



**UNIVERSITI PUTRA MALAYSIA**

***FABRICATION OF ZINC OXIDE LOW VOLTAGE VARISTOR CERAMICS  
ADDED Bi, Ti, Sb, AND Al BY CONVENTIONAL AND SOLUTION  
COATING METHOD***

**RAHELEH MOHAMMADI**

**FS 2018 51**



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SOLUTION COATING METHOD**

By

**RAHELEH MOHAMMADI**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,  
in Fulfillment of the Requirements for the Degree of Master of Science**

**September 2017**

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## DEDICATION

*To my beloved family who have been patient and caring supporting me throughout  
this journey with their endless love*

*This thesis is dedicated to  
my beloved husband  
and  
parents  
who support me with their  
endless love to carry out my education.*



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

**FABRICATION OF ZINC OXIDE LOW VOLTAGE VARISTOR CERAMICS ADDED Bi, Ti, Sb, AND Al BY CONVENTIONAL AND SOLUTION COATING METHOD**

By

**RAHELEH MOHAMMADI**

**September 2017**

**Chairman : Raba'ah Syahidah Azis, PhD**  
**Faculty : Science**

The Zinc Oxide (ZnO) based varistor ceramics, an electrical protective device from transient voltage surge, have become technologically important because of their highly nonlinear electrical characteristics enabling them to be used as reversible, solid-state switches with large-energy-handling capabilities. The aim of the present study is to optimize the soaking time, in order to maximize an electrical non-linear coefficient ( $\alpha$ ) of the varistor ceramics fabricated by the conventional ball milling, and the solution coating methods. In addition, the electrical property and microstructure of Bi<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Sb<sub>2</sub>O<sub>3</sub> additives in (ZnO) based varistor ceramics at the various soaking time. In preparing the ceramic by the solution coating method, bismuth oxide, titanium oxide, and aluminium oxide were prepared by from bismuth nitrate, titanium botoxide, and aluminium nitrate, respectively. The electrical property, microstructure and thermal characterisation of the ceramic were carried out by J-E measurement, XRD, EDX, FESEM, FTIR, and TGA analyses. The results from initial powders show that homogenously mixed ZnO powder could be made readily by coating ZnO powder with a solution of additives. The varistor ceramics prepared from the solution coating method reveal a higher  $\alpha$  value and lower break down voltage than those provided by the ball milling routes. The improved J-E properties of varistor ceramic made by this methods could be attributed to the homogenous distribution of additives in the starting powder. The effect can produce a similar profile of additives distributions at each grain-grain boundary regions across the whole microstructure. Similar composition at each grain boundary region, which could be created uniform trapping centres that lastly resulted in the formation of the uniform potential barrier through the microstructure and consequently better electrical properties. As a comparative result of the technique of fabrication, the solution coating method has better homogenous. The maximum electrical property of the varistor ceramic was at

soaking time of 150 min (sintered at 1250°C) with the  $\alpha$  value around 16.38 and 10.73 for the solution coating and for the ball milling methods, respectively.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**FABRIKASI ZINK OKSIDA SERAMIK VARISTOR VOLTAN RENDAH  
DITAMBAH Bi, Ti, Sb, DAN Al OLEH KAEDAH KONVENSIONAL DAN  
SALUTAN LARUTAN**

Oleh

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Seramik varistor berasaskan zink oksida (ZnO) merupakan peranti pelindung elektrik daripada lanjutan voltan sementara menjadi teknologi yang penting kerana ciri-ciri elektrik taklinear yang tinggi membolehkan ia digunakan sebagai boleh balik, suis keadaan pepejal dengan keupayaan pengendalian tenaga yang besar. Kajian ini bertujuan untuk pengoptimuman tempoh pensinteran, bagi memaksimumkan pekali tak linear elektrik ( $\alpha$ ) seramik varistor yang difabrikasi oleh konvensional pengilangan bola, dan kaedah salutan penyelesaian. Tambahan lagi, ciri-ciri elektrik dan mikrostruktur  $\text{Bi}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  dan  $\text{Sb}_2\text{O}_3$  aditif dalam seramik varistor berasaskan ZnO pada pelbagai tempoh penyimpanan. ke atas produk pembuatan menggunakan pengisar dan kaedah salutan larutan yang serupa, tetapi dengan kaedah fabrikasi yang berbeza. Dalam menyediakan seramik dengan kaedah salutan larutan, bismut oksida, oksida titanium, dan aluminium oksida telah disediakan oleh daripada bismuth nitrat, botanoksida titanium, aluminium nitrat, masing-masing. Ciri-ciri elektrik, mikrostruktur dan terma seramik telah dilakukan melalui pengukuran J-E, dan analisis-analisis XRD, EDX, FESEM, FTIR, TGA. Hasil dari serbuk awal menunjukkan bahawa serbuk ZnO campuran homogen dapat dibuat yang sedia ada dengan menggunakan serbuk ZnO salutan dengan larutan aditif. Seramik varistor yang disediakan dari kaedah salutan larutan mendedahkan nilai  $\alpha$  yang lebih tinggi dan voltan pecah yang lebih rendah daripada yang disediakan oleh laluan pengilangan bola. Peningkatan ciri-ciri J-E seramik varistor oleh kaedah ini boleh dikaitkan dengan pengedaran homogen dopan dalam serbuk permulaan. Kesannya dapat menghasilkan profil yang sama pengedaran aditif pada setiap regangan sempadan bijian-butir di seluruh mikrostruktur. Komposisi yang sama di setiap sempadan bijian, yang boleh diwujudkan di pusat penangkap seragam yang akhirnya menghasilkan pembentukan potensi penghalang seragam melalui struktur mikro dan akibatnya sifat elektrik yang lebih baik. Sebagai hasil komparatif teknik fabrikasi, kaedah salutan

larutan mempunyai homogen yang lebih baik. Ciri elektrik maksima seramik varistor adalah pada tempoh pensinteran 150 min (pada suhu 1250 °C) dengan nilai  $\alpha$  sekitar 16.38 dan 10.73 untuk kaedah salutan larutan dan pengilangan bola, masing-masingnya.





