UNIVERSITI PUTRA MALAYSIA

CORRELATION OF MICROSTRUCTURES WITH ELECTRICAL AND OPTICAL PROPERTIES IN ZINC OXIDE CERAMIC SEMICONDUCTOR

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By

WAN NORAILIANA BINTI WAN AB RAHMAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fullfillment of the Requirement for the Degree of Doctor of Philosophy

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Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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November 2016

Chair: Professor Azmi Zakaria, PhD
Faculty: Institute of Advanced Technology

Zinc oxide (ZnO) semiconductor is a polycrystalline ceramic exhibiting highly nonlinear (I-V) behavior. In polycrystalline ZnO materials, understanding and controlling the microstructure is very important since the electrical and optical band gap properties are directly influenced by the microstructure effect. The question about how the microstructural properties evolve with the electrical and optical properties in nanometer-to-micrometer grain-size region and what is the relationship of evolving microstructure properties with the physical properties of the ZnO has not been studied in depth. Hence, this research intend to explore the systematic study on parallel evolution from nanometere up to micrometer grain size between microstructure and material properties and the fundamental knowledge behind these parallel properties. Although there is numerous studies on the ZnO materials but the composition-microstructure relationship with the parallel evolution of the electrical and optical properties in nanometer-to-micrometer grain-size region have not yet been clarified. Doped-ZnO powders were milled using High Energy Ball Milling (HEBM) with different milling time. The doped-ZnO samples were sintered at two different ranges of sintering temperatures. The first range is from 500 until 1300 °C sintering temperatures with 100 °C increment for Batches A, C, D1, D2 and D3 samples. The second range is at lower sintering temperatures from 500 to 800 °C with 25 °C increment for Batch E samples. The phase purity of the samples were examined by XRD and the particle size distribution of the powder were observed using TEM. The surface morphology of the samples was examined using FESEM while the EDX measurement used to identify the elemental of the samples. The samples were characterized for the nonlinear coefficient (α) at room temperature using source measurement unit and for optical band gap energy, measurement was carried out by using UV-Visible spectrometer.

Decreasing particle size would lead to improved grain growth control and homogeneity for better electrical and optical band gap characteristics. The α value increased as the grain size increased while the optical band gap decreased with increasing grain size. The HEBM technique has succesfully produced good electrical properties due to the well-formed microstructure even at low-sintering temperature and improved grain boundary characteristics. The nonlinear I-V characteristic of doped-ZnO sample is a grain-boundary phenomenon, and the electrical characteristics of the samples are directly related to the size of the ZnO grain. The highest value of α was found is 8 at 1100 °C sintering temperature for Co-doped sample while for Mn-doped sample the α value was found to be 7 at 1100 °C sintering temperature. The increment of α value with grain size was due to the larger potential barrier at the grain boundaries as the sintering temperature increased from 500 until 1100 °C. At 1200 and 1300 °C sintering temperature the α value decreased due to the decrement of potential barrier at the grain boundaries. The decrement was due to the diminished of Bi-rich phase at high sintering temperature. The HEBM technique also produced samples with smaller particle size, giving rise to a systematic decrease of band gap value associated with quantum confinement. The band gap value for Co-doped sample were vary from 3.2 to 2.5 eV at nanograin size below 1µm. Higher value of band gap at nanograin size contributes by this confinement and as the grain size increased, the variation of band gap value was decreased due to the growth of interface states at the grain boundaries.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

KOLERASI ANTARA MIKROSTRUKTUR DENGAN SIFAT-SIFAT ELEKTRIKAL DAN OPTIKAL SEMIKONDUKTOR SERAMIK DI DALAM ZINK OKSIDA.

