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UNIVERSITI PUTRA MALAYSIA

OPTICAL AND THERMAL CHARACTERIZATION OF ZINC OXIDE-BASED CERAMIC USING PYROELECTRIC AND PHOTOPYROELECTRIC TECHNIQUES

SABRINA MOHD SHAPEE

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By

SABRINA MOHD SHAPEE

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

October 2008

DEDICATION

To my beloved parents Mohd Shapee Shamsudin and Nasriah Mansor
For their love and care…

To my husband Mohd Rafizu Muda
Whose make me feel that I am perfect…

To my sister Herdayu
and my brothers Mohd Safuan, Mohd Hafiz and Mohd Syukri
For making my life complete…

To all my very wonderful friends
For making my life full of joy and happiness…

To all my lecturers
For helping me a lot throughout my study…

To me
May Allah bless me always…

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

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October 2008

Chairman : Azmi Zakaria, Ph.D.

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The advantage of wide electrical band-gap of zinc oxide (ZnO) semiconductor has been used in many applications particularly as varistors, which are ceramic devices with highly non-linear current-voltage characteristics. For ZnO-based varistor system, one or more additive oxides such as antimony oxide (Sb_2O_3), bismuth oxide (Bi_2O_3) and cobalt oxide (Co_3O_4) are the main tools that improve the nonlinear response and the stability of ZnO varistor.

The thermal and optical characteristics of ZnO-based ceramic have been carried out at room temperature using pyroelectric and photopyroelectric techniques, respectively, that use polyvinylidene fluoride film as detector. In thermally thick regime, the thermal diffusivity value is obtained from the plot of the product of modulation frequency (*f*)

times pyroelectric amplitude signal versus $\sqrt{f}$. The thermal diffusivity obtained for pure ZnO ceramic sample without potassium bromide (KBr) (0.079 cm^2s^{-1}) close to literature values, indicates the reliability of the present set up. The thermal diffusivity of doped ZnO ceramic in KBr matrix was prepared by mixing the ground ceramic with KBr and pressed into a pellet form. Before the sample was attached to the pyroelectric detector it was covered with carbon soot to turn it into an optically opaque condition. It is observed that the thermal diffusivity of ceramic ZnO doped with Bi_2O_3 in the KBr matrix increases with the increase of Bi_2O_3 mol percentage.

The photopyroelectric spectrometer has been used to obtain optical absorption spectrum of ZnO based ceramic doped with various mol percentages of Bi_2O_3, Co_3O_4 and Sb_2O_3. The photopyroelectric optical spectra of thin layer of ceramic samples, put directly on photopyroelectric detector, were used to determine the band-gap energy of the samples. The results indicate that for all dopants the band-gap energy of ZnO decreases with the increase of dopant mol percentage. Microstructural characterization has been made on the ZnO-based ceramic by addition of different metal oxides. All of the samples were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

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

PENCIRIAN OPTIK DAN TERMA BAGI SERAMIK BERASASKAN-ZINK OKSIDA MENGGUNAKAN TEKNIK PIROELEKTRIK DAN FOTOPIROELEKTRIK

Oleh

SABRINA MOHD SHAPEE

Oktober 2008

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Kelebihan semikonduktor zink oksida (ZnO) yang mempunyai nilai jurang-jalur elektrik lebar telah digunakan dalam pelbagai aplikasi khususnya sebagai varistor, yang mana ia adalah peranti seramik yang mempunyai ciri-ciri arus-voltan tak-linear yang tinggi. Bagi sistem varistor berasaskan ZnO, satu atau lebih campuran oksida seperti antimoni oksida (Sb_2O_3), bismuth oksida (Bi_2O_3) dan kobalt oksida (Co_3O_4) adalah bahan utama yang digunakan untuk meningkatkan respons tak-linear dan kestabilan varistor ZnO.

Pencirian optik dan terma seramik berasaskan ZnO telah dijalankan pada suhu bilik menggunakan teknik piroelektrik dan fotopiroelektrik masing-masingnya, menggunakan filem polyvinylidene fluoride sebagai pengesan. Di dalam keadaan ketebalan secara terma, nilai keresapan terma diperolehi melalui kelok hasil-darab frekuensi modulasi (*f*)

dengan isyarat amplitud piroelektrik melawan $\sqrt{f}$. Keresapan terma diperolehi bagi sampel seramik ZnO tulen tanpa potasium bromida (KBr) (0.079 cm^2s^{-1}) menghampiri nilai literatur menunjukkan kejituan radas tersedia. Keresapan terma bagi seramik ZnO yang telah didopkan bersama-sama matriks KBr disediakan dengan mencampurkan seramik yang telah ditumbuk halus bersama-sama KBr dan dihasilkan menjadi bentuk pelet. Sebelum sampel dilekatkan kepada pengesan piroelektrik, ia disalut dengan jelaga untuk menjadikannya berkeadaan legap optik. Didapati bahawa keresapan terma seramik ZnO didopkan dengan Bi_2O_3 di dalam matriks KBr meningkat dengan peningkatan peratus mol Bi_2O_3.

