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Effect on Structural Orientation of ZnO Nanorods by Changing the Molarity and Reaction Time

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ABSTRACT

Zinc oxide (ZnO) have gained much interest since last decade to achieve desired optical and structural properties for various applications. ZnO has wide direct band gap (~3.37 eV), large exciton binding energy (~60 MeV), it is chemically stable, non-toxic and biocompatible along with abundance availability in nature. ZnO nanorods are grown on glass substrate by chemical bath deposition method. Effect of reactants concentration and reaction time on growth and morphology of ZnO nanorods is investigated. Crystal structure analyzed from X-ray diffraction reveals that as-deposited ZnO thin films are monophasic exhibiting hexagonal wurtzite structure. Increased intensity of diffraction peak corresponding to (101) plane confirms the preferential growth of ZnO nanorods. Morphology examined by SEM reveal the growth of ZnO nanorods with different dimensions, mostly less than 100nm depending upon the concentration and reaction time. Spectroscopic ellipsometry is used to study optical properties of ZnO nanorods for their viability in optoelectronic applications.

1. INTRODUCTION

ZnO is the most interesting II–VI compound semiconductor (Ali et al. 2011). ZnO has a large band gap of 3.37 eV, which has a large exciton binding energy of 60 MeV (Cruz et al. 2014). It is mostly found in wurtzite crystalline structure. ZnO nanostructure have been broadly used in surface acoustic wave devices, field effect transistor, transparent electrodes, display devices (Nithya and Radhakrishnan 2012), photonic crystals, optoelectronics (Sunandan et al. 2009), nanogenerators, UV sensors (Amjed et al. 2015), photodiodes, light emitting diodes (Jing et al. 2014), solar cell, and nano-piezoelectronics (Omer et al. 2015). ZnO nanostructure can be form in different shapes such as nanorings, nanopropellers, nanoribbons, nanobelts, nanowires/nanorods, and nanotubes (Poornajar et al. 2016).

ZnO nanostructure can be synthesized by using variety of well-established synthesis techniques, such as sputtering, spray pyrolysis (Ocakoglu et al. 2015), metal organic chemical vapor deposition (Jambure et al. 2014), thermal deposition, electro deposition, physical vapor deposition (PVD), hydrothermal, electron beam evaporation (Poornajar et al. 2016), pulsed laser deposition (PLD), molecular beam epitaxy (MBE)

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(Ahmed et al. 2015). However, these methods are highly expensive because they require high vacuum conditions, costly apparatus and high temperature conditions.

Chemical bath deposition (CBD) is one of the simple and old nanostructure fabrication technique. This technique is comparatively in-expansive because of low cost, low temperature and environmentally not dangerous. There are a number of parameters which have an effect on the properties of ZnO nanorods synthesized by chemical bath deposition (CBD) technique. Among them, type of additives, solvents, and type of precursor, time and temperature of chemical bath deposition (CBD), and types of the substrates are effective parameters for chemical bath deposition (CBD) technique (Pourshaban et al. 2015).

However, there are some challenges in the synthesis of well aligned and large aspect ratio ZnO nanorods. In aspect of morphologies of nanostructures, nanorods have large surface area. This large surface area of ZnO nanorods is beneficial for absorption of light and charge separation. It is an important factor in solar-to-electric conversion.

In this work, ZnO thin film was deposited on glass substrate by using chemical bath deposition (CBD) method at 90°C with variation in solution concentration and deposition time.

2. EXPERIMENTAL TECHNIQUE

ZnO nanorod arrays were grown on glass substrates by chemical bath deposition (CBD) technique. The glass substrates were cleaned ultrasonically for 15 minutes each in acetone and in isopropyl alcohol (IPA). All chemicals were of analytical grade. In a typical procedure, glass substrates were suspended in an aqueous solution of zinc nitrate $Zn(NO_3)_2.6H_2O$ mixed with hexamethylenetetramine (HMTA) in a glass beaker. The solution was magnetically stirred until complete dissolution. The growth temperature was 90 °C and in the first step solution concentration was varied from 25mM to 125mM. After optimization of solution concentration i.e. at 100mM deposition time was varied as 3 h, 24 h, and 48 h. Finally, ZnO nanorods grown substrates were rinsed in deionized water and dried at room temperature. Fig. 1 represents the experimental set up for the deposition of ZnO nanorods on the glass substrate.

Fig.1 Experimental set up for the deposition of ZnO nanorods

The prepared ZnO nanorods were investigated by using different characterization techniques. Structural properties were determined using Bruker D8 Advance X-ray diffractometer (XRD). Dielectric and optical properties were determined with the help of 6500B Impedance Analyzer in parallel plate configuration and by J.A. Woollam (M-2000) Variable Angle Spectroscopic Ellipsometer (VASE), respectively.