Oleh

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Zink oksida (ZnO) semikonduktor adalah polihabluran seramik mempamerkan sifat arus-voltan dengan nilai tak linear yang tinggi. Dalam bahan polihabluran ZnO, memahami dan mengawal mikrostruktur adalah sangat penting kerana sifat elektrik dan jurang jalur optik yang dipengaruhi secara terus oleh kesan mikrostruktur. Persoalan mengenai bagaimana sifat mikrostruktur berkembang dengan sifat elektrik dan optik dalam kawasan saiz butiran antara nanometer-kepada-mikrometer dan apakah hubungan yang melibatkan sifat mikrostruktur dengan sifat fizikal bahan ZnO masih belum lagi dikaji secara mendalam.Walaupun terdapat banyak kajian mengenai bahan ZnO namun hubungan antara komposisi-mikrostruktur dengan penjelasan evolusi selari sifat-sifat elektrik dan optik dalam kawasan saiz nanometer-kepada-mikrometer masih belum lagi dapat dijelaskan sepenuhnya. Serbuk ZnO yang didopkan telah dikisar menggunakan pengisar bebola berkuasa tinggi dengan masa pengisaran yang berbeza (HEBM). Sampel ZnO yang didopkan telah dibakar pada dua julat suhu pembakaran yang berlainan. Julat suhu pembakaran yang pertama adalah daripada 500 hingga 1300 °C dengan kenaikan suhu 100 °C untuk sampel kumpulan-kumpulan A, C, D1, D2 dan D3. Julat kedua ialah pada suhu pembakaran rendah, dari 500 hingga 800 °C dengan kenaikan suhu 25 °C untuk sampel kumpulan E. Ketulenan fasa sampel telah diperiksa oleh XRD manakala taburan saiz zarah serbuk diperhatikan menggunakan TEM. Morfologi permukaan sampel telah diperiksa menggunakan FESEM dan EDX digunakan untuk mengenal-pasti unsur di dalam sampel. Sampel tersebut telah dicirikan untuk pekali tak linear (α) pada suhu bilik menggunakan sumber unit pengukuran dan UV-Vis spektrometer digunakan bagi pengukuran tenaga jurang jalur optik. Pengurangan saiz zarah akan membawa kepada kawalan pertumbuhan butiran yang lebih baik dan homogen untuk ciri-ciri elektrik dan jalur jurang optik yang lebih baik. Nilai α meningkat apabila saiz butiran

meningkat manakala jalur jurang optik menurun dengan peningkatan saiz butiran. Teknik HEBM menghasilkan sifat elektrik yang baik kerana mikrostruktur telah dibentuk dengan baik walaupun pada suhu pembakaran yang rendah dan penambahbaikan pada ciri-ciri sempadan butiran. Ciri-ciri I-V tak linear oleh sampel ZnO yang didopkan adalah satu fenomena sempadan butiran, dan ciri-ciri elektrik sampel berkait secara langsung dengan saiz bijian ZnO itu. Bagi bahan yang didopkan-dengan Co, nilai tertinggi α ditemui adalah 8 pada suhu pembakaran 1100 °C manakala bagi bahan yang didopkan-dengan Mn, nilai α yang diperolehi ialah 7 pada suhu pembakaran 1100 °C. Peningkatan nilai α dengan saiz butiran adalah disebabkan oleh potensi halangan yang besar di sempadan butiran dengan peningkatan suhu pembakaran dari 500 sehingga 1100 °C. Pada suhu pembakaran 1200 dan 1300 °C nilai α menurun disebabkan oleh susutan potensi halangan di sempadan butiran. Kesusutan ini adalah disebabkan oleh berkurangan fasa yang kaya dengan Bi pada suhu pembakaran yang lebih tinggi. Teknik HEBM menghasilkan sampel dengan saiz zarah yang lebih kecil, yang membawa kepada penurunan nilai jurang jalur secara sistematik berkait rapat dengan pengurungan kuantum. Nilai jurang jalur bagi bahan yang didopkan-dengan Co adalah dalam linkungan antara 3.2 kepada 2.5 eV pada butiran-nano yang bersaiz bawah 1μm. Nilai jurang jalur yang lebih tinggi pada butiran bersaiz nano disumbangkan oleh pengurungan kuantum dan apabila saiz butiran meningkat, perubahan nilai jalur jurang telah berkurangan disebabkan oleh pertumbuhan keadaan antara muka di sempadan butiran.