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Above all, I would like to thank my family members, especially, my husband Seyyed Alireza Kaboli Mallak and my children Nika and Karina as well as my parents and my wonderful sister Ghazaleh who supported me, both spiritually and financially during the entire study process.

I certify that a Thesis Examination Committee has met on 4 December 2017 to conduct the final examination of Raheleh Mohammadi on her thesis entitled "Fabrication of Zinc Oxide Low Voltage Varistor Ceramics Added with Bi, Ti, Sb and Al by Conventional and Solution Coating Methods" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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## LIST OF ABBREVIATIONS AND SYMBOLS

### Abbreviation

XRD	X-ray diffraction
min	minute
h	hour
<i>I-V</i>	Current-Voltage
XRD	X-ray diffraction
PVA	Polyvinyl alcohol
J-E	Current density-electric field
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive x-ray analysis
VPSEM	Variable Pressure Scanning Electron Microscopy
MOV	Metal Oxide Varistor
DC	Direct current
AC	Alternating current

### Symbol

$\alpha$	Nonlinear coefficient
$V$	Voltage
$I$	Current
$K$	Material constant
$^{\circ}\text{C}$	Degree Celcius
$I_1$	Current at 1 mA
$I_2$	Current at 10 mA

$V_1$	Voltage corresponding to $I_1$
$V_2$	Voltage corresponding to $I_2$
$S$	Total surface area
$t$	Thickness
$W_{\text{air}}$	Mass in air
$W_{\text{water}}$	Mass in water



## CHAPTER 1

### INTRODUCTION

#### 1.1 Background Information

In this study, the Zinc Oxide (ZnO) varistor and relative parameters and elements are offered. Congruently, finding conducted in (Clarke, 1999) has revealed that Varistor ceramics develop technically significant since of their extremely nonlinear electrical characteristics allowing them to be used as reversible, solid-state changes with large-energy-handling abilities. Although this is including the application of ZnO, hence what makes them high demand and become the focus of interest of many research groups in the field of ceramic devices. The basic operation of ZnO varistor concern of how it works as electronic devices in the field of circuit overvoltage protection has been discussed. Lastly, research problems, the scope of research and objective of this present research work have been mentioned in this section. Additionally, the varistor ceramics were used as a protective device to detect and clamp transient voltage surge of unwanted magnitudes. Unwanted over-voltage transient surges normally refer to damaging voltage transients that exceed more than 10% of the operating voltage of the equipment being protected (Matsuoka, 1971). Their popularity is rapidly increasing due to high non-linearity exponent (Inada, 1980; Matsuoka, 1971).

Currently, the electronic components and coordination developed regularly in a minor size and lightweight and with high frequency and reliability. Nonetheless, as a result, overall insulating strength is decreased. So, in the most cases, the varistor absorbs these unsafe surges, before they try to get reach the circuitries of the electrical equipment, which is being protected. Moreover, in some other cases, the varistor absorbs and redirects the overvoltage surges to the ground. Figure 1.1 illustrations several commercial ZnO varistor ceramics of various sizes and models

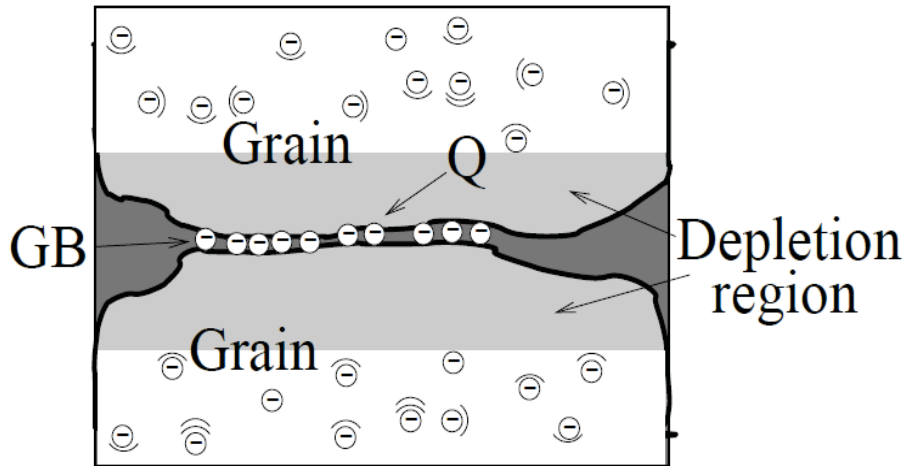


Figure 1.1 : Commercial ZnO Varistor (Mahmud, 2004)

By using their non-linearity property which depends on the varistor microstructure the assessment of the varistor ceramics will be carried out. A study conducted (Inada, 1980) the varistor ceramics microstructure are the polycrystalline material composed of ZnO grains with their attendant grain boundaries. There is non-linearity relation between the voltage, and the current is typically expressed regarding a power-law:  $I \propto V^\alpha$ . As the  $\alpha$  is nonlinear constant, inherent parameter of varistor ceramics representing the degree of nonlinearity of transmission,  $V$  is the voltage over the varistor, and  $I$  is the current through the varistor in the breakdown region. Greater the value of  $\alpha$ , better will be the device, which explains why  $\alpha$  is occasionally used as a symbol of merit (Gupta, 2005; Inada, 1980). Most of the previous works have been reviewed in Chapter 2.

