THE EFFECTS OF ZINC OXIDE MICROSTRUCTURE ON THE ELECTRICAL CHARACTERISTICS OF LOW-VOLTAGE CERAMIC VARISTORS

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THE EFFECTS OF ZINC OXIDE MICROSTRUCTURE ON THE ELECTRICAL CHARACTERISTICS OF LOW-VOLTAGE CERAMIC VARISTORS

" KESAN MIKROSTRUKTUR ZINK OKSIDA TERHADAP CIRI-CIRI ELEKTRIK VARISTOR SERAMIK VOLTAN RENDAH "

by

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ABSTRACT

The effects of ZnO microstructure, on the electrical characteristics of low-voltage ceramic varistors, have been investigated in this work. A wide-shape distribution of ZnO particle size has been found to cause a large increase in the leakage current, reduction in the dielectric constant, increase in the donor density, reduction in the interfacial trap density, rise in the junction capacitance density and big gain in grain resistivity. At a ZnO specific surface area (SSA) of 4.7-4.8 m²/g, maximum nonlinear coefficient (α =36.68) was achieved, accompanied by a donor density of 1.3×10^{14} cm⁻³, a boundary Schottky barrier of 1.8V and an average ZnO particle size of 0.23 micron. Increasing SSA of ZnO tend to raise the leakage current, reduce the interfacial trap density, reduce the junction capacitance density, decrease the grain boundary resistivity, increase degradation and raise the grain resistivity. Intrinsic defects were introduced by over-milling the ZnO powder for 100 hours prior to mixing with the additive oxides. The resulting increase of zinc interstitials and lattice defects raised the donor concentration by an amazing 63,400% $(1.3 \times 10^{17} \text{ cm}^{-3})$ and the interfacial trap density by 3,200% (5.9x10¹³ cm⁻²). Other effects due to the increased intrinsic defects were large increase in leakage current, large drop in nonlinear coefficient, big jump in the Schottky barrier, large reduction in junction capacitance density and big increase in degradation. Large concentration of bismuth was detected at the grain boundary, from the EDX data, which explains the big rise in the Schottky barrier. The immense increase in interfacial trap density could be due to the higher concentration of dangling bonds that could have originated from the bigger lattice defect concentration.

ABSTRAK

Penyelidikan ini mengkaji kesan-kesan mikrostruktur ZnO terhadap cirri-ciri elektrik varistor seramik voltan rendah. Bentuk yang lebar pada taburan saiz zarah ZnO mengakibatkan penambahan arus kebocoran, penurunan pemalar dielektrik, kenaikan densiti penderma, penurunan densiti perangkap antaramuka, penambahan densiti kapasitan simpang dan kenaikan kerintangan butiran. Pada keluasan permukaan spesifik (SSA) 4.7-4.8 m²/g, pemalar ketaklinearan mencapai tahap maksima pada 36.68, diiringi oleh densiti penderma 1.3×10^{14} cm⁻³, sawar Schottky 1.8V dan purata saiz butir ZnO 0.23 mikron. Kenaikan SSA boleh menambahkan arus kebocoran, mengurangkan densiti perangkap antaramuka, mengurangkan densiti kapasitan simpang, menurunkan kerintangan sempadan butiran, menaikkan degradasi dan menambahkan kerintangan butiran. Kecacatan jati telah dibuat dengan mengisar ZnO secara berlebihan selama 100 jam, iaitu sebelum ia dicampurkan dengan oksida-oksida lain. Interstitial zink dan kecacatan kekisi yang terhasil telah menaikkan densiti penderma pada tahap amat tinggi sebanyak 63,400% (1.3×10^{17} cm⁻³) dan menambahkan densiti perangkap antaramuka sebanyak 3,200% (5.9x10¹³ cm⁻²). Kesan-kesan lain termasuk kenaikan arus kebocoran, penurunan pemalar ketaklinearan, kenaikan sawar Schottky dan penambahan degradasi. Kepekatan bismuth yang besar yang dikesan oleh alat EDX boleh menjelaskan sebabmusabab kenaikan sawar Schottky. Penambahan mendadak densiti perangkap antaramuka mungkin disebabkan oleh bon-bon berjuntai yang berpunca dari kepekatan kecacatan kekisi yang besar.

