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IDENTIFICATION OF SUITABLE PRECURSOR FOR THE GROWTH OF VERTICALLY ALIGNED ZNO NANORODS ON SIO2/SI SUBSTRATE BY HYDROTHERMAL METHOD

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Abstract: - Nowadays ZnO nanorods playing key role in several areas like Bio-medical applications, Electronic devices and sensors etc. The properties and alignment of ZnO nanorods will be effected by growth time, temperature, seed layer and type of precursors used. In this work ZnO nanorod were grown on SiO2/Si substrate using different precursors and effect of precursor on the alignment and properties of ZnO nanorods is studied. Radio frequency dielectric sputter system is used to deposit the ZnO seed layer. Surface morphology and crystal structure of the seed layer will effects the orientation of the nanorods. To investigate the grain modification on surface, ZnO seed layer is annealed in the nitrogen atmosphere. ZnO thin film orientation, surface study and roughness of the ZnO thin film can be analyzed using XRD and AFM. Simple and low cost hydrothermal method is used to grow the nanorods. The surface morphology and orientation of the ZnO nanorod grown over annealed, unannealed ZnO thin film using different precursors namely Zinc Nitrate Hexahydrate and Zinc Acetate Dihydrate were investigated by using high resolution scanning electron microscopy (SEM).
Keywords: Hydrothermal method, XRD(X-ray diffraction), AFM(Atomic force microscopy), Precursor, Surf morphology and crystal structure, SEM, ZNH(Zinc nitrate hexa hydrate) and ZAD(Zinc acetate di hydrate)

1. INTRODUCTION

Miniaturization in size and amelioration of the performance, researchers and scientists got attracted to nano technology, it has a potential to scale down the size to the nanoscale in many fields like optoelectronics, sensing, catalysis [1-7]. Further, metal oxide based nanomaterials have drawn intense attraction because of their unique properties and flexibility in the structures [8]. Among metal oxide zinc oxide is prominent which are widely and intensively investigated for fabrication of the nanostructures. Some exciting properties of ZnO are wide band gap material 3.37eV, high exciting binding energy of 60 MeV [10], low production cost [11-13], Eco friendly, biodegradable and biocompatible[14-18]. Due to these properties ZnO used for gas sensing, optoelectronics applications. In comparison to bulk ZnO one dimensional ZnO nanostructure shows superior performance in several aspects. There are number of methods utilized to grow one dimensional structures namely Vapor-Liquid-Solid (VLS) [19-20], Metal Organic Vapor Phase Epitaxy(MOVPE) [21], Pulsed Laser Deposition (PLD) [23], Hydrothermal method [24,25]. Among these techniques, hydrothermal method is considered to be advantageous because of the minimal cost, minimal temperature, safe operation and eco-friendliness [27].Considering the advantage of hydrothermal method over other method in this work ZnO nanorod were grown by this simple hydrothermal technique. Further, the quality of the ZnO nanorod highly depends on the growth environment, concentration of precursor, type of precursor, time of growth, temperature and pressure [22]. To investigate the effect of precursor in this work two precursor were used to grow the ZnO nanorod over the SiO2/Si substrate and ZnO nanorod over silicon oxide surface will be very suitable for FET (Field Effect Transistor) fabrication where SiO2 acts a dielectric between channel and gate. Moreover, structural and surface morphology of the ZnO seed layer also effect the growth, annealing improves the ZnO thin film to study the seed layer morphology effect on ZnO nanorod growth.

2. EXPERIMENTAL PROCEDURE

All the chemicals used in our experiment were purchased from Sigma-Aldrich (France) without further purification. Deionized water (DI) used in all the experiments was prepared in three state Millipore MIlli-Q plus purification system and has a resistivity of 18.2MΩ.cm. In this work a p-type (100) silicon substrate was taken and cleaned by RCA cleaning. After the cleaning and drying of the substrate, SiO2 layer was grown by using 2-inch dry oxidation furnace at temperature 1100˚C for time period of 4hrs. The thickness of the oxide layer measured using sentech ellipsometer. ZnO seed layer of 100nm was deposited by using RF Sputter at room temperature in argon atmosphere. RF sputtered ZnO thin film classified in two samples, one sample was annealed in forming gas annealing furnace at 450˚C in nitrogen atmosphere for 20mins, whereas other sample kept without annealing, noted that these two samples were utilized to grow ZnO nanorod. After the deposition

