td>
<td>Ti$^{4+}$</td>
<td>-1318.17</td>
<td>-1298.79</td>
</tr>
<tr>
<td>+6</td>
<td></td>
<td>TiO$_2^{2+}$</td>
<td>-350.86</td>
<td>-363.12</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>Ba$^{2+}$</td>
<td>-716.71</td>
<td>-713.40</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>BaOH$^+$</td>
<td>-1299.68</td>
<td>-1278.23</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>Ba(HCO$_3$)$_2$</td>
<td>-1153.54</td>
<td>-1147.96</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>Ba(HCO$_3$)$^+$</td>
<td>-1734.64</td>
<td>-1715.56</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>BaCO$_3$(a)</td>
<td>-1103.88</td>
<td>-1094.49</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>CO$_2$(a)</td>
<td>-385.99</td>
<td>-383.68</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>HCO$_3^-$</td>
<td>-351.19</td>
<td>-343.60</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>HCO$_3$H(a)</td>
<td>-351.19</td>
<td>-343.65</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>CO$_3^{2-}$</td>
<td>-527.90</td>
<td>-512.57</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>HCO$_3^-$</td>
<td>-586.85</td>
<td>-576.38</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>H$_2$CO$_3$(a)</td>
<td>-623.20</td>
<td>-615.38</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>C$_2$O$_4^{2-}$</td>
<td>-674.09</td>
<td>-658.60</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>HC$_3$O$_4^-$</td>
<td>-698.35</td>
<td>-686.39</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>(COOH)$_2$(a)</td>
<td>-674.09</td>
<td>-658.73</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>H$^+$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>+2</td>
<td></td>
<td>H$_2$O</td>
<td>-237.16</td>
<td>-232.30</td>
</tr>
</tbody>
</table>
6.3. Construction of Eh-pH Diagrams

6.3.1. Types of Reactions Involved

Eh-pH diagrams can represent three types of reactions among the species in the system: reactions involving the transfer of electron(s) only, reactions involving the transfer of H+ ion(s) only, and the reactions involving both electron and H+ ion transfer. The reactions involving electron transfer are potential dependent, but independent of pH, and thus represented as a horizontal line on Eh-pH diagrams. Similarly, reactions involving transfer of H+ ions will only be dependent on pH, and represented as vertical lines. Reactions involving both electron and H+ ion transfer are dependent on both pH and potential, and represented as sloped lines in the diagram. The equations for the straight lines representing each type of reaction are calculated from thermodynamic data, as described below:

6.3.1.1. Reactions Involving the Transfer of Electrons Only. For electrochemical reactions, the familiar Nernst equation can be used to relate the potential and the equilibrium constant for the reaction. Considering the following reaction for the formation of a metal cation:

\[ M = M^{n+} + n \, e^- \]  

[6.7]

Note that electrochemical reactions, by convention, are written as oxidation reactions (i.e., electrons are generated by the reaction and appear on the right hand side of the equation). The equilibrium constant (\( K \)) for the above reaction can be written as:

\[ K = [M^{n+}] \]  

[6.8]

By substituting this in the Nernst equation, we have a straight line relation between the equilibrium potential and the activity of the metal cation:

\[ E = E^o + \frac{2.303*RT}{nF} \log(M^{n+}) \]  

[6.9]

where

\[ E^o = \text{Standard electrode potential for the reaction} = \frac{\Delta G^o}{nF} \]  

[6.10]
\[ \Delta G_r^o = \text{Gibbs free energy change for the reaction} \]
\[ = \Sigma \Delta G_i^o (\text{products}) - \Sigma \Delta G_i^o (\text{reactants}) \quad [6.11] \]

\[ R = \text{Universal gas constant} \]
\[ T = \text{Temperature (K)} \]
\[ n = \text{Number of electrons transferred} \]
\[ F = \text{Faraday’s constant} \]

For a given activity of the metal cation, the above relation reduces to a fixed potential value, which is represented as a horizontal line on the \( \text{E}_\text{h}-\text{pH} \) diagram, representing the equilibrium between the metal and the cation in solution. The position (\( \text{E}_\text{h} \) value) of this line represents the equilibrium potential attained by the pure metal surface in a solution containing its own ions at that particular activity. This equilibrium can be shifted to a higher or lower potential, by either changing the concentration of the cation in solution, or by changing the applied potential. By drawing several lines representing various activities of dissolved species, one can estimate the solubility of the solid substance with reasonable accuracy.

**6.3.1.2. Reactions Involving the Transfer of \( H^+ \) Ions Only.** Since these are purely chemical reactions, it is convenient to make use of the Van’t Hoff equation, which relates the equilibrium constant \( (K) \) to the Gibbs free energy change of the reaction:

\[ \Delta G_i^o = -RT \ln K = -2.303*RT \log K \quad [6.12] \]

For the following hydrolysis reaction of a metal ion, the equilibrium constant can be written and substituted in the above equation:

\[ \[ M^{n+} + nH_2O \leftrightarrow M(OH)_n(s) + nH^+ \quad [6.13] \]
\[ K = \frac{[H^+]^n}{[M^{n+}]} \quad [6.14] \]
\[ \log K = \frac{-\Delta G_i^o}{2.303*RT} = -n \ pH - \log [M^{n+}] \quad [6.15] \]

At a given activity of the metal cation, the above equation yields a straight line with a fixed pH value, which is represented as a vertical line on the \( \text{E}_\text{h}-\text{pH} \) diagram, indicating
the equilibrium between the hydroxide and the metal cation. This line, similar to the horizontal line described above, represents a constant activity for the dissolved metal cation. In other words, it defines a pH value beyond which metal hydroxide can precipitate from a solution containing the metal cations at that particular activity. The position of this line (pH value) can be shifted, by changing the concentration of the dissolved species in relation [6.15]. In the acidic regime, the metal hydroxide can precipitate only at a higher concentration of the cations.

6.3.1.3 Reactions Involving the Transfer of Both Electrons and H⁺ Ions. For electrochemical reactions involving the transfer of both electrons and H⁺ ions, the Nernst equation can be used to deduce a straight line relation between the equilibrium potential and pH. For the following equilibrium between a metal and its hydroxide:

\[ M + n H_2O \rightleftharpoons M(OH)\,n(s) + n H^+ + n e^- \]  \[ K = [H^+]^n \]  \[ E = E^° + \frac{2.303*RT}{nF} - n \, pH \]

The above relation can be represented as a sloped line on the Eh-pH diagram, indicating the equilibrium between the metal and its hydroxide. Along this sloped line, the metal and its hydroxide are in equilibrium, with the same activity of metal cation in solution. Away from this line, only one solid, either the metal or its hydroxide, is stable.

6.3.2 Stability of Water

Each of the Eh-pH diagram includes a set(s) of sloped parallel lines (a) and (b), that indicate the thermodynamic stability of water as described by the following reactions [116]:

\[ H_2(g) \rightleftharpoons 2 \, H^+ + 2 \, e^- \]  \[ E_h = 0.000 - 0.0592 \, pH, \text{ at } 25^\circ C \]  \[ 2H_2O \rightleftharpoons O_2(g) + 4 \, H^+ + 4 \, e^- \]  \[ E_h = 1.223 - 0.0592 \, pH, \text{ at } 25^\circ C \]

In the portion below line (a), representing the relation [6.19], the equilibrium hydrogen pressure is above 1 atm, and water under atmospheric pressure therefore is reduced with the evolution of hydrogen. Similarly, in the portion above line (b), representing the relation [6.20], the equilibrium oxygen pressure is above 1 atm, and water
under atmospheric pressure is oxidized to release oxygen. Between the two lines (a) and (b), the equilibrium pressures of hydrogen and oxygen are both below 1 atm, and the region included between these two lines is the domain of thermodynamic stability for water. Since all aqueous solutions contain water, this domain of stability for water is important, whenever the electrochemical equilibria in aqueous systems are considered. For this reason, all E_h-pH diagrams include the "water" lines (a) and (b). Due to slowness of the kinetics of decomposition of water and high overvoltages of gas production, a significantly wider range of E_h values is actually attainable in the electrochemical studies of aqueous solutions [100].

6.3.3. Representation of Equilibria

As mentioned in the above section, E_h-pH diagrams contain several lines, each representing a chemical or electrochemical reaction. Depending on the type of reaction, as discussed above, these are represented as horizontal, vertical and sloped lines. To facilitate easy understanding of the equilibria in E_h-pH diagrams, different line types are used by convention in this paper, to represent each kind of equilibrium. Homogeneous reactions between dissolved (neutral, ionic, and gaseous) species are always represented by thin, dashed lines. These co-existance lines represent the condition wherein the thermodynamic activity of the species on each side of that line is the same. Independent equilibria between dissolved species such as Ba-species and Ti-species in Ba-Ti-H_2O system are distinguished by different types of dashed lines. Similarly, independent equilibria between Ba-species and C-species are distinguished in the Ba-Ti-C-H_2O system. Heterogeneous reactions between dissolved substance(s) and solid substance(s) are represented by thin, solid lines, whereas the equilibria between solid substances are represented by thick, solid lines. The lines representing the effect of temperature for each reaction are individually labeled with a symbol, corresponding to that temperature, as assigned in the legend. Similarly, the lines representing the effect of activity of the dissolved substances on solid-solution equilibria are individually labeled by a digit corresponding to the common logarithm of activity. For
example, a line representing $10^{-2}$ m activity is labeled as -2. To preserve the clarity of the diagrams, some of the lines representing the effect of temperature or activity are not labeled, where they can be deduced from other sets of lines that are labeled. Some ionic equilibria exist only at a particular temperature or activity. Such lines are appropriately labeled and care should be taken to note these conditions when interpreting the data. Finally, each line or set of lines is labeled with a number, under which the reaction data is listed in the relevant appendix for each system.

6.3.4. HSC Chemistry for Windows 2.0®

The Eh-pH diagrams reported in the current work were generated using the computer program HSC Chemistry for Windows 2.03® [111]. Thermodynamic data for the species in the system can be saved in a custom database for calculating the equilibria. It also has a built-in database for more than 7600 compounds, which can be accessed for calculations. Eₜₐ-pH diagrams can be calculated by selecting one main element, for example, Ba. All species in the diagram contain this main element. One or more other elements for example, Ti and C, can be selected. HSC Chemistry® automatically selects H and O for the system. Once the system is defined, species in the system can be searched in the custom as well as the main databases. HSC Chemistry® has an option to select the kind(s) of species (aqueous, condensed, gaseous, gas ions, liquids, organic) to be included in the search. Species that are not relevant or stable can be deleted to minimize calculation time as well as probability of difficulties in the calculation. Calculation parameters such as temperature, activities of the elements, and plotting limits can be edited independently. Since HSC Chemistry® labels only those species that contain the main element, it was necessary to interchange the main and other elements and superimpose the resulting diagrams to obtain the complete equilibrium diagram. For example, in the case of the Ba-Ti-H₂O system, two separate diagrams are calculated, first with Ba as the main element and Ti as the other element, and the second with Ti as the main element and Ba as the other element. Superimposition of these two diagrams gives the complete equilibrium diagram.
6.4. Limitations of $E_h$-pH Diagrams

Inherent to any thermochemical calculation, the $E_h$-pH diagrams are subject to several limitations in accurately representing the electrochemical equilibria. As discussed in the following sections, these limitations are important and must be understood before utilizing the diagrams to predict phase stabilities.

6.4.1. Thermodynamic Data

The validity of $E_h$-pH diagrams depends, to a great extent, on the accuracy of the free energy of formation data for the species considered in the system. Unfortunately, there is no single source that provides the thermochemical data for all the species of interest. As a result, the free energies are obtained from multiple sources, which use a wide variety of techniques to determine or estimate the standard state properties of pure substances. Without a specific procedure to estimate the accuracy of the data, this can lead to a random error in the construction of the $E_h$-pH diagrams. Even though the free energy data in the current work was obtained from the most recent, critically evaluated sources of thermochemical data, care must be taken while interpreting the stability domains in the diagrams. If the diagram shows that a particular phase is stable relative to the other phase, based on a small free energy margin, the unstable phase should only be ignored with reservations.

6.4.2. Species Not Considered

While interpreting the $E_h$-pH diagrams, one should remember that the diagrams show the equilibria only between the species that are considered in the system. Therefore, the equilibria are valid only if there are no unknown species that are stable in the $E_h$-pH range of interest, and none of the species that are not considered is stable. In addition, one has to consider all possible reactions among the species in the system, a task made easier with the advent of computers. Considering these difficulties, it is appropriate to say that
many of the useful revelations made by the $E_h$-$pH$ diagrams are negative, for example, one can get an unequivocal answer that two particular phases cannot coexist at equilibrium.

6.4.3. Thermodynamics versus Kinetics

As in the case of any thermodynamic calculation, $E_h$-$pH$ diagrams are constructed with an assumption of thermodynamic equilibrium between the species and indicate regions of thermodynamic stability and boundaries of thermodynamic equilibria. However, these diagrams do not provide any information regarding the kinetics of reactions. Kinetic information such as reaction rate, activation energy, and reaction pathway are usually obtained by experimental methods.

