HYDROPHOBIC, STRUCTURAL AND OPTICAL PROPERTIES OF ZINC SILICA THIN FILMS

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A thesis submitted in fulfillment of the
requirements for the award of the degree of
Master of Science (Physics)

Faculty of Science
Universiti Teknologi Malaysia

MAY 2013

To my beloved family

Thanks for all the efforts, guidance, tender support and blessings that shower on me.

ACKNOWLEDGEMENT

Firstly, I would like to express my deepest gratitude to Almighty God; because of His Blessings, I am able to complete my final project successfully and within the stipulated time. I would like to express my appreciation and thanks to my project supervisor, PM Dr. Karim bin Deraman for his guidance and constructive criticisms. He has been the determining factor in starting and finishing this research and I learned a lot from this study.

I am highly indebted to Ministry of Science, Technology and Innovation (MOSTI) for funding my studies and provide science fund under Vot. 79388 and Sultanah Zanariah Library, UTM also deserve my appreciation for supplying the relevent literatures.

Also not forgetting to convey my deeply appreciation to Material Lab members, Mr. Md. Jaafar Raji, Puan Anisah, Thin Films Lab, Ibnu Sina Institute, UTM, and AMREC of SIRIM Kulim who had provided me with samples information and also co-operation during the process of conducting my project in the laboratory. Through their guidance and tolerance, I am now more confident with laboratory works and analysis.

Finally, an honorable mention goes to my family and friends for their understandings and supports in completing my project. Without helps from them, I would face many difficulties while doing my project.

ABSTRACT

A fundamental study was conducted to investigate the hydrophobic properties, structural characteristics, surface morphology and topology, and luminescence properties of the zinc silica thin films due to various ZnO content. Hydrophobically zinc silica thin films, xZnO-(1-x)SiO_2 with $0 < x < 20$ wt%, have been prepared using a low temperature sol-gel process and dip coating technique. The hydrophobic properties were determined using contact angle measurement which gave the static water contact angle of $102 \pm 1°$ for 20 wt% of ZnO. The structural characteristics were investigated using Infrared (IR) Spectroscopy in the range of 400 – 4000 cm^{-1}. The peaks observed on the spectra showed the C-H, C-H_3, Si-O-Si, Si-O-Zn and Zn-O bonding. The changes in morphology and topology were characterized by Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscopy (FESEM). The surface roughness of the hydrophobic coatings showed a maximum value of 148.32 nm while the maximum size of the pores was found to be 6.47 µm. The optical absorption and photoluminescence properties were studied by means of UV-Visible optical absorption and Photoluminescence (PL) spectroscopy. All samples exhibited more than 90 % optical transmittance which indicated a higher transparency of the films. The emission spectra showed broad and sharp peaks of luminescence at 390, 420, 550 and 740 nm corresponding to the characteristic of Zn^{2+} due to transitions of ${}^2S_{1/2} \rightarrow {}^2D_{5/2}$, ${}^2S_{1/2} \rightarrow {}^2D_{3/2}$, ${}^2D_{3/2} \rightarrow {}^2P°_{3/2}$ and ${}^2D_{5/2} \rightarrow {}^2P°_{3/2}$, respectively. The thin films prepared in this work have shown to be promising materials for use in hydrophobic and water-resistant applications.

