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UNIVERSITI PUTRA MALAYSIA

THERMAL, ELECTRICAL AND MICROSTRUCTURAL CHARACTERIZATION OF SnO2-BASED CERAMIC COMPOSITES

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By

AIZA MASYATI BINTI MAS'UT

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

Sept 2008

DEDICATION

To my beloved parents Mas'ut A.Samah and Rohayati Armia

for their boundless love and repeated encouragement ..

To my family members

for their wonderful support and concern…

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

THERMAL, ELECTRICAL AND MICROSTRUCTURAL CHARACTERIZATION OF SnO_2-BASED CERAMIC COMPOSITES

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Chairman: Associate Professor Zaidan Abdul Wahab, PhD

Faculty: Science

In this work, the photoflash and two-probe technique were used to measure thermal diffusivity and electrical conductivity, respectively, on tin (IV) oxide-based gas sensor materials i.e. SnO_2/CuO and SnO_2/ZnO samples. All measurements were made at room temperature.

It was found that the thermal diffusivity value of pure SnO_2 was 1.45×10^{-2} cm^2s^{-1}. The thermal diffusivity of SnO_2/CuO ceramic composites with addition of up to 30 mole% CuO increases to 7.50×10^{-2} cm^2s^{-1} but further additions of CuO decrease the thermal diffusivity value to 6.21×10^{-2} cm^2s^{-1}. For SnO_2/ZnO ceramic composites, the thermal diffusivity is in the range of 1.01 to 2.62×10^{-2} cm^2s^{-1}. Changes of the grain size or changes of the porosity volume have been suggested to be responsible for the variation in the thermal diffusivity behavior and this was supported by SEM micrographs.

The electrical resistivity of pure SnO_2 was found to be 2.11×10^1 Ωcm. Both SnO_2/CuO and SnO_2/ZnO ceramic composites indicated that their electrical resistivity values were in the range of 4.067×10^5 Ωcm to 8.667×10^6 Ωcm and 2.739×10^5 Ωcm to 5.650×10^6 Ωcm, respectively. Their electrical resistivity trends were actually decrease with increasing additions of either CuO or ZnO. The variation in the electrical resistivity of these samples has been explained based on the changes of free electron concentration.

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

PENCIRIAN TERMA, ELEKTRIK DAN STRUKTUR MIKRO KOMPOSIT SERAMIK BERASASKAN SnO_2

Oleh

AIZA MASYATI BINTI MAS'UT

Sept 2008

Pengerusi: Profesor Madya Zaidan Abdul Wahab, PhD

Fakulti: Sains

Di dalam kajian ini, teknik sinaran lampu kilat dan kaedah penduga dua titik, masing-masing telah digunakan untuk mengukur keresapan terma dan kekonduksian elektrik ke atas bahan-bahan sensor gas berasaskan SnO_2 iaitu sampel SnO_2/CuO dan SnO_2/ZnO. Semua pengukuran telah di buat pada suhu bilik.

Nilai keresapan terma bagi sampel SnO_2 tulen ialah 1.45×10^{-2} cm^2s^{-1}. Nilai keresapan terma bagi sampel seramik komposit SnO_2/CuO dengan penambahan sehingga 30 mol CuO didapati meningkat kepada 7.50×10^{-2} cm^2s^{-1}. Namun, penambahan CuO seterusnya menyebabkan pengurangan dalam nilai keresapan terma kepada 6.21×10^{-2} cm^2s^{-1}. Bagi sampel seramik komposit SnO_2/ZnO pula, nilai keresapan termanya adalah dalam julat 1.01×10^{-2} cm^2s^{-1} hingga 2.62×10^{-2} cm^2s^{-1}. Perubahan dalam saiz zarah atau isipadu liang telah dicadangkan sebagai punca kepada variasi dalam nilai keresapan terma dan keputusan ini di sokong oleh grafmikro-grafmikro SEM.

Kerintangan elektrik bagi sampel SnO_2 tulen didapati adalah sebanyak 2.11×10^1 Ωcm. Kerintangan elektrik bagi kedua-dua seramik komposit SnO_2/CuO dan SnO_2/ZnO pula maisng-masing berada dalam julat 4.067×10^5 Ωcm hingga 8.667×10^6 Ωcm dan 2.739×10^5 Ωcm hingga 5.650×10^6 Ωcm. Keputusan yang diperolehi menunjukkan kerintangan elektrik berkurang dengan penambahan CuO atau ZnO. Variasi dalam kerintangan elektrik sampel-sampel telah dijelaskan berdasarkan perubahan kepekatan elektron bebas.

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

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I certify that an Examination Committee has met on 11 September 2008 to conduct the final examination of Miss Aiza Masyati Binti Mas'ut for her Master of Science thesis entitled "Thermal, Electrical And Microstructural Characterization Of SnO_2-Based Ceramics" 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 do 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 or concurrently submitted for any other degree at UPM or other institutions.

