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THE INFLUENCE OF SEED LAYER FOR ALIGNED ZNO NANORODS FABRICATION

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ABSTRACT

Nanocrystalline zinc oxide has wide range of applications such as high power transparent thin film transistors, optical waveguides, conductive gas sensors and transparent electrodes for photo-electrochemical applications. In this paper, we demonstrated the fabrication of zinc oxide (ZnO) nanorods (NRs) with ZnO seed layers using a chemical bath deposition (CBD) method on glass substrates. This paper reports the influence of ZnO seed layer conditions which are annealed ZnO seed layer and as-prepared ZnO seed layer on the morphological, structural and optical properties of ZnO NRs. We found that annealing the seed layer at 500 ºC changes the ZnO NRs morphological and optical properties but remaining the structural property.

Keywords: Zinc oxide, nanorods, transmittance, crystalline, seed layer.

INTRODUCTION

The emerging of nanotechnology, especially for optoelectronic device applications is a new breakthrough for more efficient devices. For instance, photovoltaic solar cell is a non-polluting energy source which generates electricity by receiving solar energy into the cell, generating electrons, and simultaneously transporting electrical charge out of the cell (Xian *et al*., 2013). As another example, Wireless Sensor Networks (WSN) are collections of motes has ability to reduce energy consumption, which is motes communicate with each other and collect data such as light, vibration, moisture and temperature and then they transmit data to a main computer (Shi *et al*., 2011). Over the past few years, one dimensional (1D) Zinc Oxide nanostructures has attracted extensive attention because of their unique electrical and optical properties (Dong *et al.*, 2013). 1D ZnO is one of the most intensively studied nanorods (NRs) material. 1D nanostructure systems where electrons are free to move in one direction and confined in the other two directions are investigated intensively these years. A large number of different structures have been grown and a wide range of interesting optoelectronic devices including UV sensors, photodetectors and light emitting components such as laser and LEDs.

There are a lot of semiconductor materials being researched to develop nanostructures such as ZnO and Titanium dioxide (TiO_2). However, ZnO has attracted many researchers due to their excellent optical and electrical properties such as large wide band gap energy (3.37 eV) at room temperature and large excitonic binding energy (60 eV) (Yi *et al.*, 2007). ZnO also is a highly applicable and widely used II-IV semiconductor material with several attractive properties such as high chemical stability, good photoelectric and piezoelectric properties which leads to diversified industrial applications of the material (Chandrinou *et al*., 2007). ZnO thin films have been used in solar cells, transparent electrode, varistor, gas sensor, UV laser, surface acoustic wave system and dilute magnetic semiconductor material (Hofstetter *et al*., 2010).

Several deposition methods were used to produce ZnO nanostructures such as chemical vapor deposition (CVD) (Wu *et al.*, 2008), magnetron sputtering, pulsed laser deposition (PLD), molecular beam epitaxy (MBE) (Shanmuganathan *et al*., 2013), sol-gel methods (Kamaruddin *et al*., 2011) and chemical bath deposition (CBD). Many of these methods are expensive and require high vacuum and controlled formation conditions. Among these methods, CBD method are the extremely attractive deposition technology due to its advantageous features over other thin film deposition techniques, such as its simple, low temperature (Buba *et al.*, 2010), low cost, low evaporation temperature, easy coating of large surfaces, large area film with good uniformity and suitable for large area preparation (Jia *et al.*, 2012).

In this work, we have deposited aligned ZnO NRs using CBD method. The effect of annealing ZnO seed layer was investigated using a field emission scanning electron microscope (FESEM, JEOL JSM7600), a UV-Visible spectroscopy (UV-Vis, SHIMADZU 1100) and an X-ray Diffractometer (XRD, PANALYTICAL XPERT POWDER), to study its morphology, optical and structural properties, respectively. A surface profiler was also used to measure its thickness due to annealing effect.

EXPERIMENTAL

Figure-1 depicts the process flow for the overall experiment setup in this research. Microscope glass substrate (2×2 cm^2, 1.1 mm thick) was cleaned by acetone in ultrasonic bath for 10 minutes. Then, it was rinsed with deionized water and purge to dry with nitrogen gas.