CHAPTER 1

Page 1

INTRODUCTION

One of the success stories of solid-state ceramics is the development of zinc oxide varistors. Varistors are defined as voltage-dependent resistors (VDR) used as protective devices to regulate transient voltage surges of unwanted magnitudes [1,2,3,4,5]. Unwanted over-voltage transient surges normally refers to damaging voltage transients that exceed more than 10% of the operating voltage of the equipment being protected [1].

In most cases, the varistor literally **absorbs** these dangerous surges, or spikes, before they can reach the circuitries of the electrical equipment which is being protected. And in some other cases, the varistor **absorbs and redirects** the overvoltage surges to the ground; this grounding connection is normally employed in high voltage applications [1,6]. Figure 1 shows several commercial zinc oxide varistors of various sizes and models.

In less than 30 years of its discovery, zinc oxide varistors have now become commodity items and mass-produced in many countries including Malaysia. The applications of varistors can be categorised as follows [7].

- (a) **Power switching protection** in electrical transmission systems, which include high-voltage generators and inductive relays.
- (b) Surge protection in office equipments and household appliances, which include computers, air-conditioners, televisions and telephones.

(c) Low-voltage surge protection in automobile electronics and semiconductor electronics, especially in computer notebooks, portable cellphones, printers and scanners.



Figure 1.1: Commercial zinc oxide varistors.

More than **two billions** zinc oxide varistors have been manufactured by now and their popularity is rapidly increasing due to their low costs, high quality and amazing versatility. Three major manufacturers of zinc oxide varistors are Matsushita Corp., Siemens Corp. and AVX Corp.; while in Malaysia, there is a couple of varistor manufacturers namely TPC-AVX Components (M) Sdn. Bhd. and Megator Electronics (M) Sdn. Bhd.

In this work, focus is given to **semiconducting zinc oxide** material because of its significance of being about **90%** of the material content of varistors. Another reason is the fact that zinc oxide is locally-manufactured in Malaysia and therefore zinc oxide varistors possess immense commercial value due to their dominant local content.

1.1 **OBJECTIVE**

This work deals with the microscopic characteristics of zinc oxide (ZnO) and their effects on the electrical properties of ZnO varistors. Focus is given on low-voltage varistors because the ZnO microstructure has more profound effects on these varistors if compared with that of higher voltage ones, based on the author's industrial experience. Varistor manufacturers consider low-voltage varistor models as those components categorised as having an operating voltage of **25** V_{rms} and **below** [6,7]. To the author's knowledge, a vast majority of investigators [4,5,10,28,30,31,32,33,35] have not focused their research work on low-voltage varistor models.

The following are itemised objectives

- (i) To obtain the micro-structural characteristics of different zinc oxide powder samples obtained from two local manufacturers of zinc oxide powder, namely Approfit Zinc Oxide Sdn. Bhd. and Metoxide Sdn. Bhd.
 Micro-structural analyses include particle size distribution (PSD), specific surface area (SSA) and scanning electron microscope imaging (SEM).
- (ii) To introduce more micro-structural defects to the zinc oxide samples by over-milling, or over-crushing, for a total of 100 milling hours. The intrinsic defects may exist in the form of zinc interstitials, zinc and oxygen vacancies, and edge/screw dislocations [10].
- (iii) To analyse the effects of micro-structural characteristics of zinc oxide on the electrical properties of varistors. Electrical properties analysed in this work include voltage-current characteristics (V-I curve), resisitivity (or conductivity), non-linear coefficient, grainboundary barrier voltage and capacitance-voltage characteristics (C-V curve).

1.2 <u>SCOPE</u>

This work focuses on these areas

(i) Zinc Oxide Material

Very little research work has been done by varistor researchers on the effects of zinc oxide microstructure on varistors. Most of the research and development work which have been done involved varistor additives and fabrication processes. Zinc oxide is a **semiconducting material** with a minimal energy band gap ranging from 3.1 eV to 3.3 eV [8,10]. Additions of additives into ZnO material can create energy trap depths as low as 0.14 eV below the conduction band [5, 9].

