ZINC OXIDE NANOSTRUCTURES: THE EFFECT OF DEPOSITION PARAMETERS ON THE ELECTRICAL PROPERTIES USING SOL-GEL METHOD

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FOR MY PRECIOUS PERSON IN MY LIFE,

TO MY FATHER AND MOTHER,

TO MY BROTHERS AND SISTERS

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ABSTRACT

Nanostructured Zinc Oxide (ZnO) has been deposited on Silicon Dioxide (SiO_2) using sol-gel method. The SiO_2 was grown on Silicon (Si) using dry oxidation process in 1 atm ambient. In sol-gel method, a lot of deposition parameters need to be considered to remain the uniformity and reproducibility. Any small changes in the deposition parameters will affect the surface morphologies, electrical properties and optical properties as well. This research is done to study the deposition parameters on the electrical properties and supported by the surface morphologies and optical properties which have strong correlation. There are four deposition method have been focused in this study which are the immerse time, SiO_2 thickness, annealing temperature and the precursor solution concentration. The results have been characterized using scanning electron microscope (SEM) for the structural properties, X-ray diffractometer (XRD) for the growth orientation and IV measurement system for the electrical properties. The optical properties have been characterized using photoluminescence and UV-VIS spectrometer. Immerse time at 3 hours shows optimum electrical IV response. The SiO_2 thickness when oxidized at 5 minutes has optimum structural, electrical and optical properties. Annealing the sample at 500^oC has the optimum IV response but for the optical properties, the best annealing temperature is at 550^oC. The precursor solution concentration at 0.0001 M has optimum IV response but for the optimum optical properties, 0.01 M has the best response. At the end of this study, the optimized deposition parameters in sol-gel method to deposit nanostructured ZnO has been obtained. The result will be a contribution for the next researcher to study other parameters using sol-gel method.

ABSTRAK

Zink Oksida (ZnO) berstruktur nano telah disintesiskan di atas lapisan nipis Silikon dioksida (SiO_2) dengan menggunakan kaedah sol-gel. SiO_2 telah dihasilkan denagn menggunakan kaedah pengoksidaan kering pada 1 atm. Dalam kaedah sol-gel, beberapa parameter perlu diambil kira untuk memastikan kebolehulangan dan sekata. Setiap perubahan kecil pada perameter pendepositan akan menyebabkan perubahan pada struktur bentuk, sifat elektrik dan juga optic. Penyelidikan ini dijalankan untuk mengkaji kesan parameter pendepositan keatas bentuk permukaan, sifat elektrik dan juga sifat optik sebagai sokongan.Kajian difokuskan kepada empar parameter iaitu masa rendaman, ketebalan SiO_2, suhu pemanasan dan kepekatan bahan permulaan. Hasil eksperimen akan dicirikan menggunakan *scanning electron microscope* (SEM) untuk mengkaji bentuk permukaan bahan, *X-ray diffractometer* (XRD) untuk arah pertumbuhan dan *IV measurement system* untuk sifat elektrik. Sifat optik pula dikaji menggunakan *photoluminescence* dan *UV-VIS spectrometer*. Masa rendaman 3 jam merupakan masa yang mempunyai sifat elektrik paling baik. Ketebalan SiO_2 setelah dioksidakan dalam 5 minit menghasilkan sifat elektrik dan optik yang terbaik. Pemanasan pada suhu 500^oC mempunyai sifat elektrik yang optimum tetapi bagi sifat optic, 550^oC adalah yang terbaik. Bahan awal berkepekatan 0.0001 M mempunyai sifat elektrik yang optimum tetapi bagi sifat optik, 0.01 M adalah yang terbaik. Di akhir penyelidikan ini, kesimpulan bagi parameter-parameter yang dikaji untuk mendapatkan sifat elektrik dan optic yang terbaik telah dapat dikenalpasti.

TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 Nanotechnology

Nowadays, nanotechnology has been attracted much attentions among scientists around the world. Generally, the word "nano" means 10^{-9}, therefore a nanometer is one billionth of meter [1]. It can be imagine as about one hundred thousand times smaller than the diameter of a human hair (0.1mm)(1nm) and it is thousand times smaller than a red blood cell (1um) or about half the size of the diameter of DNA (2nm) [2].

