Deposition of non-polar a-axis nanocrystalline ZnO thin films for light emitting applications

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Non polar Zinc Oxide (ZnO) films were deposited using sol gel deposition method by using zinc acetate dihydrate, ethanol and lactic acid annealed at 300 ^{o}C to 450 ^{o}C. The ZnO films were characterized by X-ray diffractometre (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Energy dispersive analysis of x-rays (EDAX). The effects of annealing temperature on structural and chemical properties of deposited ZnO films were investigated. From XRD spectra it was revealed that, preferably a-axis oriented crystalline ZnO films were successfully deposited on silicon substrate. The grain size of 39.2 nanometer has been estimated for the film annealed at 400 ^{o}C using Scherrer's formula showing a-axis orientation. The FTIR results showed little change in the peak position and the FWHM of the ZnO stretching bond position with increase in annealing temperature from 300 ^{o}C to 450 ^{o}C. EDAX clearly show the peaks corresponding to Zn, and O element which confirms the successful growth of ZnO films. This study shows the preferential growth of non polar a-axis oriented nanocrystalline ZnO films and explore its applicability to enhance quantum efficiency for light emitting devices.

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1. Introduction

ZnO is now a widely accepted wide band gap material from II-VI group for research community world wide [1]. It is having direct optical band gap of 3.37 eV and excitonic binding energy of ~60 meV which causes the stimulated emission at room temperature [2, 3] along with its piezoelectric property. It has shown immense applications in semiconductor device fabrication like surface acoustic wave devices (SAW) filter, gas sensors and transparent conducting oxide etc. [4-6]. Due to the excellent optical properties, the heterostructures devices based on ZnO has shown a promising applications in light emitting devices [7-8]. There are various methods employed to deposit the high quality ZnO thin film like molecular beam epitaxy (MBE), chemical vapor deposition (CVD), pulsed laser deposition (PLD), sputtering etc [9-11].

ZnO crystallizes in a wurtzite type structure with 6-mm symmetry. It grows generally in polar(c-axis oriented) and non polar (a-axis oriented) planes, in which polar planes and especially (100) plane are stable [12]. The ZnO films deposited in polar plane (001) orientation has the lowest surface free energy and singular surface of films in equilibrium state. Therefore, generally, ZnO films deposited with a strong c-axis orientation on variety of substrates and heterostructures are grown using c-axis oriented ZnO active layers. These devices go through built in electrostatic field due to polar plane orientation, and this electrostatic field generates the spatial separation of electrons and holes in the active layer causing a reduction in quantum efficiency. So this problem can be eliminated by growing non polar layer surfaces used in light emitting device structures [13]. Therefore, recently more attention has been given on this aspect to improve the ultra violet light emitting efficiency for ZnO based heterostructure waveguides. Most of research work was carried out on r-plane sapphire substrates to grow ZnO based devices as it gives lower lattice mismatch. In this work we have used silicon (100) substrate to grow ZnO nanocrystalline thin films.

Recently ZnO nanocrystals were reported using synthesis at low temperatures using inorganic sols as precursors [14]. The ZnO films are mostly deposited in c-axis or polycrystalline orientation by different deposition methods on various substrates despite of the orientation of substrate. Contradictory to this, very few reports are found on the growth of the a-axis oriented ZnO films [15-17]. Neuman et al [15] have reported a-axis orientation of the ZnO crystallites deposited by MOCVD on sapphire substrate. Wang et al [16] have reported only the existence of a-axis oriented ZnO thin films on glass substrates using sol gel method, but they did not studied structural properties. ZnO films [17] were successfully grown on (100) silicon substrate by single source chemical vapour deposition method. Little work has been reported on the growth of preferential a-axis oriented ZnO film on silicon substrate by sol gel method. To the best of our knowledge, no author has reported on deposition of nanocrystalline ZnO films grown using sol gel method having non polar a-axis orientation.

In this paper, we report for the first time, on the deposition and characterization of preferential a-axis oriented nanocrystalline ZnO thin films on silicon (100) substrate by sol-gel method. Particularly, the emphasis has been given on the growth of a-axis oriented nanocrystalline ZnO films and investigation of the annealing effect on them. The characterizations of these

deposited films were carried out by XRD, FTIR, SEM and EDAX for structural, chemical composition and surface morphology evaluation respectively.