About 90 weight % of commercial variators consist of ZnO grains which are the basic building block of the ZnO variator. Micro-structural variations in the initial ZnO raw material would definitely affect the electrical properties of ZnO variators upon sintering [10]. Micro-structural characteristics that are analysed include particle size distribution, specific surface area and scanning electron microscope imaging. Another micro-structural characteristic that is synthetically introduced in this work is micro-structural defects done by over-grinding the zinc oxide powder for 100 hours. These micro-structural characteristics form one of the fundamental parameters analysed in this work; whereby variations in the parameters have clear impact on the electrical properties of ZnO varistors.

(ii) Low-Voltage Varistor Models

This work also focuses on the ZnO varistor used for low-voltage applications. Many varistor manufacturers classify low-voltage varistors as those possessing voltage values of $25 V_{rms}$ and below, and the voltage values are generally measured at an applied current of 1 mA. This rating of 25 V_{rms} is taken as a varistor "model" for low-voltage applications. Other low-voltage models include 17 V_{rms} , 14 V_{rms} and 11 V_{rms} . Some varistor models can be as low as 5 V_{rms} and 3 V_{rms} which are normally the multi-layered types, are used in microelectronics. Varistor models produced in this work fall in the model categories of 17 V_{rms} , 14 V_{rms} and 11 V_{rms} and 1

Low-voltage varistors that are manufactured in disk form normally possess small thickness values of below 1.5 mm, based on the author's experience. Thickness of lower than 0.5 mm are normally not employed for mass production due to limitations of the pressing machines. Therefore, multilayer form is a more practical form once the thickness limit has been breached.

Very little research and development is done on low-voltage varistors to date. One reason for this lack of interest could be the difficulty of fabricating samples which are very thin and electrically-stable. Thin varistor disks are sometimes electrically-unstable due to their inhomogenous nature

which may result in the thin varistor to experience physical cracking during high-current shock test of more than 200 amperes.

The second reason for the lack of interest in low-voltage variator research is due to the high rejects during pressing operation. To press thin parts, experience and skills are needed to prevent lamination problems. In this work, about 50% of pressed disks (1000 pieces) are rejected at the pressing stage.

1.3 <u>BACKGROUND</u>

The author strongly believes that the micro-structural characteristics of zinc oxide material have **profound effects** on the electrical properties of low-voltage ZnO varistors. Through his three-year stint as a varistor engineer at Thomson Electronic Parts (M) Sdn. Bhd., the author has made numerous experimentations and observations on the effects of zinc oxide on varistors which have been mass-produced. Evaluations and observations have been performed on over 200 tonnes of zinc oxide powder material and also on over 500 million pieces of manufactured varistor components. The following are the summary of the observations and evaluations

(i) The electrical properties of varistor lots, which consist of a few thousands of components per lot, **fluctuates** each time a new batch of zinc oxide is used for mass production.

- (ii) Eventhough the particle size distribution, specific surface area and purity of the zinc oxide did not vary much from one batch from the other, the electrical properties of varistors showed otherwise; especially variations in the nominal voltage (at 1 mA) and the clamping voltage (V_p).
- (iii) There must be some other **unknown** micro-structural parameters of zinc oxide that have big impact on the varistors' electrical properties.

The above findings have prompted the author to pursue a Master of Science programme in order to investigate the abovementioned phenomena in a more conclusive approach. A conclusive approach would be to set all known parameters constant except for a few parameters which are investigated. And the few parameters which become the variables for this research work are the particle size distribution (PSD), specific surface area (SSA) and intrinsic defects of zinc oxide.

CHAPTER 2

ZINC OXIDE VARISTORS AND TRANSIENTS

Most of the transient voltage surge suppressors (TVSS) manufactured today (2003) are metal-oxide varistors (MOV) especially the zinc-oxide based varistors [1]. TVSS devices are used mainly as the voltage-limiting elements which **limit or clamp** transient over-voltages; which means the transient peak voltage is reduced or limited to a level that is considered safe, as illustrated in Figure 2.1.

Normally, a varistor is located at the **incoming power line** before the power supply reaches the circuitry being protected. If during one fine day, a transient overvoltage, or spike, is passed along the power line, the varistor will detect the presence of the spike in nanoseconds speed; it will absorb most of the over-voltage spike and reduce it to a safe level slightly above the normal operating voltage of the circuit being protected, as shown in Figure 2.1. The "safe level" refers to the voltage value that the electrical circuit can handle without being damaged.