## 1.2 Introduction of ZnO Varistor

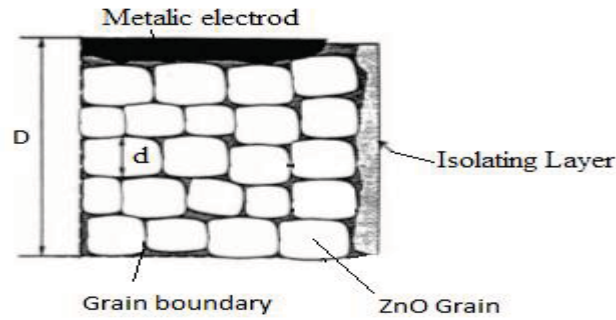
ZnO varistor ceramics are categorized as ceramic semiconductor devices. They illustrated an extreme nonlinear performance concerning current-voltage so, it will be used in electrical circuits and electronic devices as an over-voltage surge protection. Laterally with the rising demands of very-large-scale integration electronics, application of low-voltage ZnO varistors are now being attracted more attention (Abdullah, 2012). The non-linearity properties of ZnO varistor is expressed by  $I = KV^\alpha$  as known  $K$  is a constant, and also ' $\alpha$ ' is nonlinear coefficient (Wang, 2004). The study by Wang in 2008 has shown that the non-linear typical is also recognized for the formation of double Schottky barriers at the ZnO grain boundaries. Metal oxides in powder form and in different number and also the mixture are treated by liquid stage sintering to become in the form the final varistor. ZnO is the key element in the oxide mix, and also  $\text{Bi}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  are additives which improve the efficiency of the visitors. This improvement is named liquid phase sintering meanwhile, at the temperatures of the 1000-1300°C the metal oxide mixture is heated. Besides, the additives melt at these temperatures however the ZnO grains stay crystalline oxides through the sintering. It is the fact that conduction electrons close to the grain boundaries will attract to and trap in certain electron states (Leach, 2005; Peiteado, 2007). These are called interface states and are located in the grain boundaries as is indicated in Figure 1.2.



**Figure 1.2 : Sketch of the charge distribution in the vicinity of a grain boundary. Q is the charge trapped in the localized states in the grain boundary, and the shaded area is the depletion region. (Carlsson, 2002)**

Congruently, in accordance with Double Schottky Barrier (DBS) model, the evacuation region acts in the role of an obstacle for the electron present across the grain borders, since there are not any free transmission electrons, which are able to hold the electron stream from one grain to another. Trapping of electrons in a grain border is dependent on the voltage. Since the electrons start to get enough energy from the applied field to leave the interface states at a critical voltage. The barrier disappears, and the conduction electrons can maintain an electron flow also in the grain boundary region (Carlsson, 2002). The existence of potential barriers, in turn, creates critical voltages for breakdown per boundary and the total breakdown voltage of the device becomes proportionate to the number of such grain boundaries between in two electrodes (Banerjee, 2001). Furthermore, the study by (Levinson and Philipp, 1986), have shown that the schematic of Figure 1.3, it is obvious that the electrical features of ZnO varistors will be associated to the bulk of the material. This inherently multijunction feature of varistor cause its action shared between the different ZnO grain boundaries





**Figure 1.3 : Schematic of the microstructure of ZnO varistor** (Meshkatoddini, 2011)

Which indicated that the breakdown voltage,  $v_B$  is a matter of constructing a varistor related to the number of grains,  $n$ , is the sequence between the electrodes as the relation;

$$v_B = n v_g = \frac{D v_g}{d} \quad (1-1)$$

where  $d$  is the ZnO grain size,  $D$  the electrode spacing, and  $v_g$  is the breakdown voltage per grain boundary

Therefore, to attain a given breakdown voltage one could alter the varistor thickness and another one could change the grain size (for the device thickness constant). ZnO varistor ceramics are produced by sintering of ZnO powders with small amounts of other additives such as  $\text{Bi}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ , and  $\text{Sb}_2\text{O}_3$ . A common varistor ceramic consists of around 97 mol% of ZnO, and regarding (Matsuoka, 1971), the balance contains oxides of the bismuth, cobalt, aluminium, titanium manganese and antimony. Microstructurally, the sintered material is made of highly conductive ZnO grains with two major secondary phases: a spinal-type phase and a Bi-rich phase which is located at the grain boundaries which have strictly effect on nonlinear current-voltage characteristic (Zhang, et al., 2002). The microstructure of an ideal varistor has uniform grain size, shape and composition; minimal porosity and a uniform distribution of secondary phases (Puyane et al., 1996). These properties and in particular compositional homogeneity, are difficult to achieve by conventional routes. Thus, enhanced electrical properties could be achieved by using a more advanced processing technique such as nano-technology to approach the ideal ceramic detailed above. Nano-origin varistor powders with the high degree of homogeneity in additives distribution have been attempted through a variety of chemical techniques like coprecipitation, sol-gel, microemulsion and polymerized complex method (Anas et al., 2010; Wang et al., 2008). Nevertheless, the majority of these methods are complex and high- priced, or not proper for the manufacture of low voltage ZnO varistors

(Wang et al., 2008). In this excavation, researcher considers this issue and solves it by a newfound technique which is called nano-coating.