6.4.4. Activities versus Concentrations

As the $E_h$-$pH$ diagrams are constructed for activities of the dissolved species, difficulties arise when one attempts to estimate the solubilities of solids or predict their stability as a function of concentration of the dissolved species. Activity of a dissolved substance is equal to its concentration in an ideal solution, but all solutions deviate significantly from ideal behavior, except at infinitely dilute concentrations. In a non-ideal solution, activity of an ion differs from its molality by a factor $\gamma$, the activity coefficient for that particular ion in a specific solution environment. Activity coefficients can sometimes be estimated fairly accurately, from the knowledge of the ionic strength. However, for complex, multicomponent solutions, activity coefficients need to be predicted based on several solution models [28]. In order to calculate the solubility of a solid under a given set of $E_h$-$pH$ conditions, the activities of all contributing dissolved species must be known, along with their activity coefficients. A more direct situation, while utilizing the $E_h$-$pH$ diagrams is the prediction of stability of solids at a given composition of the solution. If the stability can be expressed as a function of $E_h$ and pH alone, then no difficulty arises due to lack of activity coefficients, since the equilibrium is independent of dissolved species. But in the case of an equilibrium between a solid and its aqueous species in solution, it is necessary to know the activities of the dissolved species to accurately predict the stability of
the solid. Despite this limitation, equilibrium activities obtained from $E_h$-pH diagrams can be used to estimate the minimum solubility of solids. This can be achieved by the generalization that when a solid is in equilibrium with a solution, the sum of the activities of all dissolved species containing an element is almost always less than the concentration of that element as determined by chemical analysis.

6.5. Discussion on Electrochemical Equilibria

The electrochemical equilibria as revealed by the $E_h$-pH diagrams constructed for several independent systems among Ba, Ti, and C species are discussed in the following sections.

6.5.1. Ba-H$_2$O System

Barium, similar to the other alkaline earth metals, is very reactive in aqueous solutions, exerting an extremely low solution potential ($E_h^0 = -2.908$V at 25°C), well below the thermodynamic stability domain for water. Ba is unstable with respect to BaH$_2$, which itself is unstable in the presence of water. Ba and BaH$_2$ do not coexist, as the coexistence potential lies well above the solution potentials for both Ba and BaH$_2$. For this reason, $E_h$-pH diagrams are drawn with (Figure 6-1) and without (Figure 6-2) considering the formation of BaH$_2$. Reactions and the equilibrium formulae for this system are listed in Appendix A. The diagrams at 25°C (Figures 6-1(a) and 6-2(a)) are in good agreement with those already reported by Pourbaix [117]. A significant difference, however, is the inclusion of BaOH$^+$ in the current diagrams, in equilibrium with Ba$^{2+}$ under alkaline conditions. Under oxidizing, alkaline conditions, barium peroxide (BaO$_2$) can be formed, as can be seen in the upper right corner of the $E_h$-pH diagrams. However, in the thermodynamic stability domain of water, BaO$_2$ is unstable, converting to barium hydroxide octahydrate, Ba(OH)$_2$·8H$_2$O. Higher temperatures tend to stabilize BaO$_2$, with the hydration reaction proceeding at lower potentials (Figure 6-1(b)). Barium hydroxide octahydrate precipitates at high pH, maintaining equilibrium with Ba$^{2+}$ (1.0 m activity at
Figure 6-1(a). $E_h$-pH diagram for Ba-H$_2$O system at 25°C and 1 atmosphere pressure, considering the formation of BaH$_2$. Total activity of dissolved Ba species is varied from 1 m to $10^{-3}$ m. See Appendix A for more information on reactions and equilibrium formulae.
Figure 6-1(b). $E_{H}-pH$ diagram for Ba-H$_2$O system at 25 ($\bullet$), 55 ($\Delta$), and 100°C ($\diamond$), and 1 atmosphere pressure, considering the formation of BaH$_2$. Total activity of dissolved Ba species is kept constant at 1 m. See Appendix A for more information on reactions and equilibrium formulae.
Figure 6-2(a). $E_h$-pH diagram for Ba-H$_2$O system at 25°C and 1 atmosphere pressure, not considering the formation of BaH$_2$. Total activity of dissolved Ba species is varied from 1 m to $10^{-3}$ m. See Appendix A for more information on reactions and equilibrium formulae.
Figure 6-2(b). $E_h$-pH diagram for Ba-H$_2$O system at 25 ($\bullet$), 55 ($\Delta$), and 100°C ($\diamond$), and 1 atmosphere pressure, not considering the formation of BaH$_2$. Total activity of dissolved Ba species is kept constant at 1 m. See Appendix A for more information on reactions and equilibrium formulae.
25°C) in solution at pH 13.42. The equilibrium pH is initially lowered with temperature (pH 12.95 at 55°C), indicating a decreasing solubility of Ba(OH)$_2$·8H$_2$O, as shown in Figure 6-2(b). At 100°C, however, presence of BaOH$^+$ in equilibrium with hydroxide extends the solubility of Ba(OH)$_2$·8H$_2$O (pH 13.68).

6.5.2. Ti-H$_2$O System

The E$_h$-pH diagrams for Ti-H$_2$O are drawn similar to the Ba-H$_2$O system, with (Figure 6-3), and without (Figure 6-4) considering the formation of TiH$_2$. In addition, E$_h$-pH diagrams with extended pH range (pH -10 to 15) are shown in Figure 6-5, to describe the equilibria between the dissolved species and Ti and its oxides. Appendix B lists various reactions and the equilibrium formulae for this system. As seen in Figure 6-4(a), Ti is not stable in the presence of water, but forms a passivating film of oxide on its surface. TiO$_2$(R) - titanium dioxide, rutile phase is the most stable form of native oxide on Ti, in the stability regime of water. TiO$_2$(R) protects the metal from further deterioration, through most of the pH range, except in the extremely acidic regime, where it dissolves to form Ti(OH)$_2^{2+}$ [104]. The other oxides of titanium, TiO and Ti$_2$O$_3$, are not stable in the presence of water and subsequently converted to TiO$_2$(R). For this reason, Ti is classified as a base metal, which is easily rendered passive in the presence of water, very similar to aluminum.

The electrochemical equilibria in Ti-H$_2$O system presented here are in good general agreement with Pourbaix [79], barring the deviations in the positions of equilibria due to revised thermochemical data. Corrosion and passivation regimes for Ti in the presence of several complexing agents as well as the thermodynamic stability of various forms of oxides of titanium were well described in Pourbaix [79]. One notable difference however, is the inclusion of hydrolysis products of Ti$^{4+}$ in the current work. Also, Ti$^{2+}$ and Ti$^{3+}$ ions and their hydrolysis products are not considered in the construction of these diagrams, due to the lack of reliable thermochemical data. For this reason, predominance domains for Ti$^{2+}$ and Ti$^{3+}$ do not appear in the current E$_h$-pH diagrams as they do in Pourbaix’s
Figure 6-3(a). $E_h$-pH diagram for Ti-H$_2$O system at 25°C and 1 atmosphere pressure, considering the formation of TiH$_2$. Total activity of dissolved Ti species is varied from 1 m to $10^{-3}$ m. See Appendix B for more information on reactions and equilibrium formulae.
Figure 6-3(b). $E_{0}$-pH diagram for Ti-H$_2$O system at 25 (●), 55 (Δ), and 100°C (♦), and 1 atmosphere pressure, considering the formation of TiH$_2$. Total activity of dissolved Ti species is kept constant at 1 m. See Appendix B for more information on reactions and equilibrium formulae.
Figure 6-4(a). $E_h$-pH diagram for Ti-H$_2$O system at 25°C and 1 atmosphere pressure, not considering the formation of TiH$_2$. Total activity of dissolved Ti species is varied from 1 m to $10^{-3}$ m. See Appendix B for more information on reactions and equilibrium formulae.
Figure 6-4(b). $E_{H}$-pH diagram for Ti-H$_2$O system at 25 ($\bullet$), 55 ($\Delta$), and 100°C ($\Diamond$), and 1 atmosphere pressure, not considering the formation of TiH$_2$. Total activity of dissolved Ti species is kept constant at 1 m. See Appendix B for more information on reactions and equilibrium formulae.
Figure 6-5(a). $E_h$-pH diagram for Ti-H$_2$O system at 25°C and 1 atmosphere pressure, for extended range of pH, not considering the formation of TiH$_2$. Total activity of dissolved Ti species is varied from 1 m to $10^{-3}$ m. See Appendix B for more information on reactions and equilibrium formulae.
Figure 6-5(b). $E_h$-pH diagram for Ti-H$_2$O system at 25 (●), 55 (Δ), and 100°C (♦), and 1 atmosphere pressure, for extended range of pH, not considering the formation of TiH$_2$. Total activity of dissolved Ti species is kept constant at 1 m. See Appendix B for more information on reactions and equilibrium formulae.
diagrams [79]. However, there is evidence that Ti$^{2+}$ and Ti$^{3+}$ can form by the dissolution of Ti and its oxides in the presence of acidic solutions free from oxidizing agents or by electrolytic reduction of Ti(IV) species [104]. Ti$^{2+}$ and Ti$^{3+}$ are strong reducing agents and their domains of predominance lie well below line (a), corresponding to the equilibrium of reduction of water (Figure 6-4). Ti$^{2+}$ and Ti$^{3+}$ can reduce water, liberating gaseous hydrogen at atmospheric pressure. Accordingly, the exclusion of Ti(II) and Ti(III) species should not affect the accuracy of the diagrams for the most part, as they are readily converted to hydrolyzed Ti(IV) species such as Ti(OH)$_2^{2+}$ between pH 1 and 2 in the stability domain of water [104]. At 25°C, the only ionic equilibrium that exists in solution is between Ti(OH)$_2^{2+}$ and Ti(OH)$_4$(a), at pH 2.25, as seen in Figure 6-4(a). While the less hydrolyzed TiOH$^{3+}$ is likely to be stable only at a lower pH, as shown in Figure 6-5(a), the absence of Ti(OH)$_3^{+}$ at 25°C is likely due to the decrease in coordination number when Ti(OH)$_3^{+}$ is converted to Ti(OH)$_4$(a) [104]. These ionic equilibria are consistent with the speciation diagram reported for Ti aqueous species [28]. The temperature dependence of the ionic equilibria is illustrated in Figures 6-4(b) and 6-5(b), showing the presence of Ti(OH)$_3^{+}$, and HTiO$_3^{-}$ at higher temperatures. Titanium and its oxides dissolve only with great difficulty, as evident in Figure 6-5(a), where the solid-liquid equilibria can be seen only at extremely low pH. Titanium becomes less and less noble with increasing temperature at high pH, with the stability domain for its oxides extending to lower potentials. However, TiO$_2$(R) shows higher solubility at elevated temperatures as the equilibrium with Ti(OH)$_2^{2+}$ moves to higher pH values. Formation of metastable TiO$_2$(A), the anatase form of titanium dioxide, under hydrothermal and electrochemical conditions has been reported [118, 119]. Even though it is metastable, crystallization of TiO$_2$(A) is very dominant at low temperatures, particularly under alkaline conditions (pH>7) and high concentrations of Ti precursors (e.g. TiCl$_4$). Metastable TiO$_2$(A) converts exothermally to thermodynamically stable TiO$_2$(R) only at high temperatures (about 1000°C).
As seen in the $E_h$-pH diagrams for Ti-H$_2$O system, Ti and TiH$_2$ do not co-exist in equilibrium. This is due to the relatively high temperatures (200-500°C) and pressures required for the formation of transition metal hydrides [120].

6.5.3. Ba-Ti-H$_2$O System

The Eh-pH diagrams for Ba-Ti-H$_2$O system are presented in Figure 6-6. Reactions and the equilibrium relations are listed in Appendix C. These diagrams primarily represent the phase equilibria between Ti metal and its oxides (not considering the formation of TiH$_2$), including the complex oxide BaTiO$_3$. Lack of equilibrium between the metal hydrides and pure metal states in aqueous solutions, and the overwhelming evidence for the existence of Ba and Ti in their pure, elemental states in equilibrium with their native oxides justifies the omission of BaH$_2$ and TiH$_2$. Stability domains for BaO$_2$ and Ba(OH)$_2$·8H$_2$O are also represented in equilibrium with BaTiO$_3$ and the dissolved species Ba$^{2+}$ and BaOH$^+$. The ionic equilibria between Ti species are distinguished from the equilibrium between Ba$^{2+}$ and BaOH$^+$ by a different type of dashed lines, as indicated in the captions. The line(s) corresponding to the equilibrium between Ti metal and TiO intersects the predominance domain for Ba(OH)$_2$·8H$_2$O. The portion of the line(s) present in the Ba(OH)$_2$·8H$_2$O regime is represented as broken line(s) to clarify that there is no equilibrium between Ba(OH)$_2$·8H$_2$O and Ti oxides.