History of nanotechnology was started since 1959, when physicist Richard Feynmen gave a historical speech, "There's Plenty of Room at the Bottom" that made people to start thinking seriously about the possibilities of nanotechnology [1]. At the beginning 1980s, scanning tunneling microscopes (STM) and atomic force microscopes (AFM) were invented. The invention allowed scientists to view the world from an atomic perspective and manipulate materials at the atomic level for the first time [2]. In 1991 Professor Sumio Iijima from Meiji University and also an NEC research fellow discovers single-wall carbon nanotubes and the methods to produce those using metal catalysts [3]. At present, the nanotechnology still being investigated due to the material fundamental properties at nano-sizes.

Nanotechnology can be viewed on variety of levels including molecular physics, materials science, chemistry, biology, electrical and mechanical engineering. The science, engineering and technology are related to the understanding and control of matter at the length scale. However, nanotechnology is not merely working with matter at the nanoscale, but typically concerned with materials, structures, components for exhibit the novel and significantly to improved physical, chemical and biological properties [1, 2].

Nanotechnology becomes an important field because of the properties at the atomic level, molecules can behave differently compare to its bulk material. For example, a gold property in bulk is yellow, shiny and metallic, but in nonoscale the color changes like pink depend on the material size. Thus depicts, at nano level, the material can be working with individual atoms or a handful of atoms. Besides that, with nanotechnology more energy efficient can be defined. It can be seen in batteries, whereby a battery is full of chemicals to produce electricity. However, by forming the chemicals into nano-particles, the batteries can be work much better. This is because when the nano-sized particles are produced, the number of atoms will increase and more atoms will expose to the chemical reaction [4]. Therefore, the reaction will be much faster and more efficient. Hence, the battery can store more energy and the charging process will be faster. In nanotechnology, the cost can be reduced due to less space needed to develop any device applications. Two main approaches are used in nanotechnology which is top-down and bottom-up:

1.1.1 Top-down

The top-down approach in nanotechnology refers to build something by starting with a larger component and carving away material to nano-object. This type of fabrication uses lithographic patterning techniques. Lithography technique is a process used to transfer a geometric pattern onto a substrate and etching away material, as in building integrated circuits. For instance, the micron scale of lithography process is optical, ultraviolet and focused ion beam whereas, the electron beam lithography are uses in nanoscale (20 nm to 100 nm) to fabricate small structures [3].

This technique has been able to fabricate a remarkable variety of machinery and electronics devices. However, due to the equipment limitation for cutting, molding and carving, the size produced is depending on the maximum ability of equipment technology. Hence, smaller size than the equipment limitation cannot be achieved. This indicates some nanoscale processes may never be feasible at all by top-down approaches. Nevertheless, the bottom-up solutions may eventually outrun the top-down solutions [3].

1.1.2 Bottom-up

The "bottom-up" approach refers to materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. In nanotechnology, bottom-up is self-assembly of atoms and molecules, as in chemical and biological systems. The various chemical and physical methods can be applied in this technique for creating any structures such as high temperature vapor–liquid–solid (VLS) growth with the use of catalysts, pulsed laser deposition, physical vapor transport and aqueous chemical growth.

The bottom-up technology can be implemented using two different approaches. The first one is based on self-assembly. Self-assembly is the autonomous placement of components in predefined locations. It is driven by the tendency of physical systems to minimize their potential energy. The second bottom-up approach is characterized by the controlled manipulation and positioning of atoms, molecules, clusters or nanometer-sized objects, one-by-one. This approach will involve the aid of elaborate equipment and tools such as atomic force microscopes (AFMs) or dedicated nanomanipulators in scanning electron microscopes (SEMs).

1.2 Problem Statement

In bottom-up approach, the fundamental scientific are less well understood especially for the nanostructures growth. The uniformity of deposited nanostructures on substrate as well as material properties is still under investigation by scientists. The physical properties of material include surface morphologies, growth orientation and most importantly, the electrical property. For electronics devices, good electrical property will produced better performance of devices in electronics applications.

