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Metal Oxide Varistors

From Microstructure to Macro-Characteristics

金属氧化物压敏电阻

从微观结构到宏观特性

何金良 著
Jinliang He



清华大学出版社
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内 容 简 介

金属氧化物压敏电阻是电力和电子系统的关键保护器件, 直接决定系统运行的安全可靠。本书系统介绍了氧化锌等压敏电阻的基础研究、制备工艺、性能调控及应用进展, 包括导电及老化机理、微结构电特性、微结构测试及微结构仿真分析、高梯度低残压氧化压敏陶瓷、氧化钛及氧化锡等其他体系压敏陶瓷的研究进展等, 构建了压敏电阻微结构特性与宏观特性之间的关联性。

本书可供高校和科研院所电气工程、微电子、材料等专业的师生以及电力传输、电气设备制造等行业的工程技术人员阅读和参考。

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Preface

Metal oxide varistor (MOV), or ZnO varistor, is a kind of polycrystalline semiconductor ceramics composed of multiple metal oxides and sintered by conventional ceramic technology. ZnO varistors have good nonlinear volt-ampere characteristics and excellent impulse energy-absorbing capacities. These advantages make them widely used in transient overvoltage protections for electrical/electronic systems. Now, varistors have been widely used as guardians to protect circuits over a very wide range of voltages, from a few volts in semiconductor circuits to 1000 kV AC and ± 1100 kV DC in electrical power transmission and distribution networks. Correspondingly, they can also handle an enormous range of energies from a few joules to many megajoules. Remarkably, they are also very fast, switching in nanoseconds from their high-resistance state to highly conducting state and then restores to a normal high-impedance operating conditions.

A bulk varistor is a complex multijunction device composed of large numbers of both ohmic and nonlinear elements connected in a random network. The features of bulk varistors are influenced by the geometry and the topology of the granular microstructure, as well as the properties and the distribution of electrical characteristics of grain boundaries. This book tries to bridge the Macro-Characteristics with the properties in microstructures of ZnO varistors to provide insights into some of the aspects in the microstructures of ZnO varistors, which influence the features of the bulk varistors and further the science and the understanding on microstructures of ZnO varistors and those parameters that affect the efficiency during the manufacturing process.

The book includes 12 chapters, which mainly focuses on ZnO varistors. Chapter 1 introduces and highlights the fundamental knowledge and applications of ZnO varistors. Chapter 2 introduces the conduction mechanism of the ZnO varistor, among the numerous conduction models, the one presented by G.E. Pike and further developed by G. Blatter and F. Greuter has been widely recognized and may meet most of the experimental phenomena. Various additives to improve the electrical characteristics were discovered and the synthesis conditions were optimized, which will be introduced in Chapter 3. The electrical properties of each individual grain boundary will contribute to the global electrical characteristics of ZnO varistors, Chapter 4 characterizes the microstructural electrical properties of ZnO varistors. The simulation is helpful to reveal the connection between the microstructure and the macroscopic characteristics

of varistor ceramics, the details on how to simulate varistor ceramics will be presented in Chapter 5. The breakdown of ZnO varistors is an original phenomenon during their applications, and the failure models result in different energy handling capabilities, which will be introduced in Chapter 6. ZnO varistors can be electrically, chemically, and thermally degraded during use, leading to the reduction of barrier voltage height and, consequently, to the increase of leakage current, which could be catastrophic for ZnO varistors, Chapter 7 discusses the electrical degradation of ZnO varistors. Chapter 8 introduces other ZnO varistor systems instead of bismuth, such as praseodymium, barium, and vanadium, for overcoming the shortcomings of Bi_2O_3 -based ZnO varistors.