The phrase "clamping and limiting transients" refers to the electrical action of the varistor to **absorb** the excess energy carried by the transient and to **attenuate or reduce** the excess voltage of the transient. These excess energy and overvoltage are hazardous to all electrical circuits considering that these transients occur **a few thousand times a year** for a typical household or office premise [1,6].





Figure 2.2: A general design of varistor surge protector.

A general design of a surge-protector device is shown in Figure 2.2. As shown in Figure 2.2, the varistor components or MOVs are connected between **the live (hot) wire and the ground wire**; as if the varistors are "short-circuiting" the live wire. Due to the very high resistivity of varistors, in hundreds of gigaohm.cm, the varistors **behave like open-circuits** and therefore do not interfere with the normal operation of the device.

The three-pin plug is connected to the single-phase three-pin socket that normally found in offices and households with a normal supply of 240 volts (rms). If a transient over-voltage of 300 volts (rms) is carried through the household socket, the varistors will detect the transient, absorb most of the transient energy and redirect (or shunt) the remaining transient energy to the ground [2, 11]. And the duration of the detection, absorption and shunting normally last for only a few microseconds. A typical household or office experiences about 1000 times of 500V-transients in a year [1,6]; therefore the varistor performs its varistor action for only about a few seconds a year.

Several varistors can be arranged in parallel, as shown in Figure 2.2, in order to add more lines of defense against transients; whereby if the first varistor component fails after many years of service, the second varistor can continue the protection service. Three parallel varistors can survive for **more than half a century** under normal conditions. The last line of defense is the fuse that is designed to blow if a current of more than 13 amperes passes the fuse. Some fuses blow at 10 amperes (computer plugs for example). But fuses are not good for surge suppression because they pass transient over-voltages which carry currents less than 10 amperes. That is if a lightning transient of 1000 volts, that carries 5 amperes of current, passes the fuse, it will not blow; thus resulting in the transient entering the circuit causing damage. Moreover, the fuse only works once; it will self-destruct upon receiving a current of more than 10-13 amperes.

A surge protector plug can be bought for about RM 30 and a sample plug is shown in Figure 2.3. The normal ratings of the varistor components in Figure 2.3 are either 275 volts (rms) or 300 volts (rms). There are three varistor components; two are connected to the live wire while the other is connected to the neutral wire; and all three parts are grounded. The three varistor parts can be bought for less than RM3 (market price) but the plug manufacturer has apparently quadrupled the market price of the plug since all the other components are commonly found in most plugs; this phenomenon solidifies the famous proverb "knowledge is power".

Other common applications of ZnO varistors include the power supply circuits of computers and telephone circuits, as shown by the photos in Figure 2.4 and Figure 2.5.





Figure 2.3: A commercial varistor surge protector plug.(a) External view. (b) Internal circuit.



Figure 2.4: Photograph of a power supply circuit board.

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Figure 2.5: Photograph of a telephone circuit board.

2.1 <u>HISTORY OF ZINC OXIDE VARISTOR</u>

The first transient voltage surge suppressors (TVSS) were **selenium rectifiers** that were employed to protect telephone systems in the early 20th century [10]. By 1930, the **first varistor ceramics** were developed by **Bell Systems** in which sintered compacts of **silicon carbide** (SiC) particles were the materials used to make varistors. And for low-voltage applications, the TVSS devices used in the 1930s were single crystal silicon devices, namely avalanche or **Zener diodes** [12].

After the second world war, technological improvements have been done on TVSS especially in the decades of 1960 and 1970. The United States and Japan were leading the world in research and development activities on varistors since then until now. By 1969, the first varistor ceramics based on **zinc oxide** material were developed by **Matsuoka** [13]. He unleashed significant scientific discoveries of ZnO varistors which include the roles of additives or substitutional ions, Bi₂O₃-rich liquid phase at grain boundaries and the enhancement of the degree of nonlinearity by manganese and cobalt dopants.

