International Journal of Current Advanced Research
ISSN: O: 2319-6475, ISSN: P: 2319 – 6505, Impact Factor: SJIF: 5.995
Available Online at www.journalijcar.org
Volume 6; Issue 7; July 2017; Page No. 4646-4649
DOI: http://dx.doi.org/10.24327/ijcar.2017.4649.0550

Research Article

SHORT TIME SYNTHESIS OF ZNO NANORODS PREPARED BY A HYBRID DEPOSITION TECHNIQUE: EFFECTS OF SEED LAYER

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ARTICLE INFO

Article History:

Received 12th April, 2017
Received in revised form 10th May, 2017
Accepted 26th June, 2017
Published online 28th July, 2017

Key words:

ZnO nanorods, sol-gel spin coating, chemical bath deposition, ZnO seed layers

ABSTRACT

ZnO nanorods were prepared by a hybrid deposition technique. ZnO seed layers were deposited onto glass substrates by sol-gel spin coating technique. ZnO nanorods were synthesized onto seed layers by chemical bath deposition method in very short time like 30 minutes. Effects of seed layer and the thickness of the seed layer on the crystalline structure and morphology of the ZnO nanorods were investigated using X-ray diffractometer (XRD) and field emission scanning electron microscope (FESEM). It was established that ZnO nanorod does not form without seed layer. It was found that ZnO nanorods synthesized onto seed layer have a perfect crystalline wurzite structure with a preferentially orientation of (002). The intensity of (002) peak strongly increased as the thickness of seed layer increased. It was determined that the majority of synthesized ZnO nanorods on the seed layers are vertical. An increase was observed in the density and the length of the vertically synthesized ZnO nanorods by increasing the thickness of seed layer. The increased thickness of seed layers led to improve the crystalline quality and morphological properties of ZnO nanorods.

INTRODUCTION

Zinc oxide (ZnO) with hexagonal wurtzite structure is a very popular material in semiconductors (Steiner 2004). ZnO has a wide direct band gap (3.3eV) (Salam *et al*. 2013), large binding energy at room temperature (60meV) (Hassan *et al*. 2014), high electron mobility and thermal conductivity (Könenkamp *et al*. 2002). ZnO is also low-cost (Jimenez-Garcia 2014), nontoxic and chemically-inert material (Xu and Wang 2011). Due to these properties, ZnO nanostructures are widely used in optoelectronic applications like, solar cells (Baik and Cho 1999), light-emitting diodes (LEDs), liquid crystal displays (LCDs) (Chen and Wang 2014) ultraviolet photo detectors (Znaidi *et al*. 2003; Nakamura 2013) and sensors (Chougule *et al*. 2012; Fan *et al*. 2012). Moreover, synthesized ZnO nanorods are very important to enhance performance in photovoltaic devices (Thanh *et al*. 2016). ZnO nanorods have been synthesized on ZnO seed layers prepared onto different substrates (Green *et al*. 2005; Solis-Pomar *et al*. 2011) using various methods including atomic layer deposition (Chen *et al*. 2011), molecular beam epitaxy (Zhang *et al*. 2009), chemical vapor deposition (Feng *et al*. 2015), successive ionic layer adsorption and reaction (Sutha *et al*. 2015), metal organic chemical vapor deposition (Tian *et al*. 2008), hydrothermal synthesis (Abdulgafur *et al*. 2012; Soleimanzadeh *et al*. 2015), sol–gel techniques (Yakuphanoglu *et al*. 2010; Huang *et al*. 2011) and chemical bath deposition (Bahramian *et al*. 2016). In this study, ZnO nanorods were prepared by a hybrid deposition technique. ZnO seed layers were deposited onto glass substrates by sol-gel spin coating technique in different thicknesses. ZnO nanorods were synthesized onto ZnO seed layers by chemical bath deposition method which is simple, safe and economic. In similar studies, synthesis of ZnO nanorods takes several hours and annealing is required to form nanorods (Pourshaban *et al*. 2016; Bahramian *et al*. 2016; Gawali *et al*. 2017). In this study, ZnO nanorod synthesis lasted only 30 min and annealing was not required to form nanorods. The effects of seed layer and the thickness of the seed layer on the crystalline structure and morphology of the ZnO nanorods were investigated.