Due to the fact that there are some electrostatic potential obstacles inside the ZnO grains in the depletion layers nearby the grain boundaries, ZnO varistor ceramics show a very high level of resistivity. Consequently, ZnO varistor ceramics are well-designed for use in protection of electric power lines as valve elements of lightning arresters or protection of electronic components over-voltage as surge absorbers. Also, an important suited applicability of ZnO varistor ceramics is in high-voltage resolutions. Besides, huge amounts of low-voltage varistor ceramics will be used in joined circuits and automobiles to protect surges. This emphasis that, the breakdown voltage of ZnO varistor is related to the number of ZnO grains among the electrodes. So, the varistor is obtained either by decreasing the thickness of the specimen or by increasing the size of ZnO grains (Wang et al., 2006).

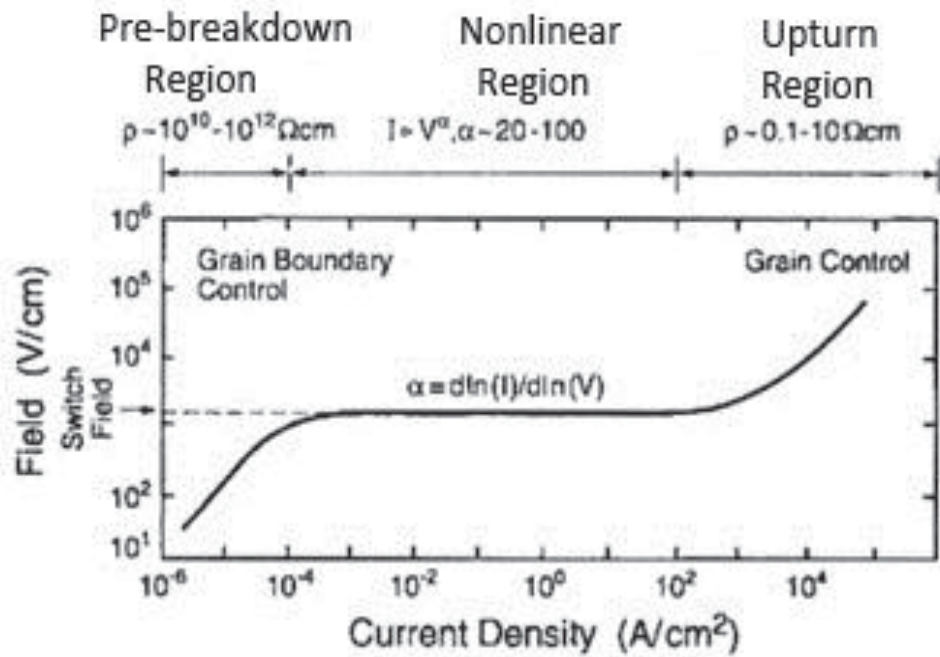
The ZnO varistor ceramics are mostly used in leveling the transient voltage peaks (i.e. unexpected increase in voltage). A lightning strike, electrostatic discharge, inductive switching and other severe damages to electronic devices and types of equipment may cause bypassing of a high transient voltage through them. Thus, components should be connected near to the protected devices to have the most favorable performance. The voltage level will be cut to its protective level when the transient voltage passes via a varistor, so the function of the machine or other types of equipment will be continued in non-destructive voltage levels.

Generally, in the case of encountering a voltage lower than the switch voltage, merely low leakage current will be permitted through the high impedance level at grain boundaries. In the case of higher voltages than the switch voltage, for example, a voltage transient or arise, the varistor resistance will be decreased rapidly which prevents surges current reaching to the protected elements and returning the varistor to its previous state after performing at a high level. Hence, the varistor has always functioned below the voltage; nevertheless, it operates as a very high resistance passive element when the voltage peaks do not happen.

### **1.3 Nonlinear Current-Voltage Characteristics**

ZnO varistor is ceramic semiconductors devices that have great nonlinearity in their current-voltage behavior, and therefore, are broadly utilized for electronic devices (Wang et al., 2008). In doped ZnO varistor the nonlinear the relationship between the electric current and the corresponding voltage is called the current-voltage characteristic that is typically responded by a graph. I-V graph is also known as J-E graph; current is responded by the current density  $J$  ( $A/cm^2$ ) while voltage represented by electric field  $E$  ( $V/cm$ ). Figure 1.4 illustrates the three major areas in the J-E curve of the ZnO varistor ceramics. Good varistors are described by high  $\alpha$  in the non-ohmic region (Banerjee et al., 2001). The non-linear response originates on its polycrystalline

microstructure and more precisely in detail through procedures happening at the grain/grain interfaces (Peiteado, et al., 2007). Furthermore, the nonlinear current-voltage (J-E) characteristic is the most important properties of ZnO varistor. Owing to this unique feature of ZnO varistor ceramics, they are broadly used as electronic devices protection adjacent to voltage surges.



