CHARACTERIZATION, ANALYSIS AND OPTICAL STUDIES OF CADMIUM SULFIDE NANOSTRUCTURES DEPOSITED ON DIFFERENT SUBSTRATES FOR OPTOELECTRONIC APPLICATIONS

By

ABDULWAHAB SALEM Z. LAHEWIL

(1141810568)

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Author's full name: **ABDULWAHAB SALEM Z. LAHEWIL**

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Dedicated to my parents

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LIST OF SYMBOLS

ml	Milliliter
mol/L	Mol Per Liter
n	Refractive Index
θ	X-ray Diffraction Angle
Eg	Energy Band Gap
ε_∞	Optical Dielectric Constant
K	Extinction Coefficient
ϕ_b	Barrier Heights
A^{**}	Richardsons Constant
m	Ideality Factor
A	Contact area
q	Electron charge
T	Temperature Centigrade
k	Boltzmann Constant
I_s	Saturation Current
β	Full Width HALF Maximum
λ	Wavelength
N	Number of crystallites per area
d	Interplanar distance
δ	Length of dislocation lines per unit area
ε	Strain of the thin film
D.	Crystallites Sizes
h	Constant
a & c	Lattice Constant
Å	Angstrom
mA	Milliampere
uA	Microampere
t	Thickness
B_o	Bulk Modulus
hkl	Miller Indices
π	ratio of a circle's circumference to its diameter
hkl	Miller Indices
π	ratio of a circle's circumference to its diameter
nm	Nanometer
%	Percentage
eV	Electron Volt

LIST OF ABBREVIATION

Si	Silicon
n-Si	n-type Silicon
p-Si	p-type Silicon
a.u	Arbitrary Unit
rpm	Revolution Per Minute
FWHM	Full Width HALF Maximum
I-V	Current – Voltage
MSM	Metal-Semiconductor-Metal
AFM	Atomic Force Microscope
TGA	Thermogravimetric analysis
DTA	Differential Thermal Analysis
DSC	Differential Scanning Calorimetry
FTIR	Fourier transform infrared spectroscopy
AFM	Atomic Force Microscope
PL	Photoluminescence
XRD	X-ray Diffraction
CdS	Cadmium sulphide
TU	Tiourea
UV	Ultraviolet

PENCIRIAN, ANALISIS DAN PENGAJIAN OPTIKAL NANO KADMIUM SULFIDA DIMENDAP DI ATAS SUBSTRAT BERLAINAN UNTUK APLIKASI OPTOELEKTRONIK

ABSTRAK

Penyelidikan mengenai teknologi nano telah menjadi semakin popular kerana sifat fizikal, kimia, optik dan pemangkin unik berbanding dengan sebahagian besar dari diri mereka. Nanoteknologi merevolusikan pelbagai sektor industri seperti tenaga, sains alam sekitar, keselamatan, sains perubatan dan peralatan perubatan dan lain-lain teknologi. Bahan semikonduktor II-VI, stuktur nano CdS merupakan bahan yang unik dan mempunyai jurang jalur sebanyak 2.45 eV dimana ia telah menarik perhatian yang besar di kalangan ahli-ahli penyelidik kerana sifat-sifatnye yang unik. Objektif kajian ini adalah untuk mensintesis struktur nano CdS yang dimendapkan di atas substrat yaug berbeza seperti kaca, kuarza, silikon jenis n dan silikon jenis p dengan menggunakan kaedah salutan putar sol-gel untuk aplikasi optoelektronik. Morfologi permukaan, struktur, sifat-sifat optik, haba dan elektrik CdS nano disintesis dan dicirikan dengan menggunakan XRD, AFM, SEM, UV-VIS, PL, FTIR, TGA, DTA, DSC dan sumber meter. Elektrod perak disejat secara terma di permukaan CdS nano menggunakan topeng bayang-bayang keluli tahan karat. CdS nano yang dimendap pada substrat kaca menunjukkan pembentukan CdS mempunyai struktur heksagon. Ketebalan Cds nano seperti yang diukur oleh AFM masing-masing didapati dalam julat 150 nm dan 10 nm pada kelajuan lapisan putaran masing-masing sebanyak 1000 rpm dan 5000 rpm. Manakala Cds nano telah dimendapkan di substrat kuarza dimana ia dipanaskan pada suhu 800 º C dengan kelajuan yang berbeza termasuk 1000, 3000 dan 5000 rpm dengan menggunakan teknik salutan putar sol-gel. Kajian struktur, morfologi dan analisis telah disiasat. Ia didapati bahawa saiz bijian CdS nano adalah dalam julat 1.81 nm hingga 4.35 nm. Jurang jalur diukur dengan petunjuk penghantaran dalam julat yang boleh dilihat, ia berubah disebabkan saiz CdS nano yang kecil. Morfologi struktur filem nipis nano Cds didapati berterusan, tebal dan juga sesuai. Permukaan filem adalah lebih licin dan zarah-zarah juga diedarkan dengan sekata. Struktur CdS nano yang telah dimendap di substrat jenis silikon n dan jenis p.dalam julat 200-600 ºC. Kesan penyepuhlindapan suhu pada struktur, sifat-sifat morfologi, optik dan elektrik telah dihuraikan untuk meningkatkan kualiti filem struktur nano CdS. Analisis XRD menunjukkan bahawa kualiti kristal CdS nano boleh diperbaiki dengan meningkatkan suhu sehingga 400 °C, tetapi pemanasan sehingga suhu 600 °C menyebabkan penurunan kualiti kristal. Modulus pukal dikira menunjukkan persamaan yang baik dari segi keputusan eksperimen dan teori untuk substrat yang berbeza iaitu dalam julat 27.6 Gpa hingga 281.3 GPa. Ciri-ciri optik penyerapan, pantulan, penghantaran, jurang jalur tenaga dan pekali kepupusan diperolehi melalui penggunaan PL dan spektroskopi UV-VIS. Keputusan kiraan indeks biasan dan dielektrik tetap optik diberi selaras dengan data eksperimen. Hasil yang terbaik untuk struktur filem nipis nano CdS adalah dengan menggunakan substrat silikon jenis-p disepuh lindap pada 400 ºC. Sifat-sifat terma Cds nano juga disiasat dan didapati jelas bahawa rawatan haba yang baik sebahagian besarnya boleh mengurangkan ketegangan filem dan meningkatkan penghabluran itu.

