Effect of Washing Treatment on the Morphology of Vertically Aligned ZnO Nanorods

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ABSTRACT

Vertically oriented ZnO nanorods were synthesized in a two steps technique involving the preparation of ZnO seed layer and the growth of ZnO nanorod on the glass substrate. ZnO seed layer was firstly deposited on the glass substrate by dip coating method, while well aligned ZnO nanorod were grown on seed layer coated substrate by hydrothermal method at 110 ^oC for 20 min. Crystalline structure, morphologies and band gap energy of the as-prepared ZnO nanorod were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM) and specular reflectance UV-Visible spectrophotometer, respectively. The XRD results showed that ZnO nanorods were wurtzite-structured with preferential orientation along (002) plane. It is shown that washing treatment on the as-prepared ZnO films provides a facile way to eliminate randomly oriented ZnO nanorods and results in vertically oriented nanorods on the glass substrate. Its textural coefficient is almost two times higher than ZnO nanorods previously reported.

Keywords : Zinc oxide, nanorod, hydrothermal method, seed layer, washing treatment.

1. INTRODUCTION

The interest in ZnO structures has increased significantly in recent years because of their potential applications in nanoelectronic devices such as light emiting diode (Park et al, 2007), UV photodetector (Lupan et al, 2008), gas sensors (Lupan et al 2008), and solar cell (Charoensirithavorn and Yoshikawa, 2006; Han et al, 2010; Ranjusha et al, 2011; Pradhan et al 2007). ZnO has shown a great deal of research interest in nanoelectronic devices due to some of its fascinating properties. Compared to other semiconductors, ZnO has unique properties such as, higher binding energy (60 meV), wide band gap (3.37 eV), high breakdown strength, cohesion, and exciton stability (Pradhan et al, 2007). Intense research by many different groups has focused on novel nanostructures with different shapes such as nanorods (Park et al, 2007; Lupan et al, 2008; Lupan et al, 2008; Charoensirithavorn and Yoshikawa, 2006; Lan et al, 2010) , nanowires (Pradhan et al, 2007), nanoflowers (Chen, 2006), nanotubes (Han et al, 2010; Ranjusha,2010) and other unique shapes. Amongst, vertically grown ZnO nanorods or nanowire arrays are the most attractive focus of interest. Various vapor-phase methods such as metal-organic vapour phase epitaxy (MOVPE) (Park et al, 2007), metal-organic chemical vapor deposition (MOCVD) (Nam et al 2011) and thermal evaporation (Wang et al, 2008) have been successfully used to grow oriented ZnO nanorod arrays at relatively high temperature of 800 - 900 ^oC. Beside the limitation of high preparation temperature and energy consuming experiment facilities, these vapor phase methods also imply complex and expensive process. Hence, an efficient and economical method for growing ZnO nanorods is desired for diverse range of applications.

Recently, hydrothermal approach to grow vertically aligned ZnO nanorods arrays was developed at low temperature. It provided simple process with simple equipment, catalyst-free growth, low cost, large area, uniform production and utilized less hazardous materials (Aneesh, 2007). This method is often used because it allows controlling particle size, morphology and crystallinity by tuning the experiment variables (Xu et al, 2010). Another attractive feature is the possibility of performing in-situ growth of film directly from aqueous precursor in solution by introducing the substrates inside the reacting medium (Baruah and Dutta, 2009).

The effects of hydrothermal growth parameters such as precursor concentration (Lan et al, 2010; Aneesh et al, 2007), temperature (Lan et al, 2010), pH (Baruah and Dutta, 2009), time (Zhao et al, 2006), seed layer crystallinity and substrates type have been investigated extensively. Tsai and Teng (2006) have reported the effect of washing treatment as post-synthesis step for preparation of TiO_2 nanotubes. It was reported that the condition of the post-treatment affected the formation, crystalline structure, or even chemical composition of the final nanotube products. However, effects of washing treatment after synthesis of ZnO nanorod are not available in the literature.

In this work, the effect of washing treatment after synthesis on the morphology and crystallinity of ZnO nanorods will be presented. The results indicate that washing treatment could eliminate the randomly oriented of ZnO nanorods and increase their bandgap energy.