AIZA MASYATI MAS'UT

Date:

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LIST OF ABBREVIATION

Al_2O_3	Aluminium Oxide
CaO	Calcium Oxide
Ce	Carium
CH_4	Methane
C_2H_5OH	Etanol
CO	Carbon Monoxide
CO_2	Carbon Dioxide
Cu	Copper
$CuCO_3$	Copper(II) Carbonate
CuO	Copper Oxide
Cu_2O	Cuprous Oxide
CVD	Chemical Vapour Deposition
DMM	Digital Multimeter
eV	Electron volt
cm	Centimeter
mm	Millimeter
nm	Nanometer
µm	Micrometer
MHz	Megahertz
Pa	Pascal
E_a	Acceptor State
E_c	Conduction Band
Ed	Donor State
E_g	Energy Gap
E_v	Valence Band
EXP	Experiment
F	Fluorine
H_2	Hydrogen
H_2S	Hydrogen Sulfide
HNO_3	Nitric Acid

In	Indium
In_2O_3	Indium Oxide
I-V	Current–voltage
ITO	Indium tin oxide
La	Lanthanum
LPG	Liquid Petroleum Gas
Mg	Magnesium
MgO	Magnesia
Mn	Manganese
MnO_2	Manganese Oxide
Nb	Niobium
NH_3	Ammonia
Ni-Cr	Nickel-Chromium
NMES	Nonmetallic Elemental Solid
NO	Nitrogen Monoxide
O_2	Oxygen
P	Phosphorus
Pd	Palladium
Pt	Platinum
Sb	Antimony
SEM	Scanning Electron Microscope
SiC	Silicon Carbide
SiO	Silicon Oxide
Sn	Tin
SnO_2	Tin (IV) Oxide
TiO_2	Titanium Oxide
WO_3	Tungsten Trioxide
wt%	Weight percentage
XRD	X-Ray Diffraction
Y	Yttrium
ZnO	Zinc Oxide
$ZnSnO_3$	Metastannate
Zn_2SnO_4	Spinnel Zinc Stannate

LIST OF SYMBOLS

α	Thermal diffusivity (cm^2s^{-1})
α_c	Corrected value of thermal diffusivity
τ	Pulse time
2θ	Scanning angle
T	Temperature
λ	Thermal conductivity ($Wcm^{-1}K^{-1}$)
Q	Total energy supplied per unit area
q	Rate of heat flow
C	Specific heat
C_p	Specific heat at constant pressure
K	Kelvin
l	Sample thickness (cm)
g	Finite thickness
m	Mass
V	Volume
ρ	Density
ρ_{th}	Theoretical density
x	Composition of ceramics
$t_{0.5}$	Half rise time
$t_{0.25}$	Time to reach 25% of maximum temperature
$t_{0.75}$	Time to reach 75% of maximum temperature
t_c	Characteristic rise time
K_R	Correction factor

l	Mean free path
l_{th}	Mean free path determined by thermal scattering
l_{im}	Mean free path determined by scattering by impurities
kV	KiloVolt
A	Surface area
Å	Amstrong
d	Diameter
E	Electric field
I	Current through the object
J	Current density
R	Resistance
V	Voltage
ρ	Resistivity
σ	Electrical conductivity
μ	Carrier mobility
v	Average velocity of the phonons
L	Lorentz number
N	Number of unit cells in the crystal lattice of solid
$\boldsymbol{\phi}_M$	Metal work functions
$\boldsymbol{\phi}_S$	Semiconductor work functions
V_{bi}.	Electrostatic potential (built-in field)

CHAPTER 1

INTRODUCTION

1.1 Ceramic

The term "ceramic" comes from the Greek work keramikos, which means "burn stuff", indicating that desirable properties of these materials are normally achieved through a high-temperature heat treatment process called firing. Ceramics can be defined as solid compounds that are formed by the application of heat and sometimes heat and pressure, comprising at least one metal and a nonmetallic elemental solid (NMES) or a nonmetal, a combination of at least two NMESs, or a combination of at least two NMESs and a nonmetal (Barsoum, 1997). Also note that ceramics are not limited to binary compounds: $BaTiO_3$, $YBa_2Cu_3O_7$ and Ti_3SiC_2 are all perfectly respectable class members.

It follows that the oxides, nitrides, borides, carbides, and silicides of all metals and NMESs are ceramics; which needless to say, leads to a vast number of compounds (Barsoum, 1997). This number becomes even more daunting when it is appreciated that the silicates are also, by definition, ceramics. Because of the abundance of oxygen and silicon in nature, silicates are ubiquitous; rocks, dust, clay, mud, mountains, sand – in short, the vast majority of the earth's crust are composed of silicate-based minerals. When it is also appreciated that even cement, bricks, and concrete are essentially silicates, the inescapable conclusion is that we live in a ceramic world.

Ceramics are hard, wear-resistant, brittle, prone to thermal shock, refractory, electrically and thermally insulative, intrinsically transparent, nonmagnetic, chemically stable and oxidation-resistant (Barsoum, 1997). As with all generalizations, there will be exceptions; some ceramics are electrically and thermally quite conductive, while others are even superconducting. An entire industry is based on the fact that some ceramics are magnetic.

Traditional ceramics are quite common, from sanitary ware to fine chinas and porcelains to glass products. Currently ceramics are being considered for uses that only two decades ago were inconceivable; applications ranging from ceramic engines to optical communications, electrooptic applications to laser materials and substrates in electronic circuits to electrodes in photoelectrochemical devices. In this project, the samples used are semiconductor ceramics.

1.2 SnO_2 Gas Sensor

Advances in technology, increased concern over domestic and industrial safety, finer control over manufacturing process steps and legislative actions governing harmful gaseous emissions from stationary and mobile sources are a few of the driving forces that have spurred increased development and implementation of gas sensors during the past three decades (Phani et al., 1999). Tin oxide, SnO_2 is most used as a material for gas sensor applications and it is the most important material for commercially