**Figure 1.4 : Nonlinear Current-Voltage Characteristics Regions on ZnO Varistor Ceramics (Clarke, 1999)**

### 1.3.1 Pre-breakdown zone

The low current linear region, below the threshold voltage ( $10^{-4} \text{A/cm}^2$ ) or can be defined as the pre-breakdown region, and J-E characteristically is linear. The AC current is higher in magnitude than DC contemporary for a specified given functioning voltage. The dissimilarity can be imputed to the chip in the insulator mislaying on the application of AC voltage. The J-E feature in this area is extremely dependent on the temperature (Eda, 1989) and determined by the impedance of the grain boundaries in the ZnO microstructure.

### 1.3.2 Non-linear Zone

The intermediate nonlinear zone between the entry voltage and a voltage at the moment is  $10^{-3}-10^3 \text{ A/cm}^2$  (breakdown region). In this current-voltage region, the ZnO varistor acts as a very good conductor and also as a very effective power surge absorber. As illustrated in Figure 1.4, the J-E graph, the flat plateau of the graph refers to the switched region. The flatter the plateau the better the protective function of the

varistor. Besides, the electrical properties of ZnO varistor are reversible after being exposed to over-voltage transient surges, or in other words, the electrical characteristics in comparison before and after the gush exposure stay same (Clarke, 1999). This means that the ZnO varistor can be exposed to millions of transients without experiencing any degradation or worsening as long as the transients are within the switched region. This non-linear region is the most important feature of a ZnO varistor. Moreover, the device conducts an increasingly a large amount of current for a small increase in voltage (Eda, 1989).

### 1.3.3 Upturn Region

The top of a present linear region in above is almost  $10^2$ - $10^3$  A/cm<sup>2</sup> which is known as an upturn region, and the J-E features are linear and it is almost similar in the low going region too. It should be considered the voltage flourishing quicker in comparison to the nonlinear region which is control by the resistance of the grains at ZnO microstructure.

### 1.4 Nonlinear Coefficient

ZnO varistor ceramics have been widely used as surge arresters because of their desired non-ohmic properties. This non-ohmic property's degree is declared by a nonlinear coefficient  $\alpha$  where it is defined as a slope of the graph of log current density (log J) versus log field strength (log E). Thus,

$$\alpha = \frac{\log J}{\log E} \quad (1.2)$$

where J is current density, E in this equation shows the field strength across. The equation above can be simplified to get the value of  $\alpha$  as follows:

$$\alpha = \frac{\log J_2 - \log J_1}{\log E_2 - \log E_1} \quad (1.3)$$

where  $J_1$  and  $J_2$  are current densities and  $E_1$  and  $E_2$  are electric fields in line with  $J_1$  and  $J_2$  respectively. Current (I) and voltage (V) can also be used in place of current density (J) and electric field (E), but the resultant values for  $\alpha$  are the same if both parameters are used (Bui, et al., 1995). Therefore, it makes no difference using either a J-E parameter or I-V parameter. It is always desirable to get the highest possible value of  $\alpha$ . This helps in protecting the electrical and electronic devices from the surge currents because of overvoltage. The  $\alpha$  of ZnO varistor ceramics ranges up to 100 compared with other varistor materials. This property makes zinc oxide the best choice for surge protection. Since, the older materials used in varistor ceramics such as silicon

carbide (SiC) and selenium (Se), do not exhibit the value of  $\alpha$  over 10. This high value of  $\alpha$  makes ZnO ceramics highly effective transient voltage protection devices.

### **1.5 Double Schottky Barrier Model**

The Schottky Barrier theory has information at the interface of ZnO semiconductor was developed by Walter Schottky material. In addition, calculations based upon the reported values of grain-boundary potentials indicate that the thermionic emission theory may be applied to the majority-carrier transport only for low bias voltages (Card & Hwang, 1980). The study conducted in Werner and Peisl (1985) have shown that Double Schottky Barriers (DSB) are created are between two layers of grain boundaries it happens when common carriers are narrowed at the edge grain boundaries. To understand the elements phenomena of polycrystalline semiconductors is the type of vacancy lattice defectiveness is a care factor element of Schottky defect which is the primary basis of the DSB model.

### **1.6 Low-Voltage Varistors**

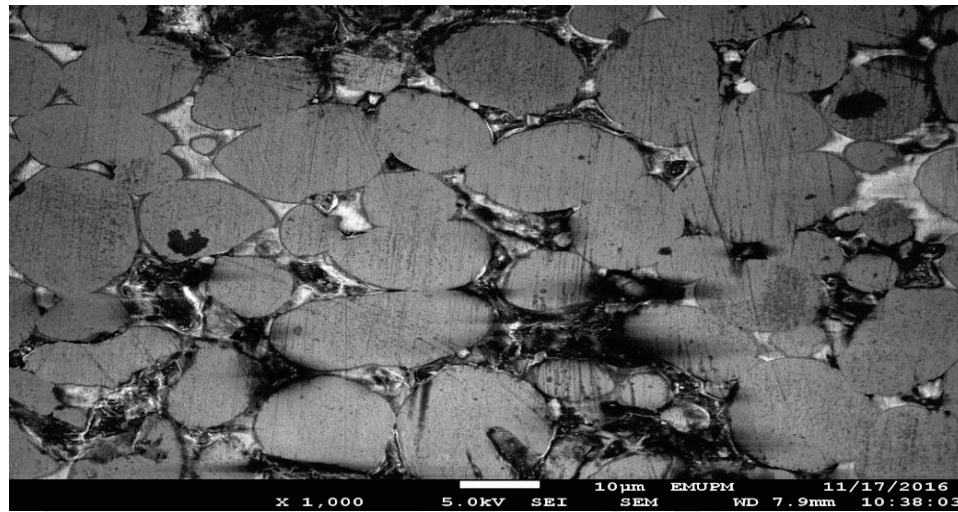
While much of varistor growth directs toward high-voltage applications, and also increase number of varistors are being used for low-voltage applications, such as in automobile electronics and semiconductor electronics. Because the switching voltage of an individual grain boundary in ZnO varistors is about 3.7 V, low-voltage varistors are typically only a few grains thick. This places severe constraints on microstructural uniformity in the manufacturing process. Two principal approaches have been used for making low-voltage varistors. One approach is the classical approach of selecting additives that encourage grain growth and, in some cases, exaggerated grain growth. The other is to adopt the approach used in making multilayer capacitors, namely, making thin layers by a process such as tape-casting and then stacking up the layers with interdigitated electrodes. Although the multilayering approach is the more suitable for high-volume manufacturing, the large number of metal/ceramic interfaces leads to an increased high-frequency capacitance that may be undesirable. An intrinsic feature of low-voltage varistors, made by either method, is their sensitivity to microstructural disorder. Much of this sensitivity results simply because of the smaller total number of grains between the electrodes.