2. EXPERIMENTAL SECTION

2.1. Material

Zinc nitrate tetrahydrate ($Zn(NO_3)_2.4H_2O$), zinc acetate hexahydrate ($Zn(CH_3COO)_2.6H_2O$), sodium hydroxide (NaOH) and ethanol were purchased from Merck.

2.2. Instrumentation

X-Ray Diffraction (XRD, Shimadzu XRD-6000 Elmer), Scanning Electron Microscope (SEM, JEOL JSM-6360 LA) and UV-Visible spectrophotometer with Specular Reflectance Attachment (SRUV, Shimadzu Pharmaspec-1700) were used to analyze crystal phase, morphology, and reflectance spectra of ZnO films, respectively.

2.3. Procedure

ZnO nanorod arrays were prepared perpendicularly on glass substrate. The methods were modified from Charoensirithavorn and Yoshikawa's methods (Charoensirithavorn and Yoshikawa, 2006,). Firstly, pre-cleaned glass substrate was seeded by 0.01 M of zinc acetate in ethanol by dip-coating method with withdrawn rate of 4 cm^2/min. Then, the film was annealed to form the crystal seeds aligned on the substrate. The annealing temperature was carried out sequentially at 130 °C for 120 min, at 180 °C for 60 min, and at 260 °C for 120 min in the air.

After the heat treatment, the seeded substrate was immersed into an aqueous solution of $Zn(NO_3)_2$ (0.03 M) and NaOH (0.8 M). The mixture was treated hydrothermally at 110 °C for 20 min. Then the as-synthesized ZnO film on the glass substrate was subjected to the post synthesis treatment. It was washed with double-distilled water by immersing the films into water for 30 minutes. The resulted films were dried in the air. Scanning electron microscopy (SEM) was used to study the morphology of the nanorods arrays. Crystalline structure of ZnO nanorods was analyzed by X-ray diffraction (XRD). The growth of ZnO crystallites on glass substrates were quantitatively characterized with calculated texture coefficient, TC(hkl), defined as follows (Park et al, 2007)

$$\mathrm{TC}\,(hkl) = \frac{\frac{I_{(hkl)}}{Ir_{(hkl)}}}{\frac{1}{n}\sum\left[\frac{I_{(hkl)}}{Ir_{(hkl)}}\right]} \qquad \text{Eq. 1}$$

where TC(hkl) is the texture coefficient, n is the number of peaks considered, I(hkl) are the intensities of the peaks of the ZnO nanorods, and Ir(hkl) are the peak intensities indicated in the JCPDS#36-1451 corresponding to the randomly oriented crystallites. A sample with randomly oriented crystallites presents a TC(hkl) of 1, while a larger value indicates an abundance of crystallites oriented to the (hkl) plane. Reflectance spectra were analyzed by Specular-Reflectance UV-Visible Spectrophotometer.

3. RESULTS AND DISCUSSION

The phase of seed layer and as-synthesized ZnO nanorods was identified by XRD measurement. Fig. 1 shows XRD patterns of ZnO seed layer (Fig. 1a) and as-grown ZnO nanorods (Fig. 1b). Both diffraction peaks can be indexed to the hexagonal wurtzite structure of zinc oxide with lattice parameter of a= 3,251 nm; c= 5,101 nm (JCPDS card no. 36-1451).

From Fig.1a, it can be seen that ZnO seed layer has two main diffraction peaks at 2θ of 35.1° and 36.9° which correspond to (002) and (101) diffraction plane of wurtzite ZnO, respectively. The same peaks are also shown in ZnO nanorods XRD pattern (Fig. 1b), with extra peak at 31.7° that corresponds to (100) diffraction plane. By using Scherrer equation, it is calculated that the crystallite size of ZnO nanorod is 52.67 nm. From Fig. 1b, it is shown that ZnO nanorods were grown at the same epitaxial as the deposited seed layer. It is suggested that seed layer have important role for the growth of ZnO nanorods. Seed layer may provide numerous nucleation sites for ZnO growth. For seed layer with good wurtzite structure, ZnO nanorods are expected to adopt the same epitaxial relationship as the seed layer (Wang et al, 2008).