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I certify that a Thesis Examination Committee has met on 23 November 2016 to conduct the final examination of Wan Norailiana binti Wan Ab Rahman on her thesis entitled "Correlation of Microstructures with Electrical and Optical Properties in Zinc Oxide Ceramic Semiconductor" 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 Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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α	Nonlinear coefficient
ρ	Resistivity
ρ_{gb}	Resistivity at grain boundary
R	Absolute reflectance
k	Molar absorption coefficient
s	Scattering coefficient
h	Planck's constant
v	Frequency of vibration
β	Absorption coefficient
a_b	Bohr radius
m	Mass
μ	Reduced mass
ε_r	Size dependent dielectric constant
d	Interplanar spacing
θ	Diffraction angle
W_a	Weight of sample in air
W_w	Weight of sample in water
ρ_w	Water density
V	Voltage
I	Current
R	Electrical resistance
A	Cross sectional area
l	Height of sample

LIST OF ABBREVIATIONS

ZnO	Zinc oxide
Bi_2O_3	Bismuth oxide
CoO	Cobalt oxide
MnO	Manganese oxide
GaN	Gallium nitride
Sb_2O_3	Antimony oxide
Cr_2O_3	Chromium oxide
SiC	Silicon carbide
UV	Ultraviolet
I-V	Current-voltage
TSS	Two-step sintering
DMCP	Direct mixing of constituent phases
hcp	Hexagonal closed-packed
AC	Alternating current
BPR	Ball to powder ratio
CIP	Cold isostatic pressing
DSB	Double Schotkky Barrier
V_{on}	Switch-on voltage
E_{on}	Switch-on electric field
E_{upon}/V_{upon}	Upturn region onset
IR	Mid-infrared
NIR	Near infrared
HEBM	High energy ball milling

PVA	Polyvinyl alcohol
E_g	Energy band gap
XRD	X-Ray diffractometer
TEM	Transmission Electron Microscopy
FESEM	Field Emission Scanning Electron Microscopy
CIP	Cold Isostatic Pressing
EDX	Energy dispersive X-Ray

CHAPTER 1

INTRODUCTION

1.1 Research Background

Zinc oxide (ZnO) semiconductor is a polycrystalline ceramic exhibiting highly nonlinear current-voltage (I-V) behavior. In polycrystalline ZnO materials, understanding and controlling the microstructure is very important since the electrical and optical band gap properties are directly influenced by the microstructure effect. The electrical and optical properties of ZnO are also influenced by the materials composition, addition of dopant and porosity. Grain growth mechanism is directly related to the microstructure and one of the fundamental subjects in material science and processing that has been studied for more than 50 years. However, the produce of this study is more on final products properties which mainly benefit the demand of the commercial applications, thus abandoned the understanding of the parallel evolution of the microstructural and physical properties of the ZnO. The evolution of the microstructural, electrical and optical properties mainly on nano or submicron scales starting materials which are important as well has been neglected in past year. In the processing of ZnO-based varistor ceramics, control of the grain growth is crucial for the successful application in overvoltage protection in a broad range, from a few volts up to several kilovolts. The nonlinear I-V of the doped-ZnO sample is a grain boundary mechanism with an ideal breakdown voltage (V_B) of the grain boundary at about 3.2 eV. The V_B of the varistor is a sum of the V_B of all the nonlinear grain boundaries between the electrodes, it depends on the number of grain boundaries per unit volume of the varistor ceramic which is inversely proportional to the ZnO grain size. Smaller grain size gives higher breakdown voltage and larger grain size results in lower breakdown voltages. This is why the influence of grain size and grain boundary on the electrical characteristics is straightforward in the case of nonlinear I-V of doped-ZnO ceramics. The optical properties of the ZnO depend closely on the microstructures of the materials, including crystallite size, orientation, and morphology, defects, lattice strain and others. In the optical band gap case, a majority of the previous studies has focused on the optical properties of ZnO nanostructures and a few studies have been carried out to understand the microstructure of ZnO nanoparticles. Hence, doped-ZnO with nanoparticles size and structure are needed to study their size-dependent properties where quantum confinement effect and surface effects may be prominent.