Spektrometer fotopiroelektrik telah digunakan untuk mendapatkan spektrum penyerapan optik bagi ZnO berasaskan seramik didopkan secara berasingan dengan pelbagai peratus mol Bi_2O_3, Co_3O_4 dan Sb_2O_3. Spektra optik fotopiroelektrik bagi lapisan nipis sampel seramik, diletakkan secara terus di atas pengesan fotopiroelektrik, digunakan untuk menentukan tenaga jurang-jalur bagi sampel. Keputusan menunjukkan bagi kesemua pendopan, tenaga jurang-jalur bagi ZnO berkurang dengan penambahan peratus mol pendopan. Pencirian mikrostruktur juga telah dijalankan bagi seramik berasaskan ZnO dengan penambahan pelbagai bahan metal oksida. Kesemua sampel telah dicirikan menggunakan mikroskopi elektron imbaan (SEM) dan pembelauan sinar-X (XRD).

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I certify that a Thesis Examination Committee has met on 16 October 2008 to conduct the final examination of Sabrina binti Mohd Shapee on her thesis entitled "Optical and Thermal Characterization of Zinc Oxide-Based Ceramic Using Pyroelectric and Photopyroelectric Techniques" in accordance with the Universities and University College 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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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 at any other institution.

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SABRINA MOHD SHAPEE

Date:

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LIST OF ABBREVIATIONS

BPPE	Back-detection PPE
C-V	Capacitor-Voltage
DLTS	Deep-level transient spectroscopy
DSB	Double Schottky Barrier
EMR	Electromagnetic radiation
FPPE	Front-detection PPE
He-Ne	Helium-Neon
ICTS	Isothermal capacitance transient spectroscopy
IPPE	Inverse PPE
I-V	Current-Voltage
NC-BPPE	Non-Contact-Back PPE
NC-FPPE	Non-Contact-Front PPE
PA	Photoacoustic
PAS	Photoacoustic spectroscopy
PE	Pyroelectric
PPE	Photopyroelectric
PPES	Photopyroelectric spectroscopy
PSD	Phase-sensitive-detection
PT	Photothermal
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene diflouride
RPPE	Reflective PPE

SEM	Scanning electron microscopy
SPPE	Standard PPE
XRD	X-ray diffraction

LIST OF SYMBOLS

α	Thermal diffusivity
β	Optical absorption coefficient
c	Specific heat
e	Thermal effusivity
E_g	Energy gap
ε	Dielectric constant
ε_o	Vacuum permittivity
f	Modulation frequency
$h\nu$	Quantized photon energy
i	$\sqrt{-1}$
I_o	Optical intensity
k	Thermal conductivity
l_β	Optical absorption length
m	Slope or gradient
L	Thickness
λ	Wavelength of light
η	Light-to-heat conversion efficiency
p	Pyroelectric coefficient
ρ	Density
Q_o	Heat source intensity
R_n	Thermal wave reflection coefficient
$R(\lambda)$	Optical reflectivity at wavelength λ
T_n	Thermal wave transmission coefficient
μ.	Thermal diffusion length
ω	Angular modulation frequency.
c	Speed of light
V	Voltage
ℓ_d	Film thickness
ΔT	Temperature rise

r	Thermal resistance
γ	Nonlinearity coefficient
V_{th}	Thermal voltage
υ	Frequency
h	Planck’s constant
β_s	Optical absorption coefficient of sample
β_p	Optical absorption coefficient of pyroelectric film
$\mu_{\beta s}$	Optical absorption depth of sample
$\mu_{\beta p}$	Optical absorption depth of pyroelectric film

CHAPTER 1

INTRODUCTION

1.1 Introduction

This thesis is presented in six chapters. The First Chapter is the general Introduction. Chapter Two discusses the literature review of the previous work for the photothermal and structural characterization of ZnO based ceramic. Chapter Three is a review of photothermal (PT) characterization theory including the thermal diffusivity measurement using pyroelectric (PE) technique, the spectrometer and a brief explanation about the optical band-gap energy. Chapter Four is concerned with the measurement set-up and apparatus. The sample preparation of ZnO ceramic is also discussed in this chapter. Chapter Five presents the results obtained through experiments conducted in the Photoacoustic (PA) Laboratory of Physics Department at Universiti Putra Malaysia of photopyroelectric (PPE) spectroscopy. Finally, Chapter Six summarizes the work conducted in this thesis and presents recommendations for future work pertaining to the area of photopyroelectric (PPE) characterizations on ceramic sample especially for ZnO sample which has wide variety of applications.

