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Structural, Morphological and Optical properties of ZnO nanorods

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Abstract: The well aligned ZnO nanorods were grown on glass substrate by using hydrothermal method. The seed layer was formed by 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 prepared ZnO nanorods were characterized by XRD, SEM, and UV – Visible spectroscopy. The prepared ZnO nano rods have wide range of applications in Photo catalytic degradation of textile colouring dyes.
Key words : ZnO nanorods – Hydrothermal method – Characterization of ZnO nanorods – Influence of pH.

Introduction

ZnO is a 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]. The efficiency and performance of any optical and electrical nano devices are determined by the properties of underlying nano structures, which are in turn greatly dependent on the crystallographic orientation, size, shape and morphology.

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]. The structural and optical properties of ZnO depend on physical and chemical parameters such as preparative methods, drying process, annealing temperature, pH of solution, chemical composition and growth conditions. It provides unique optical, chemical and electrical properties and hence most suitable for many applications like solar cells, surface acoustic devices, UV lasers and Photocatalytic degradation of textile coloring dyes. ZnO with different nano structures are mostly used in many applications in both optical and electronics field such as nano wires, nanorods, nano belts, nano ribbons, nano needles, nano rings, nano tetra pods, nano multi pods, shuttle-like, comb-like nano sheets [16].

In this paper, 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 prepared ZnO nano rods were characterized to examine the structural, morphological and optical properties are reported.

Experimental Technique

In this technique 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.

Seed Layer preparation

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. 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.

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 absorbance and transmittance of the films were measured using UV – Visible Spectrophotometer.

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 [17-19]**.** The full width at half maximum (FWHM) and grain size of crystallites was calculated using Debye Scherer's formula for (002) plane were 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.

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

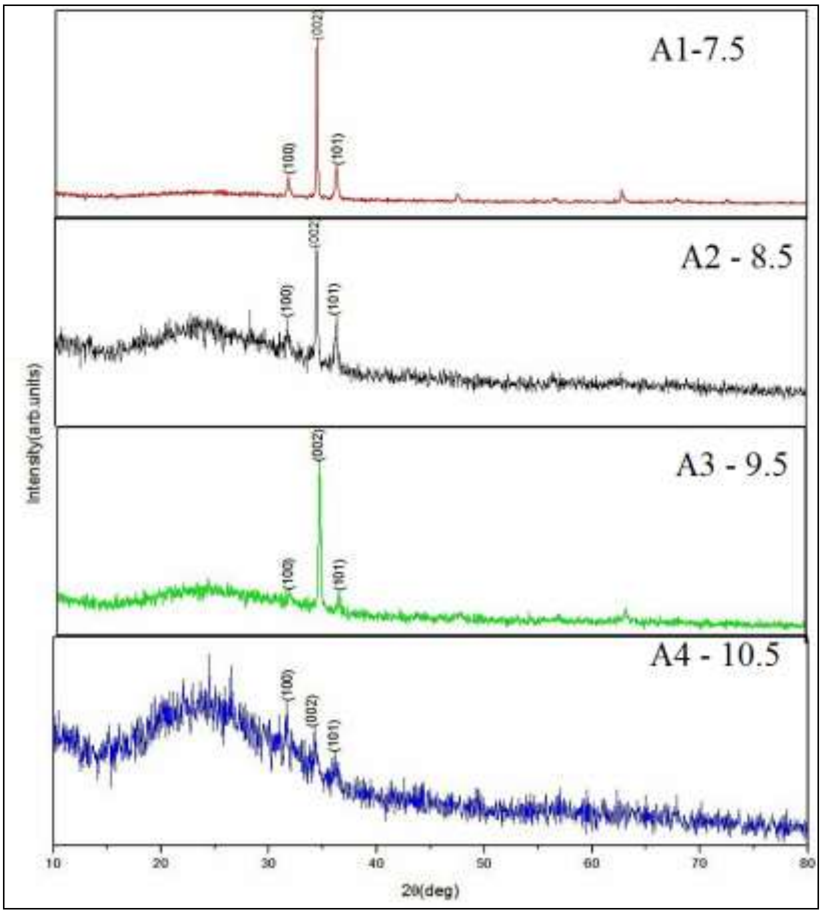

Figure 1 XRD Spectra of different pH values of 7.5, 8.5, 9.5 and 10.5.

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.

