Mechanism and Development of TiO_2-Doped ZnO-Bi_2O_3-Based Varistors

FU Jing   XU Zheng

(Department of Material Science&Engineering, Tongji University   Shanghai   200092)

Abstract   This paper reviews the history of ZnO varistor, discribes its properties and recent technological status and forecasts its evolution. The future development trend is to produce the low-voltage high-energy multi-layer ZnO varistors. After the two additives are classified by their functions，the effect mechanism of Bi_2O_3 and TiO_2 additives are researched theoretically. TiO_2 will make ZnO grain grow bigger and V_{1mA}/mm be depressed down. Especially the colloid TiO_2 additive in the scale of nanometer brings about a new method to realize the low voltage of ZnO varistor, which resolves the problem of how to disturb nanometer powder evenly. Moreover the sintering temperature has prominent effect on the electrical properties of ZnO varistors. Generally, the appropriate sintering temperature for low-voltage ZnO varistor ceramics should not be more than 1 250 ℃. These provide an effective method and rationale for studying low-voltage ZnO varistors.

Key words   ZnO varistors;   properties;   development;   additives;   grain growth

ZnO varistor is a newly developed ceramic materials with multiplefunction. It is a kind of sintered material mainly composed of ZnO as well as other oxides (mainly transitionmetal oxides) added to modify its characteristics[1]. It is widely used to build electronic devices, power system and applied in other fields for its merits such as favorable performance and expenses ratio, prominent non-Ohmic characteristics, a relatively short responding time (20~50 ns), low leakage current etc. With the popularity of miniaturization and integration of electronic devices, low-voltage varistors are in rapidly growing need.

1   Fundamental Properties

The outstanding nonlinear features of the ZnO varistor are originated from the microstructure of the sintering. The research of the chemistry, physics, electrical properties and its microstructure can be found in the published thesis[1,2].

1.1   Chemistry of ZnO Varistors

Pure ZnO is a nonstoichiometric *n*-type semiconductor with a linear *V-I* behavior. To make it nonlinear, various additive oxides are incorporated in the ZnO. The chief one among these oxides is Bi_2O_3, which can be considered as a varistor former, without which it is difficult to make a varistor. Incorporation of these oxides causes atomic defects to form at the grain and the grain boundary, with donor or donor-like defects dominating the depletion layer and acceptor and acceptor-like defects dominating the grain-boundary states. From a study of the defect equilibria in ZnO, Einzinger[3] has demonstrated that a defect-induced potential barrier can be formed from the unequal migration of defects toward the grain boundary.

1.2   Physics of ZnO Varistors

The non-linearity in the ZnO varistor is a grain-boundary phenomenon where a barrier to majority charge carriers exists in the depletion layers of the adjacent grains. The Schottky barrier has been considered to be the most likely barrier at the grain boundary of the ZnO microstructure. There is no need for physically separate, intergranular, insulating layer between two grains. The negative surface charge at the grain-boundary interface (electron traps) is compensated by the positive charge in the depletion

layer in the grain on both sides of the interface. Thermo-ionic emission and tunneling are acknowledged to be the major transport mechanisms.

