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Preparation and Characterization of ZnO Nano rods by Hydrothermal Method

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ABSTRACT

In this study, a surface structure of zinc oxide (ZnO) nano rods prepared by hydrothermal method was investigated. The crystal structure of ZnO nano rods arrays were investigated by X-ray diffractometer (XRD) with Cu Kα radiation. The surface morphologies were observed using Scanning Electron Microscope (SEM). The prepared ZnO nano rods have wide range of applications in Photo catalytic degradation of textile colouring dyes.

Introduction

ZnO films has been studied due to their numerous applications like solar cells, surface acoustic devices, UV lasers and Photo catalytic degradation of textile coloring dyes due to its multifunctional n type semiconductor with wide band gap with greater than 3.3eV, high band energy (60 meV), high thermal and mechanical stability at room temperature. The prominent crystalline structure of ZnO is wurtzite type [1, 2], although it exists in the cubic zinc blend and rock salt structures. A highly transparent ZnO films have been prepared by many different deposition techniques and their corresponding deposition parameters play an important role in controlling the morphology and physical properties of the nano structures [3,4]. ZnO with different nano structures are mostly used in many applications such as nano wires, nanorods, nano belts, nano ribbons, nano needles, nano rings, nano tetra pods, nano multi pods, shuttle-like, comb-like nano sheet

The thin films of Zinc oxide can be prepared by various techniques. They are 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) [5-9] and chemical synthetic routes including hydrothermal, solvothermal, electrochemical and chemical bath deposition [10-14] have been successfully employed to prepare a wide variety of ZnO nano structures. The physical deposition routes have the advantage of producing high quality materials, but also the disadvantage of the need for high temperature. Among these methods, 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 [15]. In this paper, the well aligned ZnO nanorods were grown on glass substrate by using hydro thermal method. The seed layer was formed using zinc acetate, ethanol and deionised water using dip coating technique. The ZnO nanorods were grown over the seed layered ZnO thin film using Zinc nitrate, Hexamethylenetetramine and deionised water. The crystal structure of ZnO nano rods arrays were investigated by X-ray diffractometer (XRD) with Cu Kα radiation. The surface morphologies were observed using Scanning Electron Microscope (SEM). The prepared ZnO nano rods have wide range of applications in Photo catalytic degradation of textile colouring dyes.

Experimental Technique

In this technique substrate cleaning plays an important 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.

Seed Layer preparation

Solution preparation, coating and drying are the three stages of thin film coating process. The ZnO nano rods were deposited by dip coating process / hydro thermal technique. 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.

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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 materials used are Zinc nitrate, Hexamethylenetetramine and deionised water 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 036-1451 card 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. 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 increased and detected at 2θ values of 31.58°, 34.33°, 36.12°. The strongest reflection observed along the (002) plane for pH 9.5 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 9.5 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 and size [16-18]**.** 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. From the table it is clearly shown that as pH value increases from 7.5 to 9.5 the grain size increases from 27.9 to 57.9. At pH 10.5 the crystal size is decreased to 27.9, 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 can be seen from SEM images, the orientation of the obtained ZnO rod arrays strongly depends on the pH of the starting solution. From SEM picture, it can be seen clearly that the samples produced from solution with pH 7.5 and pH 8.5 consist of well aligned nano granules.

In Fig.2a, the film with pH 7.5 shows that the rods were grown in all directions with small diameter. From fig.2b to 2c it is clearly seen that as pH increases from 7.5 to 8.5 and 8.5 to 9.5, the ZnO nanorods were oriented towards the vertical direction (C-axis). The density of the rods grown is decreased and diameter of rod size is increased as the pH increases. As pH increased from 9.5 to 10.5 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 [19-20].

Conclusion

Using hydrothermal method with different pH values of 7.5,8.5,9.5 and 10.5 at lower growth temperature of 90^{0C} for 4 hours, the ZnO nano rods had been successfully synthesized in a simple chemical bath deposition method.X-ray Diffraction (XRD) pattern of the synthesized ZnO film obtained by dip coating is shown in Fig.1(a) Shows that three strongest diffraction peaks indicating that the film was polycrystalline with a hexagonal wurtzite structure which is in agreement with JCPDS card no.036-1451 and preferred orientation along (100), (002)and (101) planes and SEM morphological analysis is shown in Fig.2 (a-d) revealed that grain size was 27 and 57 nm. With increase in pH, the grain size also increased and the effect of pH on grain size is summarized in Table 1.

Table 1. The structural parameters of ZnO thin films.

Samples	FWHM	2θ (angle)	Grain size d (nm)
pH 7.5	0.23	34.300	27.9
pH 8.5	0.15	34.33	45.0
pH 9.5	0.081	34.294	57.9
pH10.5	0.2	34.30	27.9

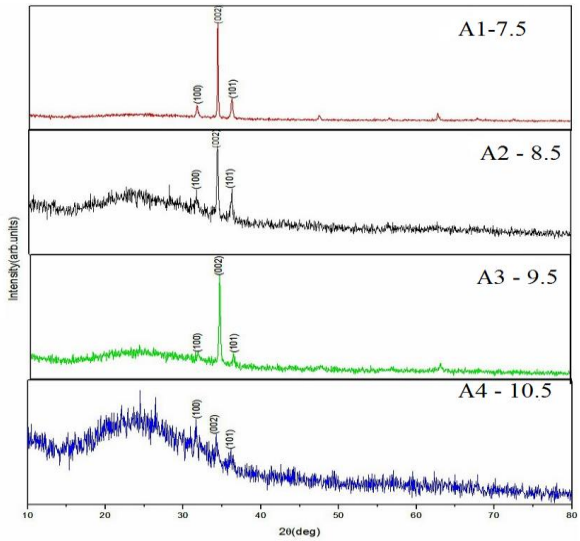

Figure 1. XRD Spectra of different pH values of 7.5, 8.5, 9.5 and 10.5.

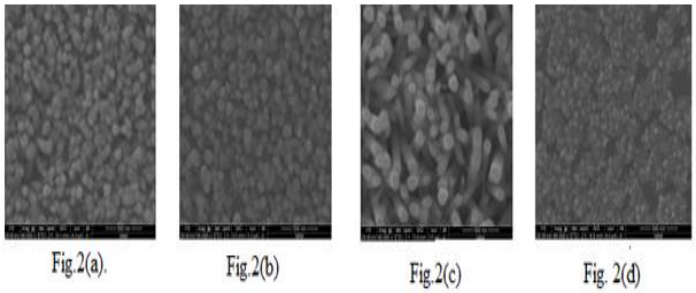

Figure 2. SEM pictures of ZnO nanorods of different pH values of 7.5, 8.5, 9.5 and 10.5.

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