1.2 Introduction to Zinc Oxide Semiconductor

ZnO is an II-VI semiconductor compound because zinc and oxygen belong to 2nd and 6th groups of the periodic table respectively. ZnO occurs as a white powder with common name zinc white and nearly soluble in water but soluble in acids and alkalis. ZnO will change colour from white to yellow when it is heated. ZnO has a density of 5.60 g/cm^3 and with a melting point of 1975 °C. The resistivity of ZnO ranges from 1 to 100 Ω.m, which corresponds to the electron concentration of the order of 10^{21}-10^{23} m^{-3}.

Pure ZnO is an n-type intrinsic with a wide band gap of 3.37 eV at room temperature. The largest exciton binding energy of 60 meV is the most desirable features of ZnO as compared to 24 meV for GaN, which is the key parameter that enables the UV laser diode and other exciton related light emitting devices to be operated at room temperature and makes ZnO a brighter emitter. ZnO is one of the "hardest" materials in II-VI compound semiconductors due to the higher melting point and large cohesive energy. The constituent elements of ZnO are abundant and of low cost. Also, the material is nontoxic, which is an important consideration for the environment. It is also a potential candidate for development of electronic and optoelectronic devices. The advantages of the wide band gap are higher breakdown voltage, ability to sustain large electric field, lower electronic noise and high power operation that make ZnO as one of the most promising materials for electronic applications. An intrinsic semiconductor is an undoped semiconductor in which the intrinsic defects originate from the semiconductor material itself and there should not be any impurity atom that can affect the electrical characteristics. For ZnO, the intrinsic defects exist in the form of excess zinc atom that acts as donor n-type conductivity (Clarke, 1999; Pierret, 1996; Mahan, 1983).

ZnO has several favorable properties such as good transparency, high electron mobility, wide band gap and strong room temperature luminescence where those properties already used in heat protecting window and electronic applications as thin film transistors and light emitting diodes. One of the common use of ZnO used until now is varistor which is also called as voltage dependent (or variable) resistor known since 1934.

1.3 Introduction to Varistor

ZnO materials have been used widely as the ZnO-based varistor. A varistor is a type of resistor with significantly has nonlinear behavior with resistivity value dependent on the applied voltage. A good varistor should have a very low leakage current, a high value of the nonlinear coefficient (α) and high value of the current at the beginning of the switched region. In normal use, they are subject to a voltage below their characteristics switch voltage and pass only leakage current. A commercial varistor is formed by adding a number of oxides such as bismuth (Bi), cobalt (Co), antimony (Sb), manganese (Mn) and others to ZnO through standard ceramic processing techniques.

After sintering, the resulting product shows highly nonlinear I-V characteristics with a microstructure consisting of semiconducting grain and insulating grain boundaries.

Such nonlinear I-V characteristics are explained on the basis of formation of the Schottky-type potential barriers at the grain boundaries where a number of free charges are trapped by the defects states. Therefore, improvement in the varistor action requires the understanding of the formation of potential barriers with different additives oxides and subsequent formation of defects states at the grain boundary regions.

Varistor devices are used mainly as the voltage-limiting elements to limit or clamp transient overvoltage which means the transient peak is reduced or limited to a safe level as illustrated in Figure 1.1. 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 over-voltage are hazardous to all electrical circuits considering that these transients could happen a few thousand times a year for a typical household of office premise.