1.3 Electrical Properties of ZnO Varistors

If we look into the volt-ampere property of the ZnO varistor, we can see that the ZnO varistor has a very high value of resistivity, which is almost several 10^6 Ω, and its leakage current is only several 10^{-6} A[4]. With the increasing of the voltage that the varistor subjects to, the resistivity decreases sharply. When it reaches the billow voltage, the resistivity may be several tens ohm, or even 0.1~1 Ω, which shows the variation of the resistivity in different value of voltages[5]. Fig.1 shows the *V-I* specific curve of the typical ZnO varistor. From Fig.1, one may see that the voltage-current characteristics can be divided into three zones, namely low current zone, medium current zone and high current zone. The *V-I* specific curve of the low and high current zones are close to linearity, while the one of the medium current zone is specified for the high nonlinear coefficient (α>50) and wide range of current volumes (may expend to 10^6~10^7 times of current volumes). Electrical properties of ZnO-based varistors prepared by combustion synthesis can be better[6].
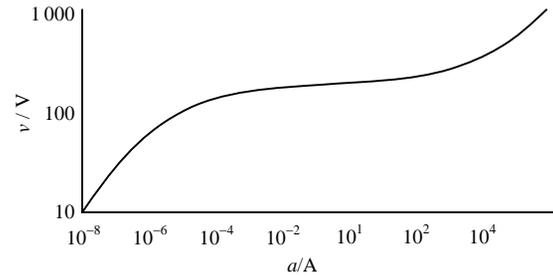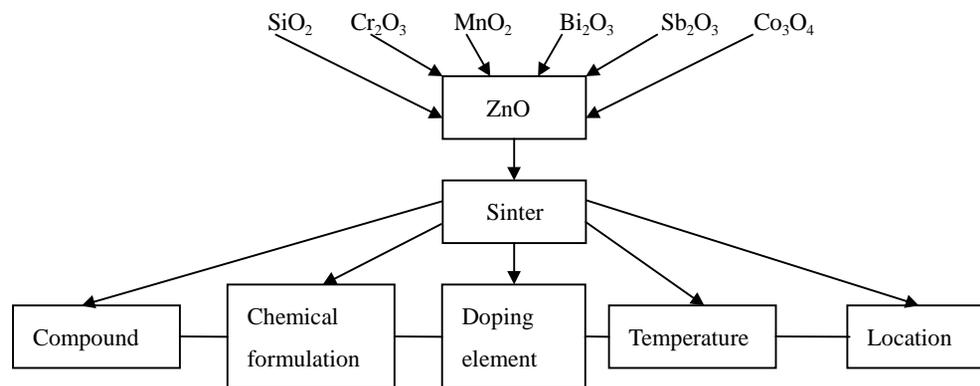

Fig.1   Typical *V-I* characteristics of the ZnO varistor

1.4 Microstructure of ZnO Varistors

It is generally believed that there are other matter phases except for the major crystal phases, for instance spinel pyrochlore and several bismuth-rich phases, etc. (as Fig.2 Shows). The ZnO phase is the major crystal phase to form varistors, and the spinel phase is non-continuum that doesn't function directly to the non-linearity of ceramics[7]. But because the spinel phase can co-exist with bismuth-rich phase in a high temperature condition, it can combine the ZnO to form the bismuth- rich phase which can increase the value of α.

ZnO phase	ZnO	Co, Mn	all	Grains
Spinel phase	Zn$_7$Sb$_2$O$_{12}$	Co, Mn, Cr	>700℃	Intergranular phase
Pyrochlore phase	Zn$_2$Bi$_3$Sb$_3$O$_{14}$	Co, Mn, Cr	(700～950)℃	Intergranular phase
Bi-rich phases:				Triple point
A phase	13 Bi$_2$O$_3$·2Cr$_2$O$_3$	Bi, Cr, little Zn	(600～900)℃	
B phase	12 Bi$_2$O$_3$·Cr$_2$O$_3$		(850～1000)℃	
C phase	14 Bi$_2$O$_3$·Cr$_2$O$_3$	Zn, Sb	(900～1250)℃	
β- Bi$_2$O$_3$ phase	β- Bi$_2$O$_3$	Zn, little Sb	>1 000℃	
δ- Bi$_2$O$_3$ phase	δ- Bi$_2$O$_3$	Zn, Sb	1 200℃	
	12 Bi$_2$O$_3$·SiO$_2$			

Fig.2   Microstructural components of the ZnO varistor comprising various crystalline phases

2   Effect of Additives

2.1   Effect of Bi$_2$O$_3$

Bi$_2$O$_3$ is an essential additive of ZnO varistors. Because Bi$_2$O$_3$ has melting point that is far lower than that of ZnO and other additives, and thus exists in liquid phase in a relatively low temperature, which promotes other oxide to be distributed evenly in the ZnO grains and grain boundary. When cooled down, Bi$_2$O$_3$ can't be found in the ZnO grains but separate in the grain boundary for the Bi^{3+} ion has a much bigger diameter (1.10×10^{-10} m)than that of the Zn^{2+} ion's(0.74 ×10^{-10} m). This will cause all additives separating together in the grain boundary to form a very thin interface that has a very high level of grain-boundary potential barrier and thus increase the nonlinear coefficient of ZnO varistors and the capacity of permitted accessing current consequently[8,9]. The distribution of the Bi-rich phase in the grain boundary of the serial of ZnO- Bi$_2$O$_3$ -TiO$_2$, which subjects to a low voltage, is non-continuum, while the width of the grain boundary of the meeting zone of every two ZnO grains is about 45 nm. This area will function as a surface phase, which will have great effect on the non-linearity. But if the Bi$_2$O$_3$ phase is added too much, bad effect may occur for not only the widening of the grain boundary but also the increase of Bi$_4$(TiO$_4$)$_3$ and thus will affect the non-linearity.

