SYNTHESIS AND CHARACTERIZATION OF ALUMINUM DOPED ZINC OXIDE NANOWIRES ON NON-CATALYTIC SILICA SUBSTRATES

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To my beloved son, RIGKUEN YESHEY CHABDAG

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ABSTRACT

The undoped and Al-doped ZnO nanostructures were fabricated on the Si (100) substrates via catalyst free thermal evaporation method using a horizontal quartz tube under controlled supply of O_2 gas. The substrate was placed vertically above the source materials unlike the conventional methods. The undoped ZnO nanowires were randomly oriented. When both Al dopant and when doping concentrations were increased, ZnO showed various morphologies in which ZnO changed from randomly orientated nanowires to hexagonal shaped, 'pencil-like' nanorods. Further increase in dopant concentrations beyond 2.4 at% lead to spikey ZnO:Al morphology. The morphology and crystalline structure of ZnO nanostructures were characterized using X-ray diffraction, field emission scanning electron microscopy, scanning electron microscopy and photoluminescence (PL) spectroscopy. ZnO:Al nanorods were found to have diameter roughly between 260 to 350 nm and the length about 720 nm. The as prepared ZnO:Al nanorods also exhibited a strong UV emission. The Al doping concentrations played an important role on the morphology and optical properties of ZnO nanostructures. The significance of the experiment is the simplicity, low cost and fewer necessary apparatus of the process that would suit the high-throughput fabrication of ZnO:Al nanorods. They are expected to have potential applications in functional Si based nanodevices.

ABSTRAK

Nanostruktur ZnO yang didopkan dan tidak didopkan dengan Al di atas substrat Si (100) tanpa penggunaan sebarang pemankin telah dihasilkan melalui kaedah penyejatan terma dengan tiub kuarza digunakan bersama gas oksigen yang dilepaskan melaluinya secara terkawal. Substrat tersebut diletakkan betul-betul di atas bahan asas tidak seperti yang selalu dipraktikkan dalam kaedah konvensional. Tanpa sebarang dopan wayar nano yang dihasilkan adalah secara rawak. Namun, apabila kesemua bahan pendopan Al dilepaskan dan kepekatan dopan meningkat, struktur ZnO yang dihasilkan menunjukkan pelbagai imej dengan struktur tersebut berubah daripada menumbuh secara orientasi rawak kepada struktur yang berbentuk heksagon seperti pensil. Jika kepekatan dopan terus ditingkatkan melebihi 2.4 at%, ZnO:Al akan membentuk struktur seperti paku-paku tajam. Morfologi dan struktur kristal ZnO yang bersaiz nano ini dianalisis ciri-cirinya dengan menggunakan alat XRD, FESEM, SEM dan Photoluminescence (PL). Rod-rod ZnO yang bersaiz nano ini didapati mempunyai jejari sekitar 260 ke 350 nm dan panjangnya mencecah sekitar 720 nm. Rod-rod tersebut juga mempamerkan sinaran UV yang kuat. Kepekatan dopan Al memainkan peranan penting kepada morfologi dan ciri-ciri optikal struktur ZnO. Kepentingan ujikaji ini adalah supaya penghasilan ZnO:Al nanorod dapat dihasilkan dalam kuantiti yang banyak dengan pengunaan kaedah yang mudah, ringkas, berkos rendah dan tidak memerlukan alatan yang banyak. Saintis menjangkakan struktur ini mempunyai potensi yang tinggi dalam alatan-alatan bersaiz nano yang bersasaskan bahan Si.

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LIST OF ABBREVIATIONS / SYOMBOLS

a, a_0	-	Lattice parameter
Å	-	Angstrom
Al_2O_3	-	Aluminate
Ar	-	Argon
Au	-	Gold
c, c_o	-	Lattice parameter
C	-	Carbon/Graphite
cm^3	-	Cubic centimeter
cm^2/Vs	-	Centimeter square per volt second
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
CROs	-	Cathode ray oscilloscopes
CVD	-	Chemical Vapour Deposition
°C	-	Degree Celsius
d	-	Interatomic spacing
D	-	Dimension
eV	-	Electron volt
EDS	-	Energy Dispersive Spectroscopy
EDAX	-	Energy Dispersive Analysis of X-rays
Eg	-	Energy band gap
FESEM	-	Field Emission Electron Microscope
FTO	-	Fluorine doped tin oxide
g	-	Gram
g/cm^3	-	Gram per cubic centimeter (density)