1.3 Objective

The objectives of this research are;

i. To prepare nanostructured ZnO using sol-gel method.
ii. To analyze the effect of deposition parameters on the nanostructured ZnO.
iii. To characterize the electrical properties of nanostructured ZnO.

1.4 Scope of work

The scopes of this research are:

i. The preparation method is using sol-gel method.
ii. The deposition parameters analyzed in this work are the immerse time, oxide thickness, annealing temperature and concentration of Zinc Oxide precursor.
iii. The characterization of nanostructured Zinc Oxide includes the structural, electrical and optical properties.

CHAPTER II

LITERATURE REVIEW

2.1 Introduction Zinc Oxide

The study of semiconductor materials has attracted much attention in recent years to scientist because of their fundamental scientific interest. Wide band gap semiconductors are being much attracted due to their possible uses as optoelectronic devices in the short wavelength and ultraviolet (UV) portion of the electromagnetic spectrum [5]. These semiconductors such as ZnSe, ZnS, SiC, GaN, SnO2 and ZnO, have similar properties with their crystal structures and band gaps.

During last decade, the first one of semiconductors to be prepared in rather pure form after silicon and germanium is Zinc Oxide. It was extensively characterized as early as the 1950s and 1960s due to its promising piezoelectric properties [5-8]. Zinc oxide is being much more extensively studied mainly due to their potential applications in nanoscale electronic and optoelectronic devices. Based on this, it encourages the scientists to explore possibilities of using them in industrial applications.

Typically, Zinc Oxide known as an *II-VI* compound semiconductor with the formula ZnO and it is hardest due to the higher melting point which decomposes into zinc vapor and oxygen at around 1975°C [5-11]. As one of transparent conductive oxide (TCO), ZnO has many valuable properties including a high piezoelectric property with direct band gap energy of 3.37 eV at room temperature and a large exciton binding energy of 60 meV [5-10], which is 2.4 times the effective thermal energy (K_{BT}=25meV) at room temperature, and biexcitation energy is 15meV [5]. This is one of the key parameters that ZnO exhibits near-UV emission, transparency, conductivity and resistance to high temperature electronic degradation.

Zinc oxide has a non-centrosymmetric wurtzite crystal structure with polar surfaces. The wurzite structure of ZnO can be considered to be composed of two interpenetrating hexagonal close packed (hcp) sublattices of cation (Zn) and anion (O) displaced by the length of cation-anion bond in the c-direction. The lattice spacing of ZnO hexagonal unit cell are a= 0.325 nm and c= 0.521 nm. Lattice parameters are considered important, when one has to develop semiconductors devices. Figure 2.1 shows the schematic of a wurzite ZnO structure.

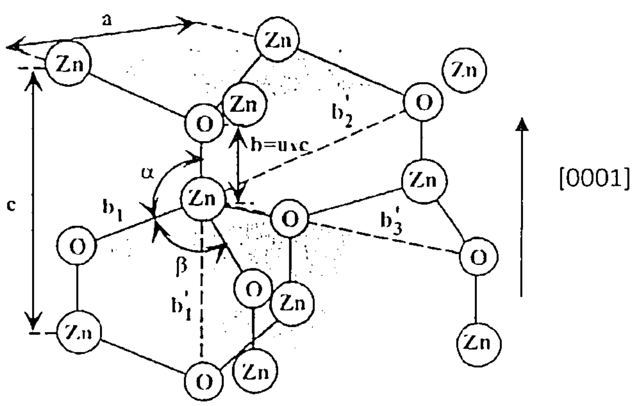

Figure 2.1: Schematic representation of a wurtzite ZnO structure [5].

Zinc oxide has three key advantages. As II-IV semiconductor, it has a direct wide band gap of 3.37 eV and a large excitation binding energy (60meV). This is an important functional oxide, exhibiting near-UV emission and visible light transparency [6-14]. Secondly, due to non-central symmetry, it is a piezoelectric, which is a key phenomenon in building electro-mechanical coupled sensors and transducers [14]. Finally, ZnO is bio-safe and biocompatible, and it can be directly used for biomedical applications without coating [14]. Based on the unique characteristics, ZnO is one of the most important nanomaterials for future research and applications.

