ELECTROCHEMICALLY DEPOSITED ZINC OXIDE MORPHOLOGIES ON GRAPHENE ON INSULATORS

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ABSTRACT

Hybrid structure of semiconductor nanostructures on graphene has attracted much attention due to their potentials in optoelectronic and electronic. A synthesis of zinc oxide (ZnO) nanostructures on graphene/insulator substrates was carried out using electrochemical deposition. Several growth parameters such as current density, temperature and supporting electrolyte have been investigated. ZnO nanostructures were directly grown onto graphene layer whereby zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) solution was used as an electrolyte. The growth temperature was varied from 75°C - 90°C at current densities of -0.1 to -3.0 mA/cm^2 for 45 minutes. Vertically aligned nanorods were obtained at low growth temperatures. The diameters of grown nanorods were increased with the current densities. Film-like structure produced by the coalescences between the neighboring nanorods with large diameters was observed on the samples grown at high current densities and high temperatures. Low temperature and low current density tended to exhibit the highest density of nanorod. The grown ZnO structures were highly oriented along the *c*-axis and at low current densities seem to show fewer structural defects. The addition of supporting electrolyte of hexamethylenetetramine (HMTA) shows improvement of hexagonal shape and smooth surface of ZnO nanorods at equimolar ratio. HMTA plays its role as mineralizer to supply additional OH^- ions in the formation of ZnO structures. Meanwhile for addition of potassium chloride (KCl) solution, instead of nanorods, vertically ZnO nanowalls were also formed. It proves that Cl^- ions as a capping agent on (0001) plane and control the formation of two dimensional (2D) ZnO nanowalls structures and one dimensional (1D) nanostructures with large diameter. The diffraction peak intensity of HMTA and KCl solution shows the crystallinity of the grown structure. This study offers significant benefit for the ZnO morphology in order to realize high crystalline and uniform ZnO nanostructures.

ABSTRAK

Struktur hibrid nanostruktur semikonduktor di atas grafen telah menarik banyak perhatian kerana berpotensi dalam optoelektronik dan elektronik. Satu sintesis nanostruktur zink oksida (ZnO) di atas grafen/penebat dengan menggunakan pemendapan elektrokimia telah dilakukan. Beberapa parameter pertumbuhan seperti ketumpatan arus, suhu dan elektrolit penyokong telah dikaji. Nanostruktur ZnO ditumbuhkan di atas lapisan grafen di mana larutan zink nitrat heksahidrat ($Zn(NO_3)_2.6H_2O$) telah digunakan sebagai elektrolit. Suhu pertumbuhan telah diubah dari 75°C - 90°C pada ketumpatan arus -0.1 sehingga -3.0 mA/cm^2 selama 45 minit. Rod nano yang menegak sejajar diperoleh pada suhu pertumbuhan yang rendah. Diameter rod nano yang tumbuh meningkat dengan peningkatan ketumpatan arus. Struktur seperti filem telah dihasilkan oleh percantuman di antara rod-rod nano berdekatan dengan diameter yang besar telah diperhatikan pada sampel yang tumbuh pada ketumpatan arus tinggi dan suhu tinggi. Suhu rendah dan ketumpatan arus rendah lebih cenderung menunjukkan kepadatan rod nano paling tinggi. Struktur ZnO yang tumbuh berorientasi di sepanjang paksi-*c* dan pada ketumpatan arus rendah seolah-olah menunjukkan sedikit kecacatan struktur. Penambahan larutan elektrolit penyokong heksametilenatetramina (HMTA) menunjukkan pembaikan bentuk heksagon dan permukaan licin rod nano ZnO pada nisbah sama molar. HMTA memainkan peranannya sebagai pemineral untuk membekalkan ion OH^- tambahan dalam pembentukan struktur ZnO. Sementara itu, bagi penambahan larutan kalium klorida (KCl), bukan sahaja rod nano, dinding nano ZnO yang menegak juga terbentuk. Ini membuktikan bahawa ion Cl^- bertindak sebagai ejen penutup pada satah (0001) dan mengawal pembentukan struktur dua dimensi (2D) dinding nano ZnO dan satu dimensi (1D) nanostruktur berdiameter besar. Keamatan puncak pembelauan larutan HMTA dan KCl menunjukkan kehabluran struktur yang tumbuh. Kajian ini menawarkan manfaat yang besar untuk morfologi ZnO bagi mewujudkan habluran yang tinggi dan nanostruktur-nanostruktur ZnO yang seragam.