h	-	Hour
HCl	-	Hydrochloric acid
HF	-	Hydrofluoric acid
H_2O	-	Water
HRTEM	-	High-resolution transmission electron Microscope
ICDD	-	International Centre for Diffraction Data
IOSCs	-	Inverted organic solar cells
ITO	-	Indium tin oxide
K	-	Kelvin scale
kJ mol^{-1}	-	Kilo joule per mole
λ	-	Lambda (Wavelength)
μ	-	Micron (10^{-6} m)
m	-	Metre
MRs	-	Microrods
mM	-	Molar mass
MOCVD	-	Metalorganic chemical vapor deposition
MOVPE	-	Metal-Organic Vapor Phase Epitaxy
meV	-	Milli electron volt (10^{-3} eV)
n	-	Wave number, Number of moles
NC	-	Nano-crystals
Ne	-	Neon gas
nm	-	Nanometer (10^{-9} m)
N_2O	-	Nitrous oxide
NPs	-	Nanoplates
NSs	-	Nanostructures / nanosheets
NTs	-	Nanotubes
$Na_2[Zn(OH)_4]$	-	Sodium zincate
NaOH	-	Sodium hydroxide (base)
NWs	-	Nanowires
O	-	Oxygen atom
Ωcm^{-1}	-	Omega per centimeter (resistivity)
PET	-	Polyethylene terephthalate
PL	-	Photoluminescence

Q1D	-	Quasi-one-dimensional
RF	-	Radio frequency
sccm	-	Standard cubic centimeter per minute
SEM	-	Scanning Electron Microscope
Si	-	Silicon
SnO_2	-	Tin oxide
SPM	-	Scanning probe microscope
T	-	Temperature
TCO	-	Transparent conducting oxide
θ	-	Theta (Diffraction angle)
UV	-	Ultraviolet radiation
VLS	-	Vapor-liquid-solid
VS	-	Vapour Solid
XRD	-	X-ray diffraction
$Zn(C_5H_7O_2)_2.xH_2O$	-	Zinc acetylacetonate hydrate
$ZnCl_2$	-	Zinc chloride
ZnO	-	Zinc Oxide
ZnO:Al	-	Aluminum doped zinc oxide
ZnS	-	Zinc sulfide

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The ease of life we enjoy can be attributed to achievements in science and technology to a very large extent. For that matter, nanotechnology has become the seed of peace and tranquility of the modern world. It has stimulated great interest due to their importance in basic scientific research and potential technological applications [1]. Zinc oxide (ZnO) is an interesting and a well-known wide band gap II-VI semiconductor with a direct band gap of ~ 3.3 eV with large exciton binding energy (60 eV). The immense excitement in this area of research arises from understanding the fact that ZnO gives rise to new phenomena and multi-functionality which ultimately leads to unprecedented integration density with nanometer-scale structures [2].

One dimensional (1D) zinc oxide nanostructures (NSs) have been synthesized by various methods [3]. Nanotechnology is an intensively and extensively pursued topic of the 21^{st} century. The influence on the electronic and optical properties due to doping of ZnO has been often reported [4]. However, there are very few studies done on the topic and only limited data is available. The influence of dopants on the formation of doped 1D ZnO NSs would indeed contribute to a better understanding of their growing mechanisms.

Curiosity and need to understand the novel physical properties of one-dimensional nanoscale has been the driving force behind the synthesis and characterization of nanowires (NWs). Undeniably, there is a wide area of applications. As the ever growing research continues, new findings are leading to new applications. The unique structural, electrical, magnetic and optical properties of ZnO NWs is due to its extremely thin nanocrystal (NC) structure which contributes to play a predominant role in the fabrication of sophisticated electronic devices. Nanowires (NWs), nanobelts (NBs), nanorods (NRs), nanotubes (NTs), nanoplates (NPs) and nanohelixes (NHs) are all sister nanostructures (NSs) which can be formed from ZnO synthesis under certain conditions. According to Kwon *et al.* [5], NWs with different compositions has been explored using various methods. Various growth mechanisms have also evolved over time. The details of growth methods will be discussed later. Since the structural, optical, magnetic and electrical properties of ZnO are dependent on growth parameters, hence their applications. So, the prime interest here is to synthesize catalyst free doped ZnO and learn the influence of dopant concentrations on the structural and optical properties. Over the time, researchers have used various dopants to dope ZnO NSs.

