博士学位論文審査要旨

２０２２年1月１１日

論文題目： Study on the Electrical Properties and Microstructure of Bismuth-Based High Voltage Zinc Oxide Varistors
（ビスマス系高電圧酸化亜鉛バリスタの電気的特性と微細構造に関する研究）

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要　　　旨：

酸化亜鉛（ZnO）バリスタは極めて優れたサージ吸収能力を有する電子セラミックスであり、構造は極めて簡単である。優れたサージ吸収能力は添加される元素（添加物）の種類や量によって ZnO 粒子内および粒子間（粒界）で形成されるドナー準位、界面準位、種々の化合物の微細構造により発現し、それ等により決定される２重ショトキー障壁（DSB）の高さ・形状がサージ吸収能力に大きな影響を与える。本研究は将来の交流送電のさらなる高圧化に対応できる小型高電圧バリスタに注目し、従来の ZnO バリスタに高電圧化に有効な希土類および酸化ケイ素の高濃度添加を行った際に、弊害として生じる耐課電劣化特性の劣化および通常課電時の漏れ電流の増加を改善する為の学術的に裏付けされた手法を確立することを目的としている。諸成果の内で最も注目されるのは、高電圧化に有効な酸化イットリウムを添加した際、弊害の改善に酸化ホウ素（B_2O_3）添加が有効であることを発見したこと。さらに、B_2O_3 添加による微細構造、電圧－電流特性、過渡容量分光法による界面準位の深さ・濃度の評価、容量－バイアス電圧特性によるドナー濃度・DSB の高さを評価し、さらに電圧－電流特性を３つの主なる伝導過程に分けて考え、それぞれの特性の解析モデルを構築して、評価結果と関連付けて解析することにより、改善メカニズムを極めて明確に明らかにしたことである。他の成果として、B_2O_3 の代わりに酸化クロムの添加が改善に有効であることを発見したことと、その改善メカニズムに界面準位の無バイアス時の非占有領域の状態密度と準位の分布の関係を関連付けたことである。さらに、高電圧化に希土類元素の代わりに環境負荷の極めて低い酸化ケイ素を添加することにより、従来に例を見ない極めて高いバリスタ電圧（約 2500 V/mm）を達成したことと、その耐課電劣化改善に、B_2O_3 添加が極めて有効であることを示したことである。

よって、本論文は、博士（工学）（同志社大学）の学位論文として十分な価値を有するものと認められる。

総合試験結果の要旨

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要　　旨：
本論文の提出者は 2018 年 9 月に本学大学院理工学研究科電気電子工学専攻博士課程後期課程 ISTC コースに入学し、現在在籍中である。 本論文の主たる内容は Journal of the European Ceramic Society, 41, pp.4841-4849 (2021)および Materials Chemistry and Physics, 276, 125390 (2021)に掲載済みであり、すでに十分な評価を得ている。2022 年 1 月 8 日午前 10 時 00 分より 1 時間 40 分にわたり、提出論文に関する博士論文公聴会が開かれた。講演後種々の質疑が行われたが、提出者の説明により十分な理解が得られた。公聴会終了後、審査委員による学力確認を実施したところ、論文提出者の十分な学力を確認することができた。また、提出者は第一著者として国際会議で 4 件の英語の発表を行っており、また公聴会も英語で行われ、高い英語能力を有するものと認められる。 以上より、論文提出者の専門分野における学力ならびに語学力は十分であることが確認された。よって、総合試験の結果は合格であると認める。

博 士 学 位 論 文 要 旨

論 文 題 目：Study on the Electrical Properties and Microstructure of Bismuth-Based High Voltage Zinc Oxide Varistors
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要　　　旨：

Consumption and demand of electricity keeps rising with the rapid development of the economy. Affordable, reliable, sustainable, and modern energy is an important goal for everyone. In recent years, a lack of electricity still occurs in poor areas and in advanced areas due to extreme weather or shortages of coal. According to united nation's report of sustainable goals, there are 759 million people lacking access to electricity. Accelerated action on renewable energy is needed especially in heating and transport sectors. Improvement of energy efficiency, and development of clean energy source is more than important for all. For a diverse electrical power grid, it is important and urgent to build a network that is efficient in combining fuel energy, solar energy, wind energy, hydroelectric energy, and other types. Development of ultrahigh voltage power transmission technologies is required to realize safe, efficient, clean, and low carbon electricity supply. Higher voltage lightning arresters, such as ZnO varistors, play a key role in increasing such transmission line voltage.