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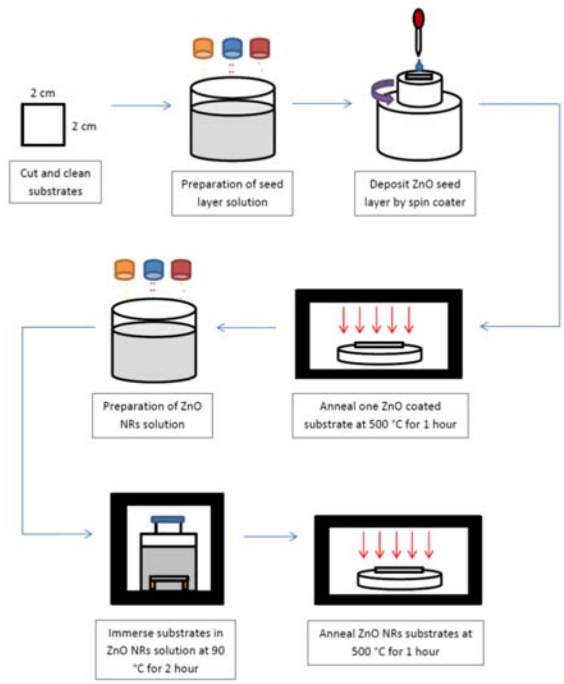


Figure-1. Fabrication process of ZnO nanostructures.

The solution preparation was divided into two parts; (i) solution for seed layer, and (ii) solution for ZnO NRs deposition. The seed layer was prepared by mixing same molarity (1:1) zinc acetate dehydrate (ZAD) and monoethanolamine (MEA) in 30 ml of isopropyl alcohol (IPA). The solution was stirred for 24 hours. After that, the seed layer was deposited on the glass substrates using a spin coater (3000 r.p.m.) with preheating substrate temperature of 280 °C for 3 minutes. In order to study the influence of annealing the seed layer, two samples were prepared. One of the sample was annealed at 500 °C for 1 hour. Finally, the sample was cooled gradually cooled at room temperature.

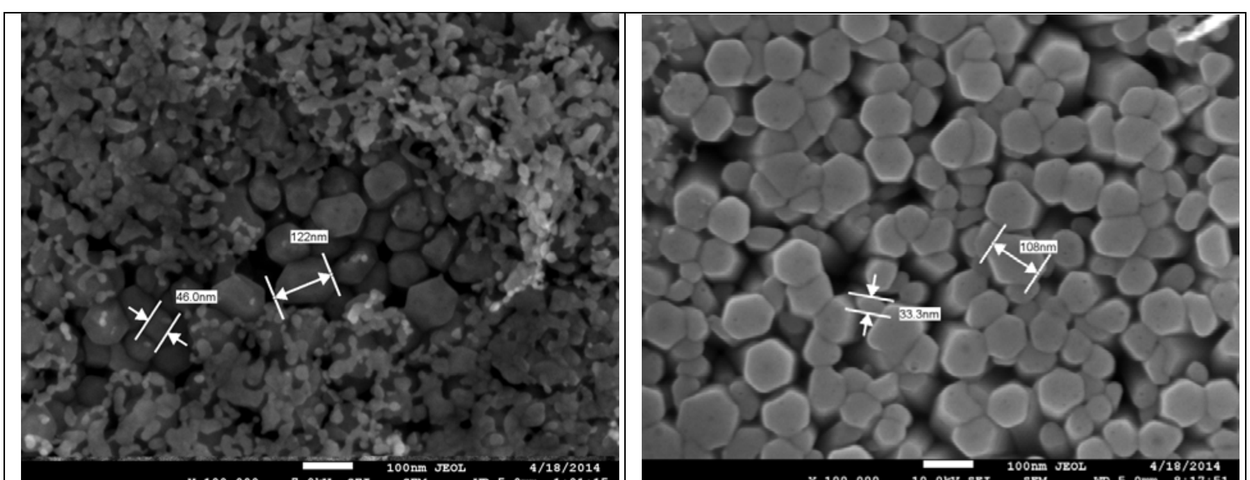
The ZnO NRs were prepared using an aqueous solution of zinc nitrate hexahydrate, mixed with hexamethylenetetramine at same molarity (1:1). The nanostructures were grown on glass substrates coated by ZnO seed surface. The solution was diluted in 100ml deionized water. After that, the solution was stirred for 1 hour at 60 °C and then was sonicated the solution with temperature 30 °C for 30 minutes. Next, the solution was stirred again for 30 minutes. Two samples of ZnO coated seed surface were immersed in the solution for 2 hours at 90 °C. Finally, after drying, the ZnO NRs samples were annealed at 500 °C for 1 hour.

All samples were characterized using FESEM to observe the surface morphologies and using XRD to obsereve the structural properties. The optical properties were measured using UV-Vis and the thickness was measured using surface profiler.