1.2 Statement of Problem

Intrinsic semiconductor is electrically neutral and not much of use. However the physical properties of semiconductors can be effectively manipulated by impurity doping. Recently, doping of nanostructures has become an important issue for the more diverse range of applications [6]. So far as we know, there are very few reports on Al-doped 1D ZnO nanowires synthesis particularly via the method we have adopted. Therefore, my focus here is to synthesize Al-doped ZnO nanowires via thermal oxidation of Zn at different dopant concentrations and understand its influence on the structural and optical properties of ZnO:Al.

In particular, catalyst free synthesis of aluminum doped zinc oxide nanowires by placing the substrate vertically above the source is a rarely attempted method. So, it is indeed an opportunity to explore this method and compare its efficiency with other methods. In the conventional systems, source and substrate lie at the same horizontal level separated by certain distance in between. Also, reduction of ZnO with graphite has been a common method unlike the current attempt.

1.3 Research Objectives

In general, aluminum doped ZnO NWs will be synthesized on silicon wafer using high purity zinc powder, aluminum powder and oxygen along with argon as carrier gas. The structural properties and optical properties under various dopant concentrations will be investigated. The following objectives will be under focus in this research;

a) To synthesize aluminum doped ZnO (ZnO:Al) nanowires by a thermal evaporation method.
b) To determine the influence of dopant concentrations on structural and optical properties of ZnO nanowires.
c) To establish the mechanism leading to the growth of ZnO:Al nanowires.

1.4 Scope of the Study

Most of the previous works being devoted on undoped ZnO, there has been very little effort devoted to investigate the doped counterparts [7]. So, it is an opportunity and little concerted effort from my part to explore little further. Doping is a powerful tool to tailor the electrical and optical properties, facilitating the construction of many electronic and optoelectronic devices. Additionally, when doped with Al, it behaves as an acceptor in ZnO with its energy level locating at 0.1 eV below the bottom of the conduction band, making itself a good candidate for creating a p-type ZnO [8]. Similarly, Al doped ZnO nanostructure is found to be one of the best n-type thermoelectric oxide. When doped with Al, the fraction of Al is expected to influence the morphologies of ZnO:Al NWs. In recent years, researchers have shifted their focus on the doped NSs because doping has brought about enhanced conductivity and optical behaviour of the NSs. Likewise, when we choose a dopant, it must possess close lattice matching with ZnO which is satisfied by group III elements which includes Al. As a consequence of limited time, we cannot experiment with dopant other than Al.

Emphasis here will be to synthesize and characterize the structural properties of aluminum (Al) doped ZnO with dopant concentrations ranging from 0.6 at% to 11.3 at% as stated in the research objectives. Also, the process will completed without use of catalyst unlike many popular methods. Thus, there awaits a huge appetite for pure Al doped ZnO NWs.

1.5 Significance of the Study

Expansion of nano research over the past decades clearly indicates the vitality of nanotechnology for the benefit of mankind. The impacts can be felt in every sphere of our life from economy, politics, entertainment, recreation, space exploration, communication, transportation, etc. Due to their unique density of electronic states, NWs in the limit of small diameters are expected to exhibit significantly different optical, electrical and magnetic properties from their bulk 3-D crystalline counterparts. It is mainly attributed to the extremely thin nanocrystals of ZnO. Nanowires, compared to other low dimensional systems, have two quantum confined directions, while still leaving one unconfined direction for electrical conduction.

The study on structural characterization of Al doped ZnO with respect to various dopant concentrations will hopefully contribute in its own manner towards nanotechnology and its pool of knowledge. Although it appears insignificant at the initial stage; however it has a large scope in fulfilling the recent surge for demand and knowledge of Al doped nanomaterials. We are optimistic that it will have a profound impact the world over and least to my needs.

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