Metal Oxides Series

Solution Processed Metal Oxide Thin Films for Electronic Applications

Edited by Zheng Cui

Solution Processed Metal Oxide Thin Films for Electronic Applications discusses the fundamentals of solution forms of metal oxide material systems and processing techniques for key electronic device applications. The book introduces basic information (materials properties and synthesis), discusses ink formulation and thin film processing methods, including sol-gel and nanoparticle inks, printing and coating methods, surface functionalization, and presents a comprehensive accounting on the electronic applications of solution processed metal oxide films, including thin film transistors, photovoltaic cells, light-emitting diodes, and other electronics devices.

This is an important reference for those interested in metal oxide electronics, printed electronics, flexible electronics, and large-area electronics.

Key Features:

- Provides in-depth information on solution processing fundamentals, techniques, considerations, and barriers combined with key device applications
- Reviews important device applications, including transistors, light-emitting diodes, and photovoltaic cells
- Includes an overview of metal oxide materials systems (semiconductors, nanomaterials, and thin films), addressing materials synthesis, properties, limitations, and surface aspects

About the Editor:

Zheng Cui

Professor Zheng Cui graduated from the Southeast University, China, in 1981 and had his Master degree and Doctoral degree in electronic engineering in 1984 and 1988. In the field of micro and nanofabrication technologies, he published over 190 technical papers and 6 books. In 2009 after working in the United Kingdom for 20 years, he returned to China and founded the Printable Electronics Research Center (PERC) at the Suzhou Institute of Nanotech and Nanobionics, Chinese Academy of Sciences, which was then the first research center in China dedicated to printed electronics R&D. His research team at the PERC has conducted more than 50 research projects with research funding over 100 million RMB. In the past 10 years working in China, he has authored or coauthored over 90 journal papers and two books on the subject of printed electronics. In addition to academic research in printed electronics, Professor Zheng Cui also devoted to transferring technologies to industry. He has filed more than 70 patents in printed electronics. He and his team at PERC developed a novel hybrid printing technique to manufacture metalmesh transparent conductive films. The invention won the Chinese outstanding patent award in 2014. The technology was subsequently transferred to a leading manufacturer of touch panels in China and implemented in mass production. Display panels integrating the metal-mesh transparent conductors as touch sensor have been commercialized and created over billions of market value. He is also the founder of two high-tech companies utilizing printed electronics technology in gas sensors and flexible electronic circuits and both have commercial products in the market.





| Contributors Volume Editor Biography Series Editor Biography Preface to the series | ix xi xiii xv |
|--|------------------------|
| 1 Introduction | 1 |
| Zheng Cui | |
| 1.1 Solution-processed electronics 1.2 Metal oxides in solution | 1 |
| 1.3 Structure of the book | 3 |
| References | 5 |
| References | 6 |
| 2 Metal oxide semiconductors and conductors | 7 |
| Haiping He | ' |
| 2.1 Introduction | 7 |
| 2.2 n-Type metal oxides | . 8 |
| $2.2.1 \text{ In}_2\text{O}_3$ | 8 |
| 2.2.2 ZnO | 12 |
| $2.2.3 \text{ SnO}_2$ | 17 |
| $2.2.4 \text{ ZnO-In}_2\text{O}_3\text{-SnO}_2 (\text{ZITO})$ | 21 |
| 2.3 P-type metal oxides | 22 |
| 2.3.1 Cu ₂ O | 22 |
| 2.3.2 NiO | 25 |
| 2.3.3 SnO | 25 |
| References | 27 |
| 3 Metal oxide dielectrics | 21 |
| Xitong Hong, Lei Liao | 31 |
| 3.1 Introduction | 31 |
| 3.2 Basics and theory of dielectrics | 32 |
| 3.3 Roles of dielectric layers in thin-film transistors | 34 |
| 3.4 High-k metal oxide dielectrics | 36 |
| References | 37 |
| 4 Sol-gel precursor inks and films | |
| Chang Liu, Qianlei Tian, Lei Liao | 41 |
| 4.1 Introduction | |
| 4.2 Fundamental of sol–gel process | 41 |
| 4.3 Sol-gel precursor inks | 41 |
| 4.4 Sol-gel process of metal oxide film | 43 |
| 4.4.1 Al ₂ O ₃ film | 45 |
| $4.4.2 \text{ HfO}_2 \text{ film}$ | 45 |