RESULTS AND DISCUSSIONS

Surface morphology

Figure-2 (a) and (b) show the FESEM images of the ZnO NRs grown on glass substrate assisted by as-prepared and annealed seed layers, respectively. It can be observed that the largest nanorod's diameter with as-prepared seed layer is 106 nm whereas for annealed seed layer is 122 nm. Meanwhile, the minimum nanorod's diameter for as-prepared and annealed sample is 46 nm and 33 nm, respectively. The changes in shape and size of the nanorods are strongly correlated with the condition of seed layer as being suggested by Kim *et al*. (Kim *et al*., 2014). The more crystalline seed layer maybe exhibit more surface energy which attract more ZnO molecules and forms other structure on top of the nanorods. The changes of crystallinity are necessary due to annealing also reported by Kim. The influence of seed layer annealing on the growth of ZnO nanorods also discussed by Kim *et al.*



(a) (b)

Figure-2. The FESEM images of ZnO NRs; (a) sample deposited using annealed seed layer (b) sample deposited using as-prepared seed layer.

XRD analysis

The normalized XRD data of ZnO nanorods grown on as-prepared seed layer and annealed seed layers at 500 °C are shown in Figure-3. It exhibits that all the diffraction peaks of the samples are crystallized into a single-phase corresponding to hexagonal wurtzite structure. All the ZnO nanorods show a strong diffraction peak at 34.44θ corresponding to ZnO (002) plane, indicating that the ZnO nanorods grow directly along the c-axis, which is consistent with the FESEM images. The diffraction patterns show small peaks corresponding to the (0 1 0), (0 1 1), (0 1 2), (1 1 0), (0 1 3) and (1 1 2) planes of hexagonal wurzite structure of ZnO with no characteristic peaks of impurities were observed, which also confirms the high purity of ZnO nanorods.

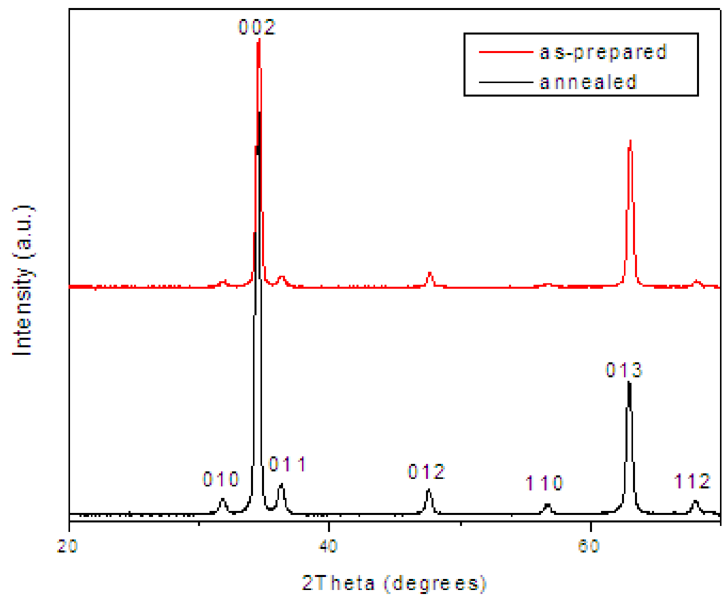


Figure-3. XRD pattern of ZnO NRs for annealed seed layer and as-prepared seed layer

From Figure-3, it shows that the annealed seed layer has higher crystalline than as-prepared seed layer. Wide ZnO seeds formed when the ZnO seed layer on the glass substrate was annealed and most of (0001) planes of these particles preferred to be parallel to the substrate under the high temperature which is 500 ◦C (Yang *et al.*, 2009). The nanorods grown from these ZnO seeds with the (0001) planes parallel to the substrate will be perpendicular to the substrate. However, as-prepared seed layer substrate make the surface is too smooth at the nanoscale, in addition to the nucleation at a relative low temperature at 90 ◦C, so the (0001) planes of the nuclei particles are likely randomly formed relative to the substrate surface, resulting in that the orientation of ZnO NRs arrays on the as-prepared substrate was poor (Yang *et al.*, 2009) .