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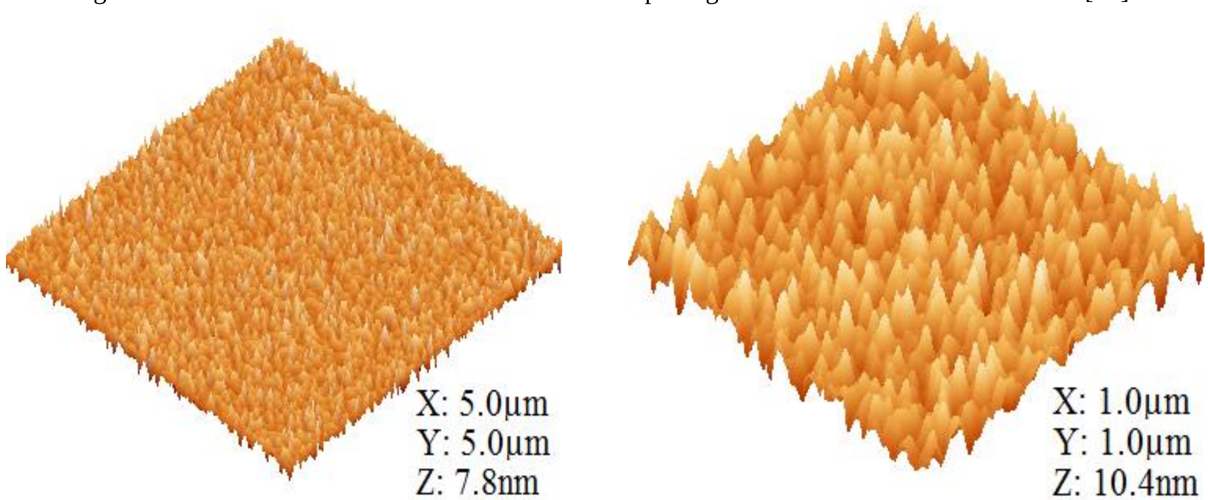
of ZnO thin film their surface morphology were studied by AFM. The AFM image of annealed and unannealed is shown in Figure.1.

To grow the ZnO nanorods hydrothermally, reactive solution was prepared by dissolving precursors Zinc Nitrate hexahydrate [Zn (NO3)2. 6^{H_2O}] and Hexamethylenetetramine [C6H12N4] in equimolar concentration of 25mM in 150 ml of DI water. Annealed and unannealed ZnO thin films were suspended upside down in the solution. Then the glass beaker was sealed and left for 4 hrs at 95˚C in the oven, after mentioned time period samples were removed and rinsed thoroughly with DI water to remove the residual reactants if present and dried in air. The same procedure repeated for other precursor namely Zinc acetate dihydrate [Zn (CH3COO) 2. 2H2O] and Hexamethylenetetramine. These two samples are further identified and were used for surface and structural characteristics.

3. RESULTS AND DISSCUSSION

To investigate the roughness of ZnO thin film which influence hydrothermally grown nano structures AFM was done. From AFM analysis it was found that the root mean square (rms) 100nm annealed thin film annealed and unannealed thin films (1.0811 and 1.1482). Annealed thin film is having surface roughness less when compared with the film without annealing. If roughness is high then there would be some bad effects on the morphologies of the resultant nanostructures [23].



(a) (b)

Figure-1: AFM images of (a) 100nm ZnO thin film with annealing (b) 100nm ZnO thin film without annealing

To know the crystal structure X-ray diffraction (XRD) studies were carried using X-ray diffraction with Cu kα radiation (λ=1. 5418 Å) in the range of 20 to 80 ˚, the XRD spectrum of the annealed and unannealed ZnO thin film shown in Figure-2 and it is clearly evident that crystalline property of ZnO surface increases for annealed thin film compared to unannealed.

The SEM image of ZnO nanorods grown by using two precursors on annealed and unannealed ZnO thin film is shown in Figure (3-6). From the images it is clearly evident that well aligned, separated nanorods of uniform cross section over annealed ZnO thin film. Because of the good density of the seeds in the deposited films which acts as nucleation centers for the growth of nanorods. Also annealed ZnO thin film gives two steps in ZnO nanorod which has half of nanorod with larger and other half showing the smaller this type of structure was not obtained by any one before this report, we also guess that the precursors also effect to get this type of structure, because this noble structure obtained for precursor Zinc Acetate Dihydrate.