It is evident from Figure 6-6(a) that BaTiO$_3$ is stable at high pH and moderate potentials. At anodic (positive) potentials higher than \(-1.0\, V\, E_h\) at 25°C, it tends to decompose to BaO$_2$ and TiO$_2$(R), whereas at low potentials (below \(-1.75\, V\, E_h\) at 25°C), Ba(OH)$_2$·8H$_2$O is the stable phase. At sufficiently high pH, barium titanate is the stable phase in the domain of thermodynamic stability of water, and the only formation reaction is the potential independent conversion of TiO$_2$(R) in the presence of Ba$^{2+}$ in solution. Concentration of Ba$^{2+}$ determines the equilibrium between TiO$_2$(R) and BaTiO$_3$. At 1 m activity of Ba$^{2+}$, the minimum pH required to form BaTiO$_3$ at 25°C is 10.2. At lower concentrations of Ba$^{2+}$, the equilibrium shifts to higher values of pH, demonstrating the
Figure 6-6(a). $E_{H}$-pH diagram for Ba-Ti-H$_2$O system at 25°C and 1 atmosphere pressure. Total activities of dissolved species are independently varied for Ba and Ti, in the range 1 m to 10$^{-3}$ m. See Appendix C for more information on reactions and equilibrium formulae.
Figure 6-6(b). $E_{h}$-pH diagram for Ba-Ti-H$_2$O system at 25 ($\bullet$), 55 ($\Delta$), and 100°C ($\circ$), and 1 atmosphere pressure. Total activities of dissolved species of Ba and Ti are kept constant at 1 m each. See Appendix C for more information on reactions and equilibrium formulae.
importance of solution alkalinity for synthesizing BaTiO$_3$. The effect of temperature on the stability of BaTiO$_3$ is illustrated in Figure 6-6(b). Equilibrium between BaTiO$_3$ and TiO$_2$(R) shifts to lower pH at elevated temperatures, extending the stability domain for BaTiO$_3$. However, the stability of BaO$_2$ extends to lower potentials with increasing temperature, which restricts the predominance of BaTiO$_3$. However, at higher temperatures, the stability of BaTiO$_3$ is extended at cathodic potentials.

6.5.4. Ba-Ti-C-H$_2$O System

Addition of carbon to the Ba-Ti-H$_2$O system drastically affects the electrochemical equilibria as shown in Figure 6-7(a) at various activities of Ba, Ti, and C. Activities of all three elements are the same in each case. Appendix D lists the reactions and equilibrium formulae for this system. The ionic equilibria between C species are distinguished from the ionic equilibria between Ba species by a different type of dashed line. To preserve the clarity of the diagrams, equilibria between Ti species (dissolved and solid) are not shown as they are not affected by the presence of carbon in the system. Even at an activity as small as $10^{-6}$ m, BaCO$_3$ is stable over a significant range of pH (9 to 14). Increasing activity extends this domain even further, with BaCO$_3$ stable over most of the pH range (2-17) at 1 m activity. This indicates the importance of eliminating the sources of carbon contamination (e.g., dissolved atmospheric CO$_2$(g)) while synthesizing BaTiO$_3$. Ionic equilibria are also affected significantly by the presence of carbon. Barium acetate ion is stable at cathodic potentials, and the ionic equilibria at higher potentials depend on the activities of Ba and C. At low activities ($10^{-4}$ m and lower), only Ba$^{2+}$ and BaOH$^+$ are in equilibrium, whereas with increasing activity, other species such as BaCO$_3$(a) at $10^{-2}$ m and BaHCO$_3^+$ at 1 m become stable. The effect of temperature on the Ba-Ti-C system at 1 m activity is shown in Figure 6-7(b). Temperature dependence of BaTiO$_3$ stability is very similar to that described in Ba-Ti-H$_2$O system. Equilibrium between BaCO$_3$ and BaTiO$_3$ shifts gradually to a lower pH with increasing temperature, extending the stability domain for BaTiO$_3$. 
Figure 6-7(a). $E_\text{H}\text{H}$-pH diagram for Ba-Ti-C-H$_2$O system at 25°C and 1 atmosphere pressure. Total activities of dissolved species are independently varied for Ba, Ti and C, in the range 1 m to $10^{-6}$ m. See Appendix D for more information on reactions and equilibrium formulae.
Figure 6-7(b). $E_{\text{H}}$-pH diagram for Ba-Ti-C-H$_2$O system at 25 ($\bullet$), 55 ($\Delta$), and 100°C ($\diamond$), and 1 atmosphere pressure. Total activities of dissolved species of Ba, Ti, and C are kept constant at 1 m each. See Appendix D for more information on reactions and equilibrium formulae.
6.6. Experimental Verification

Using the experimental data published in literature for hydrothermal and electrochemical synthesis of BaTiO₃, the Eₜₜ-pH diagrams for Ba-Ti-H₂O and Ba-Ti-C-H₂O have been verified in the following sections. Table 6-3 lists the experimental conditions along with physical and chemical nature of the reaction products obtained from hydrothermal/electrochemical synthesis of BaTiO₃ powders and films as reported in literature. Since the Eₜₜ-pH diagrams indicate thermodynamic equilibrium, and are drawn for activities of dissolved substances, experimental data often is not confined to the predominance domains defined by the Eₜₜ-pH diagrams. Moreover, reaction kinetics can be too sluggish for the equilibrium to be established. As a result, reactions may involve metastable phases and some of the metastable phases may appear to be stable, equilibrium products. Therefore, while verifying or utilizing the Eₜₜ-pH diagrams, one must bear in mind that these diagrams at best show specific "trends" in phase stability, particularly if the equilibria depend on concentrations of dissolved species or involve metastable phases.

6.6.1. Synthesis of BaTiO₃ at Low Temperatures

Hydrothermal and electrochemical synthesis of barium titanate thin films and powders at low temperatures have been reported by several authors [12, 15, 86, 87, 95, 119]. Synthesis temperatures varied from as low as 55°C [87, 95] to about 300°C [12, 15, 119]. While the success of synthesizing BaTiO₃ at low temperatures verifies the phase stability of BaTiO₃, the reason for using higher temperatures and sealed reaction vessels primarily due to the lack of understanding of the effect of parameters such as pH and solution concentration. Even though TiO₂(R) is the thermodynamically stable precursor phase to BaTiO₃, as indicated in the Eh-pH diagrams (Figure 6-6), an amorphous, metastable, hydrated titanium oxide is more likely to form under highly alkaline conditions, which is widely believed to be the precursor to BaTiO₃ in hydrothermal as well as electrochemical processes [62, 87, 91]. In most cases where a high temperature (above 100°C) was used to synthesize BaTiO₃, the solution pH and/or the Ba²⁺ concentration were
Table 6-3. Experimental conditions and synthesis products described in the published literature on hydrothermal/electrochemical synthesis of BaTiO$_3$ thin films and powders.

<table>
<thead>
<tr>
<th>Source (Ref.)</th>
<th>Method</th>
<th>Form</th>
<th>V (V)</th>
<th>C mA/cm$^2$</th>
<th>T (°C)</th>
<th>pH</th>
<th>Electrolyte</th>
<th>Products</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>119</td>
<td>EC</td>
<td>Powder</td>
<td>40-50</td>
<td>50-100</td>
<td>100-250</td>
<td>NM</td>
<td>0.1N Ba(NO$_3$)$_2$</td>
<td>BaTiO$_3$ at 250°C</td>
<td>Pure phase</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5N Ba(NO$_3$)$_2$</td>
<td>BaTiO$_3$ at 200°C</td>
<td>BaCO$_3$ contamination</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1N BaCl$_2$</td>
<td>TiO$_2$ (A)</td>
<td>At all temperatures</td>
</tr>
<tr>
<td>12</td>
<td>EC</td>
<td>Films</td>
<td>NM</td>
<td>10-100</td>
<td>RT-150</td>
<td>NM</td>
<td>0.5N Ba(OH)$_2$</td>
<td>BaTiO$_3$ at 100-150°C</td>
<td>Very thin films (50-100nm)</td>
</tr>
<tr>
<td>15</td>
<td>HT</td>
<td>Films</td>
<td>-</td>
<td>-</td>
<td>120-180</td>
<td>NM</td>
<td>0.5N Ba(OH)$_2$</td>
<td>BaTiO$_3$ at 180°C</td>
<td>Long reaction times (3-4h)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TiO$_2$ (A) below 100°C</td>
<td>BaCO$_3$ contamination</td>
</tr>
<tr>
<td>16</td>
<td>HT</td>
<td>Films</td>
<td>-</td>
<td>-</td>
<td>400-800</td>
<td>NM</td>
<td>3.0N Ba(OH)$_2$</td>
<td>BaTiO$_3$ at 150°C</td>
<td>Thicker (0.5-2.5μm) films, oriented with substrate.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BaTiO$_3$ at all temperatures</td>
<td>No BaCO$_3$ contamination.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Film thickness increased with increasing T, time and Ba$^{2+}$ concentration</td>
<td>Well faceted grain structure</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BaTiO$_3$, ~2μm thick film at 200°C, 45 min reaction</td>
<td>Thickness increases with time and temperature</td>
</tr>
<tr>
<td>18</td>
<td>EC</td>
<td>Films</td>
<td>2-3</td>
<td>10-50</td>
<td>80-200</td>
<td>13</td>
<td>0.4M Ba(OH)$_2$</td>
<td>BaTiO$_3$, TiO$_2$ (amorphous)</td>
<td>Thin, fine grained films even after long reaction</td>
</tr>
<tr>
<td>18</td>
<td>HT</td>
<td>Films</td>
<td>-</td>
<td>-</td>
<td>80-200</td>
<td>0.4M Ba(OH)$_2$</td>
<td>BaTiO$_3$, BaCO$_3$, TiO$_2$ (amorphous)</td>
<td>Lowest synthesis temperature reported.</td>
<td></td>
</tr>
</tbody>
</table>

significantly lower [15, 119]. This "trend" is evident from the temperature dependence of BaTiO$_3$ stability in Figure 6-6(b), where the equilibrium between Ba$^{2+}$ and BaTiO$_3$ gradually shifts to lower pH with increasing temperature. In other cases, a higher temperature was intentionally used to study the process kinetics, microstructure, crystallinity, and morphology [13, 16]. Higher synthesis temperatures, in general, improves kinetics of electrochemical formation of BaTiO$_3$, yielding thicker films in shorter times. Attempts to electrochemically synthesize BaTiO$_3$ films on Ti substrates at 25$^\circ$C were not successful, yielding only an unknown, amorphous phase [87]. However, Klee [121] used controlled hydrolysis of (Ba,Ti) metal organic precursors to prepare spherical BaTiO$_3$ powders at 30$^\circ$C. In the aqueous based (hydrothermal, electrochemical) processes, reaction of titanium hydrous oxide precursor with Ba$^{2+}$ in solution may be kinetically hindered at temperatures less than 50-60$^\circ$C. Hydrolysis of metal organic precursors, on the other hand, leads to a direct precipitation of BaTiO$_3$ from the elemental Ba and Ti precursors, avoiding the kinetically slow conversion of Ti oxide.

6.6.2. Effect of pH and Ba$^{2+}$ Concentration

Concentration of Ba$^{2+}$ ion plays an important role in the synthesis of barium titanate under hydrothermal and electrochemical conditions. Even though the Ba$^{2+}$ concentration is widely varied (0.01-1.5 m) among the reports published in literature, only Yoshimura and co-workers performed systematic studies on the effect of Ba$^{2+}$ on the stability of BaTiO$_3$ synthesized under electrochemical conditions [15, 119]. It has been experimentally confirmed in the above investigations that the minimum temperature required to synthesize BaTiO$_3$ decreases significantly with increasing Ba$^{2+}$ concentration in the electrolyte. Using Ba(OH)$_2$·8H$_2$O solutions as the electrolyte [15], BaTiO$_3$ thin films were synthesized on Ti at moderately high concentrations (0.5-1.5 m) of Ba$^{2+}$ in the temperature range of 150-200$^\circ$C. At lower concentrations of Ba$^{2+}$ and/or lower synthesis temperatures, only a mixture of BaTiO$_3$ and TiO$_2$-$x$ was obtained, which is in agreement with the phase stability domain for BaTiO$_3$ shown in Figures 6-6(a) and 6-6(b). However,
as the electrolyte pH also varies with the concentration of Ba(OH)$_2$·8H$_2$O, the phase stability of BaTiO$_3$ might have been affected by solution pH as well. Effect of Ba$^{2+}$ concentration on the synthesis of BaTiO$_3$ powders by anodic oxidation of Ti in Ba(NO$_3$)$_2$ solutions [119] confirms the stability of BaTiO$_3$ only above 250°C with 0.25 m Ba$^{2+}$. At lower concentrations, either a mixture of BaTiO$_3$ and metastable TiO$_2$(A) or only TiO$_2$(A) was obtained. Since the Ba(NO$_3$)$_2$ solutions possess considerably lower pH values compared to Ba(OH)$_2$·8H$_2$O solutions, and are relatively insensitive to concentration, this data confirms the effect of Ba$^{2+}$ concentration alone. Effect of solution pH at a constant concentration of Ba$^{2+}$ has also been reported [87, 95]. BaTiO$_3$ thin films were electrochemically synthesized on Ti substrates only above pH 13, in 0.5 m Ba(CH$_3$CO$_2$)$_2$ electrolytes at 55°C.

