

---



---

# *Contents*

|                              |      |
|------------------------------|------|
| <i>Chinese Abstract</i>      | i    |
| <i>English Abstract</i>      | iv   |
| <i>Acknowledgement</i>       | vii  |
| <i>Contents</i>              | viii |
| <i>List of Tables</i>        | xi   |
| <i>List of Illustrations</i> | xii  |

## ***Chapter 1 Introduction***

|   |    |
|---|----|
| 1.1 Overview of Thin Film Transistor Liquid Crystal Display (TFT-LCD) | 1  |
| 1.2 A Historical Perspective of Thin Film Transistors                 | 4  |
| 1.3 Physical Properties of ZnO  | 6  |
| 1.4 Motivation  | 8  |
| 1.5 Thesis Organization   | 10 |

## ***Chapter 2 Experiment***

|  |    |
|--|----|
| 2.1 The Fabrication of the Thin Films            | 25 |
| 2.1.1 The Sol-Gel Method                         | 25 |
| 2.1.1.1 Introduction to Sol-Gel Method           | 25 |
| 2.1.1.2 Synthesis of the Precursors              | 27 |
| 2.1.2 The Radio Frequency (RF) Sputtering        | 27 |
| 2.2 The Fabrication of the Thin Film Transistors | 29 |
| 2.3 Analysis of Material Characteristics         | 29 |

|   |    |
|---|----|
| 2.3.1 X-ray Diffraction (XRD)   | 29 |
| 2.3.2 Scanning Electron Microscope (SEM)                                | 29 |
| 2.3.3 Atomic Force Microscopy (AFM)                                     | 30 |
| 2.3.4 Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) | 30 |
| 2.3.5 X-ray photoelectron spectroscopy (XPS)                            | 30 |
| 2.4 Analysis of Electrical Properties                                   | 31 |
| 2.4.1 Current-Voltage ( <i>I-V</i> ) Measurements                       | 31 |
| 2.4.2 Capacitance-Voltage ( <i>C-V</i> ) Measurements                   | 31 |

### ***Chapter 3 Sol-Gel-Derived $Zn_{(1-x)}Mg_xO$ Thin Films Used as Active Channel***

#### ***Layer of Thin-Film Transistors***

|                            |    |
|----------------------------|----|
| 3.0 Preface                | 38 |
| 3.1 Introduction           | 38 |
| 3.2 Experiment             | 40 |
| 3.3 Results and Discussion | 42 |
| 3.3.1 Film properties      | 42 |
| 3.3.2 TFT characteristics  | 53 |
| 3.4 Conclusion             | 55 |



### ***Chapter 4 Chemical Solution Deposition of $Zn_{(1-x)}Zr_xO$ Thin Films as Active***

#### ***Channel Layers of Thin Film Transistors***

|                            |    |
|----------------------------|----|
| 4.0 Preface                | 84 |
| 4.1 Introduction           | 84 |
| 4.2 Experiment             | 86 |
| 4.3 Results and discussion | 87 |

---

|                |    |
|----------------|----|
| 4.4 Conclusion | 93 |
|----------------|----|

***Chapter 5 Electrical Performance Improvements of Sol-Gel-Derived  
 $Zn_{0.97}Zr_{0.03}O$  Thin-Film Transistors by Using (Ba,Sr)TiO<sub>3</sub> High-k  
Gate Insulators***

|                            |     |
|----------------------------|-----|
| 5.0 Preface                | 112 |
| 5.1 Introduction           | 112 |
| 5.2 Experimental           | 114 |
| 5.3 Results and discussion | 116 |
| 5.4 Conclusion             | 123 |

***Chapter 6 Conclusions and Further Recommendations***

|                             |     |
|-----------------------------|-----|
| 6.1 Conclusions             | 141 |
| 6.2 Further Recommendations | 143 |



|                                |     |
|--------------------------------|-----|
| <b><i>Publication List</i></b> | 144 |
|--------------------------------|-----|