Experimental details

The growth process of ZnO nanorods includes two steps: deposition of the ZnO seed layers onto glass substrate using sol-gel spin coating technique and synthesis of ZnO nanorods onto seed layers using chemical bath deposition method. In Fig. 1, growth process of ZnO nanorods have been presented.

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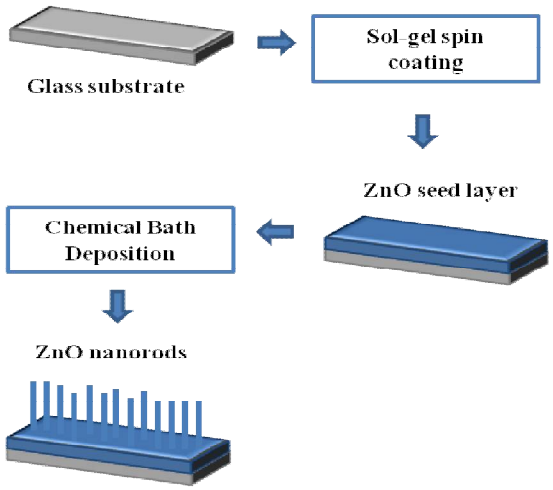

Fig. 1 Growth process of ZnO nanorods.

Deposition of the ZnO seed layers

ZnO seed layers were deposited onto glass substrates by sol-gel spin coating technique. Zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$] was used as the starting precursor. 2-methoxyethanol and monoethanolamine (MEA) were used as solvent and stabilizer respectively. The concentration of solution was 0.5 M. Prepared solution was spin coated onto glass substrates at a rotating speed of 3000 rpm for 30 seconds. The coated layers were dried at 150°C for 10 minutes (coating-drying process). To investigate the effects of seed layer three types of substrate was used as a seed layer and named as Z1, Z2, and Z3. Z1 was uncoated glass substrate. The coating-drying process was repeated for 5 times for Z2 and 10 times for Z3 to obtain seed layers in different thicknesses. Finally, the obtained seed layers were annealed at 500°C in air for 2 hours. In Table 1, the thickness values of the seed layers determined by Stokes Ellipsometer LSE-2A2W have been presented.

Table 1 The thickness values of the seed layers.

Series	Thickness (nm)
Z1	-
Z2	298
Z3	572

Synthesis of ZnO nanorods

ZnO nanorods were synthesized onto Z1, Z2 and Z3 seed layers by chemical bath deposition method. 0.1M Zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] solution was prepared in distilled water of 100 ml. In order to rapid dissolution, it was stirred with a magnetic stirrer. While the solution was stirred, the pH of the solution was fixed to 10 with adding ammonia drop by drop. After the bath was prepared, substrates were immersed in to the solution. The bath solution was stirred by temperature-controlled magnetic stirrer at 85°C for 30 min. Finally, the samples were washed with distilled water and dried at room temperature. The effects of seed layer and the thickness of the seed layer on the growth, crystalline structure and morphology of the Z1, Z2 and Z3 series were investigated using XRD and FESEM measurements.

RESULTS AND DISCUSSION

XRD measurements were performed by Panalytical Empyrean X-ray diffractometer using CuK_α (λ=1.5405 Å) radiation in the 2θ range 30°-60° with a scanning speed of 2°/min at the room temperature. In Fig. 2, XRD patterns of Z1, Z2 and Z3 series have been presented comparatively

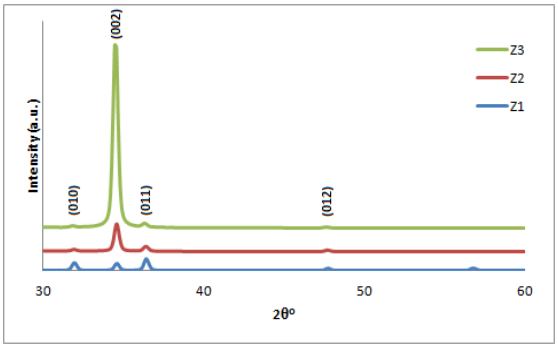

Fig. 2 XRD patterns of all series.