6.6.3. Effect of Applied Potential

As indicated in the E$_h$-pH diagrams for Ba-Ti system, the major formation reaction for BaTiO$_3$ is the equilibrium with thermodynamically stable TiO$_2$(R) and Ba$^{2+}$ ion in solution, which is independent of potential. Even though the actual reaction may involve metastable titanium hydrous oxide precursors as discussed earlier, applied potential has no direct role in the precipitation of BaTiO$_3$. This observation is supported by the data published in literature on hydrothermal synthesis of BaTiO$_3$ on Ti substrates [15, 16, 18]. BaTiO$_3$ could be synthesized without applied potential, even though the rates of deposition were significantly lower (about 4 hours for a 100 nm film). Applied potential, however, improves the rate of reaction of the deposition process, probably through the anodic oxidation of Ti, generating the suitable precursor(s) for the precipitation of BaTiO$_3$ [87]. In such case, a high anodic potential should have a favorable effect on electrochemical formation of BaTiO$_3$, through the enhanced corrosion of Ti. But the E$_h$-pH diagrams in Figure 6-6 indicate the decomposition of BaTiO$_3$ into BaO$_2$ and TiO$_2$(R) at even slightly high (>1.0 V E$_h$) anodic potential. Unfortunately, none of the reports in literature have done a systematic study on the effect of potential or the current density. Moreover, many
studies on the electrochemical synthesis of BaTiO₃ were performed galvanostatically, making it difficult to assess the effect of potential. However, a few have reported the cell potentials, which give an insight into the potential dependence of phase stability. At very high cell voltages (40-50V), only a TiO₂(R) layer was found on the surface of the Ti electrode, while BaTiO₃ powder was produced at the bottom of the vessel, through the conversion of fine TiO₂ particles ejected during the breakdown of the anodic TiO₂ film [119]. In another study [95], use of even a moderate cell voltage (4.0 V) resulted in the formation of BaCO₃, probably through the electrolytic breakdown of barium acetate electrolyte. In an earlier study [87], depth profile analysis using Auger electron spectroscopy revealed a thicker Ti oxide interface layer between Ti substrate and the BaTiO₃ film grown at higher current density, and the thickness of the film was less than those formed at smaller current densities. From these data, it is apparent that formation of BaTiO₃ is not favored at very high potentials, even though the breakdown of BaTiO₃ may not proceed at potentials as low as 1.0 V Eₜₐ as indicated in Figure 6-6.

6.6.4. Effect of Carbon Contamination

Formation of BaCO₃ as a contaminant in the synthesis of BaTiO₃ is a well known phenomenon and appropriate precautions are usually taken to avoid exposure to atmospheric CO₂. However, BaCO₃ is always in equilibrium with BaTiO₃ even at extremely low concentrations of CO₃²⁻ and Ba²⁺ species as shown in Figure 6-7(a), and as a result surfaces of hydrothermally derived BaTiO₃ powders or films are always contaminated with BaCO₃ [87, 28]. Although the formation of BaCO₃ can be easily avoided during the synthesis step, surface contamination occurs during the post-synthesis washing and handling of BaTiO₃ [87]. Washing with ammoniated water (at pH 11-12) has been reported as an effective method to minimize surface contamination. This is in agreement with the phase equilibria observed in Figure 6-7(a), where BaTiO₃ is stable with respect to BaCO₃ at high pH and low activity of dissolved species. Effect of temperature on formation of BaCO₃ in the electrochemical synthesis of BaTiO₃ was reported [119]. In
syntheses at temperatures higher than 250°C, pure BaTiO$_3$ was formed, where as a small amount of BaCO$_3$ was always associated with BaTiO$_3$ at synthesis temperatures 200°C or less. It is likely that the authors did not remove the dissolved CO$_2$ from the electrolyte solutions, which might have caused the formation of BaCO$_3$ in the first place. However, this data is consistent with the effect of temperature on BaCO$_3$/BaTiO$_3$ equilibrium as illustrated in Figure 6-7(b). At a fixed activity of carbon, formation of BaCO$_3$ is less favored at elevated temperatures.

6.7. Conclusions

$E_h$-$pH$ diagrams for Ba-H$_2$O, Ti-H$_2$O, Ba-Ti-H$_2$O, and Ba-Ti-C-H$_2$O systems are constructed at 25, 55, and 100°C. Thermochemical data for the solid and dissolved species in the above systems has been acquired from the most recent compilations.

The electrochemical equilibria obtained for Ba-Ti-H$_2$O and Ba-Ti-C-H$_2$O are consistent with the experimental data published in literature for hydrothermal and electrochemical synthesis of BaTiO$_3$.

BaTiO$_3$ is thermodynamically stable at high pH and moderate potentials. Experimental data suggests the feasibility of electrochemically synthesizing BaTiO$_3$ films at potentials higher than indicated by the stability domain for BaTiO$_3$ in the $E_h$-$pH$ diagrams. This suggests that the decomposition of BaTiO$_3$ is kinetically slower than the formation reaction, so that the equilibrium between BaO$_2$ and BaTiO$_3$ is not attained. However, at very large anodic potentials, it appears that the formation of BaTiO$_3$ on anode surface is not favored.

Presence of carbon significantly restricts the stability of BaTiO$_3$, even at very low activities, emphasizing the importance of avoiding the exposure to atmospheric CO$_2$. High synthesis temperatures minimize the BaCO$_3$ contamination by extending stability domain for BaTiO$_3$ to a lower pH.
APPENDIX A
REACTIONS AND EQUILIBRIUM FORMULAE FOR THE Ba-H₂O SYSTEM
AT 25, 55, AND 100°C AND 1 ATMOSPHERE PRESSURE

A.1. Two Dissolved Substances

A.1.1. Relative Stability of the Dissolved Substances

Z = +2

1. \( \text{Ba}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{BaOH}^+ + \text{H}^+ \)

\[
\begin{align*}
(\text{Ba}^{2+}) & : 14.25 - \text{pH} \quad \text{at 25°C} \\
\log \text{-------------------} & = 13.06 - \text{pH} \quad \text{at 55°C} \\
(\text{BaOH}^+) & : 11.62 - \text{pH} \quad \text{at 100°C}
\end{align*}
\]

A.1.2. Limits of the Domains of Relative Predominance of the Dissolved Substances

I’. \( \text{Ba}^{2+} / \text{BaOH}^+ \quad \text{pH} = \)

\[
\begin{align*}
14.25 & \text{ at 25°C} \\
13.06 & \text{ at 55°C} \\
11.62 & \text{ at 100°C}
\end{align*}
\]

A.2. Two Solid Substances

-2 \( \rightarrow \) +2

2. \( \text{BaH}_2 + 10\text{H}_2\text{O} \leftrightarrow \text{Ba(OH)}_2.8\text{H}_2\text{O} + 4\text{H}^+ + 4\text{e}^- \)

\[
\begin{align*}
-0.6649 & - 0.0592 \text{ pH} \quad \text{at 25°C} \\
\text{E} & = -0.6560 - 0.0651 \text{ pH} \quad \text{at 55°C} \\
-0.6328 & - 0.0740 \text{ pH} \quad \text{at 100°C}
\end{align*}
\]

0 \( \rightarrow \) +2

3. \( \text{Ba} + 10\text{H}_2\text{O} \leftrightarrow \text{Ba(OH)}_2.8\text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^- \)

\[
\begin{align*}
-2.1144 & - 0.0592 \text{ pH} \quad \text{at 25°C} \\
\text{E} & = -2.0762 - 0.0651 \text{ pH} \quad \text{at 55°C} \\
-1.9990 & - 0.0740 \text{ pH} \quad \text{at 100°C}
\end{align*}
\]

+2 \( \rightarrow \) +4

4. \( \text{Ba(OH)}_2.8\text{H}_2\text{O} \leftrightarrow \text{BaO}_2 + 2\text{H}^+ + 8\text{H}_2\text{O} + 2\text{e}^- \)

\[
\begin{align*}
1.5546 & - 0.0592 \text{ pH} \quad \text{at 25°C} \\
\text{E} & = 1.4931 - 0.0651 \text{ pH} \quad \text{at 55°C} \\
1.3824 & - 0.0740 \text{ pH} \quad \text{at 100°C}
\end{align*}
\]

A.3. One Solid Substance and One Dissolved Substance

-2 \( \rightarrow \) +2

5. \( \text{BaH}_2 \leftrightarrow \text{Ba}^{2+} + 2\text{H}^+ + 4\text{e}^- \)

\[
\begin{align*}
-1.0619 & + 0.0148 \log (\text{Ba}^{2+}) - 0.0296 \text{ pH} \quad \text{at 25°C} \\
\text{E} & = -1.0779 + 0.0163 \log (\text{Ba}^{2+}) - 0.0326 \text{ pH} \quad \text{at 55°C} \\
-1.1013 & + 0.0185 \log (\text{Ba}^{2+}) - 0.0370 \text{ pH} \quad \text{at 100°C}
\end{align*}
\]
0 → +2
6.  \( \text{Ba} \leftrightarrow \text{Ba}^{2+} + 2\text{e}^- \)
   \[ E = \begin{cases} 
   -2.9084 + 0.0296 \log (\text{Ba}^{2+}) & \text{at } 25^\circ C \\
   -2.9201 + 0.0326 \log (\text{Ba}^{2+}) & \text{at } 55^\circ C \\
   -2.9360 + 0.0370 \log (\text{Ba}^{2+}) & \text{at } 100^\circ C 
   \end{cases} \]

-2 → +2
7.  \( \text{BaH}_2 + \text{H}_2\text{O} \leftrightarrow \text{BaOH}^+ + 3\text{H}^+ + 4\text{e}^- \)
   \[ E = \begin{cases} 
   -0.8511 + 0.0148 \log (\text{BaOH}^+) - 0.0444 \text{ pH} & \text{at } 25^\circ C \\
   -0.8653 + 0.0163 \log (\text{BaOH}^+) - 0.0489 \text{ pH} & \text{at } 55^\circ C \\
   -0.8861 + 0.0185 \log (\text{BaOH}^+) - 0.0555 \text{ pH} & \text{at } 100^\circ C 
   \end{cases} \]

0 → +2
8.  \( \text{Ba} + \text{H}_2\text{O} \leftrightarrow \text{BaOH}^+ + \text{H}^+ + 2\text{e}^- \)
   \[ E = \begin{cases} 
   -2.4868 + 0.0296 \log (\text{BaOH}^+) - 0.0296 \text{ pH} & \text{at } 25^\circ C \\
   -0.8653 + 0.0326 \log (\text{BaOH}^+) - 0.0326 \text{ pH} & \text{at } 55^\circ C \\
   -0.8861 + 0.0370 \log (\text{BaOH}^+) - 0.0370 \text{ pH} & \text{at } 100^\circ C 
   \end{cases} \]

Z = +2
9.  \( \text{Ba}^{2+} + 10\text{H}_2\text{O} \leftrightarrow \text{Ba(OH)}_2\text{.8H}_2\text{O} + 2\text{H}^+ \)
   \[ \log (\text{Ba}^{2+}) = \begin{cases} 
   26.83 - 2\text{pH} & \text{at } 25^\circ C \\
   25.91 - 2\text{pH} & \text{at } 55^\circ C \\
   25.30 - 2\text{pH} & \text{at } 100^\circ C 
   \end{cases} \]

Z = +2
10.  \( \text{BaOH}^+ + 9\text{H}_2\text{O} \leftrightarrow \text{Ba(OH)}_2\text{.8H}_2\text{O} + \text{H}^+ \)
    \[ \log (\text{BaOH}^+) = \begin{cases} 
   12.58 - \text{pH} & \text{at } 25^\circ C \\
   12.85 - \text{pH} & \text{at } 55^\circ C \\
   13.68 - \text{pH} & \text{at } 100^\circ C 
   \end{cases} \]

+2 → +4
11.  \( \text{Ba}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{BaO}_2 + 4\text{H}^+ + 2\text{e}^- \)
    \[ E = \begin{cases} 
   2.3486 + 0.0296 \log (\text{Ba}^{2+}) - 0.1180 \text{ pH} & \text{at } 25^\circ C \\
   2.3370 + 0.0326 \log (\text{Ba}^{2+}) - 0.1304 \text{ pH} & \text{at } 55^\circ C \\
   2.3194 + 0.0370 \log (\text{Ba}^{2+}) - 0.1480 \text{ pH} & \text{at } 100^\circ C 
   \end{cases} \]

+2 → +4
12.  \( \text{BaOH}^+ + \text{H}_2\text{O} \leftrightarrow \text{BaO}_2 + 3\text{H}^+ + 2\text{e}^- \)
    \[ E = \begin{cases} 
   1.9269 + 0.0296 \log (\text{BaOH}^+) - 0.0885 \text{ pH} & \text{at } 25^\circ C \\
   1.9117 + 0.0326 \log (\text{BaOH}^+) - 0.0978 \text{ pH} & \text{at } 55^\circ C \\
   1.8891 + 0.0370 \log (\text{BaOH}^+) - 0.1110 \text{ pH} & \text{at } 100^\circ C 
   \end{cases} \]
APPENDIX B
REATIONS AND EQUILIBRIUM FORMULAE FOR THE Ti-H₂O SYSTEM
AT 25, 55, AND 100°C AND 1 ATMOSPHERE PRESSURE

B.1. Two Dissolved Substances

B.1.1. Relative Stability of the Dissolved Substances

Z=4
1. \(\text{Ti}^{4+} + \text{H}_2\text{O} \leftrightarrow \text{TiO}^{3+} + \text{H}^+\)

\[
\begin{align*}
\text{(TiO}^{3+}) & \quad 3.971 + \text{pH at 25°C} \\
\text{(Ti}^{4+}) & \quad 7.806 + \text{pH at 100°C}
\end{align*}
\]

log \(\text{------------------------} = \text{------------------------}\)