3. RESULTS AND DISCUSSION

Fig. 2 shows XRD patterns of ZnO nanorods with different molarity on the glass substrate. Diffraction pattern disclosed the deposition of polycrystalline ZnO with hexagonal wurtzite structure and peaks are in good agreement with the standard pattern in JCPDS data base (No. 00-001-1136). No impurity phases are observed and the deposited thin films are monophasic and polycrystalline. From Fig. 2 it can be seen that for all samples there is a dominant (101) diffraction peak indicating the preferential growth of ZnO nanorods along this plane. Narrow peaks show that ZnO nanorods have good crystallinity. Crystallinity of the film is improving by increasing the molarity concentration. With increasing molarity concentration, thickness of the film also increases so that the intensity of the peaks also increased. It can be seen from the Fig. 2 that crystallinity of the peaks is improving by varying molarity from 50mM to 100mM. This behavior depends on nucleation and growth rate. Nucleation / growth rate and preparation time have significant impact on the crystallinity of the ZnO nanostructure. The crystallite size of the ZnO nanorods along the (101) diffraction peak is obtained by Scherrer equation shown in Eq. (1)

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

where D, θ, λ, and β represent the average crystallite size, Bragg diffraction angle, X-ray radiation wavelength, and full width at half maximum value, respectively. Crystallite size decreases from 18.5nm to 15.5nm and 13.2nm as solution concentration was increased from 50mM to 75mM and 100mM, respectively. Different crystallite size values showed that molarity concentration is one of the parameters that influences the ZnO film structure. Decrease in crystallite size indicates that nucleation is affected, thus new sites are available for hosting the formation of thin films. This faster nucleation has consequences on the thin films density and morphology (Baneto et al. 2014).

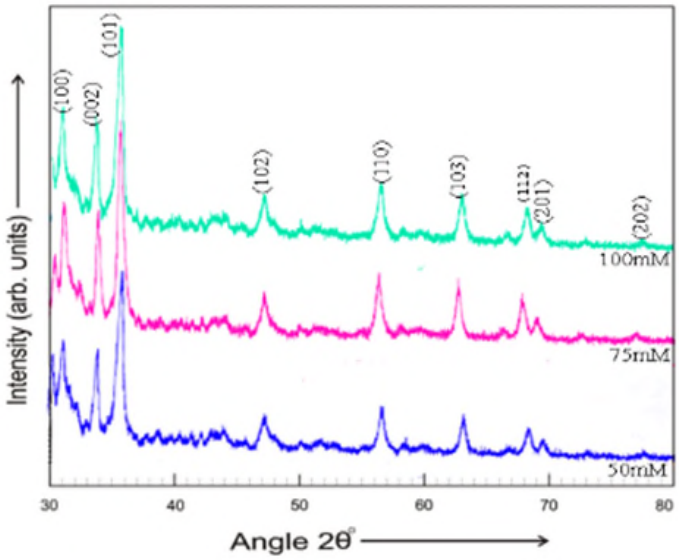

Fig. 2 XRD plots of ZnO nanorods for different molar concentrations

Optical transmission spectra of ZnO nanostructures for different molarities is shown in Fig 3. Transparency of the films depends on both growth time and concentration of the solution. From Fig. 3, it can be seen that the transparency of ZnO films is slightly improved with varying molarity from 25mM to 125mM. All the films have transmittance more than 80%. ZnO film with 100mM concentration has highest transmittance as compared to other films with different molarities. This high transmittance allows ZnO nanostructures for the optoelectronic applications as a window layer. The transparency of ZnO films can be effected by two factors; the grain boundary and the surface scattering. If the surface of the sample is relatively rough and its grain-boundary is irregular, the surface scattering and grain boundary scattering of sample are strong, accordingly inducing a low transmittance in the visible range. The transmittance of the sample increases if surface roughness is decreased or the grain sizes are more uniform and grain-boundary is clear and regular (Hwang et al. 2007).

