Preparation and characterization of aluminum doped zinc oxide (AZO) nanorods

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Abstract. Aluminum doped Zinc Oxide (AZO) nanorods with 1at.% aluminum content were prepared by Sol-gel spin coating technique. The structural and topographical properties are studied using X-Ray Diffraction (XRD) technique and Atomic Force Microscopy (AFM), respectively. Higher intensity Zinc Oxide (ZnO) peak (002) is observed in 1at.% aluminum doped nanorod with 50 s spin coated sample underwent 300°C of annealing temperature. Morphologic, compositional and crystallographic information of the samples are predicted using Transmission Electron Microscopy (TEM), the 600 nm long nanorod with an aspect ratio of 10 is obtained for 20 s and 50 s spin coating time.

Keywords. ZnO nanorods; nanoparticle; sol-gel; XRD; AFM; TEM.

1. Introduction

Zinc Oxide (ZnO) is a versatile material. It has a wide band gap which means a higher breakdown voltage, ability to sustain large electric fields, lower electronic noise, and high temperature and high power operation. Further, the band gap of ZnO can be tuned easily by doping and constricting the particle size. Zinc Oxide is an n-type semiconductor that means the majority carriers are electrons. These electrons have a mobility of $\sim 2000 \text{ cm}^2/\text{V-s}$ at 80 K and it strongly varies with temperature. However, the doping level can be altered with specific choice of dopants which make ZnO more n-type or p-type in character. High heat capacity ($C_p = 40.3 \text{ J/mol-K}$) and heat conductivity ($k = 0.6\text{--}1 \text{ W/cm-K}$), low thermal expansion ($\alpha = 2.5\text{--}4.3 \times 10^{-6}/\text{K}$) and high melting temperature (at 1974°C decomposes) of ZnO are beneficial for many applications in electronic and optoelectronic devices such as ultraviolet light-emitters, piezoelectric transducers, solar cells, nanoscale sensors and actuators [1–6].

ZnO nanostructures can be synthesized with variety of methods including MOCVD, thermal evaporation, molecular beam epitaxy (MBE), electrochemical deposition, spray pyrolysis, and sol-gel. Among these methods, the sol-gel technique is the simplest and least expensive one [7–11]. In several studies, the structural and optical properties of Aluminum doped Zinc Oxide (AZO) nanorods could be obviously improved by optimized deposition conditions and controlled doping. The primary aspiration of

this work is to examine the influence of the preparation conditions on structural and optical properties of AZO nanorods prepared by sol-gel spin coating method. The structural characteristics have been studied using X-Ray Diffraction (XRD). The morphological features have been studied using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Two-dimensional topographic information of nanorods are investigated using Atomic Force Microscopy (AFM).

2. Experimental details

Zinc acetate dihydrate ($\text{C}_4\text{H}_6\text{O}_4\text{Zn} \cdot 2\text{H}_2\text{O}$) and diethanolamine ($\text{C}_4\text{H}_{11}\text{NO}_2$) are used as a precursor material and the solvent, respectively. Diethanolamine (DEA) was first dissolved in isopropanol (iProH), Zinc acetate dihydrate (ZnAc) was added under stirring, and heated under reflux for 1 h at 70°C. Zinc acetate was dissolved in DEA by the molar ratio of 1 (DEA/Zn=1). Flowchart showing the procedure for preparing the aluminum doped ZnO nanorods in figure 1.

Doping of the solution was obtained by adding a 0.2 M solution of aluminum nitrate in ethanol. The molar ratio of dopant in the solution (Al/Zn), varied between 0.5% and 5%. Isopropanol was added to adjust the solution concentration to 0.5 Mol/L of ZnAc. The molar ratio of DEA to ZnAc was maintained 1at.%. The solution was stirred at 70°C for 2 h to yield a clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The coating was usually made one or two days

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Figure 1. Flowchart showing the procedure for preparing the aluminum doped ZnO nanorods.

after the solution was prepared, glass substrate was used for coating. To make different density of Zn seeds which will result in difference in grown nanorods density, spin coating time was altered as 20 s, 50 s and 100 s throughout the process and spin speed remained same as 3000 rpm. After spin coating, a brief annealing at 300°C for 1 h was carried out to prepare the samples.

3. Results and discussion

3.1 X-Ray Diffraction analysis

The X-Ray Diffraction analysis (XRD) was used to investigate the physicochemical process involved in the sol-gel deposition of AZO nanorods. All peaks were well-matched with hexagonal structure of ZnO and no other impurity peaks were observed in XRD pattern which shows the purity of the nanoparticle formation. XRD results reveal that nanorods have a polycrystalline hexagonal wurtzite structure with well-developed crystallinity. The crystalline volume of 1at.% aluminum doped nanorods are calculated from its most intense peak (101) of ZnO, its value is around

Figure 2. XRD patterns of the 1at.% aluminum doped nanorods.

26.2 nm. The XRD patterns of these nanorods with 1at.% aluminum contents are shown in figure 2.

3.2 Atomic Force Microscopy (AFM) analysis

The AFM is useful for obtaining two and three-dimensional topographic information. The surface morphology of sol-gel derived AZO nanorods was evaluated by AFM. Figure 3(a)–(c) shows the micrograph of 1at.% Aluminum doped sample with 20 s, 50 s and 100 s of spin coating time was annealed at 300°C (2D view). As can be observed, the film is constituted of closely-packed fluffy nanoparticle dispersed all over the surface, with the presence of nano pores. The particle size measured is 24 ± 15 nm, and the

Figure 3. 2D AFM image of 1at.% Aluminum doped ZnO Nanorods prepared with spin coating at 3000 rpm for (a) 100 s, (b) 50 s and (c) 20 s.

Figure 4. TEM image of AZO nanorods prepared with spin coating at 3000 rpm (a), (b) for 20 s, (c) for 50 s and (d) for 100 s.

surface of the films is very smooth, since the calculated roughness is 1.5 nm for the nanorods.

3.3 Transmission Electron Microscopy (TEM) analysis

TEM utilizes energetic electrons to provide morphologic, compositional and crystallographic information of samples. Figure 4(a)–(c) illustrates TEM image of AZO nanorods prepared with various spin coating time at 3000 rpm for 20 s, 50 s and 100 s. Figures reveal that all nanorods are of aspect ratio with 8–10, but their dimension purely depends on the preparation condition. 20 s and 50 s spin coated nanorods are bigger and thicker than 100 s spin coated nanorods. The 600 nm long nanorod with an aspect ratio of 10 is obtained for 20 s and 50 s spin coating time.

4. Conclusions

The AZO nanorods were fabricated on glass substrate. Furthermore, AZO nanorods were characterized by XRD, AFM and TEM. The X-ray diffraction technique reveals that, the higher intensity of the (002) peaks are observed in aluminum concentration of 1 at.% AZO nanorods, when the

annealing temperature was maintained at 300°C. According to the AFM results, 1 at.% aluminum doped film exhibits a porous microstructure and the spherical crystalline particle size of approximately 24 ± 15 nm. TEM results showed that 20 s and 50 s spin coated AZO nanorods are bigger than others and also it yielded 600 nm long rod.

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