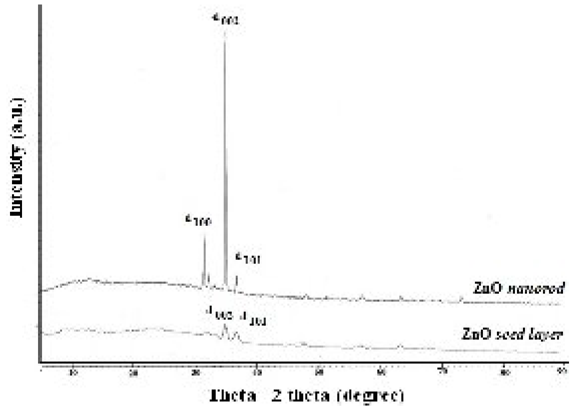

Figure 1. X-Ray Diffraction patterns of ZnO seed layer (a) and ZnO nanorods (b).

The highest peak intensity obtained for the (002) diffraction peak (Fig.1b) indicates the anisotropic growth of the nanorods in the [0001] direction, perpendicular to the glass substrate. For further evaluation, the degree of c-orientation can be calculated by the relative texture coefficient for (002) plane which is 2.36. This value is higher than that obtained by Park et al. (2007) which is ranging from 1.3 – 1.5. The XRD results confirm that the resulted ZnO is highly crystallized wurtzite ZnO with preferable c-orientation. But, SEM images of this sample (Fig. 2) show that the as-grown ZnO nanorods are not aligned perpendicularly on the glass substrate. In cross sectional view (Fig. 2a), it is observed that a large amount of ZnO nanorods was overlapping one another in randomly direction. The randomly aligned ZnO nanorods are also clearly seen from the top view (Fig. 2b). At larger magnification (Fig. 2c), the relatively uniform size of nanorods was observed from the surface of film. The size of nanorods diameter was up to 170 nm, and the length was up to 5 μm.

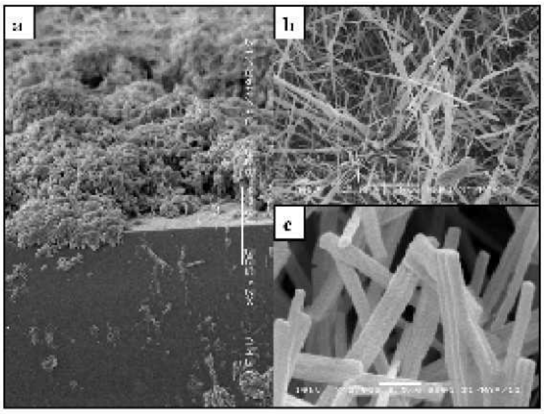

Figure 2. SEM images of deposited ZnO nanorods on glass substrate, cross section view (a), top view (b) and larger magnification of top view (c).

It is predicted that randomly oriented of ZnO nanorods on the film surface might be aligned during the cooling process that carried out after the hydrothermal synthesis. Therefore, washing treatment using distilled water was then carried out to remove the randomly oriented ZnO.

XRD result for ZnO nanorods after washing treatment is shown in Figure 3. The difractogram shows two main peaks corresponding to the crystal plane (002) and (100) for wurtzite ZnO. The absences of (101) plane indicates that the randomly oriented of nanorods have been removed after washing treatment.

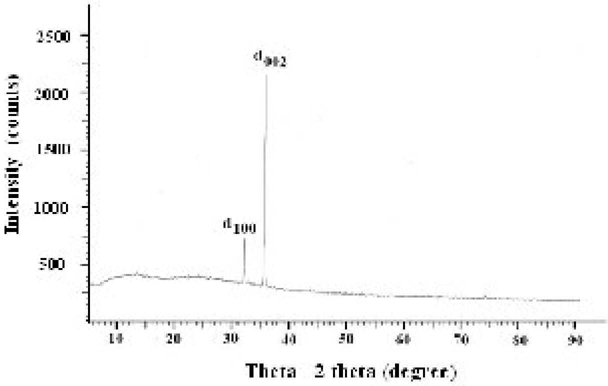

Figure 3. X-Ray Diffraction pattern of ZnO nanorods after washing treatment

Based on the XRD data, it can be evaluated that texture coefficient for the (002) ZnO nanorods thin layer after washing treatment showed an increase from 2.36 to 2.63. This indicates that preferential orientation to the [0001] direction increases. To confirm this, SEM analysis was performed (Figure 4).