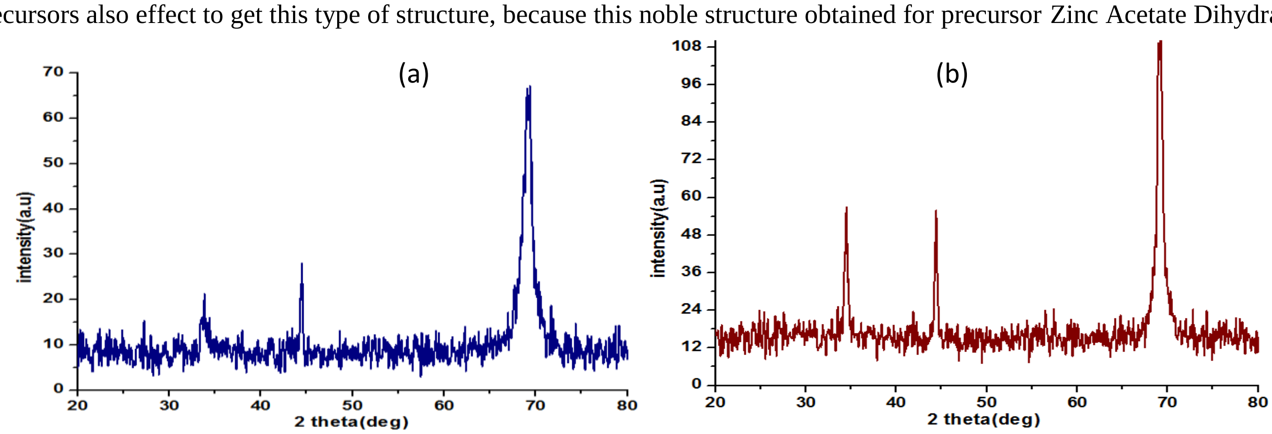


Fig-2: HRXRD peaks for 100nm (a) unannealed and (b) annealed thin film.

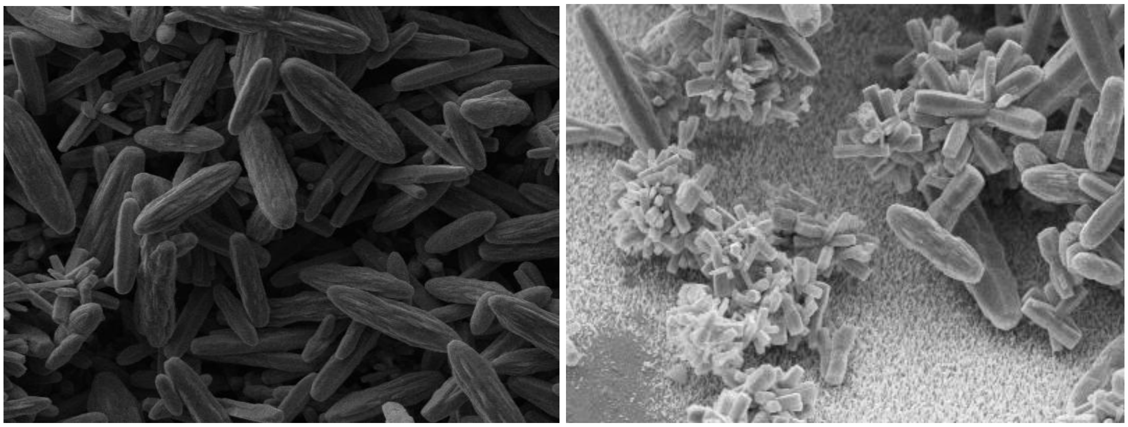


Figure-3: SEM images of the nanorods grown on 100nm without annealed thin film by using precursor ZNH

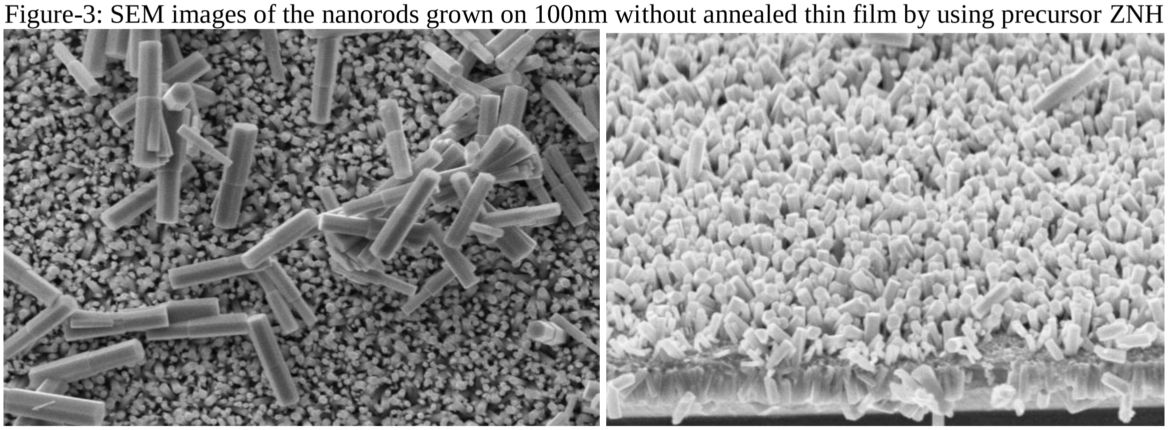


Figure-4: SEM images of the nanorods grown on 100nm without annealed thin film by using precursor ZAD