As a conclusion Zinc oxide is a versatile semiconductor which has attracted considerable attention because of its catalytic, electrical and optical properties. The exciton stability of zinc oxide provides opportunities for making highly efficient lasers which is operable at room temperature. These properties find wide technological applications.

2.2 Zinc Oxide Nanostructures

Generally, nanostructure material is refers to a broad class of materials, with microstructures modulated in zero to three dimensions on length scales less than 100 nm [2,15]. The nanostructured ZnO has different properties compare to bulk ZnO. It includes the physical, optical and electrical properties. Since ZnO has a non-centrosymmetric wurtzite crystal structure with polar surface, various structures have been successfully synthesized using several methods such as nanorods, nanocombs, nanorings, nanobelts and nanowires [7, 8, 14]. Instead of these diverse structures, it exhibits the variety of characteristics.

As known, when semiconductor materials continuously shrink down to nanometer some of their physical properties undergo changes known as the quantum size effects. The idea behind confinement is all about keeping electrons trapped in a small area. The size of the nanostructures to have the quantum confinement should be less than 30 nm for effective confinement [10].

Quantum confinement is divided into three types consist of 2-D confinement, 1-D confinement and 0-D confinement. The 2-D confinement is only restricted in two dimensional electrons movement and the result is quantum well or plane. These are most lasers are currently build form. One dimensional (1-D) confinement is restricted in one dimensional movement and occurs in nanowires or nanorods. The 0-D confinement is found only in quantum dot where electron is trapped without any movement. Instead of these, some problem such as current leakage when scaling down in transistor can be preventing.

The optoelectronic properties of ZnO nanostructures depend on their morphology, crystalline structure, defect and impurity contents. Optical transitions in ZnO nanostructures have been studied by a variety of experimental techniques such as optical absorption, transmission, reflection, photoreflection, photoluminescence and others. Photoluminescence (PL) spectra of ZnO nanostructures have been extensively reported. Excitonic emission of ZnO nanostructures were obtained at room temperature in the wavelength range from 350 nm to 650 nm by PL spectra. For instance, the green emission intensity increases with decreasing nanowires diameter. Red luminescence band also reported, which was attributed to doubly ionized oxygen vacancies. In addition, as one of the characteristics of nanoscale systems, quantum confinement was observed to cause a blue shift in the near UV emission peak in ZnO nanobelts [10, 16].

The electrical properties of ZnO nanostructures are important for developing their future applications in nanoelectronics. For example, a device developed by material with a larger band gap may have a high breakdown voltage [16]. Otherwise, the lower noise generation can be operated at higher temperatures with high power operation. In field effect transistor, the major problem is the current leakage that causes the transistor to overheat and high power dissipation. Using nanostructure such as nanowire, this current leakage can be eliminated since the electrons flow in the nanowire can be manipulated using Quantum Confinement Effect (QCE).

2.3 Application of Zinc Oxide Nanostructures

As mentioned previously, among the group of functional metal oxides semiconductor nanostructures. ZnO shows its remarkable electrical and optical properties [17]. Based on these, its promising various technology applications especially for optoelectronic and piezoelectric. With improvements in growth technology of ZnO nanostructures, single crystal, nanoparticles and epitaxial layer, it will become increasingly functional and exotic in ZnO devices.

ZnO nanostructures such as nanowires arrays depict the opportunities uses for flat screen displays, field emission sources, gas, chemical and biological sensors. Due to large exciton binding energy and wide bandgap, ZnO nanostructures allow efficient excitonic emission at room temperature. Therefore, it's suitable for optoelectronic applications such as efficient short-wavelength ultraviolet light-emitting diodes and laser diodes [17].

Besides that, an epitaxial layers and single crystals also become important for the development of optoelectronic such as blue, UV light emitters and detectors. In addition, it also has valuable for piezoelectric and spintronic devices. Epitaxial ZnO also can be uses as semiconducting transparent thin film or transparent conductive oxide, which will be important for solar cells, gas sensors, displays and wavelength selective applications [17].