2. \(\text{TiOH}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{Ti(OH)}^{2+} + \text{H}^+\)

\[
\begin{align*}
\text{(Ti(OH)}^{2+}) & \quad 3.225 + \text{pH at 25°C} \\
\text{(TiOH}^{3+}) & \quad 5.967 + \text{pH at 100°C}
\end{align*}
\]

log \(\text{------------------------} = \text{------------------------}\)

3. \(\text{Ti(OH)}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Ti(OH)}^{3+} + \text{H}^+\)

\[
\begin{align*}
\text{(Ti(OH)}^{3+}) & \quad -2.491 + \text{pH at 25°C} \\
\text{(Ti(OH)}^{2+}) & \quad 0.865 + \text{pH at 100°C}
\end{align*}
\]

log \(\text{------------------------} = \text{------------------------}\)

4. \(\text{Ti(OH)}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{Ti(OH)}_4(a) + \text{H}^+\)

\[
\begin{align*}
\text{(Ti(OH)}_4(a)) & \quad -2.012 + \text{pH at 25°C} \\
\text{(Ti(OH)}^{3+}) & \quad -7.129 + \text{pH at 100°C}
\end{align*}
\]

log \(\text{------------------------} = \text{------------------------}\)

5. \(\text{Ti(OH)}_4(a) \leftrightarrow \text{HTiO}^+ + \text{H}_2\text{O} + \text{H}^+\)

\[
\begin{align*}
\text{(HTiO}^+) & \quad -21.926 + \text{pH at 25°C} \\
\text{(Ti(OH)}_4(a)) & \quad -11.055 + \text{pH at 100°C}
\end{align*}
\]

log \(\text{------------------------} = \text{------------------------}\)

6. \(\text{Ti(OH)}_2^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Ti(OH)}_4(a) + 2\text{H}^+\)

\[
\begin{align*}
\text{(Ti(OH)}_4(a)) & \quad -4.503 + 2\text{pH at 25°C} \\
\text{(Ti(OH)}_2^{2+}) & \quad -6.264 + 2\text{pH at 100°C}
\end{align*}
\]

log \(\text{------------------------} = \text{------------------------}\)

209
B.1.2. Limits of the Domains of Relative Predominance of the Dissolved Substances

1'. TiOH$^{3+}$ / Ti$^{4+}$  
\[ pH = \begin{align*}  
-3.971 & \quad \text{at } 25^\circ\text{C} \\
-5.683 & \quad \text{at } 55^\circ\text{C} \\
-7.806 & \quad \text{at } 100^\circ\text{C} 
\end{align*} \]

2'. Ti(OH)$_2^{2+}$ / TiOH$^{3+}$  
\[ pH = \begin{align*}  
-3.225 & \quad \text{at } 25^\circ\text{C} \\
-4.440 & \quad \text{at } 55^\circ\text{C} \\
-5.967 & \quad \text{at } 100^\circ\text{C} 
\end{align*} \]

3'. Ti(OH)$_3^+$ / Ti(OH)$_2^{2+}$  
\[ pH = \begin{align*}  
2.491 & \quad \text{at } 25^\circ\text{C} \\
0.996 & \quad \text{at } 55^\circ\text{C} \\
-0.865 & \quad \text{at } 100^\circ\text{C} 
\end{align*} \]

4'. Ti(OH)$_4$(a) / Ti(OH)$_3^+$  
\[ pH = \begin{align*}  
2.012 & \quad \text{at } 25^\circ\text{C} \\
4.385 & \quad \text{at } 55^\circ\text{C} \\
7.129 & \quad \text{at } 100^\circ\text{C} 
\end{align*} \]

5'. HTO$_3^-$ / Ti(OH)$_4$(a)  
\[ pH = \begin{align*}  
21.926 & \quad \text{at } 25^\circ\text{C} \\
17.019 & \quad \text{at } 55^\circ\text{C} \\
11.055 & \quad \text{at } 100^\circ\text{C} 
\end{align*} \]

6'. Ti(OH)$_4$(a) / Ti(OH)$_2^{2+}$  
\[ pH = \begin{align*}  
2.252 & \quad \text{at } 25^\circ\text{C} \\
2.691 & \quad \text{at } 55^\circ\text{C} \\
3.132 & \quad \text{at } 100^\circ\text{C} 
\end{align*} \]

B.2. Two Solid Substances

-2 → +4

7. TIH$_2$ + 2H$_2$O ↔ TiO$_2$(R) + 6H$^+$ + 6e$^-$  
\[ \begin{align*}  
\text{Eh} = & -0.5381 - 0.0592 \text{ pH} \quad \text{at } 25^\circ\text{C} \\
& -0.5521 - 0.0651 \text{ pH} \quad \text{at } 55^\circ\text{C} \\
& -0.5728 - 0.0740 \text{ pH} \quad \text{at } 100^\circ\text{C} 
\end{align*} \]

0 → +2

8. TI + H$_2$O ↔ TiO + 2H$^+$ + 2e$^-$  
\[ \begin{align*}  
\text{Eh} = & -1.4319 - 0.0592 \text{ pH} \quad \text{at } 25^\circ\text{C} \\
& -1.4417 - 0.0651 \text{ pH} \quad \text{at } 55^\circ\text{C} \\
& -1.4557 - 0.0740 \text{ pH} \quad \text{at } 100^\circ\text{C} 
\end{align*} \]

+2 → +3

9. 2TiO + H$_2$O ↔ Ti$_2$O$_3$ + 2H$^+$ + 2e$^-$  
\[ \begin{align*}  
\text{Eh} = & -0.8821 - 0.0592 \text{ pH} \quad \text{at } 25^\circ\text{C} \\
& -0.8925 - 0.0651 \text{ pH} \quad \text{at } 55^\circ\text{C} \\
& -0.9075 - 0.0740 \text{ pH} \quad \text{at } 100^\circ\text{C} 
\end{align*} \]

+3 → +4

10. Ti$_2$O$_3$ + H$_2$O ↔ 2TiO$_2$(R) + 2H$^+$ + 2e$^-$  
\[ \begin{align*}  
\text{Eh} = & -0.5723 - 0.0592 \text{ pH} \quad \text{at } 25^\circ\text{C} \\
& -0.5851 - 0.0651 \text{ pH} \quad \text{at } 55^\circ\text{C} \\
& -0.6035 - 0.0740 \text{ pH} \quad \text{at } 100^\circ\text{C} 
\end{align*} \]
B.3. One Solid Substance and One Dissolved Substance

-2 → +4
11. \( \text{TiH}_2 + 2\text{H}_2\text{O} \leftrightarrow [\text{Ti(OH)}_2]^{2+} + 4\text{H}^+ + 6\text{e}^- \)

\[
\begin{align*}
E &= -0.5016 + 0.0099 \log ([\text{Ti(OH)}_2]^{2+}) - 0.0395 \text{pH} \\
&\quad \text{at 25°C} \\
\text{Eh} &= -0.5225 + 0.0109 \log ([\text{Ti(OH)}_2]^{2+}) - 0.0434 \text{pH} \\
&\quad \text{at 55°C} \\
\text{Eh} &= -0.5513 + 0.0123 \log ([\text{Ti(OH)}_2]^{2+}) - 0.0493 \text{pH} \\
&\quad \text{at 100°C}
\end{align*}
\]

\( Z = 4 \)
12. \( [\text{Ti(OH)}_2]^{2+} \leftrightarrow \text{TiO}_2(R) + 2\text{H}^+ \)

\[
\begin{align*}
\log ([\text{Ti(OH)}_2]^{2+}) &= -3.699 - 2\text{pH} \text{ at 25°C} \\
&\quad -2.726 - 2\text{pH} \text{ at 55°C} \\
&\quad -1.745 - 2\text{pH} \text{ at 100°C}
\end{align*}
\]

+3 → +4
13. \( \text{Ti}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{H}^+ \leftrightarrow 2[\text{Ti(OH)}_2]^{2+} + 2\text{e}^- \)

\[
\begin{align*}
\text{E} &= -0.3534 + 0.0592 \log ([\text{Ti(OH)}_2]^{2+}) + \text{pH} \text{ at 25°C} \\
\text{Eh} &= -0.4076 + 0.0651 \log ([\text{Ti(OH)}_2]^{2+}) + \text{pH} \text{ at 55°C} \\
&\quad -0.4742 + 0.0740 \log ([\text{Ti(OH)}_2]^{2+}) + \text{pH} \text{ at 100°C}
\end{align*}
\]

+3 → +4
14. \( \text{Ti}_2\text{O}_3 + 4\text{H}^+ \leftrightarrow 2\text{TiOH}^{3+} + \text{H}_2\text{O} + 2\text{e}^- \)

\[
\begin{align*}
\text{E} &= -0.1625 + 0.0592 \log ([\text{TiOH}^{3+}) + 0.1180 \text{pH} \text{ at 25°C} \\
\text{Eh} &= -0.1183 + 0.0651 \log ([\text{TiOH}^{3+}) + 0.1304 \text{pH} \text{ at 55°C} \\
&\quad -0.0321 + 0.0740 \log ([\text{TiOH}^{3+}) + 0.1480 \text{pH} \text{ at 100°C}
\end{align*}
\]

+2 → +4
15. \( \text{TiO} + \text{H}^+ \leftrightarrow \text{TiOH}^{3+} + 2\text{e}^- \)

\[
\begin{align*}
\text{E} &= -0.5223 + 0.0296 \log ([\text{TiOH}^{3+}) + \text{pH} \text{ at 25°C} \\
\text{Eh} &= -0.5054 + 0.0326 \log ([\text{TiOH}^{3+}) + \text{pH} \text{ at 55°C} \\
&\quad -0.4698 + 0.0370 \log ([\text{TiOH}^{3+}) + \text{pH} \text{ at 100°C}
\end{align*}
\]

+2 → +4
16. \( \text{TiO} + 2\text{H}^+ \leftrightarrow \text{Ti}^{4+} + \text{H}_2\text{O} + 2\text{e}^- \)

\[
\begin{align*}
\text{E} &= -0.4048 + 0.0296 \log ([\text{Ti}^{4+}) + 0.0590 \text{pH} \text{ at 25°C} \\
\text{Eh} &= -0.3203 + 0.0326 \log ([\text{Ti}^{4+}) + 0.0652 \text{pH} \text{ at 55°C} \\
&\quad -0.1806 + 0.0370 \log ([\text{Ti}^{4+}) + 0.0740 \text{pH} \text{ at 100°C}
\end{align*}
\]

0 → +4
17. \( \text{Ti} \leftrightarrow \text{Ti}^{4+} + 4\text{e}^- \)

\[
\begin{align*}
\text{E} &= -0.9183 + 0.0148 \log ([\text{Ti}^{4+}) \text{ at 25°C} \\
\text{Eh} &= -0.8810 + 0.0163 \log ([\text{Ti}^{4+}) \text{ at 55°C} \\
&\quad -0.8181 + 0.0185 \log ([\text{Ti}^{4+}) \text{ at 100°C}
\end{align*}
\]

+2 → +4
18. \( \text{TiO} + \text{H}_2\text{O} \leftrightarrow [\text{Ti(OH)}_2]^{2+} + 2\text{e}^- \)

\[
\begin{align*}
\text{E} &= -0.6177 + 0.0296 \log ([\text{Ti(OH)}_2]^{2+}) \text{ at 25°C} \\
\text{Eh} &= -0.6501 + 0.0326 \log ([\text{Ti(OH)}_2]^{2+}) \text{ at 55°C} \\
&\quad -0.6908 + 0.0370 \log ([\text{Ti(OH)}_2]^{2+}) \text{ at 100°C}
\end{align*}
\]
APPENDIX C
REACTIONS AND EQUILIBRIUM FORMULAE FOR THE Ba-Ti-H₂O SYSTEM
AT 25, 55, AND 100°C AND 1 ATMOSPHERE PRESSURE

C.1. Two Dissolved Substances

C.1.1. Relative Stability of the Dissolved Substances

Z = +2
1. \[ \text{Ba}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{BaOH}^+ + \text{H}^+ \]

\[
\begin{align*}
\text{(Ba}^{2+}\text{)} & : 14.25 - \text{pH at 25°C} \\
\log \text{-----------} & = 13.06 - \text{pH at 55°C} \\
\text{(BaOH}^+) & : 11.62 - \text{pH at 100°C}
\end{align*}
\]

Z=4
2. \[ \text{Ti(OH)}_2^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Ti(OH)}_3^+ + \text{H}^+ \]

\[
\begin{align*}
\text{(Ti(OH)}_3^+\text{)} & : -2.491 + \text{pH at 25°C} \\
\log \text{-----------} & = -0.996 + \text{pH at 55°C} \\
\text{(Ti(OH)}_2^{2+}\text{)} & : 0.865 + \text{pH at 100°C}
\end{align*}
\]

Z=4
3. \[ \text{Ti(OH)}_3^+ + \text{H}_2\text{O} \leftrightarrow \text{Ti(OH)}_4(a) + \text{H}^+ \]

\[
\begin{align*}
\text{(Ti(OH)}_4(a)\text{)} & : -2.012 + \text{pH at 25°C} \\
\log \text{-----------} & = -4.385 + \text{pH at 55°C} \\
\text{(Ti(OH)}_3^+\text{)} & : -7.129 + \text{pH at 100°C}
\end{align*}
\]