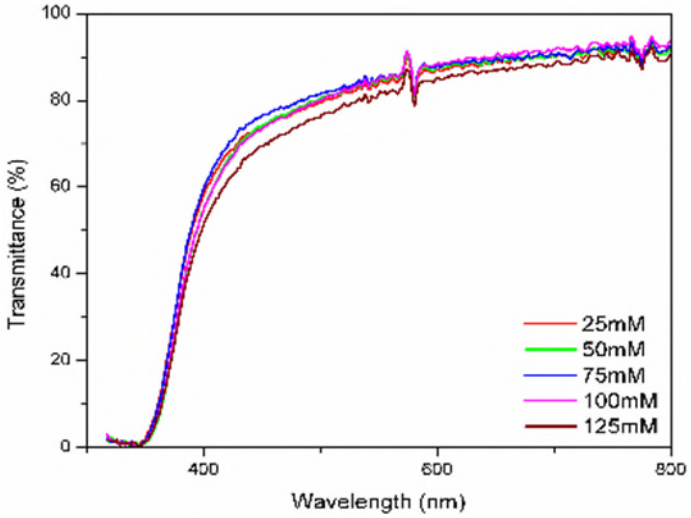

Fig. 3 Variation in transmission for different molarity

Fig. 4 shows variation in optical properties of ZnO nanorods by changing deposition time. Figure 4 (a) represents transmission spectra of ZnO as a function of wavelength for 3h, 24h and 48h deposition time. It reveals high level of transmission in the visible and near infra-red region, while the transmittance sharply decreases in the ultraviolet region by the transition of electrons between the edge of valence band and conduction band (Hwang et al. 2007). A clear effect of the variation in the deposition time on the transmission level of different specimens have also been visualized. The transmission of the ZnO thin films has been enhanced by increasing the deposition time of the bath solution. This effect has also been observed in the extinction co-efficient and refractive index of the films as shown in Fig. 4 (c) and Fig. 4 (d), respectively. By increasing the wavelength of the photons from the 400nm, the refractive index and the extinction co-efficient rapidly decreases by increasing the surface roughness of the substrate. This effect is also observed by the increase in the deposition time which reduced the diameter of nanorods.

Absorption co-efficient and then band gap of the material (Fig. 4 (b)) was calculated using transmission spectra. Blue shift has been occurred in the band gap of ZnO by changing deposition time. This shift in the band gap occurs due to the change in the diameter and number of ZnO nanorods for high deposition time.