From Figure 4, it can be seen that washing treatment has influenced the alignment of the rods. From cross sectional section (Figure 4.a and 4c.), it can be seen the appearance of nanorods with vertical orientation on the glass substrate having a length of the rods up to 800 nm. The length of rods that aligned perpendicular to the substrate is much shorter than the rods with random orientation previously presented in Figure 2. Some length has been probably cut by water during the washing treatment. However, there is still residual particle on the surface of the layer as shown in Figure 4b, that might be due to incomplete washing.

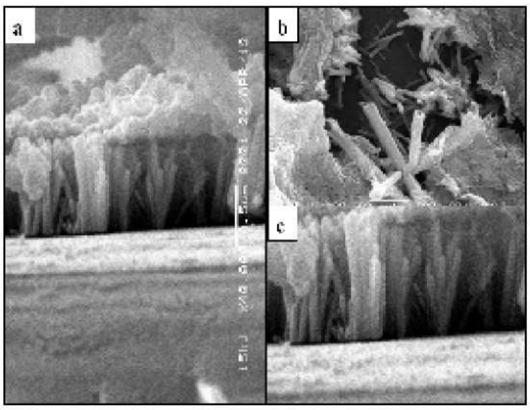

Figure 4. SEM images of deposited ZnO nanorods after washing treatment, cross section view (a), top view (b) and larger magnification of cross section view (c).

To determine the effect of washing to the bandgap energy of ZnO nanorods thin layer, the reflectance spectra of the films were taken. The band gap energy was then determined by processing data obtained from the analysis of the reflectance using Kubelka-Munk equation. Curves for determination of the bandgap energy are presented in Figure 5. Bandgap energy for asgrown ZnO nanorods was 3.73 eV, while after washing treatment was 3.78 eV. The results indicate that orientation of the nanorods on the substrate affect significantly the electronic properties of the resulted ZnO nanorods. Higher bandgap energy was obtained for vertically aligned ZnO nanorods on the glass substrate. Further investigation on the effect of alignment on the bandgap of the resulted ZnO films is still in progress.

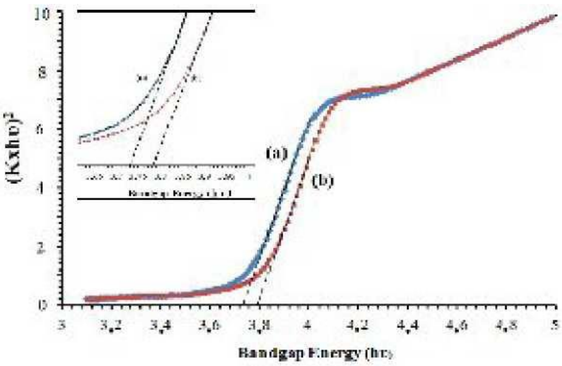

Figure 5. Plots of (Kxhα)^2 vs bandgap energy for as grown ZnO nanorods (a) and after wahing treatment (b). Inset show extrapolation line for bandgap determination

4. CONCLUSION

In summary, a simple hydrothermal technique to grow vertically aligned ZnO nanorods on the surface of amorphous glass substrate has been reported. ZnO nanorods arrrays have grown along the c-axis direction perpendicular to the substrate. It was showed that such material possesses a high quality single crystal wurtzite structure. It can be concluded that washing treatment after hydrothermal method influence the arrangement of the morphology of the asdeposited ZnO on glass substrate. Randomly oriented ZnO nanorods deposited during the cooling process and covered the surface of wellaligned ZnO nanorods can be reduced by this treatment. Post hydrothermal treatment of washing the as-deposited ZnO films with water provided facile method to increase the texture coefficient and also the bandgap energy of ZnO nanorods films on the glass substrate.