## *List of Tables*

|                  |   |     |
|------------------|---|-----|
| <i>Table 1-1</i> | The fabrication sizes and cutting efficiency of all generation factories.   | 21  |
| <i>Table 1-2</i> | Comparison of large size LCD TVs by several makers.   | 21  |
| <i>Table 1-3</i> | Major TFT/AMLCD Design Factors.   | 22  |
| <i>Table 1-4</i> | Physical properties of wurtzite ZnO.  | 23  |
| <i>Table 1-5</i> | Comparison of several printing techniques.  | 24  |
| <i>Table 2-1</i> | Specifications of rf magnetron sputtering system.   | 37  |
| <i>Table 3-1</i> | Dielectric constant $\epsilon_s$ , carrier concentration at room temperature $n_{RT}$ , Fermi energy level $E_F$ , donor energy level $E_d$ , the value of $rm_e^{3/2}$ and $rN_d$ , the normalized ratios of $r$ ( $R_r$ ) and $N_d$ ( $R_d$ ) of $Zn_{(1-x)}Mg_xO$ thin films.  | 82  |
| <i>Table 3-2</i> | Electrical characteristics (saturation mobility $\mu_{sat}$ , threshold voltage $V_{th}$ , off-state current $I_{off}$ and current modulation) of $Zn_{(1-x)}Mg_xO$ thin film transistors.  | 83  |
| <i>Table 4-1</i> | Electrical performance (field-effect mobility $\mu_{FE}$ , threshold voltage $V_{th}$ , minimum off-current $I_{off}$ and on/off current ratio) of $Zn_{(1-x)}Zr_xO$ thin-film transistors.   | 111 |
| <i>Table 5-1</i> | Electrical characteristics of $Zn_{0.97}Zr_{0.03}O$ -TFTs — including mobility ( $\mu_{sat}$ ), threshold voltage ( $V_{th}$ ), subthreshold slope ( $S$ ), and current modulation ( $I_{ON}/I_{OFF}$ ) —incorporating $SiO_2$ and BST as gate insulators of various dielectric constants ( $\epsilon_r$ ) and interface trap densities ( $D_{it}$ ); BST was deposited at various temperatures. The characteristics of the $SiO_2$ -based devices were extracted using a value of $V_D$ of 100 V; the characteristics of the devices incorporating the BST gate insulators were estimated at a value of $V_D$ of 10 V. | 140 |

## *List of Illustrations*

### *Chapter 1 Introduction*

|                   |  |    |
|-------------------|--|----|
| <i>Figure 1-1</i> | Electrical schematic of three-subpixel cross-section (bottom) of an active-matrix LCD. | 18 |
| <i>Figure 1-2</i> | TFT switching devices at the cross point with the row and column lines.                | 18 |
| <i>Figure 1-3</i> | The TFT-LCD (a) cross-sectional view of panel, (b) storage capacitor-on-gate pixel.    | 19 |
| <i>Figure 1-4</i> | The hexagonal (wurtzite) crystal structure of ZnO.                                     | 20 |

### *Chapter 2 Experiment*

|                   |   |    |
|-------------------|---|----|
| <i>Figure 2-1</i> | Flow chart of the sol-gel precursor preparation.  | 32 |
| <i>Figure 2-2</i> | Photography of the rf magnetron sputtering system.  | 33 |
| <i>Figure 2-3</i> | Process flow of the thin film transistors.  | 34 |
| <i>Figure 2-4</i> | Block diagram of current-voltage ( <i>I-V</i> ) and capacitance-voltage ( <i>C-V</i> ) measurement. | 35 |
| <i>Figure 2-5</i> | Experimental flow charts by using various analyses.   | 36 |

