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Research Article

STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF ZnO NANORODS PREPARED BY DIP COATING METHOD

Vasudevan K.P[1,2]*., Venkatachalam M[1], Saroja M[1] and Gowthaman, P[1]

[1]Thin Film Centre, Erode Arts and Science College, Erode, Tamil Nadu, India
[2]Department of Electronics, CMS College of Science &Commerce, Tamil Nadu, India

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ABSTRACT

In this study, zinc oxide (ZnO) nano rods were prepared by dip coating method. By using X-ray diffractometer (XRD) the crystal structure of ZnO nano rod arrays were investigated and it confirmed that ZnO thin films are of hexagonal wurtzite structure. The grain sizes were decreased with increasing pH value. The surface morphologies were observed using Scanning Electron Microscope (SEM) and the optical studies confirmed that the prepared films are found to have a maximum transmittance and also the band gap decreases with increasing pH value. The prepared ZnO nano rods have wide range of applications in Photo catalytic degradation of textile coloring dyes.

INTRODUCTION

The ZnO is an n-type semiconductor with wide band gap with greater than 3.3eV, high bond energy (60 meV), high thermal and mechanical stability at room temperature. The prominent crystalline structure of ZnO is wurtzite type(K.Hara., *et al*, 2000, Y. Zhizhen *et al*, 2003), due to its multifunctional property it has been studied and used for many applications like solar cells, surface acoustic devices, UV lasers and photo catalytic degradation of textile coloring dyes. The ZnO films were prepared by different deposition techniques and based on the deposition the morphology and physical properties of nanostructures changes (Zhong Lin Wang 2004, M. Suchea *et al*, 2006). The thin films of Zinc oxide can be prepared by various techniques viz., sputtering, chemical vapour deposition (CVD), laser ablation, sol-gel process, spray pyrolysis, thermal evaporation, metal organic chemical vapor deposition (MOCVD), pulsed laser deposition, molecular beam epitaxy (MBE) (HB. Kang *et al*, 2009, M. Lorenz, *et al*., 2005, G. Zhang *et al*., 2007, Y. Segawa *et al*., 1997, P. Puspharajah *et al*., 1997) and chemical synthetic routes including hydrothermal, solvothermal, electrochemical and chemical bath deposition (S.K.N. Ayudhya *et al*., 2006, G.Dhivya *et al*., 2015, S. Peulon *et al*., 1996, Wang, B. Mao *et al*., 2007) have been successfully employed to prepare a wide variety of ZnO nano structures. The hydrothermal method is promising for fabricating ideal nano material with special morphology because of the simple, fast, less expensive, low growth temperature, high yield and scalable (A.D.A. Buba *et al*.,) Also, the hydrothermal process is usually substrate independent and the morphology of the nanorods can be easily controlled through slight changes in the reaction conditions (Sunandan Baruah *et al*., 2009).

In this paper, well aligned ZnO nanorods were grown on glass substrate by using hydro thermal method. By using zinc acetate, ethanol and deionised water the seed layer was formed through dip coating technique. The ZnO nano rods were grown over the seed layered ZnO using zinc nitrate, Hexamethylenetetramine and deionised water**.** By using X-ray diffractometer (XRD) the crystal structure of ZnO nano rods arrays were investigated and the grain size was calculated. The surface morphologies were observed using Scanning Electron Microscope (SEM). The optical studies were taken using UV-Vis spectrophotometer (UV-Vis) and the band gap was studied.

Experimental Technique

The substrate cleaning plays a vital role in the deposition of thin films. First, commercial microscopic glass slides were boiled in chromic acid for 2 hours, washed with detergent, rinsed three times in acetone and finally ultrasonically cleaned with distilled water before deposition.

**Corresponding author:* *Vasudevan K.P*
Thin Film Centre, Erode Arts and Science College, Erode, Tamil Nadu, India

Seed Layer preparation

Seed layers were prepared in three stages of a) Solution preparation, b) Drying and c) Coating. Initially the seed layer solution was prepared for 0.1 mol concentration by mixing Zinc acetate (0.2 gms) and Ethanol (10 ml). The initial pH of solution is 7.5. The solution was mixed in a magnetic stirrer for 2 hours. The 0.25 ml of de-ionised water added to the prepared solution drop by drop in the mixer. The prepared seed layer solution was used for producing ZnO seed coated thin films using automatic dip coating machine. The dipping time and retrieval time was set to 1 min and 15 minutes set to 70 °C for drying. The same process was repeated for 5 times to get desired thickness. After that the seed coated glass substrates were kept in muffle furnace at 200°C for 1 hour annealing and left it for auto cooling until it reaches room temperature. The same seed coating process was repeated for different values pH 8.5, 9.5 and 10.5.