For all series, XRD diffraction patterns have matched with the hexagonal structured ZnO [ICDD data: 98-003-1052]. No distinct peak due to any impurity was observed in the XRD spectrum, showing that synthesized ZnO nanocrystals have high purity. Z1 series have polycrystalline structure. (010), (002), (011) and (012) peaks of hexagonal ZnO structure have been formed in Z1 series. There is no preferential growth in the Z1 series. It was determined that ZnO nanorod does not form in Z1 series. For Z2 and Z3 series, strong (002) peaks appear which are indexed to hexagonal ZnO crystal. Z2 and Z3 series have a strong c-axis orientation. As can be seen in Fig 2, the intensity of (002) peak strongly increases as the thickness of seed layer increases in Z3 series. These results indicate that the crystalline structure of the nanorods can be controlled by changing thickness of the seed layers.

The grain size (D) of samples was calculated with Scherrer's equation (Cullity 2001);

$$D = \frac{0{,}9\lambda}{\beta cos\theta} \qquad (1)$$

where λ; the wavelength of X-rays, β; the full width at half maximum value and θ is the angle of diffraction. The calculated grain size value for the Z3 series is 40-42 nm.

Synthesized Z3 nanorods have a perfect crystalline wurzite structure with a diameter of approximately 40-42 nm and preferentially orientation of (002). These results are in good agreement with FESEM observations.

The surface morphology of the samples was studied by FESEM (Zeiss Supra 40VP). Fig. 3(a), 3(b) and 3(c) shows the top view FESEM images of Z1, Z2 and Z3. Also Fig 4(a) and 4(b) shows the tilted FESEM images of Z2 and Z3 nanorod arrays.

In Fig. 3(a), it is seen that the Z1 structure is formed continuously and independently from each other by nanoparticles. It is also seen that these nanoparticles combine to form a flower-like structure and it is established that ZnO nanorod does not form in Z1 without seed layer. This result is also supported by XRD measurements. In Fig. 3(b) and 3(c), it is seen that the Z2 and Z3 structure is formed by nanorods. These synthesized nanorods are clearly distinguished from nanoflower structure of Z1. ZnO nanorods have a hexagonal shape of crystal structure of ZnO. As it seen from Fig. 3(b) and 4(a), in Z2, some nanorods stand vertically some nanorods stand slanted.

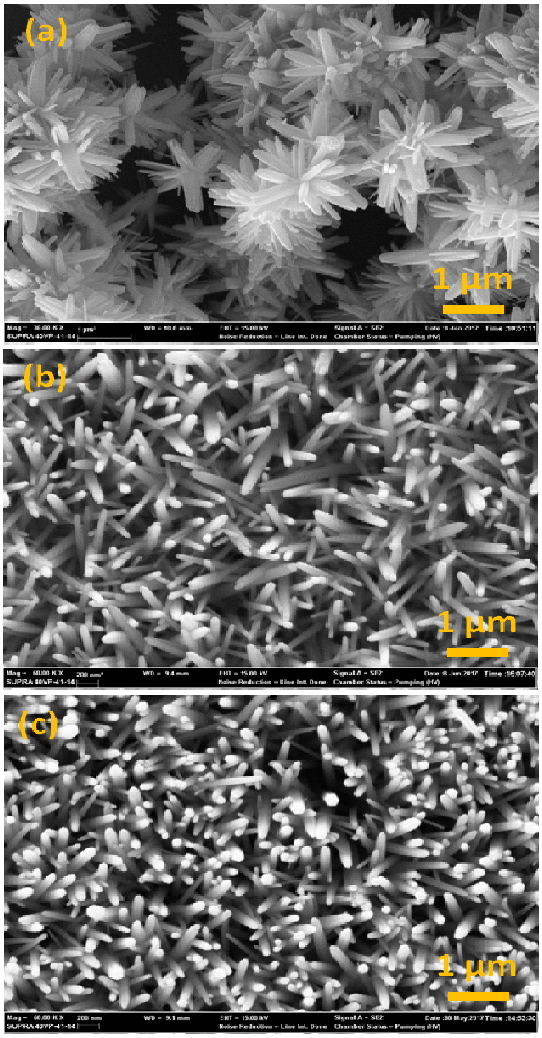

Fig. 3 Top view FESEM images of (a) Z1, (b) Z2, (c) Z3.