The sintering temperature has prominent effect on the electrical properties of ZnO varistors. According to the SEM and XRD analysis, if the temperature is too high, many of the Bi atoms will volatilize, and thus bring about many air pores in ZnO varistor to deteriorate the structural uniformity so as to affect its electrical properties. On the other hand, since that phase is relevant to the material's leakage current I_L and the nonlinear coefficient α，with the increasing of the sintering temperature, the electric field strength of the low-voltage ZnO varistor E_{1mA} will decrease, while I_L will increase and α will decrease[10~12]. Generally, the appropriate sintering temperature for low-voltage ZnO varistor ceramics should not be more than 1250℃.

2.2   Effect of TiO$_2$

The relationship among nonlinear voltage V_{1mA} of varistors and voltage decreasing of every grain V_0, the average quantity of grains between the both electrodes N, the diameter of the grain d_0 and the agglomeration's thickness L can be summarized as following [13]

$$V_{1\,mA}=N\,V_0=(L/\,d_0)V_0 \qquad (1)$$

The traditional method to depress $V_{1\,mA}$ is to make the component thinner, so that its mechanical strength can be reduced. We are aiming at developing a low-voltage varistor with a high-energy capacity, namely, we want a varistor with a low C value (the variable voltage in per unit of thickness) and a low leakage current value. From Eq.(1), the key point is to produce the relatively larger sized ZnO sintering ceramics grain whose properties can satisfy the demand. What's more, the resistivity ρ of ZnO grain is relatively low (0.5～2.7Ω·cm). So, one effective way to produce low-voltage varistors is to enlarge the size of the grain, namely, increase the value of d_0 to reduce $V_{1\,mA}$/mm[14,15].

Sung and Kim[16] believed that for ZnO varistor ceramics with the doping of Bi$_2$O$_3$ and TiO$_2$, TiO$_2$ would enhance the reaction activity of the bismuth-rich liquid phase and the ZnO phase, and effect ZnO grain growth through the phase-boundary reaction. During the initial period of the sintering of the liquid phase, TiO$_2$ would saturate quickly into the bismuth-rich liquid phase and react with Bi$_2$O$_3$ liquid phase

$$2Bi_2O_3(l)+ 3TiO_2(s) \rightarrow Bi_4(TiO_4)_3 \qquad (2)$$
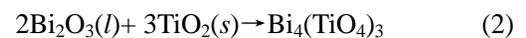
While the solubility of ZnO grain in the Bi$_4$(TiO$_4$)$_3$ liquid phase is bigger than that in the Bi$_2$O$_3$ liquid phase, which will accelerate the speed of ZnO transfer in the Bi$_4$(TiO$_4$)$_3$ liquid phase, and thus will accelerate ZnO grain growth with a small grain growth exponent n . Bi$_4$(TiO$_4$)$_3$ will discompose at the temperature of about 1 050℃ and react with ZnO:

$$Bi_4(TiO_4)_3(s)+6ZnO(s) \rightarrow 2Bi_2O_3(l)+3Zn_2TiO_4 \quad (3)$$
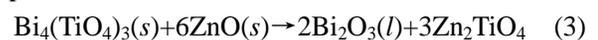
Zn$_2$TiO$_4$ spinel particle pins the ZnO grain-boundaries creating a drag mechanism that reduces the grain-boundary mobility and increase the apparent activation energy [17,18]. So after the sintering temperature exceeds 1 100℃, the growth speed of the grain will slow down.

TiO$_2$ additive affects mostly the gradient of ZnO varistor ceramics potential; also it can act as the

grain-growing promoter for its solid-phase transfer mechanism. The diameter of Ti^{3+} ion is 0.69×10^{-10} m and that of the Ti^{4+} ion is 0.68×10^{-10} m, which are smaller than that of Zn^{2+}(0.74×10^{-10} m). However, those ions are similar in their diameters, so the Ti^{3+} and Ti^{4+} ions will replace Zn^{2+} ions in ZnO, which will cause the aberrances in crystal lattice, so that the Zn^{2+} and O^{2-} ions will be activated, and the value alterable element will be deoxidized to form some oxygen lack lattice in the neighborhood. This kind of oxygen lack lattice is beneficial very much to the particle disperse and thus promotes the solid-phase transfer and will form TiO$_2$ and Bi$_2$O$_3$ into low inter-dissolving liquid phase in ZnO varistor ceramics with the doping of Bi$_2$O$_3$ families[19,20]. This liquid phase has the functions of embellishing, felting and tension. It will not only enhance the contact of the grains to strengthen the diffusing effect of TiO$_2$ and promote the grain growth consequently, but also be ionized into +1 or +2 valued effective donor in the crystal lattice and increase the concentration of effective donor in the depletion layer. At the same time, the height of the potential barrier will be reduced and thus decrease the gradient of ZnO varistor ceramics potential with the corresponding decreasing in non-linearity coefficient.