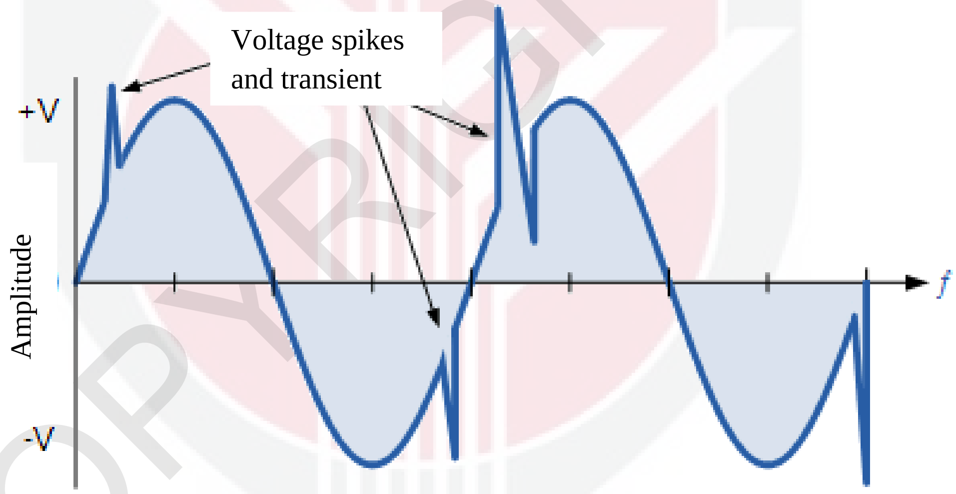

Figure 1.1: Varistor action to limit or clamp over voltage transient
(Source: http://www.electronics-tutorials.ws/resistor/varistor.html)

When the voltage exceeds the switch voltage, for instance during a voltage transient or surge, the varistor becomes highly conducting and draws the current through it, usually to ground. When the voltage returns to normal, the varistor returns to its highly resistive state. The switch is reversible and the resistance of varistor is depending upon the applied voltages. Under normal operating condition the resistance of the varistor is very high but when the voltage applied across the varistor is larger than the breakdown voltage value, the resistance of the varistor falls drastically and it continues to decrease as the voltage applied increase as shown in Figure 1.2.

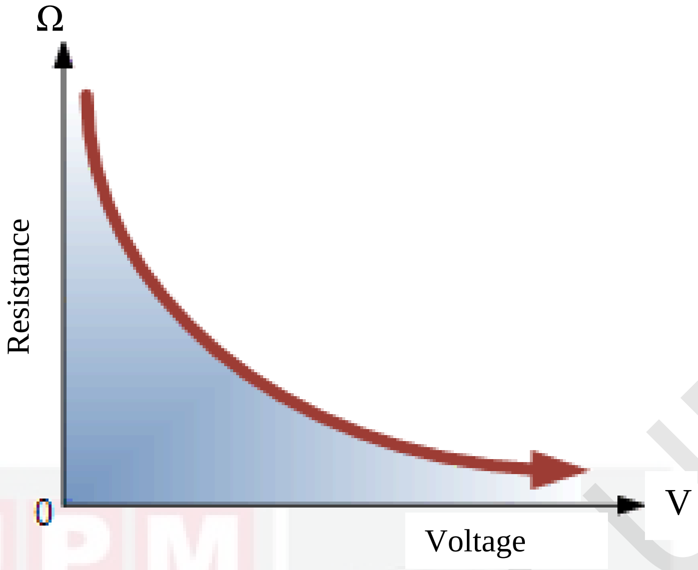

Figure 1.2: Resistance of varistor with respect to its applied voltage
(Source: http://www.electronics-tutorials.ws/resistor/varistor.html)

Varistor is used to protect circuits by voltage clamping method over a wide range of voltages from a few volts for low voltage varistor in semiconductor circuits to tens of kilovolts for electrical power distribution networks and a wide range of currents from microampere to kiloampere. The varistor also has the additional property of high-energy absorption capability ranging from a few joules to many megajoules. They also very fast switch in a nanosecond from their resistive to highly conductive state. Their I-V characteristics are similar to a Zener diode. But unlike a diode, varistor can limit overvoltage equally in both polarities, thus giving rise to I-V characteristics, which is analogous to two back-to-back Zener diodes. Varistor is normally connected in parallel with an electric device and located at the incoming power line before the power supply to protect electrical circuit from voltage surges shown in Figure 1.3.