### *Chapter 3 Sol-Gel-Derived Zn<sub>(1-x)</sub>Mg<sub>x</sub>O Thin Films Used as Active Channel*

#### *Layer of Thin-Film Transistors*

|                   |  |    |
|-------------------|--|----|
| <i>Figure 3-1</i> | Schematic diagram of TFT using Zn <sub>(1-x)</sub> Mg <sub>x</sub> O as active channel layer.  | 59 |
| <i>Figure 3-2</i> | XRD patterns of Zn <sub>(1-x)</sub> Mg <sub>x</sub> O films after annealing at 500°C for 2 hr. | 60 |

|                    |  |    |
|--------------------|--|----|
| <i>Figure 3-3</i>  | Transmittance spectra of $Zn_{(1-x)}Mg_xO$ films deposited on glass substrates.  | 61 |
| <i>Figure 3-4</i>  | Relative absorption coefficients of the $Zn_{(1-x)}Mg_xO$ thin films, where $x$ ranged form 0.00 to 0.30.  | 62 |
| <i>Figure 3-5</i>  | $c$ -axis length and band gap energies of $Zn_{(1-x)}Mg_xO$ thin films, where $x$ ranged form 0 to 0.30.   | 63 |
| <i>Figure 3-6</i>  | SEM images of un-doped ZnO thin films annealed at (a) 400 °C, (b) 450 °C, (c) 500 °C, (d) 550 °C, and (e) 600 °C.  | 64 |
| <i>Figure 3-7</i>  | AFM surface observations of un-doped ZnO thin films annealed at (a) 400 °C, (b) 450 °C, (c) 500 °C, (d) 550 °C, and (e) 600 °C.  | 65 |
| <i>Figure 3-8</i>  | SEM images of $Zn_{(1-x)}Mg_xO$ thin films of (a) $x = 0.00$ , (b) $x = 0.10$ , (c) $x = 0.20$ , (d) $x = 0.30$ , and (e) $x = 0.40$ .                                   | 66 |
| <i>Figure 3-9</i>  | AFM surface observations of $Zn_{(1-x)}Mg_xO$ thin films of (a) $x = 0.00$ , (b) $x = 0.10$ , (c) $x = 0.20$ , (d) $x = 0.30$ , and (e) $x = 0.40$ .                     | 67 |
| <i>Figure 3-10</i> | (a) Roughness of un-doped ZnO films annealed at various temperatures. (b) Roughness of $Zn_{(1-x)}Mg_xO$ films as a function of Mg content.                              | 68 |
| <i>Figure 3-11</i> | XPS survey scan analysis of un-doped ZnO thin film annealed at 500 °C under air atmosphere for 2 hr.   | 69 |
| <i>Figure 3-12</i> | X-ray photoelectron spectroscopy survey scan analysis of $Zn_{(1-x)}Mg_xO$ thin films of (a) $x = 0.10$ , (b) $x = 0.20$ , (c) $x = 0.30$ , and (d) $x = 0.40$ .         | 70 |
| <i>Figure 3-13</i> | X-ray photoelectron spectroscopy spectra of O 1s of $Zn_{(1-x)}Mg_xO$ thin films, where $x$ ranged from 0.00 to 0.40.  | 71 |
| <i>Figure 3-14</i> | Dependence of relative intensity of the O 1s peak of the $Zn_{(1-x)}Mg_xO$ thin films, on the values of $x$ .  | 72 |
| <i>Figure 3-15</i> | X-ray photoelectron spectroscopy spectra of Zn 2p <sub>3/2</sub> of $Zn_{(1-x)}Mg_xO$ thin films, where $x$ ranged from 0.00 to 0.40.                                    | 73 |
| <i>Figure 3-16</i> | X-ray photoelectron spectroscopy spectra of Mg 2s and Zn 3p <sub>1/2</sub> of $Zn_{(1-x)}Mg_xO$ thin films, where $x$ ranged from 0.10 to 0.40.                          | 74 |
| <i>Figure 3-17</i> | C-V curves obtained for MOS structure Al/SiO <sub>2</sub> /ZnO (25°C). The charge carrier density $n$ of the ZnO films was evaluated from the slope of $C^{-2}$ vs $V$ . | 75 |
| <i>Figure 3-18</i> | Energy band diagram of the double Schottky barrier of the $Zn_{(1-x)}Mg_xO$ thin films. All energy levels are referenced to the  | 76 |

minimum energy level  $E_V = 0$  and the maximum  $E_{vac}$ .