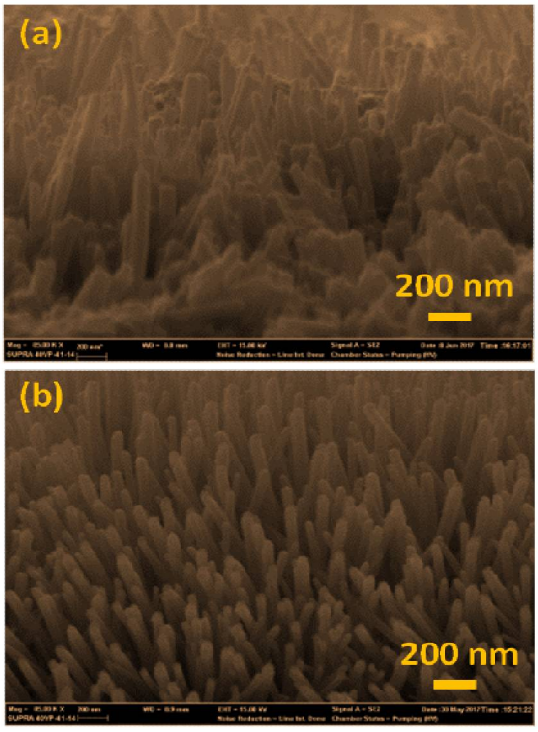

Fig. 4 Tilted FESEM images of (a) Z2 and (b) Z3.

In Fig. 3(c) and 4(b), Z3 nanorods are almost vertically synthesized on the seed layers. A strongly increase was observed in the density and the length of the vertically synthesized ZnO nanorods by increasing the thickness of seed layer in Z3 series. Synthesis of ZnO nanorods is highly related to the seed layer thickness. The orientation, density and configuration of the nanorods can be improved by increasing the thickness of seed layer. The average diameter calculated from FESEM images for the Z3 series is 45-50 nm. These results are in good agreement with XRD measurements.

CONCLUSION

ZnO nanorods were synthesized by a hybrid deposition technique include two steps: deposition of the ZnO seed layers and synthesis of ZnO nanorods onto seed layers. ZnO seed layers were deposited onto glass substrates by sol-gel spin coating technique. Three different seed layers in different thicknesses were prepared. ZnO nanorods were synthesized onto seed layers by chemical bath deposition method. ZnO nanorod synthesis lasted only 30 min and annealing was not required to form nanorods with the chemical bath conditions used in this study. Effects of seed layer on the crystalline structure and morphology of the ZnO nanorods were investigated by XRD and FESEM measurements. Z1 series have polycrystalline structure and there is no preferential growth in the Z1 series. Also, as can be understood from the FESEM image, Z1 is formed like a nanoflower structure and it is established that ZnO nanorod does not form in Z1 without seed layer. For Z2 and Z3 series, strong (002) peaks appear which are indexed to hexagonal ZnO crystal. Z2 and Z3 series have a strong c-axis orientation. As the thickness of seed layer increases in Z3 series, the intensity of (002) peak strongly increased. As can be seen from FESEM images, Z2 and Z3 structure is formed by nanorods. In Z2, some nanorods stand vertically some nanorods stand slanted but Z3 nanorods are almost vertically synthesized on the seed layers. A strongly increase was observed in the density and the length of the vertically synthesized ZnO nanorods by increasing the thickness of seed layer in Z3 series. These results indicate that the crystalline structure of the nanorods can be controlled by changing thickness of the seed layers and the density and alignment of the nanorods can be improved by increasing the thickness of seed layer.

Acknowledgments

This work was supported by Scientific Research Project Commission of Bilecik Seyh Edebali University (project number is 2016-01.BŞEÜ.06-02). XRD and FESEM measurements were performed in Bilecik Seyh Edebali University Central Research Laboratory.

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How to cite this article:

Sinan Temel *et al* (2017) ' Short Time Synthesis Of Zno Nanorods Prepared By A Hybrid Deposition Technique: Effects Of Seed Layer', *International Journal of Current Advanced Research,* 06(07), pp. 4646-4649.
DOI: http://dx.doi.org/10.24327/ijcar.2017.4649.0550

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