REFERENCES

Park, S. H., Kim, S. H. and Han, S. W., 2007, Growth of Homoepitaxial ZnO film on ZnO Nanorods and Light Emitting Diode applications, *Nanotechnol.*, 18, 055608

Lupan, O., Chow, L., Chai, G., Chernyak, L., Tirpak, O.L., and Heinrich, H., 2008, Focused-ion-beam Fabrication of ZnO nanorod-based UV photodetector using the in-situ lift-out technique, *Phys. Stat. Sol. (a),* 11, 2673-2678

Lupan, O., Chai, G. and Chow, L., 2008, Novel Hydrogen Gas Sensor based on Single ZnO Nanorod, *Microelectron. Eng.*, 85, 2220 – 2225

Charoensirithavorn, P., and Yoshikawa, S., 2006, Dye Sensitized Solar Cell Based on ZnO Nanorod Arrays, The 2th Joint International *Conference on "Sustainable Energy and Environment (SEE 2006)"*, 21-23 November 2006, Bangkok, Thailand.

Han, J., Fan, F., Xu, C., Lin, S., Wei, M., Duan, X. and Wang, L., 2010, ZnO nanotube-based Dye-sensitized Solar Cell and its Application in Self-powered Devices, *Nanotechnol.,* 21, 1-7

Ranjusha, R., Lekha, P., Subramanian, K. R. V., Shantikumar, V. N. and Balakrishnan, 2011, A., Photoanode Activity of ZnO Nanotube Based Dye-Sensitized Solar Cells, *J. Mater. Sci. Technol.,* 27, 961-966

Pradhan, B., Batabyal, S. K. and Pal, A. J.,2007, Vertically Aligned ZnO Nanowire Arrays in Rose Bengal-based Dye-sensitized Solar Cells, *Sol. Energy Mater. Sol. Cells,* 91, 769-773

Wang, H., Zhang, Z. P., Wang, X. N., Mo, Q., Wang, Y., Zhu, J.H., Wang, H.B., Yang, F.J., Jiang, Y., 2008, Selective Growth of Vertical aligned ZnO Nanorod Arrays on Si Subtrate by Catalyst-free Thermal Evaporation, *Nanscale Res. Lett*., 3:309-314

Lan, S. Y., Ming, B. J., Wei, L.Q, Min, L. Y., 2010, Effects of Substrate on the Structure, Morphology and Optical Properties of Vertically Aligned ZnO Nanorod Arrays Grown by Low-temperature CBD Method, *J. Inorg. Mat.*, 25, 1115-1120

Chen, Y., Zhu, C. L. and Xiao, G., 2006, Reduced-temperature Ethanol Sensing Characteristics of Flower-like ZnO nanorods Synthesized by a Sonochemical Method, *Nanotechnol.*, 17, 4537 - 4541

Nam, S. H., Jeong, S. H., and Boo J. H., 2011, Growth Behavior and Characteristics of One Dimensional ZnO Nanostructures by Metalorganic Chemical Vapor Deposition, *J. Nanosci. Nanotechnol.*, 11, 1648-1651

Aneesh, P. M., Vanaja, K. A. dan Jayaraj, M. K., 2007,Synthesis of ZnO Nanoparticles by Hydrothermal Method, *Proc. SPIE,* 6639, 1-9

Xu, F., Lu, Y., Xie, Y. and Liu, Y., 2010, Seed Layer-free Electrodeposition and Characterization of Vertically Aligned ZnO Nanorod Array Film, *J. Solid State Electrochem.,*14, 63 - 70

Baruah, S. and Dutta, J., 2009, pH-dependent Growth of Zinc Oxide Nanorods, *J. Cryst. Growth*, 135, 1-6

Zhao, J., Jin, X. G., Liu, X. X. and Liu, Z. F., 2006, Growth and Morphology of ZnO nanorods Prepared from $Zn(NO_3)_2$/NaOH Solution. *J. Eur.Ceram. Soc.*, 26, 3745-3752

Tsai, C. C. and Teng, H., 2006, Structural Features of Nanotubes Synthesized from NaOH Treatment on TiO_2 with Different Post-Treatments, *Chem. Mater.* , 18, 367-373