UNIVERSITI PUTRA MALAYSIA

PHOTOTHERMAL AND ELECTRICAL CHARACTERIZATION OF ZnO-BASED VARISTOR SYSTEMS

ZAHID RIZWAN

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By

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

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DEDICATION

I dedicate these humble efforts, the fruit of my thoughts
and studies to my affectionate mother (late)
who inspired me to higher ideals of life.

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

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Chairman: **Azmi Zakaria, PhD**

Faculty: **Science**

Photopyroelectric spectroscopy is a powerful tool for examining the optical properties related to non-radiative de-excitation processes in materials. This technique consists of using a thin photopyroelectric (PPE) film in intimate contact with a solid sample on which modulated monochromatic light beam is incident. The non-radiative de-excitation process within the solid causes the sample temperature to fluctuate and PPE signal is produced in PPE transducer as a result of this temperature fluctuation. Varistor is a voltage dependant resistor and is used as a protective device to regulate transient voltage surges of unwanted magnitudes caused by lightning and switching of circuits containing inductors, capacitors, and can inflict serious damages on machinery and other equipments. In this study, the electrical properties of ZnO based varistor doped with different additives are investigated in conjunction with the photothermal properties. The wavelength of incident light is kept in the range from 300 to 800 nm and the PPE spectrum with reference to the doping level, sintering conditions is

discussed. The energy band-gap or shortly as band-gap is determined from the plot $(\rho h\upsilon)^2$ vs $h\upsilon$. The band-gap is reduced from 3.2 eV (pure ZnO) to about 1.9 eV for single additive MnO_2 or when it is used with the combination of other additives. The steepness factors σ_A (in A-region), and σ_B (in B-region), which characterize the slope of exponential optical absorption are discussed in conjunction with the band-gap which give the information about the disordering of the structure. It was also found that the value of band-gap slightly increases or decreases in 13 material systems in the range of 0.03 to 0.05 eV. It was found that the secondary phases such as $Bi_4Ti_3O_{12}$, Zn_2TiO_4, $Zn_7Sb_2O_{12}$ are grain suppressors. The maximum and minimum relative densities for all systems in this study are about 96 %, 78 %, respectively. The maximum grain size was found to be 82 μm when ZnO was doped with MnO_2, Co_3O_4, Bi_2O_3, TiO_2 for 3 hour sintering time. It was found that the TiO_2 is a strong grain enhancer; Sb_2O_3 is a strong grain suppressor upto certain doping level. SEM and EDX results show that the additives Bi_2O_3, Y_2O_3, Er_2O_3, Dy_2O_3 and Pr_6O_{11} are segregated at the grain boundaries and at the triple point junctions. EDX analysis show that the Co, Mn, Ti ions are distributed on the grain surfaces as well as grain boundaries. Current-voltage characteristics of the varistor show that the varistor voltage increases with the decrease of grain size. The value of barrier height increases with the increase of the nonlinear coefficient and vice versa but it deviates in some cases. The value of band-gap decreases due to the increase in the structural disordering and increases due to the decrease in the structural disordering. It is found that the increase or decrease in the band-gap ranges from 0.03 to 0.05 eV in all cases but this ranges from 0.1 to 0.3 eV only for xBi_2O_3 and xPr_6O_{11} doped ZnO system. The change in the value of the band-

gap in conjunction with the nonlinearity of the doped ZnO can be categorized in four cases as both band-gap and nonlinearity increases in system 5, band-gap decreases and nonlinearity increases in system 2, system 10 and system 11, band-gap increases and nonlinearity decreases in system 6, system 8 and system 13, both band-gap and nonlinearity decreases in system 7, system 9, and system 12. System 12 which is Bi_2O_3, TiO_2, Co_3O_4, doped ZnO with and without Sb_2O_3 at different sintering temperatures is the best system found in which both band-gap and nonlinearity decreases having the maximum value of nonlinearity that is 7.9 at the sintering temperature of 1210 ^oC for one hour sintering time with 0.02 mol% Sb_2O_3. The second best system found in the project is System 13 which is Bi_2O_3, TiO_2, MnO_2, doped ZnO with and without Sb_2O_3 at different sintering temperatures in which band-gap increases and nonlinearity decreases with the maximum value of nonlinearity that is 18.6 at the sintering temperature of 1180 ^oC for one hour sintering time with Sb_2O_3.

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

CIRI-CIRI FOTOTERMA DAN ELEKTRIK BAGI SISTEM-SISTEM VARISTOR BERASASKAN ZnO

Oleh

ZAHID RIZWAN

September 2007

Pengerusi: **Azmi Zakaria, PhD**

Fakulti: **Sains**

Spektroskopi fotopiroelektrik adalah peralatan berkebolehan tinggi untuk menganalisis ciri-ciri optik berkaitan proses-proses nyah-pengujaan bukan-radiasi dalam bahan. Teknik ini melibatkan penggunaan filem fotopiroelektrik (PPE) nipis yang bersentuh rapat dengan sampel pepejal yang mana alur cahaya monokromatik termodulasi menimpa. Proses nyah-pengujaan bukan-radiasi di dalam pepejal menyebabkan suhu sampel turun-naik dan signal PPE akan terhasil di dalam transduser PPE sebagai hasil dari penurun-naikan suhu ini. Varistor adalah resistor sandaran voltan dan digunakan sebagai peranti pelindung untuk mengawal-atur pendadakan voltan fana bermagnitud berlebihan yang disebabkan oleh kilat dan pensuisan litar-litar mengandungi induktur kapasitor, dan boleh menyebabkan kerosakan serius pada mesin dan peralatan-peralatan lain. Di dalam kajian ini, ciri-ciri elektrik varistor berasaskan ZnO terdop dengan tambahan-tambahan berbeza diselidiki sehubungan dengan sifat-sifat fototerma. Panjang gelombang cahaya tuju ditetapkan dalam julat 300 ke 800 nm dan spektrum