- Figure 3-19* Plot of  $\ln(n/T^{3/2})$  vs.  $1/kT$ , where  $n$  is the measured electron concentration in the  $Zn_{(1-x)}Mg_xO$  films, showing a constant Fermi level within the temperature range 25~125 °C. 77
- Figure 3-20* Plot of  $\ln\{2/[f - n/rN_d] - 2\}$  vs  $1/kT$ . The constant slope ( $=E_d - E_F$ ) shows a definite donor level below the Fermi level in the  $Zn_{(1-x)}Mg_xO$  films. 78
- Figure 3-21* (a) Output and (b) transfer characteristics of the un-doped ZnO thin film transistor, recorded at a value of  $V_D$  of 100 V. 79
- Figure 3-22* (a) Output and (b) transfer characteristics of  $Zn_{(1-x)}Mg_xO$  thin film transistor, where  $x = 0.20$ , recorded at a value of  $V_D$  of 100 V. 80
- Figure 3-23* Output characteristics of  $Zn_{(1-x)}Mg_xO$  TFTs of  $x = 0.25$ . 81

## **Chapter 4 Chemical Solution Deposition of $Zn_{(1-x)}Zr_xO$ Thin Films as Active Channel Layers of Thin Film Transistors**

- Figure 4-1* Schematic diagram of TFT utilized  $Zn_{(1-x)}Zr_xO$  films as active channel layer. 96
- Figure 4-2* XRD spectra of  $Zn_{(1-x)}Zr_xO$  thin films annealed at 500 °C for 4h. 97
- Figure 4-3* SEM surface images of  $Zn_{(1-x)}Zr_xO$  thin films of (a)  $x = 0.00$ , (b)  $x = 0.01$ , (c)  $x = 0.03$ , (d)  $x = 0.05$ , and (e)  $x = 0.10$ . 98
- Figure 4-4* AFM surface morphologies of  $Zn_{(1-x)}Zr_xO$  thin films of (a)  $x = 0.00$ , (b)  $x = 0.01$ , (c)  $x = 0.03$ , (d)  $x = 0.05$ , and (e)  $x = 0.10$ . 99
- Figure 4-5* Roughness of  $Zn_{(1-x)}Zr_xO$  films as a function of the Zr content. 100
- Figure 4-6* XPS survey scan analysis of un-doped ZnO thin film annealed at 500 °C under oxygen atmosphere for 2 hr. 101
- Figure 4-7* X-ray photoelectron spectroscopy survey scan analysis of  $Zn_{(1-x)}Zr_xO$  thin films of (a)  $x = 0.01$ , (b)  $x = 0.03$ , (c)  $x = 0.05$ , and (d)  $x = 0.10$ . 102
- Figure 4-8* X-ray photoelectron spectroscopy spectra of O 1s of  $Zn_{(1-x)}Zr_xO$  thin films, where  $x$  ranged from 0.00 to 0.10. 103