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CHAPTER 1

INTRODUCTION

1.1 Research background

Nowadays, great attention has been attracted to the synthesis of semiconductor nanostructures materials due to their enhanced optical, electrochemical and electrical properties intrinsically associated with their low dimensionality. Among the various semiconductors materials, zinc oxide (ZnO) has become a technologically important material that has been most extensively studied among the researchers due to its versatile properties such as wide direct bandgap (3.37 eV) and large exciton binding energy of 60 meV which is much larger than that of GaN (21meV) [1]. ZnO has been commonly used for many applications in electronic and optoelectronic devices such as light-emitting diodes (LED) [2,3], photodetectors [4,5], gas sensor [6], solar cells [7,8] and UV lasers [9]. Furthermore, from various oxide materials, ZnO have the richest family of nanostructures such as nanorods, nanowires, nanoflowers, nanosheets, nanobelts, nanowalls and nanorings. ZnO nanowires has been explored for gas sensors due to large surface area versus nanowires volume whose widths are much narrower than that of lithography-based thin film technology which can increase the sensitivity of sensors beyond the limitations of planar thin film device. These diverse groups of ZnO nanostructures have been synthesized using various growth methods [10,11].

The methods employed for the growth of ZnO nanostructures can be performed either by vapor-phase method or by liquid-phase method. For the vapor-phase method such as chemical vapor deposition [12,13], thermal

Finally, chapter 7 concludes the results obtained and discusses the future research directions.

1.6 Thesis Overview

This thesis is organized into 7 chapters. Chapter 1 gives a brief introduction of the research background on the growth of ZnO nanostructures. The objectives, research scopes and research activities are also presented.

Chapter 2 presents a comprehensive review of literature on the ZnO and graphene properties together with their application. The first part of this chapter explains the structural, optical and electronic properties of ZnO in order to provide in-depth knowledge of ZnO materials. Growth method and application of ZnO nanostructures are also been described. The next part focused on the graphene structure together with its properties and their application.

In chapter 3, the details of experimental procedures in this research are described. The substrate preparation and the experimental setup are explained in the first part. Second parts describe the growth procedure and condition of the grown ZnO structures. The characterization techniques and equipment used are mentioned in the last part.

In chapter 4, the effects of current density and temperature on the structure of the grown ZnO on graphene/glass substrate in purely zinc nitrate solution are discussed. The morphology, compositional, structural and optical properties of ZnO nanorods is systematically characterized and described.

In chapter 5, the effects of supporting electrolyte of HMTA and KCl solution on the grown ZnO structures on graphene/glass substrate are discussed. The morphology, compositional, structural and optical properties of ZnO structures is systematically characterized and described.

In chapter 6, the effects of supporting electrolyte of HMTA and KCl on the grown ZnO structures on graphene/SiO_2/Si substrate are discussed. The morphology, compositional, structural and optical properties of ZnO structures is systematically characterized and described.

The optical properties are characterized using PL measurement and UV-Vis spectrometer. All the data collected is analyzed.