This paper is organized in four sections. Second section of the paper describes the experimental procedure used to deposit the ZnO films; third section discusses the results in detail and last section concludes the paper.

2. Experimental procedure

The silicon (100) substrate was used in this study for the deposition of ZnO films. To remove the contamination from the surface of the silicon, it was cleaned in trichloroethylene, acetone and methanol and finally dried.

The starting precursor used were zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$], ethanol (C_2H_5OH) and lactic acid ($CH_3.CHOH.COOH$) [18]. Solution was prepared by dissolving the 2.195 gm of Zinc acetate in the ethanol to obtain the 0.4 m/l concentration, with a few drops of lactic acid. The solution was prepared at ~ 60 ^oC under continuous stirring for one hour. The transparent solution was obtained, which was used for the deposition of nanocrystalline ZnO. The deposition was carried out on the home made spin coater maintained at the constant rotation so that the layers of the same thickness can be obtained per coat. The deposition was carried out in relative humidity and room temperature of ~66% and 33 ^oC respectively. After each deposition, samples were dried at 200 ^oC for 10 minutes to evaporate the solvent. To attain the desired thickness, the procedure of deposition and heat treatment was carried for six times for each sample separately. The crystallization was accomplished by annealing the samples at 300 ^oC, 350 ^oC, 400 ^oC and 450 ^oC temperature in the tube furnace for one hour each. Finally homogeneous and crack free films were obtained on the silicon substrates.

The deposited samples were characterized by Bruker AXS D8 for XRD spectra having CuK_α X-Ray source of wavelength 1.54059 Å. The FTIR absorption spectrum was recorded within 4000 cm^{-1} to 400 cm^{-1} wave number range by Nicollet 380 FTIR instrument at resolution of 4 cm^{-1} at room temperature for determination of bonds present in the films. The morphological study and EDAX was carried out by the SEM-JSM-6360.

3. Results and discussion

The ZnO film structure was measured in θ-2θ mode with 0.1 step size. The XRD spectra recorded for the deposited films at various temperatures are shown in Fig. 1. It was observed from the film annealed at 300 ^oC, that the strong diffraction peak of (100) and weak diffraction peaks of (002), (101) at 2θ = 31.7 and 34.5, 36.2 were present respectively attributed to polycrystalline ZnO films. However, strong orientation in (100) plane occurs. It indicates that polycrystalline orientation of ZnO films was already started at annealing temperature of 300 ^oC. In literature, it was found that the crystallization process was completed even at low annealing temperature using sol gel deposition technique [19]. At 350 ^oC annealing temperature, the intensity of the (100) diffraction peak was increased, and intensity of other remaining diffraction peaks present was decreased. It further suggests the orientation effect towards a-axis. Yoshihiro et al. [20] prepared ZnO thin films with preferential orientation on silica glass substrates by sol gel deposition method using same precursor as in the present study and discussed the effect of heat treatment temperature on ZnO crystallization. While increasing the annealing temperature at 400 ^oC, it was seen that the peak of the (100) plane became highly intense showing the strong preferential growth of a-axis oriented ZnO films. But, unexpectedly at 450 ^oC annealing temperature, intensity of (100) diffraction peak decreased. It indicates the degradation of crystal quality of ZnO films at 450 ^oC. One possible explanation for this degradation can be the abrupt evaporation of the solvent which gives the less time for the gel to undergo structural relaxation at higher heating rates [21]. In the annealing treatment it was observed that the position of (100) diffraction peak remained at $2\theta = 31.7^0$. To make clear the preferential a-axis orientation of deposited ZnO films the intensity ratio was determined. It clearly indicates the preferential growth of the films in a particular plane. Previously the intensity ratio was already used for c-axis oriented ZnO films [22]. We have used this formula to verify the orientation of ZnO films along a-axis. Therefore, the intensity ratio for (100) plane was determined by the following formula.

$$i_{(100)} = \frac{I_{(100)}}{I_{(100)} + I_{(002)} + I_{(101)}} \quad (1)$$

Where $I_{(100)}$, $I_{(002)}$ and $I_{(101)}$ represent the intensities of (100), (002) and (101) x-ray diffraction peaks, respectively. Fig. 2 shows the graph plotted for the intensity ratio as a function of annealing temperature. It was observed from the plot, that the intensity ratio for (100) diffraction peak improved up to 400 ^oC annealing temperature clearly signifying the preferential growth along a-axis of deposited ZnO thin films. At 450 ^oC, intensity ratio was decreased indicating the degradation of the crystal quality; though we would expect that it would increase further significantly.