CHARACTERIZATION, ANALYSIS AND OPTICAL STUDIES OF CADMIUM SULFIDE NANOSTRUCTURES DEPOSITED ON DIFFERENT SUBSTRATES FOR OPTOELECTRONIC APPLICATIONS

ABSTRACT

Recently the research on nanotechnology has become increasingly popular due to their unique physical, chemical, optical and catalytic properties compared to their bulk counterparts. Nanotechnology revolutionizes many technology and industry sectors such as energy, environmental science, safety, medical sciences, medical instrumentation and many others. An II-VI semiconductor material, CdS nanostructure with a band gap of about 2.45 eV, has attracted great attention among the researches due to the peculiar properties. The objective of this research is to synthesize CdS nanostructure thin films deposited on different type of substrates glass, quartz, n-type and p-type silicon using sol-gel spin coating technique for optoelectronic applications. The CdS nanostructure thin films was synthesized and characterized using XRD, AFM, SEM, UV-VIS, PL, FTIR, TGA, DTA, DSC and Keithley 2400 Source Meter. Silver electrodes were thermally evaporated on the surface of CdS nanostructure thin films using stainless steel shadow mask. For CdS nanostructure thin films deposited on glass substrates, the results have indicated that the CdS has hexagonal structure. The thickness of CdS nanostructure thin films as measured by AFM is found to be in the range of 150 nm and 10 nm at 1000 rpm and 5000 rpm spin coating speeds respectively. For CdS nanostructure thin films deposited onto quartz substrates and annealed at 800 ^{o}C with different spin coating speeds 1000, 3000 and 5000 rpm, the structural, morphological and analytical studies were investigated and found that the grain size of CdS nanostructure thin films found to be in the range 1.81 nm to 4.35 nm. The band gap was measured with an indication of transmission within the visible range. It is found that the band gap changed due to small grain size of CdS nanostructure thin films. The morphology of CdS nanostructure thin films are found to be continuous, dense and well adhered. The films surface is much smoother and the particles are well distributed. For CdS nanostructure thin films deposited into n-type and p-type silicon substrates at different annealing temperatures in the range from 200 ^{o}C to 600 ^{o}C. The effects of annealing temperatures were investigated on the structural, morphological, optical and electrical properties to improve the CdS nanostructure thin films. The XRD analysis shows that the crystalline quality of CdS nanostructures can be improved by increasing the temperature to 400 ^{o}C, but further increase to 600 ^{o}C leads to degradation of the crystalline quality. The bulk modulus was calculated and showed good agreement with experimental and theoretical results for different substrates to be found in the range 27.6 to 281.3 GPa. The optical properties of absorption namely; reflection, transmission, extinction coefficient and the energy band gap were obtained by PL and UV-VIS spectroscopies. The calculated refractive index and optical dielectric constant, the results are in agreement with experimental data. The best results for CdS nanostructure thin films are found using p-type silicon substrates annealed at 400 ^{o}C. The thermal properties of CdS nanostructures also investigated and found to be evident that a good thermal treatment can largely decrease the film strain and improve its crystallinity.