ABSTRAK

Satu kajian asas telah dijalankan untuk menyiasat sifat hidrofobik, ciri-ciri struktur, morfologi dan topologi permukaan, dan sifat-sifat luminesen daripada zink silika saput tipis terhadap kepelbagaian kandungan ZnO. Secara hidrofobik, zink silika saput tipis, xZnO-(1-x) SiO_2 dengan $0 < x < 20$ % berat, telah disediakan dengan menggunakan proses sol-gel bersuhu rendah dan teknik lapisan celup. Ciri-ciri hidrofobik telah ditentukan dengan menggunakan pengukuran sudut sentuh yang memberikan sudut sentuhan air statik iaitu 102 ± 1 ° untuk 20 % berat ZnO. Ciri-ciri struktur telah disiasat menggunakan Inframerah (IR) Spektroskopi dalam julat 400-4000 cm^{-1}. Didapati puncak pada spektrum menunjukkan terdapat ikatan C-H, C-H_3, Si-O-Si, Si-O-Zn dan Zn-O. Perubahan dalam morfologi dan topologi telah diukur dengan menggunakan Mikroskopi Tenaga Atom (AFM) dan Mikroskopi Elektron Pengimbasan Pancaran Medan (FESEM). Kekasaran permukaan lapisan hidrofobik menunjukkan nilai maksimum 148.32 nm manakala saiz maksimum liang udara didapati sebanyak 6.47 μm. Penyerapan optik dan sifat-sifat fotoluminesen dikaji melalui penyerapan UV-optik nyata dan Spektroskopi Fotoluminesen (PL). Semua sampel menunjukkan penghantaran optik lebih daripada 90 % iaitu menunjukkan ketelusan cahaya yang lebih tinggi daripada filem. Pancaran spektrum menunjukkan puncak luminesen yang luas dan tajam pada 390, 420, 550 dan 740 nm sepadan dengan ciri-ciri Zn^{2+} disebabkan oleh peralihan daripada $^2S_{1/2} \rightarrow {}^2D_{5/2}$, $^2S_{1/2} \rightarrow {}^2D_{3/2}$, $^2D_{3/2} \rightarrow {}^2P°_{3/2}$ dan $^2D_{5/2} \rightarrow {}^2P°_{3/2}$, masing-masing. Saput tipis yang disediakan dalam kerja ini telah menunjukkan bahan-bahan yang berpotensi untuk digunakan dalam aplikasi hidrofobik dan kalis air.

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LIST OF ABBREVIATIONS

AFM	-	Atomic Force Microscopy
C	-	Carbon
CH_3	-	Methyl
CH_3OH/MeOH	-	Methanol
EDAX	-	Energy Dispersive X-ray Analysis
FESEM	-	Fourier Transform Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared
H_2O	-	Deionized water
MTMS	-	Methyltrimethoxysilane
NH_4F	-	Ammonium Flouride
O	-	Oxygen
PL	-	Photoluminescence
SEM	-	Scanning Electron Microscope
SiO_2	-	Silica / Silicon Dioxide
T	-	Transmittance
UV	-	Ultra violet
wt%	-	Weight percentage
WCA	-	Water Contact Angle
XRD	-	X-Ray Diffraction
Zn	-	Zinc
ZnO	-	Zinc oxide

LIST OF SYMBOLS

^{o}C	-	Degree celcius
c	-	Speed of light
d	-	Thickness of thin film
D	-	The average size of crystallites
eV	-	Electron Volt
E_g	-	Energy band gap
g	-	Gravity
h	-	Coating thickness
H	-	Humidity
$h\nu$	-	Photon energy of light
ml	-	Milliliter
M	-	Molarity
P_0	-	Vapor pressure
r	-	The roughness factor
v	-	Withdrawal Speed
α	-	Absorption coefficient
λ	-	X-ray wavelength
θ	-	Bragg angle
η	-	Viscosity
ρ	-	Density
γ_{LV}	-	Liquid vapour surface tension

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nowadays, hydrophobic surface have gained a lot of attention among researchers in both academic and industrial field. Solid surfaces exhibit contact angle more than 90° was called hydrophobic surface while contact angle more than 150° known as superhydrophobic surface. The hydrophobic surfaces have great interest because their potential applications in diverse field such as water repellent and stainless coating, anti-contamination, laboratory-on-a-chip devices and self-cleaning properties for solar cells, building walls and roof glasses, satellite dishes and photovoltaics.

The well-known example for hydrophobic self-cleaning properties is lotus leaves with scientific name *'Nulembo nucifera'*. In 1997, Barthlott and Neinhuis investigated the hydrophobicity and surface roughness of Lotus leaves act as self-cleaning properties. The Lotus leaves show the bigger pores size in the range of 20–40 µm using electron micrograph and have smaller surface roughness on the surface. Numerous researchers confirmed that the combination of micro and nano-scale of surface roughness can produce higher hydrophobicity with low surface energy and low sliding angle contributed for self-cleaning applications. In order to mimicking Lotus leaf behavior, different chemical methods are investigate for the synthesis of water repellent surfaces such as air brushing (Tsai *et al.,* 2011), sol gel method (Rao *et al.,* 2006), layer-by-layer assembly technique (Bravo *et al.*, 2007 and Zhang *et al.*, 2007), and combustion synthesis (Chakradhar *et al.,* 2011). However, a few methods can produce good and transparent thin films with simple and low cost processing method.