Astonished by Matsuoka's findings, General Electric Corporation and Matshushita Corporation formed an alliance in research and development to further pursue the science and technology of ZnO varistors; and a few years after the joint venture, so many research publications were made on ZnO varistors. Concurrently, new ZnO varistor products were developed and they were found to be far superior to SiCbased varistors in terms of these application properties

- (a) ZnO varistors have excellent energy-handling capabilities of up to megajoules range.
- (b) They are very versatile whereby they can be used in low-voltage circuits, medium-voltage applications and even high-voltage power electronics, in which the voltage ratings range from a few volts until a few million volts; this is something not achievable by other materials.
- (c) ZnO varistors have remarkable switching speeds in nanoseconds range for them to change from a highly resistive state to a highly conductive state [14].

ZnO-based varistor devices have been actively employed as the **main TVSS** since the 1980s until now due to their **superior quality and lower costs** [1,10]. And by the early 1990s, all surge suppressors for power supply system in Japan have been replaced by ZnO varistors [7] and as a result, there is hardly any power failure case in Japan. Unfortunately, Malaysia has been far behind than other developed nations in employing ZnO varistors in its power systems; this fact may be the reason why in Malaysia, power failure occurrence is common especially in industrial sectors whereby large power surges and over-voltage transients occur frequently.

2.2 <u>DEFINITION OF ZINC OXIDE VARISTORS</u>

Zinc oxide varistors are **electro-ceramic** devices used as transient voltage surge suppressors (TVSS) to detect and clamp over-voltage transients [1,10,12]. With zinc oxide (ZnO) as the base material, ZnO varistors exhibit **non-ohmic** behaviour with resistivity values dependent on the applied voltage. The main properties of ZnO varistors are described as follows

- (a) ZnO varistors have super-fast response to over-voltage transients whereby they can sense and clamp (limit) transients in nano-seconds speed.
- (b) ZnO varistors can sense and clamp transients **repeatedly**, in thousands of times, without being destroyed [1,12].
- (c) Their current-voltage (I-V) characteristic is **nonlinear** similar to the current-voltage characteristic of a Zener diode.

- (d) They can perform surge suppressing functions equally in **both polarities**, which means they can work in both forward and reverse biases; similar to two diodes arranged back-to-back.
- (e) ZnO varistors can be used in circuits which employ both alternating current (ac) and direct current (dc) over wide ranges of voltage (one volt to megavolts) and current (1 microampere to kiloamperes) [14].
- (f) They have very large energy-handling capabilities ranging from a few joules for smaller models up to thousands of kilojoules for larger models.

Since Dugan [1] and Clarke [10] emphasised the importance of ZnO varistors as the most popular TVSS to date, it would be fun to examine the **advantages** of ZnO varistors as compared to other TVSS devices. Below are a list of the advantages [10,12]

- (a) **High non-linear coefficient** values ranging from 10 to 100 which is important for fast response and better protective function.
- (b) Sharp switching voltage with no hysteresis, that is the current-voltage characteristic is **reversible**.
- (c) High energy-absorption capability with energy density up to 300 J/cm^3 .
- (d) **Low power loss** of only $10 100 \text{ mW/cm}^3$.
- (e) Fast response to over-voltage transients.
- (f) Gapless design, making ZnO varistors compact.
- (g) Small sizes with various geometries.
- (h) Long life span under hostile environments of more than 10 years.

- (i) Highly versatile with applications from low-voltage range up to mega-volt range applications.
- (j) **Low price** of less than RM0.10 per piece if bought in bulk

2.3 <u>ELECTRICAL TRANSIENT SURGES</u>

Transients, or surges, are **sudden pulses of over-voltage** in electrical circuits which last a **very short time** from microseconds up to milliseconds duration [1, 2,15] .Over-voltage transients are voltage pulses with peak voltage values that exceed the circuit steady-state voltage by more than 10%; therefore, if the steady-state operating voltage is 20 volts, then an over-voltage event should be more than 22 volts. In general, the transient over-voltages are followed by a rise in current. Electrical transients are caused by sudden release of stored energy in circuit **inductance and capacitance** [1,6]; which means circuits which contains inductors and capacitors are highly susceptible to transients.