Growth Layer Preparation

In this process, The ZnO nano rods were grown over the seed layered ZnO by using the materials zinc nitrate, Hexamethylenetetramine and deionised water. All these materials were put it into the beaker and mixed in magnetic stirrer for 2 hours at room temperature. After preparation of growth layer solution it was taken in a beaker and the seed coated substrates are dipped inside the growth solution and kept in oven at 90°C for 4 hours. After that the slides were taken out from the beaker and rinsed in water for separation of residuals. These substrates are kept in 500°C annealing process for 1 hour. The ZnO nanorods were prepared for four different pH values of 7.5, 8.5, 9.5 and 10.5.

RESULTS AND DISCUSSION

Structural studies

Figure 1 show the XRD patterns of pH 7.5, 8.5, 9.5 and 10.5 termed as A1, A2, A3 and A4 respectively. At pH 7.5, the patterns of the ZnO nanorod array films deposited on glass revealed three dominant peaks at 2θ values of 31.61°, 34.29° and 36.11° corresponding to (100), (002) and (101) planes respectively. The (h k l) peaks are in good agreement with the standard JCPDS card (036-1451) for hexagonal wurtzite ZnO. The XRD pattern of pH 7.5 shows that, it has a strong (002) peak and weak (100) and (101) peaks.

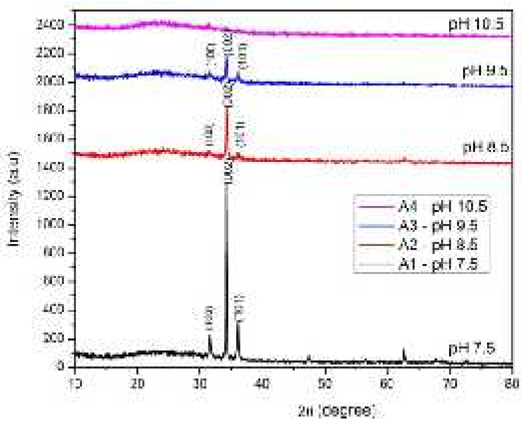

Fig.1 XRD patterns of ZnO nanorods at different pH values

The strongest reflection observed along the (002) plane for pH 7.5 sample indicates that the ZnO nanorods arrays are preferentially well-oriented in the direction of the c-axis. The presence of broad peaks in the pH 7.5 samples shows that the grains have started to grow on pH and the films are of nano crystalline nature.

The strong and narrow diffraction peaks indicate that the material has a good crystalline nature and size (Sugapriya S *et al*., 2015, Suganya. R *et al*., 2015, Vanaja A *et al*., 2016). From fig.1 the intensities of the reflection peaks changes as the pH increases from 7.5 to 8.5, the intensity of the (100), (002) and (101) peaks has been decreased. When the pH value increased from 8.5 to 9.5, the intensity of the (100), (002)and (101) peaks has been further decreased and detected at 2θ values of 31.58°, 34.33°, 36.12°. The full width at half maximum (FWHM) and grain size of crystallites was calculated using Debye Scherer's formula for (002) plane was given in Table 1. FWHM of ZnO thin films show changes with changing pH values.

Table 1 The structural parameters of ZnO thin films.

Sample	FWHM	2θ (angle)	Grain size d (nm)
pH 7.5	0.08	34.29	94
pH 8.5	0.15	34.33	50
pH 9.5	0.23	34.30	33
pH10.5	0.3	36.12	25

From the table 1 it is clearly shown that as pH value increases from 7.5 to 9.5 the grain size decreased from 94 to 33. At pH 10.5 the crystal size is decreased to 25, because the c-axis orientation is decreased.

Morphological Studies

Surface morphology was examined by a (JEOL JSM 5610) scanning electron microscope. The figure 2 (a-d) shows the SEM images of ZnO nanorods prepared at pH values of 7.5, 8.5, 9.5 and 10.5. They show the dense arrays of hexagonal ZnO nanorods having different diameters that are formed under different pH. The pH of the precursor solution was found to play a major role in the deposition of ZnO nanorod arrays. As seen from SEM images, the orientation of the obtained ZnO rod arrays strongly depends on the pH of the starting solution.

SEM image (Fig 2a), shows the ZnO nanorod prepared at pH 7.5 were well aligned nanorods were grown and they were oriented towards the vertical direction (C-axis). The density of the rods grown is decreased and diameter of rod size is decreases as the pH increases. From fig.2b to 2c it is clearly seen that as the pH increased from 7.5 to 8.5 and 8.5 to 9.5 we observe that it consist of well aligned nano granules. The morphology changed from nanorods to nano granules. As pH further increased from 9.5 to 10.5 as shown in fig 2d, the rod formation has been collapsed. The reason for this should be higher reaction rate, when precipitates start to dissolve. The SEM results are in accordance with the XRD.

From SEM observations, it is clear that the morphological characteristics of ZnO can be controlled by the pH value of starting solution. In addition, as clearly seen from SEM images, although the shape of the structures remains the same their overall dimensions change with increasing pH. In other words, one can tune-up the size of the ZnO structures from macro to nanorods by adjusting the pH of the solution (Kiruthiga A *et al*., 2015, Panchavarnam D *et al*., 2016).