Z=4
4. \[ \text{Ti(OH)}_4(a) \leftrightarrow \text{HTiO}_2^+ + \text{H}_2\text{O} + \text{H}^+ \]

\[
\begin{align*}
\text{(HTiO}_2^+\text{)} & : -21.926 + \text{pH at 25°C} \\
\log \text{-----------} & = -17.019 + \text{pH at 55°C} \\
\text{(Ti(OH)}_4(a)\text{)} & : -11.055 + \text{pH at 100°C}
\end{align*}
\]

Z=4
5. \[ \text{Ti(OH)}_2^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Ti(OH)}_4(a) + 2\text{H}^+ \]

\[
\begin{align*}
\text{(Ti(OH)}_4(a)\text{)} & : -4.503 + 2\text{pH at 25°C} \\
\log \text{-----------} & = -5.381 + 2\text{pH at 55°C} \\
\text{(Ti(OH)}_2^{2+}\text{)} & : -6.264 + 2\text{pH at 100°C}
\end{align*}
\]

C.1.2. Limits of the Domains of Relative Predominance of the Dissolved Substances

1'. \[ \text{Ba}^{2+} / \text{BaOH}^+ \quad \text{pH= 14.25 at 25°C} \]

2'. \[ \text{Ti(OH)}_3^+ / \text{Ti(OH)}_2^{2+} \quad \text{pH = 2.491 at 25°C} \]

212
\[ Z = +2 \text{(Ba), } +2 \rightarrow +4 \text{(Ti)} \]

6. \[
\begin{align*}
\text{TiO}^+ &+ \text{Ba(OH)}_2\cdot8\text{H}_2\text{O} &\leftrightarrow &\text{BaTiO}_3 &+ 8\text{H}_2\text{O} &+ 2\text{H}^+ &+ 2e^- \\
\text{Eh} &= -0.9184 - 0.0592 \text{ pH} \quad \text{at } 25\text{°C} \\
\text{Eh} &= -0.9771 - 0.0651 \text{ pH} \quad \text{at } 55\text{°C} \\
\text{Eh} &= -1.0843 - 0.0740 \text{ pH} \quad \text{at } 100\text{°C}
\end{align*}
\]

\[ Z = +4 \text{(Ti), } +2 \rightarrow +4 \text{(Ba)} \]

7. \[
\begin{align*}
\text{BaTiO}_3 &+ \text{H}_2\text{O} &\leftrightarrow &\text{BaO}_2 &+ \text{TiO}_2 &+ 2\text{H}^+ &+ 2e^- \\
\text{Eh} &= 1.7458 - 0.0592 \text{ pH} \quad \text{at } 25\text{°C} \\
\text{Eh} &= 1.7313 - 0.0651 \text{ pH} \quad \text{at } 55\text{°C} \\
\text{Eh} &= 1.7113 - 0.0740 \text{ pH} \quad \text{at } 100\text{°C}
\end{align*}
\]

C.3. Two Solid Substances

0 \rightarrow +2

8. \[
\begin{align*}
\text{Ti} &+ \text{H}_2\text{O} &\leftrightarrow &\text{TiO}^+ &+ 2\text{H}^+ &+ 2e^- \\
\text{Eh} &= -1.4319 - 0.0592 \text{ pH} \quad \text{at } 25\text{°C} \\
\text{Eh} &= -1.4417 - 0.0651 \text{ pH} \quad \text{at } 55\text{°C} \\
\text{Eh} &= -1.4557 - 0.0740 \text{ pH} \quad \text{at } 100\text{°C}
\end{align*}
\]

+2 \rightarrow +3

9. \[
\begin{align*}
2\text{TiO}^+ &+ \text{H}_2\text{O} &\leftrightarrow &\text{Ti}_2\text{O}_3 &+ 2\text{H}^+ &+ 2e^- \\
\text{Eh} &= -0.8821 - 0.0592 \text{ pH} \quad \text{at } 25\text{°C} \\
\text{Eh} &= -0.8925 - 0.0651 \text{ pH} \quad \text{at } 55\text{°C} \\
\text{Eh} &= -0.9075 - 0.0740 \text{ pH} \quad \text{at } 100\text{°C}
\end{align*}
\]

+3 \rightarrow +4

10. \[
\begin{align*}
\text{Ti}_2\text{O}_3 &+ \text{H}_2\text{O} &\leftrightarrow &2\text{TiO}_2 &+ 2\text{H}^+ &+ 2e^- \\
\text{Eh} &= -0.5723 - 0.0592 \text{ pH} \quad \text{at } 25\text{°C} \\
\text{Eh} &= -0.5851 - 0.0651 \text{ pH} \quad \text{at } 55\text{°C} \\
\text{Eh} &= -0.6035 - 0.0740 \text{ pH} \quad \text{at } 100\text{°C}
\end{align*}
\]

\[ Z = +2 \text{(Ba), } +4 \text{(Ti)} \]

11. \[
\begin{align*}
\text{Ba}^{3+} &+ \text{TiO}_2 &\leftrightarrow &\text{BaTiO}_3 &+ \text{H}_2\text{O} &\leftrightarrow &\text{BaTiO}_3 &+ 2\text{H}^+ \\
\log (\text{Ba}^{2+}) &= 20.367 - 2\text{pH} \quad \text{at } 25\text{°C} \\
\log (\text{Ba}^{3+}) &= 18.594 - 2\text{pH} \quad \text{at } 55\text{°C} \\
\log (\text{Ba}^{4+}) &= 16.419 - 2\text{pH} \quad \text{at } 100\text{°C}
\end{align*}
\]
Z = +2 (Ba), +3 → +4 (Ti)

12. \[ \text{Ti}_2\text{O}_3 + 2\text{Ba}^{2+} + 3\text{H}_2\text{O} \leftrightarrow 2\text{BaTiO}_3 + 6\text{H}^+ + 2\text{e}^- \]

\[
\text{Eh} = 0.6333 - 0.0592 \log(\text{Ba}^{2+}) - 0.1770 \text{ pH at 25°C}
\]

13. \[ \text{TiO} + \text{Ba}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{BaTiO}_3 + 4\text{H}^+ + 2\text{e}^- \]

\[
\text{Eh} = -0.1244 - 0.0296 \log(\text{Ba}^{2+}) - 0.1180 \text{ pH at 25°C}
\]

14. \[ \text{TiO} + \text{BaOH}^+ + \text{H}_2\text{O} \leftrightarrow \text{BaTiO}_3 + 3\text{H}^+ + 2\text{e}^- \]

\[
\text{Eh} = -0.5461 - 0.0296 \log(\text{BaOH}^+) - 0.0885 \text{ pH at 25°C}
\]

15. \[ \text{Ti(OH)}_2^{2+} \leftrightarrow \text{TiO}_2(\text{R}) + 2\text{H}^+ \]

\[
\log(\text{Ti(OH)}_2^{2+}) = -3.699 - 2\text{pH at 25°C}
\]

\[
-2.726 - 2\text{pH at 55°C}
\]

\[
-1.745 - 2\text{pH at 100°C}
\]

16. \[ \text{Ti}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{H}^+ \leftrightarrow 2\text{Ti(OH)}_2^{2+} + 2\text{e}^- \]

\[
\text{Eh} = -0.3534 + 0.0592 \log([\text{Ti(OH)}_2^{2+}] + \text{pH}) at 25°C
\]

\[
-0.4076 + 0.0651 \log([\text{Ti(OH)}_2^{2+}] + \text{pH}) at 55°C
\]

\[
-0.4742 + 0.0740 \log([\text{Ti(OH)}_2^{2+}] + \text{pH}) at 100°C
\]

17. \[ \text{Ba}^{2+} + 10\text{H}_2\text{O} \leftrightarrow \text{Ba(OH)}_2.8\text{H}_2\text{O} + 2\text{H}^+ \]

\[
\log(\text{Ba}^{2+}) = 26.83 - 2\text{pH at 25°C}
\]

\[
25.91 - 2\text{pH at 55°C}
\]

\[
25.30 - 2\text{pH at 100°C}
\]

18. \[ \text{BaOH}^+ + 9\text{H}_2\text{O} \leftrightarrow \text{Ba(OH)}_2.8\text{H}_2\text{O} + \text{H}^+ \]

\[
\log(\text{BaOH}^+) = 12.58 - \text{pH at 25°C}
\]

\[
12.85 - \text{pH at 55°C}
\]

\[
13.68 - \text{pH at 100°C}
\]

19. \[ \text{Ba}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{BaO}_2 + 4\text{H}^+ + 2\text{e}^- \]

\[
\text{Eh} = 2.3486 + 0.0296 \log(\text{Ba}^{2+}) - 0.1180 \text{ pH at 25°C}
\]

\[
2.3370 + 0.0326 \log(\text{Ba}^{2+}) - 0.1304 \text{ pH at 55°C}
\]

\[
2.3194 + 0.0370 \log(\text{Ba}^{2+}) - 0.1480 \text{ pH at 100°C}
\]

C.4. One Solid Substance and One Dissolved Substance

Z = 4

15. \[ \text{Ti}(\text{OH})_2^{2+} \leftrightarrow \text{TiO}_2(\text{R}) + 2\text{H}^+ \]

\[
\log(\text{Ti(OH)}_2^{2+}) = -3.699 - 2\text{pH at 25°C}
\]

\[
-2.726 - 2\text{pH at 55°C}
\]

\[
-1.745 - 2\text{pH at 100°C}
\]

+3 → +4

16. \[ \text{Ti}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{H}^+ \leftrightarrow 2\text{Ti(OH)}_2^{2+} + 2\text{e}^- \]

\[
\text{Eh} = -0.3534 + 0.0592 \log([\text{Ti(OH)}_2^{2+}] + \text{pH}) at 25°C
\]

\[
-0.4076 + 0.0651 \log([\text{Ti(OH)}_2^{2+}] + \text{pH}) at 55°C
\]

\[
-0.4742 + 0.0740 \log([\text{Ti(OH)}_2^{2+}] + \text{pH}) at 100°C
\]

Z = +2

17. \[ \text{Ba}^{2+} + 10\text{H}_2\text{O} \leftrightarrow \text{Ba(OH)}_2.8\text{H}_2\text{O} + 2\text{H}^+ \]

\[
\log(\text{Ba}^{2+}) = 26.83 - 2\text{pH at 25°C}
\]

\[
25.91 - 2\text{pH at 55°C}
\]

\[
25.30 - 2\text{pH at 100°C}
\]

Z = +2

18. \[ \text{BaOH}^+ + 9\text{H}_2\text{O} \leftrightarrow \text{Ba(OH)}_2.8\text{H}_2\text{O} + \text{H}^+ \]

\[
\log(\text{BaOH}^+) = 12.58 - \text{pH at 25°C}
\]

\[
12.85 - \text{pH at 55°C}
\]

\[
13.68 - \text{pH at 100°C}
\]

+2 → +4

19. \[ \text{Ba}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{BaO}_2 + 4\text{H}^+ + 2\text{e}^- \]

\[
\text{Eh} = 2.3486 + 0.0296 \log(\text{Ba}^{2+}) - 0.1180 \text{ pH at 25°C}
\]

\[
2.3370 + 0.0326 \log(\text{Ba}^{2+}) - 0.1304 \text{ pH at 55°C}
\]

\[
2.3194 + 0.0370 \log(\text{Ba}^{2+}) - 0.1480 \text{ pH at 100°C}
\]
APPENDIX D
REATIONS AND EQUILIBRIUM FORMULAE FOR THE Ba-Ti-C-H₂O SYSTEM
AT 25, 55, AND 100°C AND 1 ATMOSPHERE PRESSURE

D.1. Equilibrium Between Dissolved Substances

D.1.1. Relative Stability of the Dissolved Substances

1. \[ \text{H}_2\text{CO}_3(a) \leftrightarrow \text{HCO}_3^- + \text{H}^+ \]
   \[ \text{(HCO}_3^-) \quad \text{pH} = 6.369 \quad \text{at} \quad 25^\circ\text{C} \]
   \[ \text{(H}_2\text{CO}_3(a)) \quad \text{pH} = 6.208 \quad \text{at} \quad 55^\circ\text{C} \]
   \[ \log \frac{\text{(HCO}_3^-)}{\text{(H}_2\text{CO}_3(a))} = \frac{\text{pH} - 6.369}{\text{pH} - 6.208} \quad \text{at} \quad 25^\circ\text{C} \]
   \[ \text{pH} = 6.002 \quad \text{at} \quad 100^\circ\text{C} \]

2. \[ \text{CO}_2(a) + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \]
   \[ \text{(HCO}_3^-) \quad \text{pH} = 6.359 \quad \text{at} \quad 25^\circ\text{C} \]
   \[ \text{(CO}_2(a)) \quad \text{pH} = 6.304 \quad \text{at} \quad 55^\circ\text{C} \]
   \[ \text{pH} = 6.563 \quad \text{at} \quad 100^\circ\text{C} \]

3. \[ \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \]
   \[ \text{(CO}_3^{2-}) \quad \text{pH} = 10.328 \quad \text{at} \quad 25^\circ\text{C} \]
   \[ \text{(HCO}_3^-) \quad \text{pH} = 10.159 \quad \text{at} \quad 55^\circ\text{C} \]
   \[ \text{pH} = 10.174 \quad \text{at} \quad 100^\circ\text{C} \]

\[ Z = +2 \]