1.2 Motivation and Problem Statement

This thesis is concerned with the topic of PPE study of ZnO ceramics. One of its wide applications is as a varistor in electronic ceramic materials area whose electrical behavior is dominated by grain-boundary interface states. Many research studies that are concerned with the grain boundary of ZnO ceramics have been performed. It has been confirmed that the electrical behavior of ceramics is closely related to the Double Schottky Barrier (DSB) formed at the grain boundary. The donor density has been determined using the modified C-V characteristics and infrared reflection spectrum. The bulk traps on ZnO varistors have also been characterized by many researchers. Also, much attention has been paid to the interface states which directly affect the nonlinear I-V characteristics of ZnO varistors and are closely related to the formation of DSB. The interface states have been investigated using transient capacitance methods such as deep-level transient spectroscopy (DLTS) and isothermal capacitance transient spectroscopy (ICTS).

In spite of the many investigations carried out on ZnO varistors, detailed analysis of the defects and associated states has not been sufficiently elucidated. Although numerous investigations have been carried out on the electrical properties, few investigations concern the relationship between the optical absorption and the I-V characteristics for ceramic ZnO containing metal impurities because of the difficulty with the conventional transmission methods due to strong scattering. PT spectroscopy such as PPE and PA spectroscopy is the useful tool to study the optical absorption spectra of ceramic ZnO containing suitable metal oxides. Using these methods, a study of the non-radiative recombination processes and the evaluation of the optical and thermal properties of materials can be conducted. It is also effective for non-contact detection of the energy state and the deep level in the scattering sample such as ceramics and powders.

1.3 Objectives

The objectives of this research are:

1. To investigate the thermal diffusivities of zinc oxide doped with bismuth oxide using the pyroelectric method, and

2. To determine the band-gap energy of zinc oxide doped with transition metal material by using photopyroelectric method.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The photopyroelectric (PPE) technique is one of the useful methods to determine the thermal parameters of a sample such as thermal diffusivity and to investigate optical properties of materials. This technique is based on a photothermal effect where a pyroelectric (PE) transducer is used to detect the temperature variation from a light-induced periodic heating in a sample. The transducer possesses a temperature-dependent spontaneous polarization below the Curie temperature that changes as the temperature of a material change (Blackburn, 1970). When there is absorption of incident light, the non-radiative de-excitation processes within the solid cause the sample temperature to fluctuate and, through heat diffusion to the surrounding pyroelectric film, the temperature of the sample-PE film interface fluctuates (John *et al.*, 1986). Due to this temperature change, a PE voltage is produced in the PE film and is given by;

$$V = \frac{pl_d}{\varepsilon}\Delta T \tag{2.1}$$

where p is the PE coefficient of the film, l_d is the film thickness, ε is the film dielectric constant and ΔT is the temperature rise in the film (John *et al.*, 1986).

Zinc oxide varistors are ZnO-based ceramic semiconductor devices with highly non-linear current-voltage characteristics (Levinson *et al.*, 1986). The varistors are typically fabricated by sintering of ZnO with small amounts of additives with other metal oxides material such as Bi_2O_3, CoO, MnO, Sb_2O_3, SnO_2, Cr_2O_3 and etc. These additives are the main tools that are used to improve the nonlinear response and the stability of ZnO. Many authors reported that the Bi_2O_3 are typically used at the first stage of varistor fabrication. Wong (1980) reported that the Bi_2O_3-rich liquid phase enhanced densification during the initial stages of sintering and also increased the final grain size of the resulting ZnO structures.

This chapter is concerned with the review of the evolution of PPE techniques for the optical and thermal purpose. The overview will also mention the ZnO as a varistor and the significant characterizations.

2.2 Review on Thermal Diffusivity of ZnO-Based Ceramic

Historically, the search for PE materials has been focused on their infrared radiation detectivity and their efficient high frequency responsivity (Bergman *et al.,* 1971). The most commonly used PPE configurations are shown in Figure 2.1. In standard PPE (SPPE) configuration, the modulated radiation is illuminated on the front surface of the sample, refer to Figure 2.1 (a). The PE sensor is in thermal contact with rear side of the sample. It is also known as back-detection PPE (BPPE) because the detect signal relies on the diffusion of the heat across the sample. Quantitative description of the basis phenomena in SPPE detection which was given by Mandelis and Zver (1985) shows that the particularization of the general PPE responses leads to six special cases based upon the optical, thermal and physical thickness of the sample. Chirtoc and Mihailescu (1989) mark a step further to consider the role