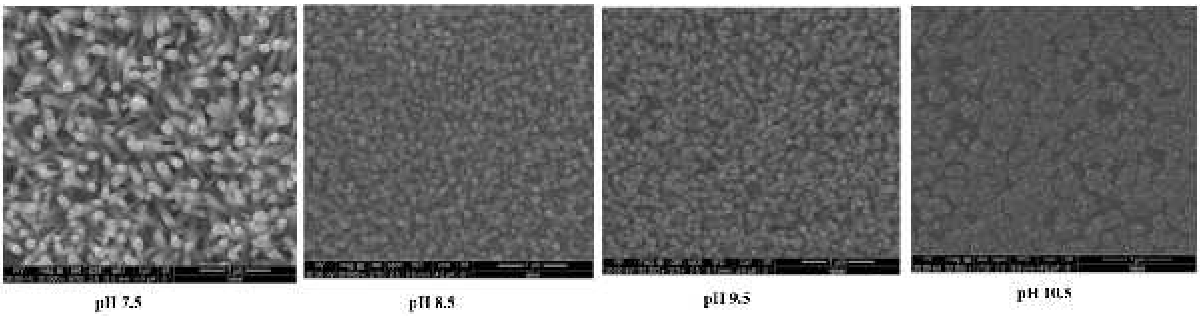

Fig.2 SEM images of ZnO nanorods at different pH values

Optical studies: UV-Vis Absorption

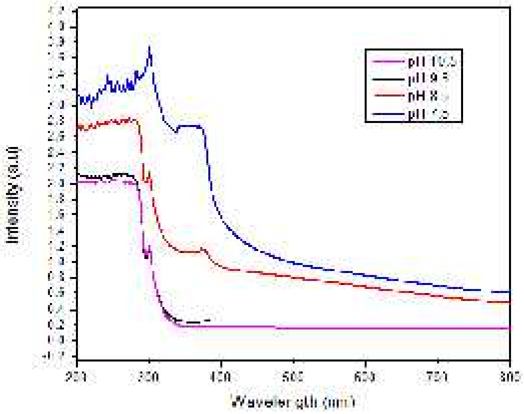

Fig.3 Absorption spectra of ZnO nanorods at different pH values

Absorption studies of the ZnO nanorods are further checked by optical properties. The optical absorption spectrum is as shown in the figure 3. The studies were performed in the wavelength range of 200 to 800 nm. From the result it is observed that at pH 7.5 the intensity is high. As the pH value increased from to 8.5 and to 9.5 the absorption intensity is decreased. At pH 10.5 the intensity is further decreased.

Optical studies: UV-Vis Transmittance

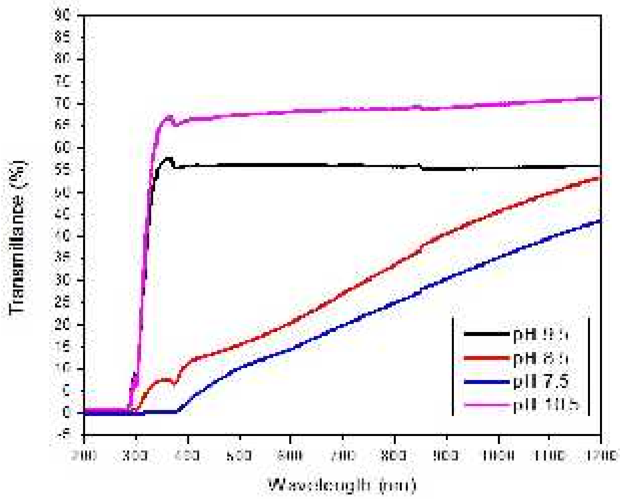

Fig.4 Transmittance spectra of ZnO nanorods at different pH values

Transmittance studies of the ZnO nanorods were shown in the figure 4. The percentage of transmittance is very low for 7.5 pH. The lower absorption and higher transmittance in the visible region observed in the pH range 7.5, illustrates the good optical quality of the crystals with low scattering and absorption losses which leads to industrial application especially as a transparent electrode. As the pH increases from 7.5 to 10.5, through 8.5 and 9.5 the value transmittance percentage increases.

CONCLUSION

The hydrothermal process is substrate independent and most energy efficient method for synthesizing ZnO nanorod. It had been successfully synthesized in a simple chemical bath deposition method. From XRD patterns it is observed that the strongest reflection observed along the (002) plane for pH 7.5 sample indicates that the ZnO nanorods arrays are preferentially well-oriented in the direction of the c-axis. From SEM analysis it is shown that well aligned nanorods were found at pH 7.5 and the grain size was 94 nm and found to decrease with increase in pH. The optical analysis confirmed that the absorption intensity was high at pH 7.5 and vice versa in transmittance which shows good optical properties. The prepared ZnO nanorods can be used for the photocatalytic degradation of textile dyes.

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