CHAPTER 1

INTRODUCTION

1.1 Overview

The purpose of this chapter is to provide a general framework and introduction for the work presented in the current thesis. This chapter is divided into five sections, addressing the CdS properties and application, problem statement, research objectives, research scopes, and thesis organogram.

1.2 CdS Properties and Applications

Nanostructured materials have an explosion of scientific and industrial interest over the last fifty years (Lahewil et. al., 2012). Nanostructured and microstructures have obtained for ceramic, metallic, diamond, semiconducting, polymer and composite materials. The different forms in which these materials may appear include dry powders, liquid dispersions, coatings, films and bulk solids. Increased interest in nanomaterial is a resulted of the unique properties that can be obtained and the exciting applications that result from these properties. Enhanced morphology, analysis, thermal, optical and electrical properties have been reported for these nanomaterials. Nanocrystalline materials are three dimensional solids composed of nanometer sized grains, or crystallites (building blocks)

(Pan et. al., 2011). Because of their unique structure, which is characterized by ultrafine grains and a rather high density of crystal lattice defects, these material have extraordinary fundamental properties that could be exploited to make next-generation super strong metals, ductile ceramics and wear-free materials. Nanostructured materials have characteristic length of which is of a few (typically 1-100) nanometers and therefore may be in or far away from thermodynamic equilibrium.

The reduced size in the nonmetric range also characterizes the material to transmit visible light considerably. This feature helps the nanomaterial to act as transparent envelopes over various substrates without affecting their aesthetic/original look. Besides, the extremely high surface to volume ratio possessed by the nanomaterial makes them highly energetic in terms of surface energy, which in turn let the surface to undergo suitable reactions to reduce the surface energy. This possibility can be exploited by using the nanomaterial in catalysis/photocatalysis (Li et. al., 2011).

Cadmium sulfide (CdS) is an important chalcogenide semiconductor with a wide band gap of 2.42 eV at room temperature. Extensive research has been done in the last fifty years on CdS compound, mainly due to their interesting electrical, optical and photoconductive properties. CdS offers a large number of applications in solid state technologies as the solar cells and transistors for flat panel displays, piezo-electronic and semiconducting devices. A large number of studies on the synthesis and characterization of nanocrystallines, crystalline with sizes of crystallites below hundred nanometers, of different II-VI compound semiconductors have been published in the recent years (Dobson et. al., 2000, Hiie et. al., 2006, Murali et. al., 2010, Pan et. al., 2011 & Li et. al., 2011). Many properties of nanocrystalline materials are found to deviate from those of coarse grained crystalline materials with the same average chemical composition. These deviations result from dimensionality of nanometer sized grains and numerous interfaces between adjacent crystallites (Dong et. al., 2003). The CdS thin films have been prepared by various methods; including evaporation metal organic chemical vapour deposition (MOCVD) (Frigo et. al., 1989), molecular beam epitaxy (Samarth et. al., 1990), electrodeposition (Nishino et. al., 1999), photochemical deposition (Ichimura et. al., 1999 & Ye et. al., 2000), spray pyrolysis (Hiie et. al., 2006) and sputtering (Lee et. al., 2007).

Among these techniques, sol-gel spin coating technique is an attractive method with the advantage of simplicity, convenience and easy control of the parameters by changing the substrates temperature, spin coating speed, deposition time, and material quantity. II-VI compounds obtained at room temperature and use this method are generally amorphous, crystalline, or nanocrystalline, showing high resistivity and larger optical band gaps than those reported in the bulk (Singh et. al., 2004 & Mondal et. al., 2007). Different studies of electronic and optical properties of Cd-based materials of bulk structure (Reshak et. al., 2006, Reshak et. al., 2008, Reshak et. al., 2008 & Reshak et. al., 2011 & nano-crystallites Reshak et. al., 2010) are available in the literature. Otherside, structural (Ouahrani et. al., 2010), magnetic (Saeed et. al., 2010) properties of alloys (Tit et. al., 2010) and nanodevices (Umar et. al., 2012) are focused for optoelectronic devices.