4. \[ \text{Ba}^{2+} + \text{H}_2\text{CO}_3(a) \leftrightarrow \text{BaHCO}_3^+ + \text{H}^+ \]
   \[ \text{(BaHCO}_3^+) \quad \text{pH} = 5.347 \quad \text{at} \quad 25^\circ\text{C} \]
   \[ \text{(H}_2\text{CO}_3(a))(\text{Ba}^{2+}) \quad \text{pH} = 4.860 \quad \text{at} \quad 55^\circ\text{C} \]
   \[ \text{pH} = 4.265 \quad \text{at} \quad 100^\circ\text{C} \]

\[ Z = +2 \]

5. \[ \text{Ba}^{2+} + \text{HCO}_3^- \leftrightarrow \text{BaCO}_3(a) + \text{H}^+ \]
   \[ \text{(BaCO}_3(a)) \quad \text{pH} = 7.679 \quad \text{at} \quad 25^\circ\text{C} \]
   \[ \text{(Ba}^{2+})(\text{HCO}_3^-) \quad \text{pH} = 7.164 \quad \text{at} \quad 55^\circ\text{C} \]
   \[ \text{pH} = 6.517 \quad \text{at} \quad 100^\circ\text{C} \]

\[ Z = +2 \]

6. \[ \text{Ba}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{BaOH}^+ + \text{H}^+ \]
   \[ \text{(Ba}^{2+}) \quad \text{pH} = 14.25 - \text{pH} \quad \text{at} \quad 25^\circ\text{C} \]
   \[ \text{(BaOH}^+) \quad \text{pH} = 13.06 - \text{pH} \quad \text{at} \quad 55^\circ\text{C} \]
   \[ \text{pH} = 11.62 - \text{pH} \quad \text{at} \quad 100^\circ\text{C} \]

\[ Z = +2 \]

7. \[ \text{BaHCO}_3^+ \leftrightarrow \text{BaCO}_3(a) + \text{H}^+ \]
   \[ \text{(BaCO}_3(a)) \quad \text{pH} = 8.701 \quad \text{at} \quad 25^\circ\text{C} \]
   \[ \text{(BaHCO}_3^+) \quad \text{pH} = 8.512 \quad \text{at} \quad 55^\circ\text{C} \]
   \[ \text{pH} = 8.254 \quad \text{at} \quad 100^\circ\text{C} \]
Z = +2
8. \[ \text{BaCO}_3(a) + H_2O \leftrightarrow \text{BaOH}^+ + \text{CO}_3^{2-} + H^+ \]

(BaOH\(^+\))(CO\(_2^\text{-}\)) pH - 16.895 at 25°C

\[
\log \frac{\text{(BaCO}_3(a))}{\text{BaOH}^+} = \text{pH} - 15.275 \quad \text{at 100°C}
\]

Z = +2
9. \[ \text{Ba(CH}_3\text{CO}_2)_2(a) + 8H_2O \leftrightarrow 4\text{H}_2\text{CO}_3(a) + \text{Ba}^{2+} + 14H^+ + 16e^- \]

Eh = \[ \log (\text{H}_2\text{CO}_3(a)) + 0.0037 [\log (\text{Ba}^{2+}) - \log (\text{Ba(CH}_3\text{CO}_2)_2(a))] = 0.0517 \quad \text{pH at 25°C} \]

Z = +2
10. \[ \text{Ba(CH}_3\text{CO}_2)_2(a) + 8H_2O \leftrightarrow 3\text{H}_2\text{CO}_3(a) + \text{BaHCO}_3^+ + 15H^+ + 16e^- \]

Eh = \[ \log (\text{H}_2\text{CO}_3(a)) + 0.0037 [\log (\text{BaHCO}_3^+) - \log (\text{Ba(CH}_3\text{CO}_2)_2(a))] = 0.0555 \quad \text{pH at 25°C} \]

Z = +2
11. \[ \text{Ba(CH}_3\text{CO}_2)_2(a) + 8H_2O \leftrightarrow 3\text{H}_2\text{CO}_3^- + \text{BaHCO}_3^- + 18H^+ + 16e^- \]

Eh = \[ \log (\text{H}_2\text{CO}_3^-) + 0.0037 [\log (\text{BaHCO}_3^-) - \log (\text{Ba(CH}_3\text{CO}_2)_2(a))] = 0.0666 \quad \text{pH at 25°C} \]

Z = +2
12. \[ \text{Ba(CH}_3\text{CO}_2)_2(a) + 8H_2O \leftrightarrow 3\text{CO}_3^{2-} + \text{BaCO}_3(a) + 19H^+ + 16e^- \]

Eh = \[ \log (\text{CO}_3^{2-}) + 0.0037 [\log (\text{BaCO}_3) - \log (\text{Ba(CH}_3\text{CO}_2)_2(a))] = 0.0703 \quad \text{pH at 25°C} \]

Z = +2
13. \[ \text{Ba(CH}_3\text{CO}_2)_2(a) + 8H_2O \leftrightarrow 3\text{CO}_3^{2-} + \text{BaCO}_3(a) + 22H^+ + 16e^- \]

Eh = \[ \log (\text{CO}_3^{2-}) + 0.0037 [\log (\text{BaCO}_3) - \log (\text{Ba(CH}_3\text{CO}_2)_2(a))] = 0.0814 \quad \text{pH at 25°C} \]

Z = +2
14. \[ \text{Ba(CH}_3\text{CO}_2)_2(a) + 8H_2O \leftrightarrow 4\text{CO}_3^{2-} + \text{Ba}^{2+} + 18H^+ + 16e^- \]

Eh = \[ \log (\text{CO}_3^{2-}) + 0.0037 [\log (\text{Ba}^{2+}) - \log (\text{Ba(CH}_3\text{CO}_2)_2(a))] = 0.0666 \quad \text{pH at 25°C} \]

Z = +2
15. \[ \text{Ba(CH}_3\text{CO}_2)_2(a) + 8H_2O \leftrightarrow 4\text{CO}_3^{2-} + \text{Ba}^{2+} + 22H^+ + 16e^- \]

Eh = \[ \log (\text{CO}_3^{2-}) + 0.0037 [\log (\text{Ba}^{2+}) - \log (\text{Ba(CH}_3\text{CO}_2)_2(a))] = 0.0814 \quad \text{pH at 25°C} \]
Z = +2

16. \[ \text{Ba(CH}_3\text{CO}_2\text{)}_2\text{(a)} + 9\text{H}_2\text{O} \leftrightarrow 4\text{CO}_3^{2-} + \text{BaOH}^+ + 23\text{H}^+ + 16e^- \]

\[
\text{Eh} = 0.3927 + 0.0148 \log (\text{CO}_3^{2-}) + 0.0037 [\log (\text{BaOH}^+) - \log (\text{Ba(CH}_3\text{CO}_2\text{)}_2\text{(a)})] - 0.0851 \text{pH} \text{ at } 25^\circ \text{C} \\
0.3924 + 0.0163 \log (\text{CO}_3^{2-}) + 0.0041 [\log (\text{BaOH}^+) - \log (\text{Ba(CH}_3\text{CO}_2\text{)}_2\text{(a)})] - 0.0943 \text{pH} \text{ at } 55^\circ \text{C} \\
0.3971 + 0.0185 \log (\text{CO}_3^{2-}) + 0.0046 [\log (\text{BaOH}^+) - \log (\text{Ba(CH}_3\text{CO}_2\text{)}_2\text{(a)})] - 0.1058 \text{pH} \text{ at } 100^\circ \text{C}
\]

D.1.2. Limits of the Domains of Relative Predominance of the Dissolved Substances

1'. \[ \text{H}_2\text{CO}_3\text{(a)} / \text{HCO}_3^- \]  
\[ \text{pH} = \begin{cases} 
6.369 & \text{at } 25^\circ \text{C} \\
6.208 & \text{at } 55^\circ \text{C} \\
6.002 & \text{at } 100^\circ \text{C} 
\end{cases} \]

2'. \[ \text{CO}_2\text{(a)} / \text{HCO}_3^- \]  
\[ \text{pH} = \begin{cases} 
6.359 & \text{at } 25^\circ \text{C} \\
6.304 & \text{at } 55^\circ \text{C} \\
6.563 & \text{at } 100^\circ \text{C} 
\end{cases} \]

3'. \[ \text{HCO}_3^- / \text{CO}_3^{2-} \]  
\[ \text{pH} = \begin{cases} 
10.328 & \text{at } 25^\circ \text{C} \\
10.159 & \text{at } 55^\circ \text{C} \\
10.174 & \text{at } 100^\circ \text{C} 
\end{cases} \]

4'. \[ \text{Ba}^{2+}, \text{H}_2\text{CO}_3\text{(a)} / \text{BaHCO}_3^+ \]  
\[ \text{pH} = \begin{cases} 
5.347 & \text{at } 25^\circ \text{C} \\
4.860 & \text{at } 55^\circ \text{C} \\
4.265 & \text{at } 100^\circ \text{C} 
\end{cases} \]

5'. \[ \text{BaCO}_3\text{(a)} / \text{Ba}^{2+}, \text{HCO}_3^- \]  
\[ \text{pH} = \begin{cases} 
7.679 & \text{at } 25^\circ \text{C} \\
7.164 & \text{at } 55^\circ \text{C} \\
6.517 & \text{at } 100^\circ \text{C} 
\end{cases} \]

6'. \[ \text{Ba}^{2+} / \text{BaOH}^+ \]  
\[ \text{pH} = \begin{cases} 
14.25 & \text{at } 25^\circ \text{C} \\
13.06 & \text{at } 55^\circ \text{C} \\
11.62 & \text{at } 100^\circ \text{C} 
\end{cases} \]

7'. \[ \text{BaCO}_3\text{(a)} / \text{BaHCO}_3^+ \]  
\[ \text{pH} = \begin{cases} 
8.701 & \text{at } 25^\circ \text{C} \\
8.512 & \text{at } 55^\circ \text{C} \\
8.254 & \text{at } 100^\circ \text{C} 
\end{cases} \]

8'. \[ \text{BaOH}^+, \text{CO}_3^{2-} / \text{BaCO}_3\text{(a)} \]  
\[ \text{pH} = \begin{cases} 
16.895 & \text{at } 25^\circ \text{C} \\
16.051 & \text{at } 55^\circ \text{C} \\
15.275 & \text{at } 100^\circ \text{C} 
\end{cases} \]

9'. \[ \text{Ba}^{2+}, \text{H}_2\text{CO}_3\text{(a)} / \text{Ba(CH}_3\text{CO}_2\text{)}_2\text{(a)} \]  
\[ \text{Eh} = \begin{cases} 
0.0929 - 0.0517 \text{pH} & \text{at } 25^\circ \text{C} \\
0.0726 - 0.0570 \text{pH} & \text{at } 55^\circ \text{C} \\
0.0437 - 0.0648 \text{pH} & \text{at } 100^\circ \text{C} 
\end{cases} \]

10'. \[ \text{BaHCO}_3^+, \text{H}_2\text{CO}_3\text{(a)} / \text{Ba(CH}_3\text{CO}_2\text{)}_2\text{(a)} \]  
\[ \text{Eh} = \begin{cases} 
0.1127 - 0.0555 \text{pH} & \text{at } 25^\circ \text{C} \\
0.0924 - 0.0610 \text{pH} & \text{at } 55^\circ \text{C} \\
0.0634 - 0.0694 \text{pH} & \text{at } 100^\circ \text{C} 
\end{cases} \]

11'. \[ \text{BaHCO}_3^+, \text{HCO}_3^- / \text{Ba(CH}_3\text{CO}_2\text{)}_2\text{(a)} \]  
\[ \text{Eh} = \begin{cases} 
0.1833 - 0.0666 \text{pH} & \text{at } 25^\circ \text{C} \\
0.1683 - 0.0732 \text{pH} & \text{at } 55^\circ \text{C} \\
0.1468 - 0.0833 \text{pH} & \text{at } 100^\circ \text{C} 
\end{cases} \]

12'. \[ \text{BaCO}_3\text{(a)}, \text{HCO}_3^- / \text{Ba(CH}_3\text{CO}_2\text{)}_2\text{(a)} \]  
\[ \text{Eh} = \begin{cases} 
0.2155 - 0.0703 \text{pH} & \text{at } 25^\circ \text{C} \\
0.2029 - 0.0773 \text{pH} & \text{at } 55^\circ \text{C} \\
0.1850 - 0.0879 \text{pH} & \text{at } 100^\circ \text{C} 
\end{cases} \]

13'. \[ \text{BaCO}_3\text{(a)}, \text{CO}_3^{2-} / \text{Ba(CH}_3\text{CO}_2\text{)}_2\text{(a)} \]  
\[ \text{Eh} = \begin{cases} 
0.3302 - 0.0814 \text{pH} & \text{at } 25^\circ \text{C} \\
0.3270 - 0.0895 \text{pH} & \text{at } 55^\circ \text{C} \\
0.3263 - 0.1018 \text{pH} & \text{at } 100^\circ \text{C} 
\end{cases} \]
14'. \( \text{Ba}^{2+}, \text{HCO}_3^- / \text{Ba(CH}_3\text{CO}_2)_2(a) \)  
\[ \text{Eh} = \begin{align*} &0.1871 - 0.0666 \text{ pH} \quad \text{at 25°C} \smallskip \\
&0.1737 - 0.0732 \text{ pH} \quad \text{at 55°C} \smallskip \\
&0.1548 - 0.0833 \text{ pH} \quad \text{at 100°C} \end{align*} \]