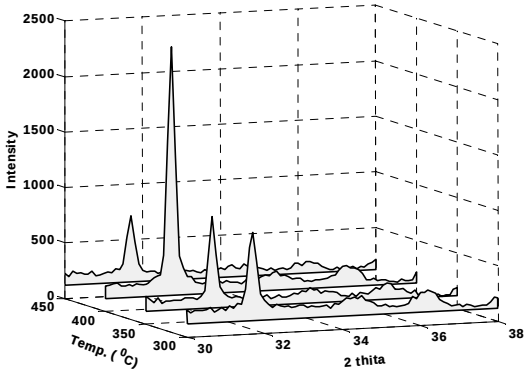

Fig. 1. X-ray diffraction spectra of ZnO films on Si substrate at different annealing temperature.

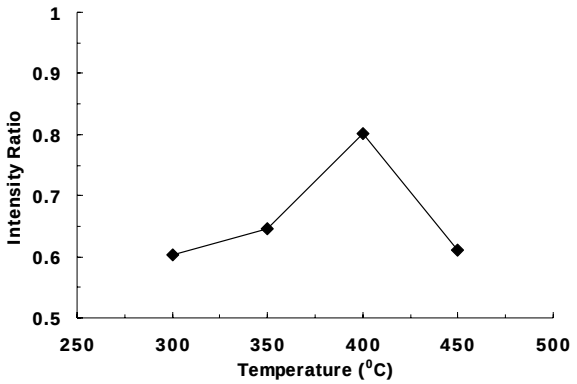

Fig. 2. Relative intensity of (100) peak vs annealing temperature for ZnO films.

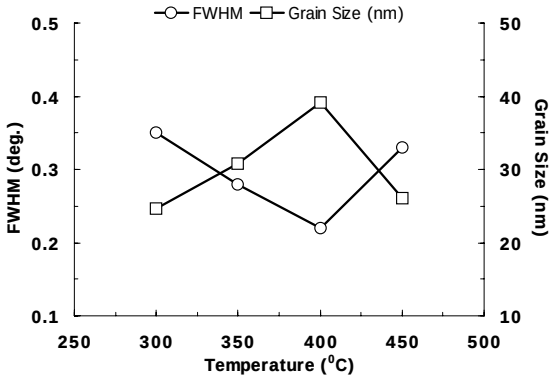

Fig. 3. FWHM and grain size values of the (100) diffraction peak of ZnO films.

The grain size of the a-axis oriented ZnO crystals was determined from full width at half maximum (FWHM) at (100) diffraction peaks. It was observed that, a-axis orientation was improved significantly after the annealing process, with FWHM reducing from 0.35 to 0.22. The width of the peak became narrow at 400 ^{o}C temperature, than the other annealing temperatures demonstrating the high quality of ZnO film. The grain size of these a-axis oriented ZnO films were estimated using the well known Scherrer's formula as follows [23],

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{2}$$

Where λ = 0.154056 nm, θ is the Bragg diffraction angle at peak position, and β is FWHM in radians corresponding to peak. The graph was plotted for FWHM and grain size as a function of annealing temperatures as shown in Fig. 3. The grain size estimated were 24.6, 30.8, 39.2, 26.1 nm corresponding to 300^{o}, 350^{o}, 400^{o} and 450 ^{o}C annealing temperatures respectively. The annealing temperature influenced the grain size of the grown ZnO crystal. The a-axis lattice constant *a* for this ZnO films is 0.3257 nm which is very close near to the wurtzite ZnO value, *i.e. a* = 0.3249 nm [24], at the preferential a-axis crystal grown at 400 ^{o}C. The step size was kept 0.1 while scanning the samples by XRD. Thus annealing shows noticeable improvement in crystalline quality of ZnO films in a-axis plane as noticed in c-axis oriented ZnO thin films. Estimated grain size for deposited ZnO films clearly shows nanocrystalline growth along a-axis for all the annealing temperatures.