The applications in electronic systems require the miniaturized varistors and low-voltage varistors. Chemical processing, such as sol-gel, solution, precipitation, microemulsion techniques, etc., facilitates a homogeneous doping at the molecular level to obtain a miniature device with a higher breakdown voltage, which will be introduced in Chapter 9. Interestingly, the ceramic-polymer composite varistor is a composite one, incorporating varistor particles or semiconducting particles, and its field-dependent property varies with the filler concentration. The composite varistor, with a lower breakdown voltage, can be a suitable substitute for ZnO-based varistors for the purpose of protection for low-voltage systems, which will be introduced in Chapter 1.

Besides works on improving the performance of the ZnO varistor material, other new materials have also been searched in order to achieve a better stability and be used for new applications. The titanium-based capacitor-varistor dual-function varistor ceramics, such as TiO_2 , SrTiO_3 , $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO), and BaTiO_3 varistor ceramics, have realized the goal to achieve component miniaturization and provide a superior high-frequency and high-amplitude transient voltage protection, which will be introduced in Chapter 10. Different from the multiphase structure of the ZnO-based varistor, the SnO_2 -based varistor has a simple microstructure, good stability, and better thermal conductivity, which makes the SnO_2 -based varistor one of the most promising candidates to commercially compete with the ZnO-based varistor. The SnO_2 -based varistors will be introduced in Chapter 11. The WO_3 -based varistor ceramic is another kind of low-voltage varistor with a low threshold electric field of $5\text{--}10\text{ V mm}^{-1}$ and a high dielectric constant, which enables it to act as a varistor in parallel with a capacitor, which will be introduced in Chapter 12.

This book covers main aspects of metal oxide varistors, which introduce fundamental and advanced theories and technologies related to metal oxide varistors, research achievements in the this field, and has reflected the recent research works of the authors and their students and colleagues in Tsinghua University, especially the Ph.D. dissertations of Dr. Chen Qingheng, Dr. Hu Jun, Dr. Liu Jun, Dr. Long Wangcheng, Dr. Zhao Hongfeng, Dr. Xie Jingcheng, Dr. Cheng Chenlu, and MSc thesis of Ms. Wei Qiaoyuan. The author tried to cover all the aspects of metal oxide varistors, but it is hard to avoid ten thousand may have been left out.

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Enormous references had been cited in our book, all had been listed in every chapter, but it is hard to avoid careless omission, in this case, I beg your pardon. I am so sorry, some formulas are unable to find the original references where they came from.

I have had a long-term cooperation in the research of metal oxide varistors with Prof. Nan Cewen of Tsinghua University, who is an Academician of Chinese Academy of Sciences, and Prof. Lin Yuanhua, who is the Dean of the School of Materials Science and Technology in Tsinghua University, I have learnt a lot from them, and many cooperation results have been collected in the book. I would like to extend my sincere thanks to them.

Special thanks go to Dr. Han-Goo Cho and Dr. Se-Won Han, from Korea Electrotechnology Research Institute (KERI), for providing me the chance to do research works in the field of metal oxide varistors during 1997–1998. KERI is where I started my research in this field.

Special thanks also go to my students, including Dr. Long Wangcheng, Dr. Luo Fengchao, Dr. Xie Jingcheng, Ms. Wei Qiaoyuan, and Mr. Meng Pengfei, for their assistance on preparing the draft of the book and to my colleagues for their generous help in many ways so as to allow me to allocate time working on the book. Great gratitude is given to Prof. Hu Jun for preparing the manuscript of Chapter 5, Dr. Cheng Chenlu for preparing part manuscripts of Chapters 2 and 7, and Dr. Liu Jun for preparing the part manuscript of Chapter 7.

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Lastly, but not least, my most special gratitude goes to my supporting and understanding family, my mother, Yang Ruiru, who taught me working hard and enjoying the wonderful life; my wife, Prof. Tu Youping, who had done and has been still doing a great job on supporting the family. Most of all, I am indebted to my son, Ziyu, I have not spent much time to enjoying his grow-up process, but it is gratifying that he is working hard to become a scientist in the field of statistics and machine learning.