Ti atoms in ZnO varistors may emit four electrons to form Ti^{4+}, or emit three electrons to form Ti^{3+}, depending on the different environments in which the atoms exist. Ti^{3+} is unstable, thus may very easily emit another electron to become Ti^{4+}. In this condition, a Ti^{3+} electron trap will exist besides the grain boundary, which may emit electrons under the effect of the electric field to increase the leakage current, so that the nonlinear property will be deteriorated, with the value of α reduced. The doping of TiO$_2$ will accelerate the grain growth, so that the grain defects will increase to enhance the leakage current. Another thing is, for ZnO ceramics, which has been sintered but yet annealing, TiO$_2$ will exist in the intergranular phase of Zn$_2$TiO$_4$ in large quantity, while a minority of them will be saturated in the Bi$_2$O$_3$-rich phase. In the process of anneal, the Ti^{4+} will diffuse to the surface of ZnO grains to replace the Zn^{2+} ions, which have similar size of diameter with the Ti^{4+} icons, so the Ti^{4+} icons can be saturated in ZnO grains in solid, which can increase the thickness of the effectual donor lying in the electron depletion layer of the grain- surface. This may reduce the height of the Schottky barrier to decrease the nonlinear coefficient α of ZnO ceramics and increase the leakage current I_L[21]. It is reported that if doped appropriate amount of boron and process in a temperature of 850℃，the weak current property and non-linearity can be improved, and the leakage current I_L can be increased, with the improvement of the stability[22].

According to some research results[23], TiO$_2$ additive in the scale of nanometer can provide the low-voltage ZnO varistor with a better effect, but the problem is how to make it disturbed evenly. The colloid TiO$_2$ additive in the scale of nanometer brings about a new method to realize the low voltage of the ZnO varistor.

3   Development

The appliance of ZnO varistors in China began at 1976, and has a developing history of almost 30 years. The bulk production was only initiated several years ago, with the properties and quantity meeting the domestic demand, but this industry is still left behind the international standard. The international tycoons are Panasonic, Simens, Harris, and Northland etc, each of whom has an output of more than a hundred million annually. The manufacturers in Taiwan are catching up with an output of 100 M per month totally. Few of the domestic manufacturers have an annual output of more than a hundred million. In addition, the equipments are frequently out of date; the automatic degree is far lower than needed with several manufacturers still staying the level of handicrafts. Thus, the level and quality of the products are undesirable and then don't enjoy a favorable competitive with the international counterparts. We must go all out to carry on the technical renovation in the following three major aspects:1) catch up with the international marketing development trend, continue to develop those high-tech products, which enjoy a good marketing potential; 2) rely on the capability and superiority of the technical renovation that domestic manufacturers

enjoy to deploy the front field research, watch intimately the market demand, aim at the developing trend if the international electronic technology, and try to make the result of research and development on the new product and technology at the first time;3) carry out the cooperation with the developed countries and regions in the field of manufacture, market and research, so as to enlarge the output rapidly and catch up with the international level.

In 1968, Panasonic Company developed successfully for the first time the ZnO varistor ceramics. The progress of ZnO varistor ceramics can be roughly divided into three phases[24]:

Phase 1: The development of the surface vinculum ZnO varistor ceramics, whose nonlinear coefficient is 12~20,

Phase 2: The discovery of the three-dimensional ZnO varistor ceramics.

Phase 3: The experimental research on the function of the admixture. From the serendipitous diffusion effect, a lot of researches have been carried out on the categories, quantity and formulas of the admixture and the sintering condition. Measures have been taken to find out the principle functions of each kind of admixture, so as to choose the appropriate formula and processing procedures to produce different needed ZnO varistor ceramics.