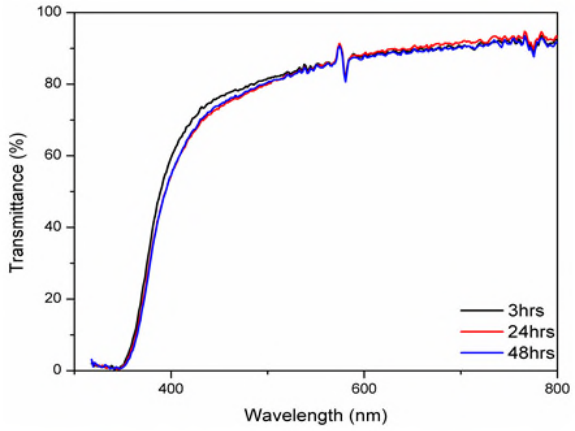

Fig. 4 (a) Transmission Coefficient

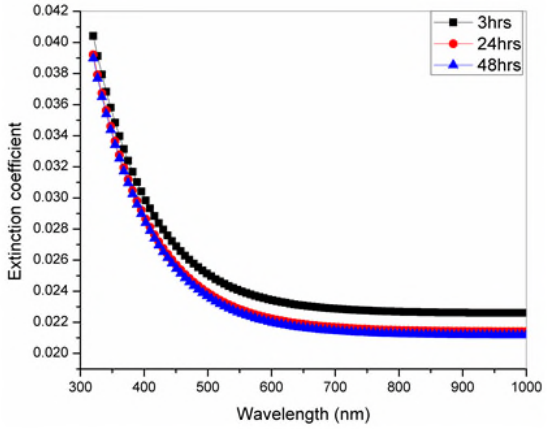

Fig. 4 (c) Extinction Coefficient

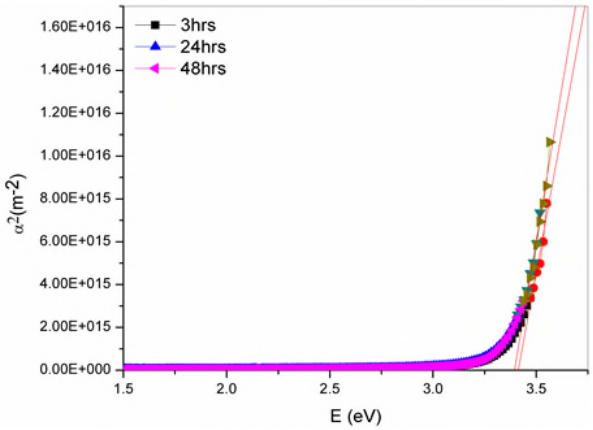

Fig. 4 (b) Band Gap

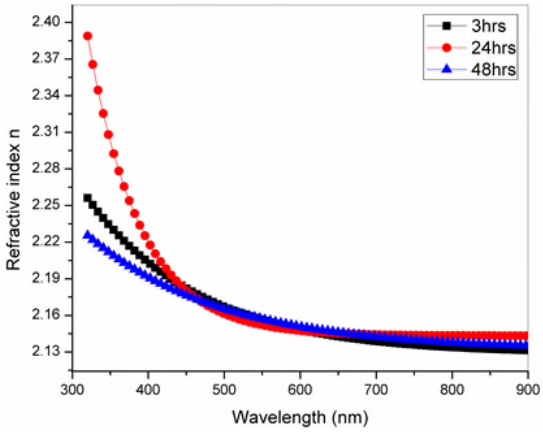

Fig. 4 (d) Refractive Index

Fig. 4 (a) Transmission Coefficient, (b) Band Gap, (c) Extinction Coefficient and (d) Refractive Index

Fig. 5 (a) represents the dielectric response, as a function of frequency, of as prepared ZnO thin films by varying the deposition time. It has been visualized from the graphs that the dielectric constant of ZnO remains almost same at lower frequencies and increases sharply near frequencies of 15kHz, while there is also slight increase in the values of dielectric constant by increasing the deposition time. On the other hand, there is a decrease in the values of tangent loss with respect to dielectric constant by increasing the frequencies as shown in Fig. 5 (b)

The dielectric constant (ε) of a material has low values initially because of the space charge distribution below 100Hz. While by increasing the frequency there should be further decrease in the value of dielectric constant as the dipoles could not follow the applied ac electric field resulting in the decrease of dielectric constant at higher frequencies (Li et al. 2005). However, in the current work, increase in the dielectric value is observed at high frequencies which shows anomalous behavior. Such behavior might have observed because of the surface compactness of the thin films (Rao and

Kumar 2009) i.e. increased number of nanorods with decreased diameter. Thus, increased dielectric constant and decreased tangent loss was observed at higher frequencies.

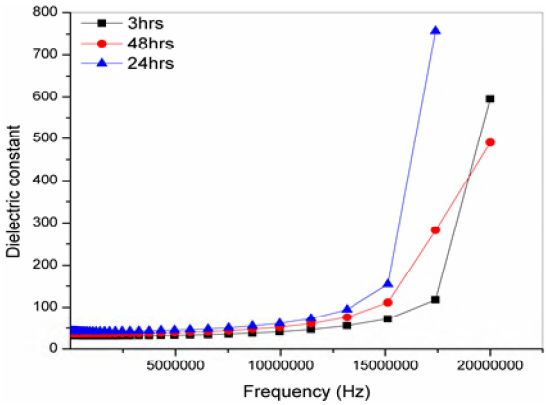

Fig. 5 (a) Dielectric Constant

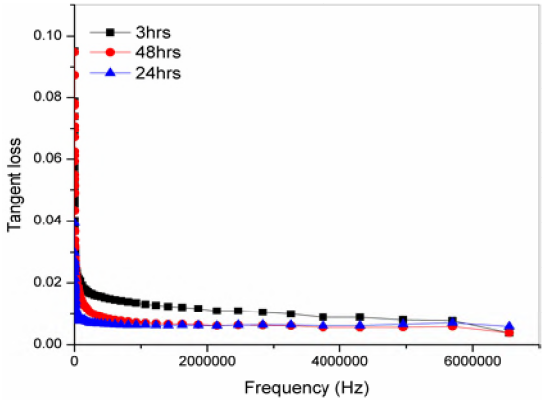

Fig. 5 (b) Tangent Loss

4. CONCLUSIONS

In summary, ZnO nanorods have been successfully grown on glass substrate by chemical bath deposition technique. Structural, optical and dielectric properties were investigated based on different molarity concentrations and reaction time. XRD results revealed that the deposited films were monophasic with hexagonal wurtzite structure. Intensity of diffraction peak confirmed the vertical growth of ZnO nanorods along c-axis in (002) plane. Optical spectra of different molarity and time based thin films revealed that all the films have transmittance more than 80%. By varying the molarity from 50mM to 100mM, transparency of the films slightly improved and this high transmittance is good for ZnO in optoelectronic applications as window layer. Dielectric Response of ZnO films for different deposition time showed that there is slight increase in the dielectric constant by increasing the deposition time but on the other hand decrease in tangent loss is observed.

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