fotopiroelektrik dengan rujukan kepada tahap dop, keadaan-keadaan pensinteran adalah dibincangkan. Tenaga jurang jalur atau ringkasnya jurang jalur ditentukan daripada plot $(\rho h\upsilon)^2$ lwn $h\upsilon$. Jurang jalur adalah berkurangkan daripada 3.2 eV (ZnO tulen) kepada 1.9 eV untuk tambahan tunggal MnO_2 atau bila ia digunakan dengan kombinasi dari tambahan-tambahan lain. Faktor kecerunan σ_A (dalam rantau A) dan σ_B (dalam rantau B), yang mana mencirikan cerun dari eksponen penyerapan optik adalah dibincangkan sehubungan dengan jurang jalur yang mana memberikan maklumat tentang ketaktertiban struktur. Didapati juga bahawa nilai jurang jalur menaik atau menurun secara lemah dalam 13 sistem bahan dan perubahan ini adalah dalam julat 0.03 ke 0.05 eV. Didapati bahawa fasa-fasa sekunder seperti $Bi_4Ti_3O_{12}$, Zn_2TiO_4, $Zn_7Sb_2O_{12}$ adalah penindas butiran. Ketumpatan relatif maksimum dan minimum untuk semua sistem dalam kajian ini adalah kira-kira 96 % dan 78%, masing-masingnya. Saiz butiran maksimum didapati adalah 82 μm apabila ZnO didop dengan MnO_2, Co_3O_4, Bi_2O_3, TiO_2 untuk 3 jam masa pensinteran. Adalah didapati bahawa TiO_2 adalah penggalak butiran kuat; Sb_2O_3 adalah perencat butiran kuat sehingga ke paras dop tertentu. Keputusan-keputusan SEM dan EDX menunjukkan bahawa bahan tambahan Bi_2O_3, Y_2O_3, Er_2O_3, Dy_2O_3 dan Pr_6O_{11} adalah terasing di sempadan butiran dan di simpang-simpang titik tigaan. Analisis EDX menunjukkan bahawa ion-ion Co, Mn, Ti adalah teragih di atas permukaan-permukaan butiran dan juga di sempadan-sempadan butiran. Pencirian arus-voltan dari varistor menunjukkan bahawa voltan varistor menaik dengan penurunan saiz butiran. Nilai tinggi sawar menaik dengan penaikkan pekali tak linear dan sebaliknya, tetapi ia menyisih dalam kes-kes tertentu. Nilai jurang jalur menurun dengan peningkatan tahap pendopan dan meningkat dengan pengurangan tahap

pendopan. Didapati jurang jalur meningkat atau menurun dari 0.03 hingga ke 0.05eV dalam semua kes tetapi jurang dari 0.1 hingga 0.3eV adalah hanya untuk sistem ZnO terdop xBi_2O_3 dan xPr_6O_{11}. Perubahan dalam nilai jurang jalur sehubungan dengan ketak-linearan daripada ZnO terdop boleh dikategorikan dalam empat kes dengan kedua-dua jurang jalur dan ketak-linearan meningkat di sistem 5, jurang jalur menurun manakala ketak-linearan meningkat di sistem 2, sistem 10 dan sistem 11, jurang jalur meningkat manakala ketak-linearan menurun di sistem 6, sistem 8 dan sistem 13, kedua-dua jurang jalur dan ketak-linearan menurun di sistem 7, sistem 9 dan sistem 12. Sistem 12 iaitu ZnO terdop Bi_2O_3, TiO_2, Co_3O_4 dengan atau tanpa Sb_2O_3 pada suhu pensinteran berbeza adalah sistem yang terbaik yang ditemui di mana kedua-dua jurang jalur dan ketak-linearan menurun mempunyai nilai maksimum iaitu 7.9 pada suhu pensinteran 1210 ^oC untuk satu jam masa pensinteran dengan 0.02 mol% Sb_2O_3. Sistem kedua terbaik ditemui dalam kajian ini adalah sistem 13 iaitu ZnO terdop Bi_2O_3, TiO_2, MnO_2 dengan atau tanpa Sb_2O_3 pada suhu pensinteran berbeza di mana jurang jalur meningkat dan ketak-linearan menurun dengan nilai maksimum dari ketak-linearan iaitu 18.6 pada suhu pensinteran 1180 ^oC untuk satu jam masa pensinteran dengan Sb_2O_3.

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I certify that an Examination Committee has met on 27-September-2007 to conduct the final examination Zahid Rizwan on his Doctor of Philosophy thesis entitled "Photothermal and Electrical Characterization of ZnO-Based Varistor Systems" 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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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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Date: 13 December 2007

DECLARATION

I hereby declare that the thesis is based on 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 at any other institution.

ZAHID RIZWAN

Date: 23 October 2007

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