In view of economic concern, over-voltage transients cause power system **disturbances** which can result in huge losses of about **RM 30,000** per year for a medium-sized factory in the USA [1]. Power disturbances can create power failures that result in loss of product output and big downtime because electrical machineries need about 4 hours to re-start and re-stabilise. Moreover, affected factories cannot meet customer orders in time and they lose business. TVSS devices

such as ZnO varistors play a major role in preventing these power disturbances from causing power failures.

Electrical transients may be repeatable or random.

(i) Repeatable transients are predictable, easily studied and suppressed. Causes of repeatable transients are commutation voltage spikes, inductive load switching and transformer primary circuit switching. Figure 2.6 shows an example of repeatable transient. Repeatable transients can be quite severe because they can be as high as ten times the operating voltage [6] and if these bursts of energy enter semiconductor devices, chances are the devices will be damaged. Common energy levels of these transients range from a millijoules up to a few joules. Energy discharges of a few joules may look like sparks coming from a welding process.



Figure 2.6: Example of repeatable transient over-voltage.

Another common predictable transients are **automobile transients** caused by inductive loads such as alternators, motors and solenoids. Abrupt changes in these inductive loads can create transient overvoltages as high as 100 volts lasting up to 500 ms [6], eventhough the car battery operate at only 12 volts. Low-voltage varistors play an important role in automotive surge protection because the varistor action must be triggered at a low voltage of about 14 volts.

(ii) Random transients, which are unpredictable, normally originate from the power supply units that supply power to electrical circuits. The amplitude, duration and energy content of random transients are difficult to analysed. Common causes are due to lightning and power system faults. Due to their unpredictability, random transients may have peak amplitudes from hundreds of volts to hundreds of kilovolts and duration from microseconds up to a few second. Since Malaysia possess among the highest cases of lightning strikes, random transients become more menacing than other parts of the world. If a lightning struck a ground area where underground power cables and telecommunication lines are located, then high voltage transients can be **induced** between the internal conductors and the insulating layer. This over-voltage induction is due the immense level of electro-magnetic (E-M) wave generated by the lightning strike. Lightning transients may travel to houses and offices; and if the houses or offices do not have TVSS, then electrical equipments

may be damaged or even may catch fire. Figure 2.7 illustrates how a lightning can cause random transients.



Figure 2.7: Illustration of random transient due to lightning strike.

2.4 EFFECTS OF OVER-VOLTAGE TRANSIENTS

(i) Effects on Semiconductors

Semiconductor devices such as integrated circuits (ICs) are not tolerant toward over-voltage transients. Even a few microseconds of transient can cause ICs to fail. Normally the transient exists as a large reverse voltage that is applied to a non-conducting PN junction [16]. Due to localised build-up of electric field, the PN junction may avalanche at the localised point which results in thermal runaway; thermal runaway is a melt-through which destroy the junction due to localised heating build-up. If the PN junction is not destroyed, it may still function but with degraded performance in the form of lower gain and higher leakage current.

(ii) Effects on Electromechanical Contact

Over-voltage transients due to capacitance discharges and recharges can cause **repeated arcings** across the air gaps of electromechanical contacts. Inductive circuit switching can also be another culprit that causes contact arcings. The very high energy at very high over-voltage of about 10,000V/cm [6] at the contact gaps can cause melting, oxidation and burning of the metallic contacts. As a consequence, the electromechanical contacts up.

(iii) Effects on Insulation

Organic insulation such as PVC, which is normally used for wire insulation, is vulnerable to **breakdown** by transient over-voltages. The high resistivity of the insulation combined with the high voltage transients can generate a lot of heat inside the insulation, as presented by the power equation [6,7,15]

$$\mathbf{P} = \mathbf{V}\mathbf{I} = \mathbf{I}^2 \mathbf{R} \quad \text{in watts}$$
 (2.1)

whereby P = dissipated power (W) V = potential difference across a material (V) I = the current flowing through the material (A) $R = the resistance of the material (\Omega)$

If the heat dissipation, P, is high enough to raise the temperature of the insulation up to 250° C, then local carbonisation of the organic material can occur. And if the temperature is raised further up to 400° C, the organic material can burn and cause a fire. Over long usage, the insulation exposed to repeated transients can degrade until it almost loses its insulative capabilities; this phenomenon may eventually cause short-circuiting that can also cause fire. This is one of the reasons why the wiring of old houses of more than 20 years must be replaced with new ones.