Despite the c-axis oriented ZnO films evidence the applicability in the light emitting devices, the photoluminescence has shown the possibility of preferentially a-axis oriented ZnO films suitable for light emitters in ultra violet region [25]. Furthermore, the successful a-axis oriented ZnO homojunction light emitting device was demonstrated [26]. The work carried out by these authors, demonstrates that the a-axis oriented ZnO films are useful for optoelectronics applications. Our work confirms a-axis oriented nanocrystalline growth of ZnO films deposited on Si substrate using the sol-gel method.

The FTIR characterization was carried out to identify the presence of specific impurities in these deposited films and to understand the conversion process in to ZnO films on silicon substrate after heat treatment. The absorbance spectrum was recorded in the 400 cm^{-1} to 4000 cm^{-1} wavenumber range for the films at room temperature with a resolution of 4 cm^{-1}. The film annealed at 300 ^{o}C shows the O-H absorption bond at ~3400 cm^{-1}, C=O stretching bond related to the symmetric and asymmetric modes of COO groups in Zinc monoacetate respectively [27,28] between 1400 to 1600 cm^{-1}, with the broad absorption peak situated at ~417 cm^{-1} showing the bond formation of ZnO bond [29]. It was reported that the decomposition process of zinc acetate was started at 300 ^{o}C. In our work, the films annealed at 350 ^{o}C shows increase in intensity of this bond. At 400 ^{o}C, annealing temperature, the strong absorption peak related to Zn-O stretching was appeared shifted at 415 cm^{-1}. Fig. 4 shows the IR absorbance spectra recorded for a-axis oriented nanocrystalline ZnO films as a function of wavenumber annealed at 400 ^{o}C. By comparing the XRD and FTIR spectra for these deposited ZnO films, we observe that the crystallization process has started at lower temperature and completed at higher annealing temperature. It was confirmed that the films were transformed in to a-axis orientation through the dehydration and the removal of organic compounds by annealing process.

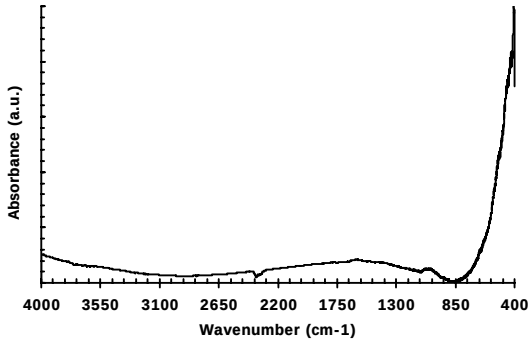

Fig. 4. FTIR absorbance spectra of ZnO film deposited on Si substrate annealed at 400 ^{o}C.

As found shift in the peak position of ZnO stretching bond, it is interesting to study the peak position as well as FWHM of this peak as a function of annealing temperature as shown in Fig. 5. At lower annealing temperature the peak position of ZnO stretching bond was detected at 417 cm^{-1}, while it was found to be stable at 415 cm^{-1} for increasing annealing temperature. It was due to the large amount of organic compound present initially in the film and then completion of a crystallization process takes place. The FWHM was found to be affected by the annealing temperature. It was broad initially and then became narrower for increasing annealing temperature indicating the strong possession of ZnO stretching bond.

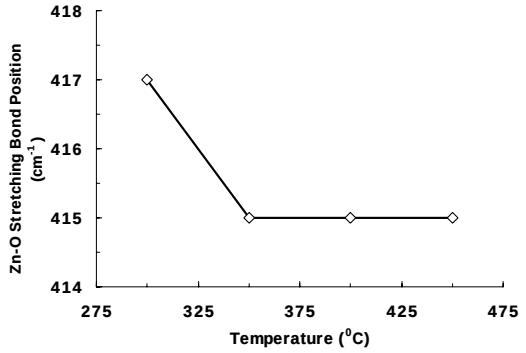

Fig. 5(a). Peak position of ZnO stretching bond vs annealing temperature.