The major current developing trends of ZnO varistor materials can be summarized as the following:

1) Research on the manufacturing technology of ceramic powder. The powder is the fundamental of ceramics, and the high-tech ceramics like ZnO varistors have a special sensitive responce to the property of the powder such as the pureness, form and shape, and granularity distribution, and thus it is essential to improve ZnO varistor ceramics' properties by enhancing the powder material so as to manufacture the material with better characteristics and realizing the standard producing procedures under the condition of optimization. Only by this, we can make the same block of products' qualities more stable and coherent. In terms of varistor ceramic powder producing technology, domestic producers have done little in the research on wet chemical method[25] except introduced

spraying technology from Japanese companies. However, the dry method cannot ensure nice and uniform ingredient and the mechanical sphere grind can't guarantee the powder with uniform granularity, especially nanometer powder. Even worse, it will bring about the pollution problem for the rubbing medium, and thus can't improve the ceramics' properties radically. The wet chemical method combines the powder through liquid phase. This method is especially suited to produce multi-ingredient super fine powder. The common wet chemical methods currently being widely used are depositing calcinations, liquid heating, colloid methods and spray thermal decompose method. Moreover, the key point to produce compound powder[26] is to achieve the even dispersal and stability for the multi-ingredient compound system. Liquid chemical method is better for synthesizing compound powder of ZnO varisors[27].

2) Previously, varistors were mainly used as over-voltage protector and surge-voltage restrainer in the electrical devices and lighting arresters. Since the early 1980s, the low-voltage TiO_2 varistors have taken the place of SiC ceramics in the telephone line[28,29]. Ever since then, the research and production of the low-voltage varistors have drawn the wide concern of the people. That kind of varistors can be widely used in the fields like automobile, communication device, railway signal, micro-electromotor and various electric devices protectors. The developing trend of low-voltage ZnO varistors is miniaturization, multi-function and membrane, and gradually aiming at super low voltage and low temperature sintering[30]. Meanwhile, microwave sintering technology will be appointed[31]. Efforts are taken to produce a new type of varistor that can function at the periodical work frequency load.

3) The shapes of varistors will gradually become piece-like, multi-layer-like, miniaturizing, and multi-functional. The piece-like multi-layer ZnO varistors produced recently have favorable properties like short responding time, good clamping-voltage features, and small temperature disturbance etc, and are thus widely used as IC, CMOS, MOSFET and

automobile circuit protectors. Domestic major development current of these devices is the multi-layer varistor (MLV) in SMD[32~34].

4) The fundamental theories have been strengthened and perfected. The rewarding research has been carried out especially in the fields of grain-boundary phenomena, conductivity mechanism, defect theory, failure model and the origin of the microstructure[35]. Since America grasped the technology of the manufacturing the ZnO varistor ceramics, great efforts have been taken on the fundamental research. The major research topics are the microstructure of the conducting model, the formula mechanism and sintering technology, the nonlinear net topological model, the manufacture technology of the powder and the application of the nanometer material in the varistor ceramics[36,37]. Nanometer material is undoubtedly better for electrical properties, but its dispersal in larger batch production is a big puzzle. Someone adopted high energy ball milled nanocrystalline ZnO varistors[38]. Although its electrical properties improved, the cost of energy is high and the coherent of nanocrystalline is uncertain[39]. The future research will focus on the application of the computer technology in the material research such as the computer simulation on the grain growth process and the microstructure of ceramics, and make deeper researches by experiments. Emphatically changing many practical properties of ZnO varisors by doping all kinds of additives is a workable way, such as Pr$_6$O$_{11}$, Er$_2$O$_3$, Y$_2$O$_3$ and Nb$_2$O$_5$[40,41].

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Brief Introduction to Author(s)

FU Jing(傅静)was born in 1978. She is now pursuing M.S. degree in Tongji University. Her research interests include: functional material. E-mail:fujing1978@hotmail.com

XU Zheng(徐政)was born in 1942. He is a Professor in Tongji University. His research interests include: functional material. E-mail:xuzheng1178@yahoo.com.cn

Synthesis Mechanism of Low-Voltage Praseodymium Oxide Doped Zinc Oxide Varistor Ceramics Prepared Through Modified Citrate Gel Coating.

Wan Rafizah Wan Abdullah 1, Azmi Zakaria 1,2,* and Mohd Sabri Mohd Ghazali 2.

1. The proposed varistors exhibited comparable non-linearity properties to that of Bi_2O_3 based ZnO varistors with minimum number of additives. The non-linearity coefficient of the varistors could reach up to 60 with the general Vgb of 2–3 V. However, most of the Pr_6O_{11} based ZnO varistor systems that have been reported so far are developed towards high-voltage applications. The work by Horio et al., [21] is one of the very few attempts to extend the use of Pr_6O_{11} based ZnO ceramics for low-voltage applications.