15'. \( \text{Ba}^{2+}, \text{CO}_3^{2-} / \text{Ba(CH}_3\text{CO}_2)_2(a) \)  
\[ \text{Eh} = \begin{align*} &0.3400 - 0.0814 \text{ pH} \quad \text{at 25°C} \smallskip \\
&0.3392 - 0.0895 \text{ pH} \quad \text{at 55°C} \smallskip \\
&0.3433 - 0.1018 \text{ pH} \quad \text{at 100°C} \end{align*} \]

16'. \( \text{BaOH}^+, \text{CO}_3^{2-} / \text{Ba(CH}_3\text{CO}_2)_2(a) \)  
\[ \text{Eh} = \begin{align*} &0.3927 - 0.0851 \text{ pH} \quad \text{at 25°C} \smallskip \\
&0.3924 - 0.0943 \text{ pH} \quad \text{at 55°C} \smallskip \\
&0.3971 - 0.1058 \text{ pH} \quad \text{at 100°C} \end{align*} \]

D.2. Three Solid Substances in Equilibrium with Dissolved Substances

\[ Z = +2 \text{ (Ba)}, +4 \text{ (Ti)} \]

17. \( \text{BaCO}_3 + \text{TiO}_2 + \text{H}_2\text{O} \leftrightarrow \text{BaTiO}_3 + \text{CO}_3^{2-} + 2\text{H}^+ \)

\[ \log (\text{CO}_3^{2-}) = \begin{align*} &2 \text{ pH} - 33.688 \quad \text{at 25°C} \smallskip \\
&2 \text{ pH} - 31.521 \quad \text{at 55°C} \smallskip \\
&2 \text{ pH} - 29.187 \quad \text{at 100°C} \end{align*} \]

+2 \( \rightarrow +4 \text{ (Ba)}, Z=+4 \text{ (Ti)} \)

18. \( \text{BaTiO}_3 + \text{H}_2\text{O} \leftrightarrow \text{BaO}_2 + \text{TiO}_2(R) + 2\text{H}^+ + 2e^- \)

\[ \begin{align*} &1.7458 - 0.0592 \text{ pH} \quad \text{at 25°C} \smallskip \\
&1.7313 - 0.0651 \text{ pH} \quad \text{at 55°C} \smallskip \\
&1.7113 - 0.0740 \text{ pH} \quad \text{at 100°C} \end{align*} \]

D.3. Two Solid Substances in Equilibrium with Dissolved Substances

+2 \( \rightarrow +4 \)

19. \( \text{BaCO}_3 + 2\text{H}_2\text{O} \leftrightarrow \text{BaO}_2 + \text{H}_2\text{CO}_3(a) + 2\text{H}^+ + 2e^- \)

\[ \begin{align*} &2.2552 + 0.0296 \log (\text{H}_2\text{CO}_3(a)) - 0.0592 \text{ pH} \quad \text{at 25°C} \smallskip \\
&Eh = 2.2315 + 0.0326 \log (\text{H}_2\text{CO}_3(a)) - 0.0651 \text{ pH} \quad \text{at 55°C} \smallskip \\
&2.1998 + 0.0370 \log (\text{H}_2\text{CO}_3(a)) - 0.0740 \text{ pH} \quad \text{at 100°C} \end{align*} \]

+2 \( \rightarrow +4 \)

20. \( \text{BaCO}_3 + 2\text{H}_2\text{O} \leftrightarrow \text{BaO}_2 + \text{HCO}_3^- + 3\text{H}^+ + 2e^- \)

\[ \begin{align*} &2.4437 + 0.0296 \log (\text{HCO}_3^-) - 0.0888 \text{ pH} \quad \text{at 25°C} \smallskip \\
&Eh = 2.4337 + 0.0326 \log (\text{HCO}_3^-) - 0.0977 \text{ pH} \quad \text{at 55°C} \smallskip \\
&2.4221 + 0.0370 \log (\text{HCO}_3^-) - 0.1110 \text{ pH} \quad \text{at 100°C} \end{align*} \]

+2 \( \rightarrow +4 \)

21. \( \text{BaCO}_3 + 2\text{H}_2\text{O} \leftrightarrow \text{BaO}_2 + \text{CO}_3^{2-} + 3\text{H}^+ + 2e^- \)

\[ \begin{align*} &2.7494 + 0.0296 \log (\text{CO}_3^{2-}) - 0.1184 \text{ pH} \quad \text{at 25°C} \smallskip \\
&Eh = 2.7646 + 0.0326 \log (\text{CO}_3^{2-}) - 0.1302 \text{ pH} \quad \text{at 55°C} \smallskip \\
&2.7989 + 0.0370 \log (\text{CO}_3^{2-}) - 0.1480 \text{ pH} \quad \text{at 100°C} \end{align*} \]

\[ Z = +2 \text{ (Ba)}, +4 \text{ (Ti)} \]

22. \( \text{Ba(CH}_3\text{CO}_2)_2(a) + \text{TiO}_2(R) + 9\text{H}_2\text{O} \leftrightarrow \text{BaTiO}_3 + 4\text{CO}_3^{2-} + 24\text{H}^+ + 16e^- \)

\[ \begin{align*} &0.4153 + 0.0148 \log (\text{CO}_3^{2-}) - 0.0037 \log (\text{Ba(CH}_3\text{CO}_2)_2(a)) - 0.0888 \text{ pH} \quad \text{at 25°C} \smallskip \\
&Eh = 0.4149 + 0.0163 \log (\text{CO}_3^{2-}) - 0.0041 \log (\text{Ba(CH}_3\text{CO}_2)_2(a)) - 0.0977 \text{ pH} \quad \text{at 55°C} \smallskip \\
&0.4193 + 0.0185 \log (\text{CO}_3^{2-}) - 0.0046 \log (\text{Ba(CH}_3\text{CO}_2)_2(a)) - 0.1110 \text{ pH} \quad \text{at 100°C} \end{align*} \]
D.4. One Solid Substance in Equilibrium with Dissolved Substances

+2 → +4
23. \[ \text{Ba}^{2+} + 2H_2O \leftrightarrow \text{BaO}_2 + 4H^+ + 2e^- \]

\[
\text{Eh} = \begin{align*}
2.3486 - 0.0296 \log (\text{Ba}^{2+}) - 0.1184 \text{pH} & \quad \text{at } 25^\circ \text{C} \\
2.3370 - 0.0326 \log (\text{Ba}^{2+}) - 0.1302 \text{pH} & \quad \text{at } 55^\circ \text{C} \\
2.3194 - 0.0370 \log (\text{Ba}^{2+}) - 0.1480 \text{pH} & \quad \text{at } 100^\circ \text{C}
\end{align*}
\]

\( Z=+2 \)

24. \[ \text{Ba}^{2+} + \text{H}_2\text{C}_03(\text{a}) \leftrightarrow \text{BaC}_03 + 2H^+ \]

\[
\log [(\text{Ba}^{2+})(\text{H}_2\text{C}_03(\text{a}))] = \begin{align*}
3.154 - 2 \text{pH} & \quad \text{at } 25^\circ \text{C} \\
3.238 - 2 \text{pH} & \quad \text{at } 55^\circ \text{C} \\
3.231 - 2 \text{pH} & \quad \text{at } 100^\circ \text{C}
\end{align*}
\]

\( Z=+2 \)

25. \[ \text{Ba}^{2+} + \text{HCO}_3^- \leftrightarrow \text{BaCO}_3 + \text{H}^+ \]

\[
\log [(\text{Ba}^{2+})(\text{HCO}_3^-)] = \begin{align*}
-3.215 - \text{pH} & \quad \text{at } 25^\circ \text{C} \\
-2.970 - \text{pH} & \quad \text{at } 55^\circ \text{C} \\
-2.771 - \text{pH} & \quad \text{at } 100^\circ \text{C}
\end{align*}
\]

\( Z=+2 \)

26. \[ \text{Ba(}\text{CH}_3\text{C}_02\text{)}_2(\text{a}) + 8\text{H}_2\text{O} \leftrightarrow \text{BaCO}_3 + 3\text{H}_2\text{CO}_3(\text{a}) + 16\text{H}^+ + 16e^- \]

\[
\text{Eh} = \begin{align*}
0.1045 + 0.0111 \log (\text{H}_2\text{CO}_3(\text{a})) - 0.0037 \log (\text{Ba(}\text{CH}_3\text{C}_02\text{)}_2(\text{a})) - 0.0592 \text{pH} & \quad \text{at } 25^\circ \text{C} \\
0.0858 + 0.0122 \log (\text{H}_2\text{CO}_3(\text{a})) - 0.0041 \log (\text{Ba(}\text{CH}_3\text{C}_02\text{)}_2(\text{a})) - 0.0651 \text{pH} & \quad \text{at } 55^\circ \text{C} \\
0.0586 + 0.0139 \log (\text{H}_2\text{CO}_3(\text{a})) - 0.0046 \log (\text{Ba(}\text{CH}_3\text{C}_02\text{)}_2(\text{a})) - 0.0740 \text{pH} & \quad \text{at } 100^\circ \text{C}
\end{align*}
\]

\( Z=+2 \)

27. \[ \text{Ba(}\text{CH}_3\text{C}_02\text{)}_2(\text{a}) + 8\text{H}_2\text{O} \leftrightarrow \text{BaCO}_3 + 3\text{HCO}_3^- + 19\text{H}^+ + 16e^- \]

\[
\text{Eh} = \begin{align*}
0.1752 + 0.0111 \log (\text{HCO}_3^-) - 0.0037 \log (\text{Ba(}\text{CH}_3\text{C}_02\text{)}_2(\text{a})) - 0.0703 \text{pH} & \quad \text{at } 25^\circ \text{C} \\
0.1616 + 0.0122 \log (\text{HCO}_3^-) - 0.0041 \log (\text{Ba(}\text{CH}_3\text{C}_02\text{)}_2(\text{a})) - 0.0773 \text{pH} & \quad \text{at } 55^\circ \text{C} \\
0.1420 + 0.0139 \log (\text{HCO}_3^-) - 0.0046 \log (\text{Ba(}\text{CH}_3\text{C}_02\text{)}_2(\text{a})) - 0.0879 \text{pH} & \quad \text{at } 100^\circ \text{C}
\end{align*}
\]

\( Z=+2 \)

28. \[ \text{Ba(}\text{CH}_3\text{C}_02\text{)}_2(\text{a}) + 8\text{H}_2\text{O} \leftrightarrow \text{BaCO}_3 + 3\text{CO}_3^{2-} + 22\text{H}^+ + 16e^- \]

\[
\text{Eh} = \begin{align*}
0.2899 + 0.0111 \log (\text{CO}_3^{2-}) - 0.0037 \log (\text{Ba(}\text{CH}_3\text{C}_02\text{)}_2(\text{a})) - 0.0814 \text{pH} & \quad \text{at } 25^\circ \text{C} \\
0.2857 + 0.0122 \log (\text{CO}_3^{2-}) - 0.0041 \log (\text{Ba(}\text{CH}_3\text{C}_02\text{)}_2(\text{a})) - 0.0895 \text{pH} & \quad \text{at } 55^\circ \text{C} \\
0.2833 + 0.0139 \log (\text{CO}_3^{2-}) - 0.0046 \log (\text{Ba(}\text{CH}_3\text{C}_02\text{)}_2(\text{a})) - 0.1018 \text{pH} & \quad \text{at } 100^\circ \text{C}
\end{align*}
\]
REFERENCES


220


BIOGRAPHICAL SKETCH

Sridhar Venigalla was born December 6, 1964, in Dondapadu, Andhra Pradesh, India. He attended public schools in Krishna District of Andhra Pradesh, and studied the Intermediate Course in Siddhartha College, Vijayawada. In the Fall of 1985, he graduated from the Regional Engineering College, Warangal, India, with a B. Tech degree in metallurgical engineering. Two years later, he received M. Tech degree in process metallurgy from the Indian Institute of Technology, Bombay, India. After working as a Senior Research Fellow with the Department of Metallurgical Engineering at IIT, Bombay, he moved to the United States to attend University of Florida, Gainesville in the Fall of 1990, and enrolled in the Ph. D. program in the Department of Materials Science and Engineering. He is a member of the American Ceramic Society, Materials Research Society, NACE International, ASM International, International Society for Hybrid Microelectronics, the honor society of Phi Kappa Phi, and Keramos.
I certify that I have read this study and that in my opinion it confirms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

James H. Adair, Chairman
Associate Professor of
Materials Science and Engineering

I certify that I have read this study and that in my opinion it confirms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Ellis D. Verink, Jr.
Distinguished Service Professor Emeritus of
Materials Science and Engineering

I certify that I have read this study and that in my opinion it confirms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John R. Ambrose
Associate Professor of
Materials Science and Engineering

I certify that I have read this study and that in my opinion it confirms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Rajiv K. Singh
Associate Professor of
Materials Science and Engineering

I certify that I have read this study and that in my opinion it confirms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Daniel R. Talham
Associate Professor of
Chemistry

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy in December, 1995.

Winfred M. Phillips
Dean, College of Engineering

Karen A. Holbrook
Dean, Graduate School