UNIVERSITI PUTRA MALAYSIA

MICROSTRUCTURE AND ELECTRICAL AND OPTICAL PROPERTIES OF ZnO BASED VARISTOR CERAMICS WITH SMALL - AMOUNT OF MnO2 AND Co3O4 AS DOPANT

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By

NOORFAUZANA BINTI ADNIN

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

January 2012

DEDICATION

To my beloved family, supervisor and all my dearest friends.

Thanks for their guidance, supports, understanding, caring, love and encouragements.

May ALLAH bless us always.

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

MICROSTRUCTURE AND ELECTRICAL AND OPTICAL PROPERTIES OF ZnO BASED VARISTOR CERAMICS WITH SMALL - AMOUNT OF MnO_2 AND Co_3O_4 AS DOPANT

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Chairman : Professor Azmi Zakaria, PhD

Faculty : Science

Various stresses such as high electric fields, high temperature and aggressive ambient can inflict serious damages on machinery and other equipments and may degrade the performances of ZnO varistor devices. To develop a high performance of ZnO varistor ceramics, the influences of dopant are very crucial to be understood since dopants are responsible for the formation of varistor behavior. Therefore, small amount of MnO_2 and Co_3O_4 as dopant is added to ZnO system respectively to improve the varistor properties. Although there were numerous studies on the effect of dopant on ZnO varistor, the exact roles of "small amount" dopant in ZnO varistor and how it can improve the nonlinear Current - Voltage (*I*-*V*) characteristics have not yet been clarified.

In this study, the microstructure, electrical and optical properties of the ZnO - $xMnO_2$ and ZnO - xCo_3O_4 systems have been investigated for small amount of x ranging from 0.011 - 0.026 mol % at various sintering temperatures from 1180 - 1300 ºC for the sintering time of 1 and 2 hours. XRD analysis shows that the main

phase was ZnO with $ZnMnO_3$, $ZnMnO_7$ and Co_3O_4 as the secondary phases developed in the material systems. The maximum density have been achieved up to about 98% of theoretical density at 1300 ºC sintering temperature at 0.011 mol % doping level of Co_3O_4 and the relative density in general, has the value above 85%. The maximum grain size was found to be 14 µm at the highest sintering temperature which is at 1300 ºC at 0.021 mol % of Co_3O_4 doping level. It was also found that MnO_2 is a grain enhancer and promotes the grain growth of the ZnO samples. SEM and EDAX results verify that Mn and Co ions are distributed in the grain interior as well as in the grain boundaries. The value of nonlinear coefficient α, is found to increase with the amount of MnO_2 up to 0.016 mol% doping level, while slightly change with the amount for Co_3O_4 mol%. Also, the value of nonlinear coefficient increases with the increase of sintering temperature and time for all ZnO system. An optimum sintering temperature of 1300 ^oC at 2 hour sintering time for ZnO + 0.016% MnO_2 gave the best electrical properties, with the non-linear coefficient value α, attaining a highest value of 9.11 in which represent fast response to transient voltage, thus give high protective function of ZnO varistor. The band gap energy E_g, decreases with the increase of Co_3O_4 and MnO_2 doping level and also sintering temperature respectively. For both dopants, the maximum decrease in the band gap occur at 0.026 mol % doping level at 1300 ºC for 1 hour sintering time with the value of 2.65 and 2.46 respectively.

It is found that, the introduction of "small amount" MnO_2 and Co_3O_4 dopant influences the microstructure, electrical and optical properties of all ZnO systems. The electrical characteristics of all ZnO samples depend on their microstructure properties. For both dopant, the growth of interface states are responsible for the decrement of the energy band gap value.