|                    |   |     |
|--------------------|---|-----|
| <i>Figure 4-9</i>  | Dependence of relative intensity of the O 1s peak of the $\text{Zn}_{(1-x)}\text{Zr}_x\text{O}$ thin films, on the values of $x$ .  | 104 |
| <i>Figure 4-10</i> | X-ray photoelectron spectroscopy spectra of Zn 2p <sub>3/2</sub> of $\text{Zn}_{(1-x)}\text{Zr}_x\text{O}$ thin films, where $x$ ranged from 0.00 to 0.10.                          | 105 |
| <i>Figure 4-11</i> | X-ray photoelectron spectroscopy spectra of Zr 3d <sub>3/2</sub> and Zr 3d <sub>5/2</sub> of $\text{Zn}_{(1-x)}\text{Zr}_x\text{O}$ thin films, where $x$ ranged from 0.10 to 0.10. | 106 |
| <i>Figure 4-12</i> | Output characteristics of $\text{Zn}_{(1-x)}\text{Zr}_x\text{O}$ -TFTs of (a) $x = 0.00$ and (b) $x = 0.03$ .   | 107 |
| <i>Figure 4-13</i> | Transfer characteristics of $\text{Zn}_{(1-x)}\text{Zr}_x\text{O}$ -TFTs with various Zr content.   | 108 |
| <i>Figure 4-14</i> | The capacitance-voltage characteristics and a plot of $1/C^2$ as a function of voltage of $\text{Zn}_{(1-x)}\text{Zr}_x\text{O}$ MOS structure where $x = 0.03$ .                   | 109 |
| <i>Figure 4-15</i> | Carrier concentration ( $n$ ) of $\text{Zn}_{(1-x)}\text{Zr}_x\text{O}$ thin films as a function of the Zr content.   | 110 |

**Chapter 5 Electrical Performance Improvements of Sol-Gel-Derived  $\text{Zn}_{0.97}\text{Zr}_{0.03}\text{O}$  Thin-Film Transistors by Using  $(\text{Ba},\text{Sr})\text{TiO}_3$  High- $k$  Gate Insulators**

|                   |   |     |
|-------------------|---|-----|
| <i>Figure 5-1</i> | Schematic diagram the $\text{Zn}_{0.97}\text{Zr}_{0.03}\text{O}$ thin-film transistor.  | 127 |
| <i>Figure 5-2</i> | XRD spectra of BST films grown on $\text{BaRuO}_3$ at various deposition temperatures.  | 128 |
| <i>Figure 5-3</i> | Dielectric constant of BST as a function of deposition temperatures.  | 129 |
| <i>Figure 5-4</i> | Leakage current density variation as a function of electric field for BST capacitors (Al/BST/BRO) with various deposition temperatures.                         | 130 |
| <i>Figure 5-5</i> | AFM surface observations of BST deposited at (a) 100 (b) 300 and (c) 500 °C.  | 131 |
| <i>Figure 5-6</i> | Roughness of BST films as a function of various deposition temperatures.  | 132 |
| <i>Figure 5-7</i> | SEM surface images of $\text{Zn}_{0.97}\text{Zr}_{0.03}\text{O}$ films deposited on (a) $\text{SiO}_2$ (b) BST ( $T_d = 100$ °C) and (c) BST ( $T_d = 300$ °C). | 133 |



---

|                    |  |     |
|--------------------|--|-----|
| <i>Figure 5-8</i>  | Output characteristics of $\text{Zn}_{0.97}\text{Zr}_{0.03}\text{O}$ -TFTs by using $\text{SiO}_2$ as gate insulator at $V_D = 100\text{V}$ .  | 134 |
| <i>Figure 5-9</i>  | Transfer characteristics of $\text{Zn}_{0.97}\text{Zr}_{0.03}\text{O}$ -TFTs by using $\text{SiO}_2$ as gate insulator at $V_D = 100\text{V}$ .  | 135 |
| <i>Figure 5-10</i> | Drain current — drain voltage characteristics of the $\text{Zn}_{0.97}\text{Zr}_{0.03}\text{O}$ -TFTs incorporating the BST gate insulator deposited at room temperature.                        | 136 |
| <i>Figure 5-11</i> | Log and square root of drain current as a function of gate voltage of the devices incorporating BST gate insulators, prepared at various values of $T_d$ , recorded at a value of $V_D$ of 10 V. | 137 |
| <i>Figure 5-12</i> | Frequency effects on the capacitance-voltage curves of the ZnO MISM structure.   | 138 |
| <i>Figure 5-13</i> | Dependence of interface trap density ( $D_{it}$ ) on various gate insulators. Open and solid squares refer to $\text{SiO}_2$ and BST deposited at different $T_d$ , respectively.                | 139 |