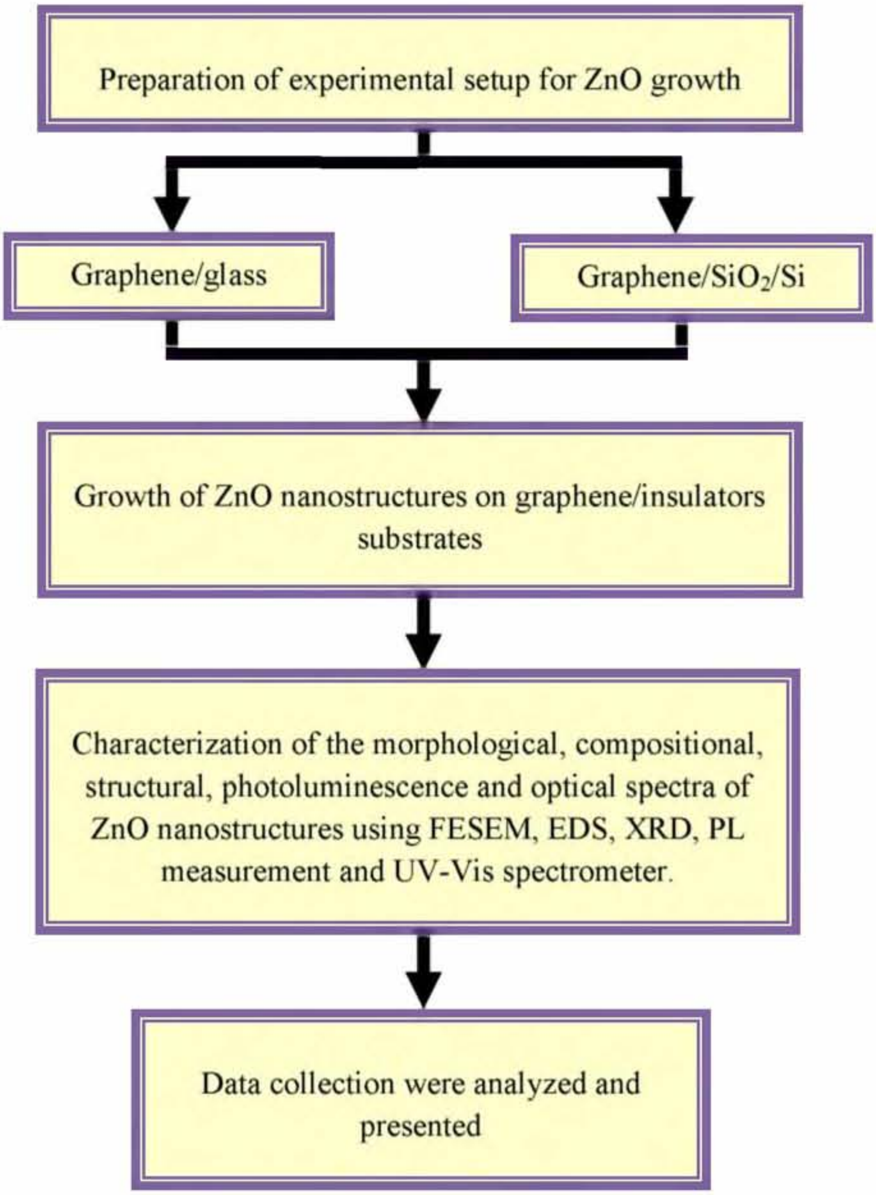

Figure 1.1 Research activities

1.4 Research Scope

This study is focused on the growth of ZnO nanostructures on monolayer graphene/glass by electrochemical deposition method. ZnO nanostructures are synthesized using purely zinc nitrate ($Zn(NO_3)_2$) solution at different current densities of -0.1, -0.5, -1.0, -2.0 and -3.0 mA/cm^2 with the growth temperatures of 75, 80 and 90°C. However, the effects of adding supporting electrolyte from hexamethylenetetramine (HMTA) and potassium chloride (KCl) solution on the ZnO structures grown on monolayer graphene/glass and monolayer graphene/SiO_2/Si are also been studied. The molar ratio of $Zn(NO_3)_2$:HMTA and $Zn(NO_3)_2$:KCl was set to 9:1, 7:3, 1:1 and 1:9.

The morphological and compositional characterization is carried out using field-emission scanning electron microscopy (FESEM) equipped with energy dispersive X-ray spectroscopy (EDS). The structural and optical properties are performed using X-ray diffraction (XRD), photoluminescence (PL) measurement and UV-Vis spectrometer, respectively.

1.5 Research activities

The implementation of this study has been summarized into a flowchart as shown in Figure 1.1. This study is focused on the growth of ZnO nanostructures on graphene substrate by electrochemical deposition method. Firstly, the preparation of the experimental setup is performed. The formation of ZnO structures on graphene substrate is carried out in a simple electrochemical deposition cell. There are two types of graphene substrates are used in this work which is graphene/glass and graphene/silicon dioxide substrate. The growth of ZnO nanostructures on graphene substrates are investigated by varying a few parameters such as current density, temperature and molar ratio concentration of supporting electrolyte. Next, the morphological and elemental study on the grown ZnO structures are performed using FESEM equipped with EDS. The structural properties are investigated using XRD.

Nowadays, the hybrid structures of ZnO nanostructures on graphene have attracted much attention because the nanostructures can offer additional functionalities to graphene for realizing advanced nanoscale applications due to the superior properties of nanostructures such as quantum confinement effects and high surface-to-volume ratio [53,54,60]. Based on the previous studies, they manage to grow the ZnO on graphene with high crystallinity and uniformity [29,53-55]. Xu et al. reported the seedless growth of ZnO nanotubes and nanorods on graphene by electrochemical deposition [29,55]. They reported the growth of highly dense vertically aligned ZnO nanostructures by using solely zinc nitrate as the electrolyte with the introduction of oxidation process of graphene prior to the actual growth. In this study, we directly grow the ZnO nanostructures on graphene by a single-step cathodic electrochemical deposition method by studying in details about the current density, temperature and supporting electrolyte because the deposition techniques and deposition parameters play an important role in controlling the morphology and physical properties of the nanostructures.