### **1.7 General Microstructure of ZnO Varistor**

During the sintering of ZnO powder, which is doped with small amounts of additives such as  $\text{Bi}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ , the microstructural behavior of the varistor will be developed. In the sintering process, a few compositions which are ZnO grains, spinel ( $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ ), pyrochlore ( $\text{Zn}_2\text{Bi}_3\text{Sb}_3\text{O}_{14}$ ) and bismuth-rich phases are formed.  $\text{Bi}_2\text{O}_3$ -rich and  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$  can be found at the boundaries of the ZnO grain, while a  $\text{Zn}_2\text{Bi}_3\text{Sb}_3\text{O}_{14}$  existence is possible as well. The main contributing factors in varistor



effect are ZnO-ZnO grain boundary and highly resistive phase in bismuth-rich, whereas, the spinel-ZnO junction has no effect on the nonlinear characteristic.



**Figure 1.5 : General microstructure of the ZnO varistor**

The general microstructure of ZnO varistor ceramics is shown in Figure 1.5. ZnO grains which form about 90% of the content volume, the boundaries of the grains, triple junctions and the secondary phases include spinel, pyrochlore and bismuth phases which are the major components of the ZnO based varistors.

## **1.8 Role of Additives**

Additives can easily fill the empty sites in the structure of the ZnO, which are many in its lattice. Consequently, external defects are formed by external sources. There are three chief functions for additives: controlling the grain growth during the sintering process, affecting the re-wetting feature of the liquid phase during the cooling process and adjusting the electronic defect statuses. According to Clarke, 1999; Gupta, 1992; Matsuoka, 1971 and Lagrange, 1991, additives are categorized concerning their contributions as it is listed below:

### **1.8.1 Varistor Formers**

For forming the charged depletion layers of the varistor ceramics which shape the main action of them, varistor formers which are metal oxides additives are needed to be added in varistor ceramics. Bismuth oxide can be an example of these additives. Oxygen diffusion path provision for grain boundary formation facilitation is possible through bismuth oxide (Elfwing et al., 2000). Because of the bismuth oxide larger ionic radius, it inclined to be separated to the grain boundaries which results in the non-ohmic feature of the ZnO varistor ceramics.

### 1.8.2 Varistor Enhancers

Since the early 1970's, the solid-state varistor has been the dominant surge protection device in the electronic marketplace. In order to improve the non-linear J-E feature of the varistor ceramics and to enhance the energy handling capability of the varistor ceramics, which is for overcoming multiple overvoltage e surges, varistor enhancers are employed. Titanium and aluminium oxides are examples of this group of additives. These additives that are placed in the category of additives fill the empty spaces in the ZnO structure for optimizing the grain resistivity characteristic. Grain resistivity is for reducing the heat dispersal and for improving the energy handling capability. Also, for enhancing the trap state density of the depletion layers, these additives can be used as donors.

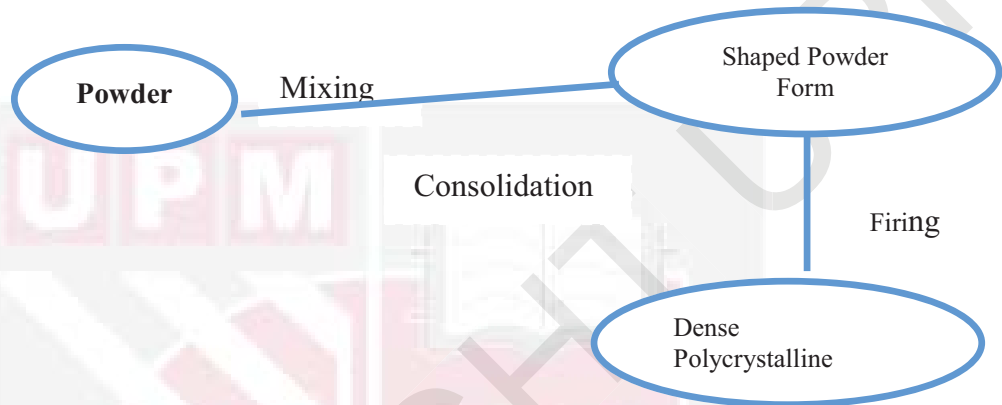
### 1.8.3 Varistor Highlighters

By the use of some additives, the stability of varistor will be enhanced. These additives are used for reducing the degradation effects of the varistor ceramics. As an instance, antimony trioxide provides stability for commercially produced ZnO varistor. The number of grain boundaries, which is the same as a number of the potential barrier across the terminals of the varistor, can be reduced by grain growth. This causes both the lower voltage terminals and the varistor as a low voltage model in our case. Titanium oxide is a good example for grain growth enhancers. Using more types of additives will result in a better nonlinearity and a higher terminal voltage.