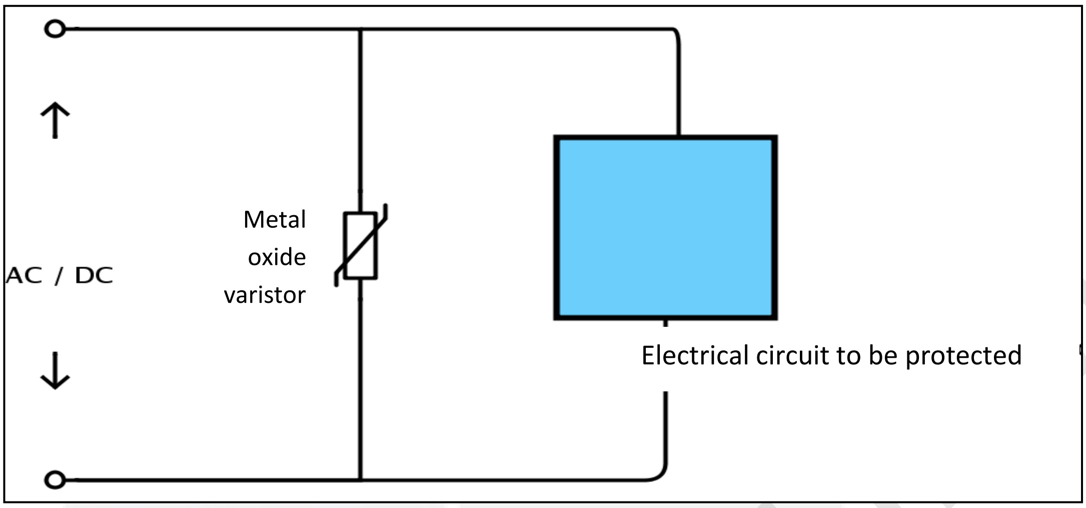

Figure 1.3: Metal oxide varistor protecting electrical circuit
(Source: http://www.electronicshub.org/varistor/)

Since the early 1970s the ZnO varistor has been the dominant surge protection device and attract more attention compared to silicon carbide in the electronic appliances due to the excellent nonlinear I-V characteristics and their large withstand capabilities. The main properties of ZnO-based varistor are described as follows;

1. ZnO-based varistor has a super-fast response to overvoltage transients where they can sense and clamp transients in nanoseconds speed.
2. ZnO-based varistor can sense and clamp over-voltage transients repeat and in thousands of time without being damaged.
3. ZnO-based varistor has high α which is important for fast response and better protection function
4. ZnO-based varistor has high energy-handling capability ranging from a few joules to thousands of kilojoules.
5. ZnO-based varistor can be used in alternating current and direct current over wide range of voltage
6. ZnO-based varistor has sharp switching voltage where the IV characteristics are reversible.

1.4 Selection of Materials

The distinctive composition in doped-ZnO samples consists of ZnO and other oxides dopants such as Bi_2O_3, TiO_2, Sb_2O_3, MnO_2 and $C_{O3}O_4$. The characteristics of varistor ceramics are closely related to the microstructure (Bernik and Daneu, 2007) where each dopant plays an important role to improve the α property of ZnO varistor. An addition of dopant in this research based on several important criteria such as selected dopants should be accepted and extensively applied by other researchers and the selected dopant also should give good properties of doped-ZnO samples. Thus, judicious choice of dopant is very important from the beginning of this research because our primary in this research is to unravel the relationship between the microstructure and physical properties in doped-ZnO samples and the addition of dopant is an indispensable because based on previous literature, undoped ZnO sample unable to show good properties of ZnO samples. From the numerous literature, dopants of Bi_2O_3, CoO and MnO are chosen and added to ZnO system respectively where these additives are the main tools that used to improve the stability of ZnO varistor.