1.3 Research Objectives

The objective is to grow high dense ZnO nanostructures on graphene substrates by electrochemical deposition method.

1. To investigate the effects of current density and temperature on the vertically aligned ZnO nanostructures grown on monolayer graphene/glass.
2. To study the influences of supporting electrolyte effect on the structure of ZnO deposited on monolayer graphene/insulator.
3. To characterize the morphological, compositional, structural and optical properties of the structure.

compositional, structural and optical properties of the grown ZnO nanostructures were characterized.

1.2 Research motivation

Nowadays, rapidly increasing demand for energy together with more concerns about the environment force us to seek sustainable energy resources and clean energy technologies. As a result, solar cells have received increased interest in recent years. Solar cells based on titanium dioxide (TiO_2) nanoparticles with a size of 10 to 30 nm have been used as photoanodes with demonstrated 11% photovoltaic conversion efficiency [56]. Recently, ZnO has emerged as a promising candidate due to its semiconducting properties which are very similar to the most used semiconductor oxide, TiO_2, but are especially due to the possibility of obtaining ZnO nanostructures by easy and low-cost techniques. It has similar energy levels to TiO_2. More importantly, it is much higher carrier mobility which is more favorable for the collection of photo-induced electrons [57,58]. Besides that, another advantage of ZnO over TiO_2 is that it can be synthesized applying a wide range of synthesis techniques in order to obtain a great variety of different morphologies and nanostructured electrodes, especially vertically-aligned nanostructures.

It was reported that nanostructured thin film made of vertical-aligned nanowires provides a higher interfacial area between the donor and the acceptor material (polymer/oxide, respectively) with highly-efficient electron transport pathways. In the case of dye-sensitized solar cells (DSSCs), the replacement of the nanoparticle electrode by vertically-aligned nanostructures has also emerged as a possible way to obtain faster electron transport thus improving solar cell efficiency [59]. In recent years, graphene has to be found as replacement to transparent conductive oxides such as FTO and ITO as solar cell electrode. Graphene is expected to act as an excellent conducting transparent electrode material [47,48] because of its extraordinary electrical, thermal, and mechanical properties including a carrier mobility exceeding 10^4 cm^2/Vs and a thermal conductivity of 10^3 W/mK [49-52].

evaporation [14-20] and pulsed laser deposition [21], it requires high temperature and is also considered as a high-cost method. Thus, considerable attention has been focused on liquid-phase method such as chemical bath deposition [22], hydrothermal [23,24], sol-gel [25-28] and electrochemical deposition [29-35]. Among these methods, the electrochemical deposition has advantages over other methods because of its simplicity, low cost and low process temperature [36]. In addition, this method gives good controllability of both growth rate and structure dimension. Furthermore, the performance and efficiency of electrical and optical nanodevices are directly determined by the underlying nanostructures properties which are greatly dependent on the size, shape, crystallographics orientation and morphology. Besides deposition technique, corresponding parameters such as temperature [37], substrate [38], precursor [39,40] and electrolyte [41] play an important role in controlling the morphology and physical properties of the nanostructures[42].

Recently, ZnO has been shown to be able to enhance the power conversion efficiency of conjugated polymer-based solar cells [43,44]. Typically, the electrode of solar cell is formed by the transparent conductive oxides such as fluorine-doped tin oxide (FTO) or indium tin oxide (ITO) deposited on glass [45,46]. However, FTO and ITO are expensive and non-flexible in contrast to graphene which is cheap and flexible. Graphene which has two dimensional honeycomb-like carbon structures is expected to act as an excellent conducting transparent electrode material [47,48] because of its extraordinary electrical, thermal, and mechanical properties including carrier mobility exceeding 10^4 cm^2/Vs and a thermal conductivity of 10^3 W/mK [49-52]. Interestingly, the direct growth of ZnO nanorods on graphene with high crystallinity and uniformity has also been reported in several literatures so far [29,53-55].

In this study, the formation of ZnO nanostructures on graphene/insulator by electrochemical deposition process is carried out. Firstly, the effects of current density and growth temperature of ZnO structures grown on monolayer graphene/glass in purely zinc nitrate solution were studied. Next, the effects of supporting electrolyte on the growth of ZnO nanostructures on graphene/glass substrate and graphene/SiO_2/Si substrate were performed. The morphological,

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