There are other additives such as Al in the group of monovalent and trivalent additives, which also has an impact on the form of the potential barriers as well as the J-E features of the varistor by playing the role of the donors or acceptors in ZnO. Typically, ZnO varistor ceramics which are produced for commercial use are made of four primary additives which are  $\text{Bi}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{Sb}_2\text{O}_3$  together with other additives for controlling the size of the grains, the resistivity of the ZnO and the stability of the ZnO (Eda, 1989). This current, study focus on  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  as an additive of ZnO. Fabrication of Polycrystalline Ceramics from Powders. Because of its extremely nonlinear J-E feature, the varistor works instead of an open flow up to the voltage put into trespass a feature for breaking down the voltage, bringing about the varistor to become a low opposition to the current path. The fabrication of ceramics from powder is illustrated in Figure 1.6.

Most instances, the construction procedure begins with condense of the powder received from trading sources. Despite that, understanding of powder mixture methods is very significant. Moreover, determining the methods for finding out the chemical as well as physical features of the powder are vital too. Powder characteristics strongly depend on the techniques used to produce it, which in turn influence the impact of subsequent ceramic processing. Details are given in Section 1.4. Combining the ceramic powders for making a grain boundary is universally alluded to as forming. The primary set-up way contains the dry or semi-dry powder which is pressed. The

grain boundary microstructure is discovered as a significant factor which impacts on the following firing stage. If intense transformations in packing density happen in grain boundary and afterwards, it is in the conventional firing status, the created the grain boundary usually attain a heterogeneous and diverse micro structure which restricts the features and validity. When consolidation happened, the green grain boundary will be heated to make reference microstructure. The changes which are happening during this stage will be in fact very complicated, depend on the adversity of the trigger materials. (Rahaman, 2007).

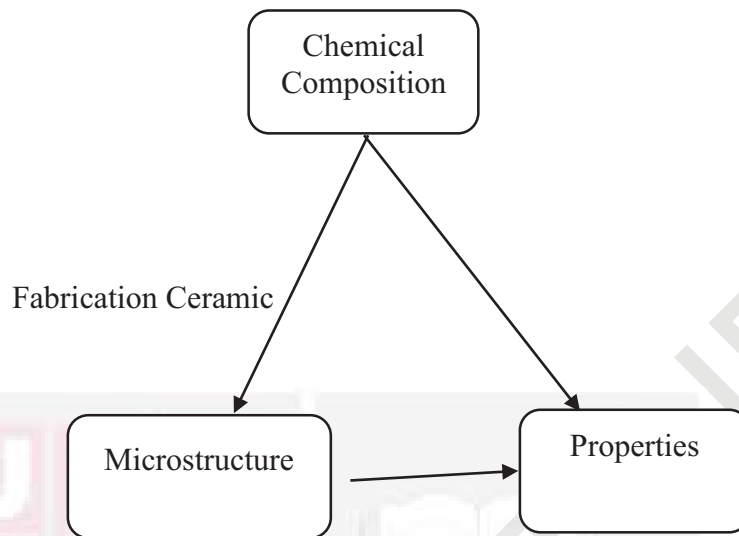


**Figure 1.6 : Basic flow chart for the production of polycrystalline ceramics by firing of consolidated powders. (Rahaman, 2007)**

## 1.9 Synthesis of Powders

The characteristics of the powder have a remarkable effect on subsequent processing, such as consolidation of the powder into a grain boundary and firing to produce the desired microstructure. The significant relations between atomic structure, chemical composition, microstructure, fabrication, and properties of polycrystalline ceramics are illustrated in Figure 1.7. As a result, powder synthesis is very important to the overall fabrication of ceramics. The desirable characteristics that a powder should possess for the production of successful ceramics are explained in the next topic (Rahaman, 2007).





**Figure 1.7 : The important relationships in ceramic fabrication**

### 1.10 Desirable Powder Characteristic

Advanced ceramics must meet very specific property requirements, and therefore their chemical composition and microstructure must be well controlled. Advanced ceramics include ceramics for electrical, magnetic, electronic, and optical applications. Careful attention must be paid to the quality of the starting powders. For advanced ceramics, the important powder features are the size, size distribution, shape, state of agglomeration, chemical composition. These properties have a significant influence on both the powder consolidation stage and the microstructure of the fired grain boundary. The most profound effect of the particle size, however, is on the sintering. The rate at which the grain boundary densifies increases strongly with a decrease in particle size. Normally, if other factors do not cause severe difficulties during firing, a particle size of less than  $\sim 1\mu\text{m}$  permits the attainment of high density in a sensible time. Homogeneous packing of a narrow size distribution powder allows greater control of the microstructure. Agglomerates result in heterogeneous packing in the grain boundary that, in turn, result in differential sintering during the firing stage. Differential sintering occurs when diverse areas of the grain boundary shrink at diverse rates (Ma and Li 2002; Rahaman, 2007). This can lead to serious problems such as the development of large pores and crack-like voids in the fired grain boundary. Surface impurities may have a significant influence on the dispersion of the powder in a liquid, but the most serious effects of variations in chemical composition are encountered in the firing stage. Impurities may lead to the formation of a small quantity of liquid phase at the sintering temperature, which causes the selected growth of the major individual grains. In such a case, the achievement of a fine uniform grain

size would be impossible (Rahaman, 2007). To summarize, the desirable powder characteristics for the fabrication of advanced ceramics are listed in Table 1.1.