Furthermore in the making material for self-cleaning applications, sol gel method is one of the most efficient methods for preparation of transparent water repellent materials. Sol gel makes a promising in producing precise ability in controlling the silicate (SiO_2) microstructure with properties that cannot be achieved by other materials. Rao and co-workers have done variety investigation for transparent silica thin films hydrophobic coatings on the glass surfaces. Mahadik and colleagues (2010) has developed transparent silica superhydrophobic coatings using methylmethoxysilane (MTMS) by sol gel method. Besides, silica base nanocomposite films offer a better control of the shape, size and properties for quantum confinement of semiconductor crystallites such as luminescence.

Zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor which also can be made transparent thin films for the whole visible range. Moreover, ZnO films allows in producing a great luminescent material at room temperature. For example, the optical properties of ZnO dispersed into SiO_2 shows good photoluminescence properties where ZnO-SiO_2 emits violet, blue, green and red band emission. After all, less study has been made for hydrophobic properties using zinc oxide materials whereas zinc oxide promising good hydrophobic properties for the thin films.

In the present research work, an easy and efficient method will be prepare to synthesize hydrophobic zinc silica thin films with high transparency and good luminescence by simple dip coating technique using sol gel method exhibiting the self-cleaning behavior. These films will be deposited with different composition of zinc materials between 0 to 20 wt% keeping the other deposited parameters fixed at certain values. The effects of zinc composition on silica thin films will change the microstructural and the optical properties which produced a good quality of films.

1.2 Problems of Statement

Although properties of zinc silica thin films have been studies and attracted a number of researchers because their wide-ranging in industrial and technical applications, most researchers were more interested to study the structural and optical properties of the zinc silica thin films without more specific studies on hydrophobicity characteristic of the films (Hong *et al.*, 2010; Zhang *et al.*, 2011; Mohamed *et al.*, 2012). Therefore, an investigation on the hydrophobic characteristic of ZnO-SiO_2 thin films will be carried out and the results of this study are presented in this thesis.

1.3 Objectives of the study

The objectives of the study are as below:

(i) To determine the influence of ZnO content on the hydrophobic properties of silica thin films.

(ii) To determine the influence of ZnO content on the phase formation and structure feature of silica thin films.

(iii) To determine the influence of ZnO content on the surface morphology and topology of silica thin films.

(iv) To determine the influence of ZnO content on the optical and luminescent properties of silica thin films.

1.4 Scope of the study

In order to achieve the objectives of the study, the scope of the study as follows:

(i) The thin film samples based on composition of xZnO-(1-x)SiO_2 with ($0 \leq x \leq 20$ wt%) have been prepared using sol gel technique and dip coating technique. In this case, silica thin films sample also be prepared and can be used as reference.

(ii) The water contact angle of zinc silica thin films will be measured by water contact angle meter or goniometer.

(iii) The phase formation and structure feature was conducted by X-Ray diffraction (XRD), Fourier Transform Infrared (FTIR), and Energy Dispersive X-Ray Spectroscopy (EDAX).

(iv) The surface morphology and topology of zinc silica thin films will be measured using Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscope (FESEM).

(v) The optical and luminescence properties of zinc silica thin films will be measured using UV-Visible and photoluminescence spectroscopy (PL).

1.5 Significance of Study

The study focuses on the influence of ZnO content through hydrophobic silica thin films properties. Due to limited studies on luminescence properties in hydrophobic thin films, this present study has been developed because the promising in luminescence performance. The study of zinc silica thin films is important to determine the influence ZnO content on the surface structure of the films. Furthermore, the sol gel technology considered to be among the most effective method for the better control of shape, size and properties of hydrophobic thin films. By the end of this research, zinc silica thin films expected to have excellent hydrophobic properties with high transparency and high luminescence properties.

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