Bismuth oxide, Bi_2O_3 has a purity of 99.99% and ionic radii of 1.20 Å. During liquid-phase sintering, Bi_2O_3 will melt and form a second phase segregated at ZnO grain boundaries allowing a significant fraction of ZnO-ZnO grain contact and thus, produces the interface states. The existence of Bi_2O_3 at the grain boundaries and grain junction controlled the densification and grain growth of ZnO (Wong, 1980; Asokan et al., 1987). Bi_2O_3 also has high oxygen diffusion coefficient (Haifeng and Chiang, 1998). The improvement of α and prevention of Bi_2O_3 to evaporate during the heat treatments can achieve by the addition of MnO_2 or Co_3O_4.

Cobalt (II) oxide, CoO has a purity of 99.998% and ionic radii of 0.74 Å**.** The addition of transition metal elements such as cobalt that act as a donor and produces interfaces state, thus, improves the nonlinear (I-V) characteristics. Due to its radius, Co ions can substitute Zn^{2+} or interstitials (Bahadur and Rao, 1992). The substitution of Co^{2+} in an interstitial position would affect the concentration of the interstitial Zn, oxygen, and Zn vacancies (Vijayaprasath et al., 2014).

Manganese oxide, MnO has a purity of 99.99% with ionic radii of 0.80 Å acts as a grain enhancer (Han et al., 2002) and donors that produce the interface states (Eda, 1978; Bui et al., 1995) and consequently contributed to the physical properties of doped-ZnO samples.

1.5 Problem Statement

Doped-ZnO samples are among the most widely used for varistor application including voltage stabilization and transient surge suppression in electronic devices. The development of ZnO semiconductor for electrical and optical application had been studying for many years ago by other researchers but in previous literature, they focused mainly on yielding the final outcome only. For an example the effect of variation addition of dopants to electrical properties of the doped-ZnO samples. Until now, many researchers keep investigating the properties of doped-ZnO samples with complexed dopants and cause them to neglect the fundamental line of scientific enquiry: what would be the composition-microstructure relationship with the parallel evolution of the electrical and optical properties in nanometer-to-micrometer grain size region? Doped-ZnO samples are obtained by the addition of small amounts of oxide of bismuth (Bi), antimony (Sb), cobalt (Co), manganese (Mn) and others to ZnO powder, and then sinter from 1100 to 1300 °C, usually at

1200 °C sintering temperature. A few investigations have been done about studies on microstructure development at low temperatures, where the grain growth kinetics is still slow. Hence in this research, we intend to study the microstructure-electrical and optical properties relationship during the parallel evolution of the microstructure and the semiconductor ZnO properties from low sintering temperature until high sintering temperature.

1.6 Research Objectives

In the present research work, the main aim is to track down the parallel evolution of microstructural and electrical, optical properties from low sintering temperature to high sintering temperature.
The objectives of this research are:

1. To study the parallel evolution of the electrical and optical properties with microstructure changes and their relationship from an amorphous-crystalline mixture state to a complete polycrystalline zinc oxide in nanometer-to-micrometer grain-size regime.
2. To investigate the development of parallel evolving microstructure, electrical and optical properties of the material.
3. To study the effect of the dopant on the evolving electrical, optical properties and microstructure of ZnO ceramic.

1.7 Scope of the Study

This research is involved of fabrication of nanoparticle starting powder doped-ZnO (98 mol% ZnO + 1 mol% Bi_2O_3 + 1 mol% CoO and 98 mol% ZnO + 1 mol% Bi_2O_3 + 1 mol% MnO) samples via high energy ball milling (HEBM) method. There are divided of six batches with different parameters and analysis on the effect of minimum addition of dopant, varying milling time and different sintering temperatures to the doped-ZnO samples are observed. The particle size of doped-ZnO powders were measured using (TEM) and the phase formation of the doped-ZnO samples using XRD. The parallel evolution of the electrical and optical properties with microstructure changes is investigated by using FESEM, nonlinear I-V and UV-Vis Spectrophotometer. Investigation of the relationship between the evolution of electrical and optical properties to the microstructural changes are critically done.

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