**Table 1.1 : Desirable Powder Characteristics for Advanced Ceramics**

Powder characteristic	Desired property
Particle size	Fine ( $< \sim 1\mu\text{m}$ )
Particle size distribution	Narrow or monodisperse
State of agglomeration	No agglomeration or soft agglomerate
Chemical composition	High purity

### 1.11 Sintering Process

The action of compacting objects from the powder employing heating till sticking its particle together is called sintering. It also can be defined as a method of density-controlled components production from metal or ceramic powders by using thermal energy. The sintering process resulted from the era with the firing of property. A primarily and scientific study of the sintering process was started in 1940. The sintering, which was initiated with pottery and stoneware firing, was the human civilization emblem. According to (Mc Ketta, 1996), sintering is broadly used in producing useful parts from metal or ceramic powders these days. During the sintering process, the particles of the powder bond to each other and cause the matter transport occurrence, which results in a micro-pores elimination, higher density, and stronger pieces. A wide range of technological important products could be made by the sintering process. (Ristic, 1979) stated that, as the particles bond to each other throughout the solid-state atomic or molecular attraction, via heating which results in powder mass strength. It may also cause densification and recrystallization as a result of material transport. It is mentioned that the fundamental theory about the sintering was originated by Pines, Levensen, and Kuczynski back to nineteen century. Other researchers continued the previous research works. Their research and developments were still derived from the solid state atomic process, in which the physical basis of the sintering process still exhibits. Regarding Lee, 1994), sintering is removing the holes between initial atoms, together with component contraction, accompanied by growth and sturdy bond formation between adjacent particles. There are two types of sintering process: solid state and liquid phase sintering. To gain the former one, the ceramic that is comprised of ions must have the optimum pliability in the microstructure when the temperature is greater than about 80% of the melting point of the compound temperature. The latter one takes place in order for the texture elements to experience densification enhancement. In other words, the liquid phase sintering through dissolution and precipitation of the solid paves the way for a spontaneous mass transport.

### 1.12 Problem Statement

Technologically, the zinc-based varistor ceramics is the critical matter of producing quality electrical devices, because highly nonlinear electrical characteristics enable them to be used as reversible, solid-state switches with large-energy-handling capabilities. The main problem is that inhomogeneous microstructure of varistor ceramic has a negative impact on the current density-electronic field (J-E) characteristics; therefore, highly uniform nanoparticles with a narrow size distribution is required. Other problem of present study mention that in comparing the methods of fabrication variation such as ball milling and solution coating methods the time using has a significant result on non-linearity, which is face to weak research.

### 1.13 Objective of Current Study

The present objectives are to study the electrical property and microstructure of  $\text{Bi}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{Sb}_2\text{O}_3$  additive in ZnO based varistor ceramics at a various soaking time on fabricated by ball milling, and solution coating methods which are similar studies on varistor ceramic but different fabricated methods. Specifically the objectives are;

- 1) to determine the effect of electrical property and microstructure of  $\text{Bi}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{Sb}_2\text{O}_3$  additive in ZnO based varistor ceramics at various soaking time on fabricated by ball milling method,
- 2) to determine the effect of electrical property and microstructure of  $\text{Bi}(\text{NO}_3)_3$  Titanium butoxide  $\text{Al}(\text{NO}_3)_2$   $\text{Sb}_2\text{O}_3$  additive in ZnO based varistor ceramics at various soaking time fabricated by solution coating method.

### 1.14 Scope of Study

The current study reports the results of the ZnO based varistor ceramics prepared by ball milling, and solution coating methods at various soaking times with the small addition of additives such as  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Sb}_2\text{O}_3$ . J-E characterization of varistor ceramics for obtaining the electrical non-linear coefficient ( $\alpha$ ). Microstructure characterization of the ceramic was carried out by using X-ray diffraction (XRD), variable pressure scanning electron microscopy (VPSEM), and energy dispersive X-ray (EDX).

### 1.15 Hypothesis

The hypothesis is that the nano-solution coating method could be more efficient than the conventional method in increasing  $\alpha$ , because it provides the desired microstructures and consequently improved electrical properties. Hence by

manipulating the soaking time it is expected that the optimum grain size and non-linearity of varistor would be obtained.

The non-linearity coefficient ( $\alpha$ ) of ZnO varistor ceramic could be optimized by optimizing the soaking time.

### **1.16 Outline of Thesis**

The dissertation is organized in five chapters. The current chapter presents the background of the study, theoretical framework, problem statement, objectives and scope of the study, definition of key concepts, and outline dissertation. Chapter 2 reviews the literature on the fabrication of ZnO varistor ceramics, the effect of the sintering process on varistor ceramics. Chapter 3 will be devoted to the description of experimental design that has been used for fabrication of ZnO varistor ceramics. Chapter 4 explains the findings regarding fabrication and characterization of varistor ceramics. Lastly, Chapter 5 states the research conclusion.

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