| | 4.4.3 ZnO film | 50 |
|---|--|------|
| | 4.4.4 TiO ₂ film | 54 |
| | 4.5 Other precursors-based metal oxides inks and films | 56 |
| | References | 57 |
| 5 | Nanoparticles inks | 63 |
| | Qun Luo | |
| | 5.1 Introduction | 63 |
| | 5.2 Synthesis of metal oxide nanoparticles | 63 |
| | 5.2.1 Hot-injection method | 63 |
| | 5.2.2 Hydrothermal or solvothermal method | 66 |
| | 5.2.3 One-pot heating method | 67 |
| | 5.2.4 Microwave-assisted method | 68 |
| | 5.2.5 Precipitation method | 72 |
| | 5.2.6 Sol-gel method | 73 |
| | 5.2.7 Continuous flow method | 73 |
| | 5.2.8 Ball-milling method | 75 |
| | 5.3 Characterization and properties of metal oxide nanoparticles | 76 |
| | 5.3.1 Measurement methods | 76 |
| | 5.3.2 Physical and chemical properties | 77 |
| | 5.4 Formulation of metal oxide nanoparticles inks | 77 |
| | 5.4.1 Surfactants | 79 |
| | 5.4.2 Long-term stability | 79 |
| | References | 80 |
| 6 | Coating and printing processes | 83 |
| | Zheng Cui, Lei Liao | |
| | 6.1 Introduction | 83 |
| | 6.2 Nonpatternable solution processes | 83 |
| | 6.2.1 Spin coating | 83 |
| | 6.2.2 Spray coating | 84 |
| | 6.2.3 Bar coating | 87 |
| | 6.3 Patternable solution processes | / 88 |
| | 6.3.1 Inkjet printing | 88 |
| | 6.3.2 Templated printing | 91 |
| | 6.4 Roll-to-roll solution processes | 92 |
| | 6.5 Self-aligned solution processes | 94 |
| | References | 95 |
| 7 | Thermal processes | 99 |
| | Lei Liao, Zheng Cui | |
| | 7.1 Introduction | 99 |
| | 7.2 Internal annealing | 99 |
| | 7.3 External annealing | 102 |
| | 7.3.1 UV annealing | 102 |
| | 7.3.2 Microwave annealing | 103 |
| | | |

| | 7.3.3 High-pressure annealing | 104 |
|----|--|-----|
| | 7.4 Low-temperature enabled flexible electronics | 105 |
| | References | 107 |
| 8 | Applications in photovoltaics | 109 |
| | Qun Luo | |
| | 8.1 Introduction | 109 |
| | 8.2 Metal oxides as buffer layers for OPVs | 109 |
| | 8.3 Electron transport layer | 112 |
| | 8.3.1 ZnO | 112 |
| | 8.3.2 TiO ₂ | 113 |
| | 8.3.3 Other metal oxides | 113 |
| | 8.4 Hole transport layer | 114 |
| | 8.4.1 MoO ₃ | 115 |
| | $8.4.2 \text{ V}_2\text{O}_5$ | 116 |
| | $8.4.3 \text{ WO}_x$ | 116 |
| | 8.4.4 NiO | 117 |
| | $8.4.5 \text{ CuO}_x$ | 118 |
| | 8.4.6 Metal oxide composites | 119 |
| | 8.5 Metal oxides as buffer layer for perovskite PV | 120 |
| | 8.6 Electron extraction layer | 121 |
| | 8.6.1 TiO ₂ | 122 |
| | 8.6.2 ZnO | 122 |
| | 8.6.3 SnO ₂ | 124 |
| | 8.6.4 Other metal oxides | 126 |
| | 8.7 Hole extraction layer | 127 |
| | 8.7.1 NiO | 127 |
| | $8.7.2 \text{ Cu}_x\text{O}$ | 128 |
| | $8.7.3 \text{ MoO}_x$ | 129 |
| | 8.7.4 Metal oxide composites | 130 |
| | 8.8 Metal oxides as electrode | 130 |
| | 8.9 Metal oxides as other functional layers | 132 |
| | References | 133 |
|) | Applications in OLED and QLED | 141 |
| | Haiping He | |
| | 9.1 Introduction of OLED and QLED | 141 |
| | 9.1.1 OLED | 141 |
| | 9.1.2 QLED | 142 |
| | 9.2 Metal oxides in OLEDs and QLEDs | 146 |
| | 9.2.1 Metal oxides as electron transport layer | 146 |
| | 9.2.2 Metal oxides as hole transport layer | 150 |
| | References | 152 |
| nd | lex | 155 |

I