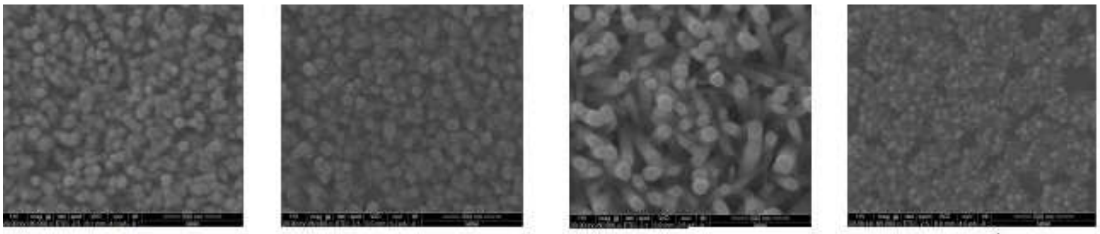

Fig.2(a). Fig.2(b) Fig.2(c) Fig. 2(d)

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

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 [20-22].

Optical Studies

Absorption

The optical characterization of the films was carried out by UV-VIS spectroscopy. The optical absorption was found in the UV region and this can be used for the photo degradation of industrial effluent dyes with the influence of the ZnO nanorods for photo catalytic activities. Fig.3(a) shows the absorption spectra of ZnO nanorods. The optical absorption edge has a tendency to shift to an upper wavelength with increase in pH value. It is well identified that the optical absorption determines the optical band gap of ZnO films which has a direct band gap. The optical band gap of ZnO nanorods at pH values of 7.5, 8.5, 9.5 and 10.5 was found to be 3.13 eV, 2.5 eV, 2.17 eV and 3.14 eV respectively as given in Table 2. From the Table 2 it shows that the band gap was found to decrease from 3.13 eV to 2.17 eV, with the increase of pH from 7.5 to 9.5. The decrease in band gap of ZnO films may be attributed to the improvement in the crystalline quality of the films along with the reduction in porosity and increase in grain size.[23]

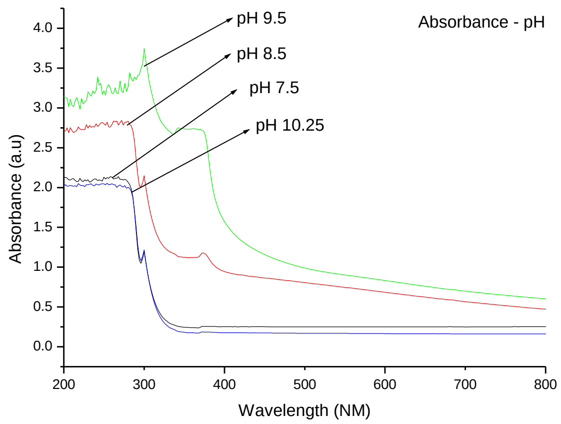

Fig.3(a) Absorption spectra of ZnO nanorods with different pH

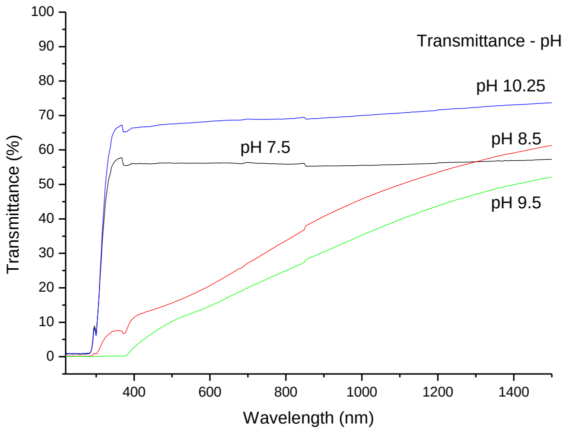

Fig.3(b) Transmittance spectra of ZnO nanorods with different pH

Table 2. The bandgap of ZnO thin films

Samples	Bandwidth
pH 7.5	3.13
pH 8.5	2.5
pH 9.5	2.17
pH 10.5	3.14

Transmittance

Fig 3(b) shows the optical transmittance spectra of pH values of 7.5, 8.5, 9.5 and 10.5. The transmittance spectra is within the visible range nearer to infrared wavelength region that is always higher than 60%, which reveals the superior optical properties in the ZnO thin films produced by Chemical Bath Deposition method. The effect of pH on the optical transmittance for sample was investigated from pH of 7.5, 8.5, 9.5 and 10.5. A slight decrease in average transmission was observed with the increase of pH and was attributed to the increase of surface roughness. The optical transmittance of ZnO films was found to decrease from 60%, 55%, and 50% to 45% with the increase of pH.[24]

Conclusion

ZnO nano rods had been successfully synthesized in a simple Chemical bath deposition method at low growth temperature of 90°C for 4 hours via hydrothermal method with different pH values of 7.5, 8.5, 9.5 and 10.5. From the results of XRD, SEM and UV, it was clearly indicated that at pH 9.5 the film leads to fast growth rate through size of the nano rods. This leads to the improvement in the crystalline quality of the films. A slight decrease in average transmission was observed with the increase in pH and those results are attributed to the increase of surface roughness. Results showed that the different pH values would influence structure, morphology and optical properties of the prepared ZnO nano rods.

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