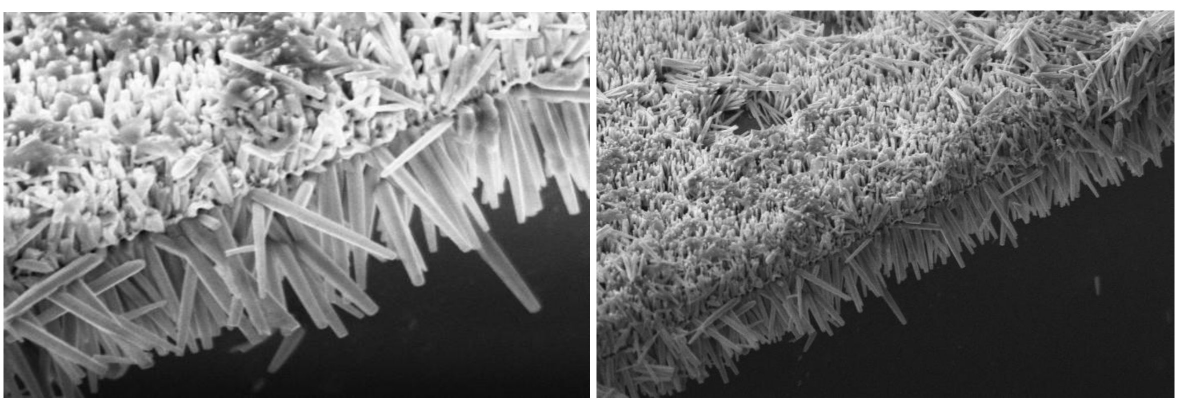


Figure-5: SEM images of the nanorods grown on 100nm with annealed thin film by using the precursor ZNH

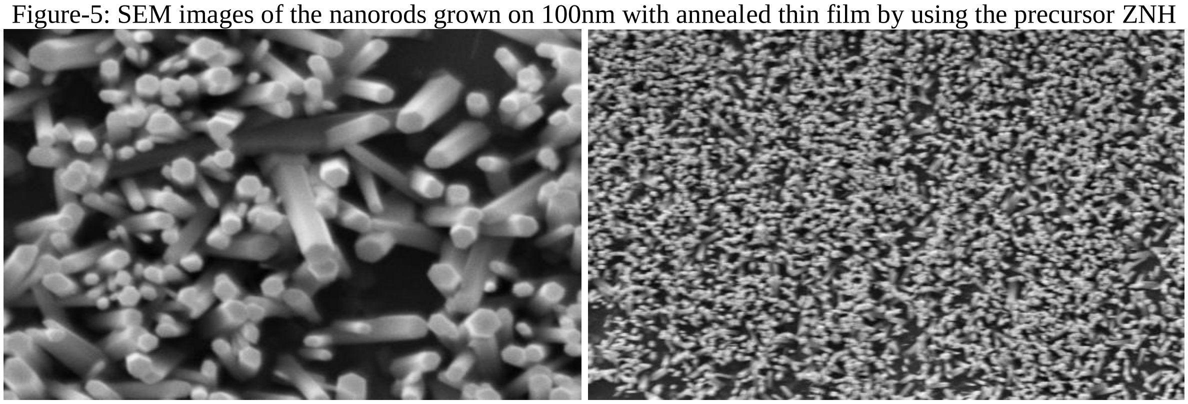


Figure-6: SEM images of the nanorods grown on 100nm with annealed thin film using precursor ZAD

4. CONCLUSION

In this work hydrothermal method was used to grow ZnO nanorod over the SiO2/Si substrate by using the RF deposited ZnO seed layer. It was identified that crystal and surface morphology of ZnO seed layer decided the orientation and shape of the grown ZnO nanorods, where annealing of ZnO thin film was utilized to tune the surface and structure of seed layer. It was obtained that annealed ZnO thin film gives good result. Further, precursor also effect the overall properties of the ZnO nanorod, to study the precursor effect in this work two precursors were used, and from the SEM it was observed that ZnO nanorod grown by using Zinc acetate dihydrate is giving the one dimensional nanostructures even in both annealed and un annealed conditions while nanorods grown by Zinc nitrate hexahydrate exhibiting flower like structures in un annealed condition and straight nanorods in the annealed conditions.

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