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

PENCIRIAN STRUKTUR – MIKRO DAN ELEKTRIK DAN OPTIK VARISTOR SERAMIK BERASASKAN ZnO DENGAN KUANTITI SEDIKIT MnO_2 DAN Co_3O_4 SEBAGAI BAHAN DOP

Oleh

NOORFAUZANA BINTI ADNIN

Januari 2012

Pengerusi : Profesor Azmi Zakaria, PhD

Fakulti : Sains

Pelbagai tekanan seperti medan elektrik dan suhu yang tinggi serta persekitaran yang agresif boleh mengakibatkan kerosakan serius pada mesin dan peralatan - peralatan lain dan merosotkan prestasi peranti ZnO varistor. Untuk meningkatkan prestasi varistor seramik ZnO, pengaruh dopan adalah sangat penting untuk difahami dimana dopan bertanggungjawab terhadap pembentukan perilaku varistor. Oleh itu, MnO_2 dan Co_3O_4 digunakan di dalam kuantiti yang sedikit sebagai bahan dop dimana setiap satu ditambah kepada sistem ZnO untuk meningkatkan sifat - sifat varistor. Walaupun terdapat banyak kajian mengenai kesan pendopan pada ZnO varistor, peranan sebenar bahan dop dalam "kuantiti sedikit" di dalam ZnO varistor dan bagaimana ia boleh meningkatkan sifat-sifat tak linear arus - voltan (*I-V*) masih belum dijelaskan secara terperinci.

Di dalam kajian ini, pencirian mikrostruktur, elektrik dan optik bagi sistem ZnO - $xMnO_2$ dan ZnO - xCo_3O_4 telah dijalankan bagi perubahan nilai x dari 0.011 - 0.026 mol% pada pelbagai suhu pensinteran dari 1180 - 1300 ºC dan dengan masa pensinteran selama 1 dan 2 jam. Analisis XRD menunjukkan bahawa fasa utama

adalah ZnO dengan $ZnMnO_3$, $ZnMnO_7$ dan Co_3O_4 sebagai fasa - fasa kedua yang terbentuk di dalam sistem bahan. Ketumpatan maksimum telah dicapai sehingga 98% dari ketumpatan teori pada suhu pensinteran 1300 ºC pada tahap 0.011 mol% Co_3O_4 dan ketumpatan relatif secara umumnya mempunyai nilai di atas paras 85 %. Saiz butiran maksimum didapati adalah 14 µm pada suhu pensinteran yang tertinggi iaitu 1300 ºC pada tahap 0.021 mol% Co_3O_4. Didapati bahawa MnO_2 adalah penggalak butiran dan menggalakkan pertumbuhan butiran sampel ZnO. Keputusan SEM dan EDAX menunjukkan bahawa ion Mn dan Co bertaburan di dalam butiran dan juga di sempadan butiran. Nilai pekali tak -linear, α didapati meningkat dengan peningkatan jumlah MnO_2 sehingga tahap 0.016 mol% manakala sedikit perubahan berlaku dengan peningkatan jumlah Co_3O_4. Nilai pekali tak-linear juga meningkat dengan peningkatan suhu dan masa pensinteran bagi kesemua sistem ZnO. Suhu persinteran yang optimum pada 1300 ºC bagi masa persinteran selama 2 jam, memberikan sifat elektrik yang terbaik dengan nilai pekali tak-linear, α mencapai nilai 9.11 yang mewakili tindakan pantas terhadap voltan fana, seterusnya melindungi ZnO varistor. Jurang jalur tenaga masing - masing menurun dengan peningkatan jumlah MnO_2 dan Co_3O_4 dan suhu persinteran. Bagi kedua - dua bahan dop, penurunan maksimum dalam jurang jalur berlaku pada tahap 0.026 mol% pada suhu pensinteran 1300 ºC dan masa pensinteran selama 1 jam masing-masing dengan nilai 2.65 dan 2.46.

Didapati bahawa, bahan dop MnO_2 and Co_3O_4 di dalam kuantiti yang sedikit masing - masing mempengaruhi pencirian mikrostruktur, elektrik dan optik bagi kesemua sistem ZnO. Pencirian elektrik bagi kesemua sistem ZnO bergantung kepada pencirian struktur - mikro. Bagi kedua - dua bahan dop, pertumbuhan antara muka merupakan penyebab utama penurunan nilai jurang jalur tenaga.

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

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I certify that an Examination Committee has met on **18 January 2012** to conduct the final examination of Miss **Noorfauzana binti Adnin** for her Master of Science thesis entitled **"Microstructure, Electrical and Optical Properties of ZnO Varistor Ceramics With Small - Amount MnO_2 and Co_3O_4 As Dopant"** in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or other institutions.

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NOORFAUZANA BINTI ADNIN

Date: 18 January 2012

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