Zinc oxide varistors are widely used as a key part in surge arresters to protect electronic and electrical devices from abnormal overvoltages, such as lightning attacks. This special ceramic material is a mixture of mainly ZnO and a minor number of additives such as Bi, Co, Mn, Sb, Si, and others. Their protective abilities originate from the nonlinear voltage−current (V−I) characteristics generated between ZnO grain boundaries and intergranular layers due to the formation of double Schottky barriers. It is a voltage-dependent switching device that exhibits nonohmic V−I characteristics above the breakdown voltage, and becomes conductors when they are exposed to voltages higher than their operating limits, shunting current to ground to prevent damage to devices connected in parallel. The withstand level, set amount, and position of surge arresters are designed according to the overvoltage caused by lightning strikes and switching surges in power systems. However, increasing the number of surge arresters for UHV transmission will also increase the cost. Furthermore, although the arrester's working voltage (also called varistor voltage) can be increased by simply increasing the number of ZnO varistors in device, in this case, the size of surge arresters will also be largely increased which may be more than a few meters. Considering the layout of the transmission system and the limited area in the city, downsizing of surge arresters is also needed. Hence, ZnO varistors need to be improved in order to be used in UHV transmission. Varistors exhibiting high ZnO voltage, good nonlinearity, low leakage current, and high electrical stability are essential for reducing energy loss and enhancing protection.

The author's aim is to investigate ZnO varistors with high voltage to 1000V/mm (double the commercial varistor voltage) and good resistance to electrical degradation, which could be applied to the UHV transmission systems and reduce ZnO varistor element amounts in surge arresters. The conduction processes in ZnO varistors need to be clarified, especially the mechanisms of electrical degradation which have not been fully studied and reported. Varistor voltage is dependent on the number of grain boundaries between two electrodes and the voltage per grain boundary. To increase it, one method is to reduce the ZnO grain size, and the other is to increase the voltage per boundary. By adjusting additive type and amounts in ZnO the electrical properties of ZnO varistors can be controlled. On the basis of this recipe, Y, Cr, Ni, B, Si oxides were added

in this study. These oxides can be divided into two categories, the Y doping group and the Si doping group. Firstly, Y were introduced into commercial varistors and varistor voltage was increased to around 1000V/mm, however, electrical degradation occurred severely and leakage current was large. Chapters 5 and 6 discussed how Cr, Ni, or B could improve electrical degradation properties in Y-doped varistors. Another recipe that contained less additives and without Y was studied by adding SiO_2 to Zn-Bi-Co-Mn varistors. The effects of B and Sb on Si-doped varistors were further studied in chapter 7.

The thesis is divided into eight chapters.

In Chapter 1, ZnO varistors and their history are generally explained, and the importance of improving and developing new recipes for ZnO varistors for ultra-high voltage transmission lines is demonstrated. The objective of the study is to develop a high voltage varistor which shows good electrical stability for the use in UVH systems.

In Chapter 2, the properties of ZnO varistors such as the nonlinear electrical properties, microstructure and grain boundary structure, chemical reaction mechanisms during sintering are demonstrated. The application of ZnO varistors in various types of devices is described. The ZnO varistors are complex ceramic materials with addition of many additives. The microstructure and electrical properties of ZnO varistors are influenced by the chemical reaction occurring between additives and ZnO during sintering at high temperatures. Now, ZnO varistors are applied from a few volts for low voltage varistors in circuits to 1100kV in electrical power transmission networks.

In Chapter 3, the principles of ZnO varistors are demonstrated. The nonlinear V–I characteristics and specific phenomena are explained. Reported additive effects have been summarized. A double Schottky barrier and other mechanisms are discussed for the origin of V–I characteristics. Electrical degradation is explained and degradation phenomena are illustrated in various conditions. Various mechanisms can lead to electrical degradation.