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1

Introduction of Varistor Ceramics

Zinc oxide (ZnO) varistor, which is a kind of polycrystalline semiconductor ceramic composed of multiple metal oxides and sintered using conventional ceramic technology, is a voltage-dependent switching device, which exhibits highly nonohmic current–voltage characteristics above the breakdown voltage. Basic information on ZnO varistors, including the fabrication, microstructure, and typical electrical parameters, is introduced. The history and applications of ZnO varistors are also presented. The panorama of alternative varistor ceramics for Bi₂O₃-based ZnO varistors is mapped out. Especially, the ceramic–polymer composite varistors with lower breakdown voltage, incorporating varistor particles such as semiconducting particles, a combination of metal and semiconducting particles, and ZnO microvaristors, in a polymeric matrix are reported. Now, varistors are available that can protect circuits over a very wide range of voltages, from a few volts for low voltage varistors in semiconductor circuits to 1000 kV AC and ± 1100 kV DC in electrical power transmission and distribution networks. Correspondingly, they also can handle an enormous range of energies from a few joules to many megajoules.

1.1 ZnO Varistors

A varistor is an electronic component with a “diode-like” nonlinear current–voltage characteristic, which is a portmanteau of variable resistor [1]. Functionally, varistors are equivalent to a back-to-back Zener diode and are typically used in parallel with circuits to protect them against excessive transient voltages in such a way that, when triggered, they will shunt the current created by the high voltage away from sensitive components.

The most common type of varistor is the metal oxide varistor (MOV), which contains a ceramic mass of ZnO grains, in a matrix of other metal oxides, such as small amounts of bismuth, cobalt, and manganese, sandwiched between two metal electrodes. The boundary between each grain and its neighbor controls the current according to the applied voltage, and allows current to flow in two directions. The mass of randomly oriented grains is electrically equivalent to a network of back-to-back diode pairs, each pair in parallel with many other pairs. A varistor’s function is to conduct significantly increased current when voltage is excessive. Only nonohmic variable resistors are usually called varistors [1].

In normal use, a varistor is subject to a voltage below its characteristic breakdown voltage and passes only a tiny leakage current. When the voltage exceeds the breakdown voltage, the varistor becomes highly conducting and draws a large current through it, usually to ground. When the voltage returns to normal, the varistor returns to its high-resistance state [2]. The result of this behavior is a highly nonlinear current–voltage characteristic [3–5], in which the MOV has a high resistance at low voltages and a low resistance at high voltages; usually, the resistivity of a ZnO varistor is more than $10^{10} \Omega \text{ cm}$ below the breakdown voltage, whereas it is less than several ohm-centimeters above the breakdown voltage [6]. The switch is reversible with little or no hysteresis although it can degrade under electrical loading [2]. A varistor remains nonconductive as a shunt-mode device during normal operation when the voltage across it remains well below its “clamping voltage”; thus varistors are typically used for suppressing line voltage surges. However, a varistor may not be able to successfully limit a very large surge from an event such as a lightning strike where the energy involved is many orders of magnitude greater than it can handle. Follow-through current resulting from a strike may generate excessive current that completely destroys the varistor [1].

ZnO varistors are voltage-dependent switching devices, which exhibit highly nonohmic current–voltage (I – V) characteristics above the breakdown voltage. The nonohmic I – V characteristics are usually expressed logarithmically, as shown in Figure 1.1 [6]. The degree of nonohmic property is usually expressed by a nonlinear coefficient α defined by the following equation:

$$\alpha = \frac{V}{I} \frac{dV}{dI} \quad (1.1)$$

Empirically, the following simple equation is used:

$$I = \left(\frac{V}{C}\right)^\alpha \quad (1.2)$$

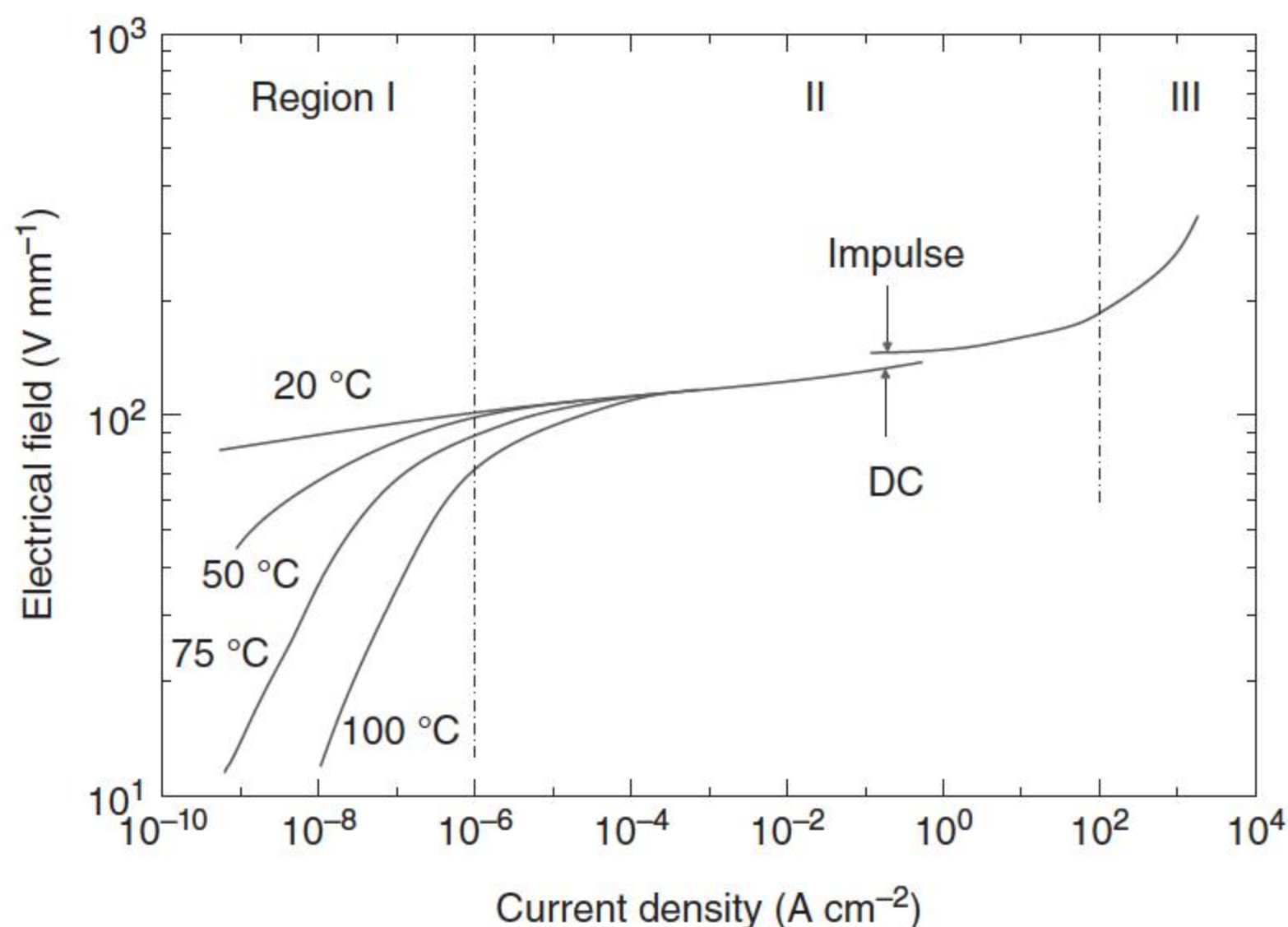


Figure 1.1 I – V characteristics of a typical ZnO varistor. Source: Adapted from Eda [6].