Optical properties

Figure-4 shows the annealing of seed layer influence on the transmittance of the ZnO NRs thin films. To study that, a sample was annealed at temperature 500 °C while the other sample do not annealing. All ZnO thin-film samples were measured transmission spectra in the range between 350 nm and 800 nm for indicate that the films are rather transparent in the visible region. However, the transmission drops dramatically in the ultraviolet region around 375 nm and it is due to the bandgap absorption. In this graph, the annealed seed layer film has high transmittance which is over than 90% approaching 100% in the visible range while as-prepared seed layer film has a low transmittance which is approaching 60%. From Figure-4, the highest transmittance occurs for annealed seed layer ZnO NRs thin film with approximately 100% transmission. This annealed seed layer result shows, it has a good transmission for making best solar cell which is required 95% above transmission (Kamaruddin *et al.*, 2011).

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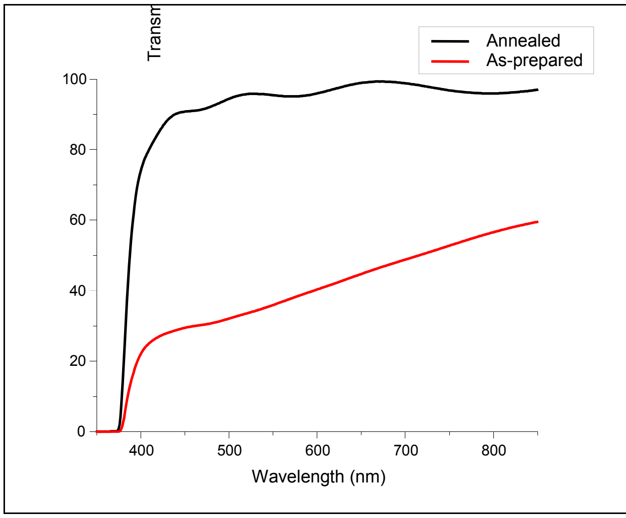

Figure-4. The transmittance of ZnO NRs films for annealed seed layer and as-prepared seed layer.

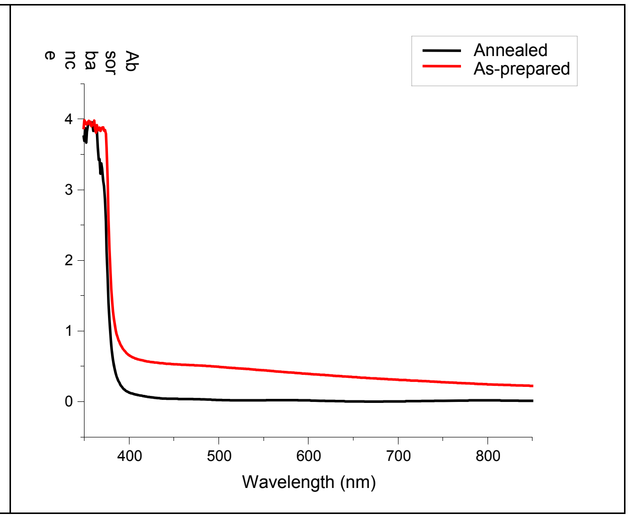

Figure-5. The absorbance of ZnO NRs films for annealed seed layer and as-prepared seed layer.

Figure-5 shows the UV-visible absorbance spectroscopy of annealed seed layer and as-prepared seed layer. The absorbance of annealed seed layer is lower than as-prepared seed layer. The absorption edge was observed to be located at 365 nm. The UV cured films of the present work absorbs in the region 350-390 nm hence blocking 85% of the UV radiation above 400 nm.

Thickness

We also measured the thickness of the films by using surface profiler. From this measurement, we found that the thickness of annealed seed layer is 166 nm and the thickness of as-prepared seed layer is 661 nm. Other than that, we found from the results of surface profiler is the ZnO NRs surface of the as-prepared seed layer is rougher than ZnO NRs surface of the annealed seed layer.

CONCLUSIONS

The difference of surface morphologies, structural properties, optical properties and thicknesses between annealed ZnO seed layer and as-prepared seed layer was investigated. The properties of aligned ZnO nanorods are influenced by the seed layer condition. From the FESEM images, the nanorods fabricated using annealed seed layer film has big particle grain size. The NRs particle size becomes larger when annealing ZnO seed layer at high temperatures. The structural property of the sample such as crystalline measured using XRD shows annealed seed layer has higher crystalline and strong diffraction peak at (002) plane. The absorption spectrum of annealed sample using an UV-Vis also demonstrated more transparent behavior and more crystalline. The absorption edge was observed to be located at 365 nm. We also observed that the NRs grown on the as-prepared seed layer thicker than the NRs grown on the annealed seed layer. Several parameters such as time deposition and deposition temperature should be studied to improve the growth of NRs with better properties.

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