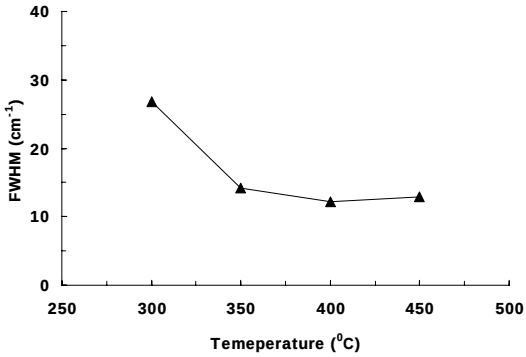

Fig. 5(b). FWHM of ZnO stretching bond vs annealing temperature.

Fig. 6 and 7 shows the SEM and EDAX of the ZnO film deposited at 400 ^{o}C annealing temperature magnified at 20,000X for evolution of surface morphology and film composition. The SEM shows the granular ZnO nano-crystal formation. In EDAX, the strong peak appeared at 1.8 eV represents the signal coming from Si substrate because of the large thickness of Si substrate than ZnO film. The main peaks of ZnK_{α}, ZnK_{β} and $OK\alpha$ were present at 8.63 eV, 9.6 eV and 0.52 eV respectively. Thus, EDAX spectrum has shown the clear composition of ZnO on the Si substrate.

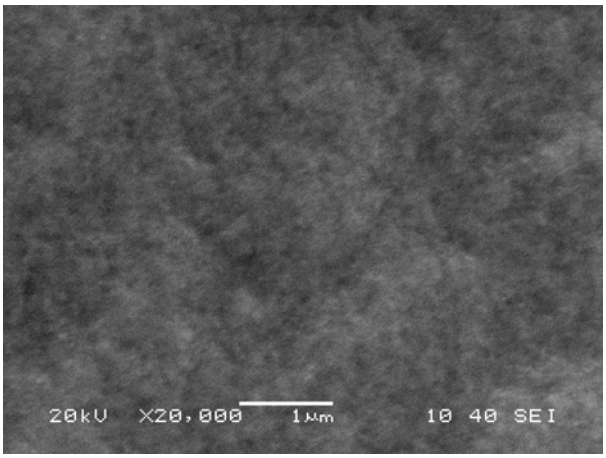

Fig. 6. SEM micrograph of ZnO film deposited on Si substrate annealed at 400 ^{o}C annealed.

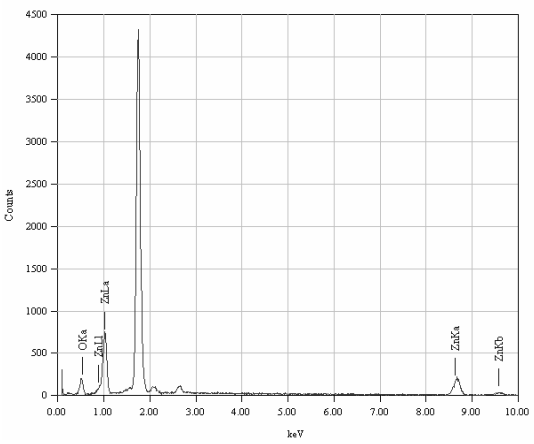

Fig. 7. EDAX spectrum of ZnO film deposited on Si substrate at annealing at 400 ^{o}C annealed.

4. Conclusion

In this work, ZnO films were deposited on Si substrate by the sol gel method using solution of Zinc acetate dihydrate, ethanol and lactic acid. The deposited nanocrystalline ZnO films were found to be oriented preferably in a-axis (100) rather than reported c-axis orientation by other authors. The XRD study reveals that,

crystalllinity and the a-axis orientation of these deposited ZnO films was improved by increasing annealing temperature. The FTIR analysis has shown the evidence of the ZnO stretching bond. SEM and EDAX confirm the film composition of ZnO. Thus, the structural and optical properties of preferentially non polar a-axis oriented nanocrystalline ZnO films can be used to improve quantum efficiency for exploring its use in the light emitting devices.

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