In Chapter 4, the experimental methods and evaluation methods are demonstrated. Solid-state reaction at high temperature is used to make samples. The electrical properties such as V–I characteristics, electrical degradation test are explained. The capacitance–voltage measurement and isothermal capacitance transient spectroscopy are introduced and used to investigate the Schottky barrier and interface states. Microstructures are observed by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, energy-dispersive spectroscopy, and emission electron probe micro analyzer.

In chapter 5, the effects of Cr and Ni on Y-doped varistors are examined, including electrical properties, electrical degradation, microstructure, Schottky barriers and interface states. Incorporating 0.35 mol% Cr_2O_3 in Y-doped varistors increased single-grain varistor voltage V_{NNGB} from 2.6 to 3.3 V and decreased the leakage current density by a factor of 40, from 2×10^{-5} to 5×10^{-7} A/cm^2. Nonlinearity index α before and after degradation increased from 21 to 35. 1.2 mol% NiO increased V_{NNGB} to 4V. The highest varistor voltage was 1500 V for 0.3 mol% NiO. Resistance to electrical degradation improved with optimal amounts of Cr or Ni by reduction in grain boundary oxygen vacancies. Though donor density was changed by addition of Cr and/or Ni prominently, the change of barrier height was suppressed by the change of interface state density. As a result, the change of V_{NNGB} was related mainly to the empty interface state density under no bias.

In chapter 6, the effects of B_2O_3 addition to Y-doped varistors are studied. The optimal amount of B_2O_3 (0.75 mol%) drastically improved the electrical properties of Y-doped varistors, reducing the leakage current to 0.8 μA/cm^2 while maintaining exceptionally long-term stability to DC electrical degradation and a voltage around 900 V/mm. Boron ions are found with Bi ions in Y-compounds, which contribute to formation of a Bi-rich glass phase containing B at grain boundaries when B_2O_3 is above 0.75 mol%. The change in microstructure affected the donor density and barrier structure leading to a change in electrical properties. The Bi-rich phase first reduced Co concentration in the ZnO grain, decreasing donor density N_D. Then, when B_2O_3

was greater than 1 mol%, the excessive B ions acted as donors to increase N_D. In addition, the relationship between B_2O_3 and SiO_2 in Y-doped varistors is also discussed.

A new analytical method using differential resistance R_D of the nonlinear voltage–current density relation was proposed and explained also in chapter 6, to clarify the effects of B_2O_3 addition. This method separates the three-differential resistance R_{Di} values ($i = 1, 2, 3$) and was used to analyze the corresponding conduction process located in forward-biased region I, reverse-biased region III, and interface region II of the energy band. The R_{D1} and R_{D2} values exhibited a junction diode-like property in regions I and III. The value of R_{D2} that correlated with α_{asMAX} and long-term stability of varistor and R_{D3} may be related to region II.

In Chapter 7, SiO_2 addition to Zn-Bi-Co-Mn varistors are investigated. Varistor voltage increased as Si content increased because the formation of second phase Zn_2SiO_4 that inhibits the ZnO grain growth. However, the resistance to electrical degradation also decreased. Therefore, B was added into Si-doped ZnO varistors to improve the resistance to degradation. It is considered that the resistance to electrical degradation is improved upon addition of B by its combination with ions in grains and prevention of ion movement. Furthermore, it was found that Bi-Mn-Co-Si-B added ZnO varistors have good resistance to electrical degradation characteristics and the varistor voltage can be controlled by manipulating the amounts of Si and B.

In Chapter 8, the summary of the whole thesis and pathways for future work are explained.

This study discussed the additives' effects on fabrication of high voltage ZnO varistors, improved the electrical properties of Bi-based ZnO varistors by doping Y, Cr, Ni, B, Si oxides as additives, clarified the degradation phenomena, and summarized and created a guideline for the measurement of ZnO varistors. A new differential resistance R_D of the nonlinear voltage–current density is proposed, that is suggested for devices such as other types of ZnO varistors, TiO_2 varistors, and SnO_2 varistors, and may also be suitable for avalanche diodes or heterojunctions, especially because the equation for R_{D3} may result from the tunneling effect.