Joshi et. al., (2011) have reported on growth of stoichiometric and nonstoichiometric nanostructured heterojunction solar cell of $CdS/CuInS_xSe_{2-x}$ varying x from 0 to 2 in the interval of 0.5 using cost effective, simple, chemical ion exchange method at room temperature on ITO glass substrate. They have investigated structural, compositional, optical and illumination studies. They have achieved the solar energy conversion efficiency which corresponds for stoichiometric dependent electron-hole pair generation and separation phenomenon. Also (Rios-Flores et. al., 2010) have reported the effect of $CdCl_2$ vapor treatment on the photovoltaic parameters of CdS/CdTe solar cells. Such solar cells are examined by measuring their current density versus voltage (J-V) characteristics. The open-circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) of their best cell, corresponding to a total area conversion efficiency of η = 5 %.

Bai & Liu, (2012) have reviewed the nanomaterials and nanostructures implanted on the surface of solid due to those is one of the most attractive topics in the interdisciplinary fields of nanoscience and nanotechnology, surface science, material science, bioscience, supramolecular engineering, etc. This review has presented some recent progress in how to implant the nanomaterials and nanostructures such as nanoparticles, nanowires, nanotubes and chiral nanostructures on the surface of certain supports and their potential application opportunities, with a focus on several sophisticated and typical strategies for the formulation of nanostructured surface, where the unique physicochemical and biochemical properties and potential application possibilities are emerged, in addition to their proposition on the future trends and developments in nanoscience and nanotechnology arena. Otherside, sol-gel technique has been implemented to tailing materials and creating various nanostructures for dye-sensitized solar cells (DSC) by (Zhang & Cao, 2011). They have classified the nanostructures into;

i. Nanoparticles, which offer large surface area to photoelectrode film for dye-adsorption.

ii. Core-shell structures, which are derived from the nanoparticles however with a consideration to reduce charge recombination by forming a coating layer.

iii. One-dimensional nanostructures such as nanowires and nanotubes, which provide direct pathways for electron transport much faster than in the nanoparticle films.

iv. Three-dimensional nanostructures such as nanotetrapods, branched nanowires or nanotubes, and oxide aggregates, which not only emphasize providing large surface area but also aim at attaining more effective light harvesting and charge transport or collection. They have briefly elicited an outlook proposing that the oxide aggregates are potentially promising structure which may possibly achieve higher efficiency than the record by reason that the bifunction of aggregates in providing large surface area and generating light scattering allows for photoelectrode film thinner than usual and thus decreases the charge recombination of DSC's.

Merdes et. al., (2013) have reported externally confirmed total area efficiencies reaching up to 12.9 % for CdS/Cu(In,Ga)S_2 based solar cells. They have confirmed the highest externally efficiencies for such cells, and mentioned the absorbers were prepared from sputtered metals subsequently sulfurized using rapid thermal processing in sulfur vapor. Also, they have presented the structural, compositional and electrical properties of these cells and discussed the correlation between the gallium (Ga) distribution profile and solar cell properties. Otherside, (Kim et. al., 2013) have fabricated CdTe/CdS heterostructure on fluorine tin oxide (FTO) glass to produce thin-film photovoltaic devices. A $CdCl_2$ layer was deposited onto CdTe absorber layer and the subsequent annealing of the stack was performed in a He atmosphere. They have investigated the influence of $CdCl_2$-activation step on the interfaces by monitoring the phase transition of $CdCl_2$-heat-treated

CdTe specimens during temperature ramp annealing via high-temperature X-ray diffraction, and confirmed the interdiffusion between the CdTe and CdS layers through observation of the binding energy shifts and atomic ratio by X-ray photoelectron spectroscopy depth profiling data.

1.3 Problem Statement

Extensive research has been done in the last fifty years on CdS materials due to its applications in electronic devices such as field-effect transistors, solar cells, photoconductors, optical thin films filter, nonlinear integrated optical devices, light emitting diodes (LEDs) and laser heterostructures for emission in the visible spectral range (Dai et. al., 1992, Trujillo et. al., 1996, Ullrich et. al., 2000, Perna et. al., 2001, Hernandez-Contrerasa et. al., 2002 & Chediak et. al., 2004). For these purposes, CdS nanostructures have been deposited by different techniques including spray pyrolysis (SP), close space vapor transport (CSVT), vacuum evaporation (Ullrich & Oeder, 2001), chemical bath deposition (CBD), solution growth technique (SGT) (Wang et. al., 2000), sputtering, chemical vapor deposition (CVD), pulsed laser deposition (PLD) and spin coating method. It is proven that the spin coating has many features and can create a highly energetic growth precursor, leading to growth conditions, so that high quality films can be obtained at a fairly low substrate temperature. (Ullrich et. al., 2001 & Erlacher et. al., 2004) have used the spin coating deposition technique up to date in the laboratory research to obtain CdS nanostructures.