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Effect of annealing temperature on structural, optical and electrical properties of hydrothermal assisted zinc oxide nanorods

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ABSTRACT

Zinc oxide nanorods were grown employing a low cost hydrothermal method on microslide glass substrates pre-coated with ZnO seed layer. The as grown nanorods were annealed in air at 350 °C, 450 °C and 550 °C. The effect of annealing at different temperatures on morphology, structural, optical and electrical properties was investigated using field emission scanning electron microscopic, X-ray diffraction, UV–vis spectral, photoluminescence and electrical studies. The X-ray diffraction pattern of all the samples showed wurtzite structure preferentially oriented along the c-axis (0 0 2) direction. It was found that diameter of the nanorods increased with increasing of annealing temperature. The UV–vis absorption spectra showed a red shift from which it was inferred that the optical bandgap of the material decreases from 3.33 eV to 3.28 eV with increase in annealing temperature. Photoluminescence measurements showed increase in the UV emission intensity with respect to annealing temperature and also produced additional peaks attributed to defects and impurities. Annealing the ZnO nanorod structures at various temperatures evidently showed that the sample annealed at 550 °C acquired the lowest resistivity about 1.62×10^{-4} Ω-cm.

1. Introduction

The interest in zinc oxide (ZnO) nanostructures has been increased drastically and ZnO material has been studied widely due to its excellent properties such as wide direct band gap (3.37 eV) with high exciton binding energy (60 meV) at room temperature [1,2]. ZnO is a potential material which finds applications in light emitting diodes [3,4], field emission devices [5,6], piezoelectric nanodevices [7], solar cells [8–10], photocatalysis [11–13], varistors [14], UV sensors [15–17] and gas sensors [18–21]. Owing to extremely high surface to volume ratio of one-dimensional nanostructures [22] and the dependence of optical, electrical and structural properties on the synthesis conditions, control over these properties is challenging and highly desirable [23–26].

Various methods have been developed to grow well aligned ZnO nanorods such as pulsed laser deposition [27], radio frequency magnetron sputtering [28], thermal evaporation [29] and templating against anodic alumina membrane [30], but these methods are complicated and expensive. In order to overcome the above challenges, solution phase routes which include microemulsion, solvothermal, hydrothermal, self-assembly and template assisted sol gel process have been investigated [31]. Among all the methods stated above, hydrothermal approach [32,33] appears to be the most promising one for ZnO nanorods growth due to its high growth rate, cost effectiveness and simplicity [34]. Preparation of ZnO seed layers using different solvents (isopropyl alcohol (IPA) [35–37], methanol (MeOH) [37], 2-methoxyethanol (2-ME) [38] and ethanol (EtOH) [39]) has been widely reported. ZnO seed layers were deposited on different substrates (ITO-coated glass [35,38,40,41], sapphire [35,42,43], quartz [44,45], glass [39,46] and silicon [35–37,47,48]) and different ZnO nanostructures were grown on the seed layer. Foo et.al [32], in their report showed that crystal qualities, grain size, diameter and optical band gap of the ZnO nanorods grown on silicon substrate were affected by the type of solvent used in seed preparation. However, there are no reports of the growth of ZnO nanorods on the ZnO seed layer prepared on the microslide glass substrates using IPA based precursor solution. Hence, in this work we report on the growth of ZnO nanorods on the ZnO seed layer coated glass substrate (using IPA based precursor solution) and studied the effect of annealing at 350 °C, 450 °C and 550 °C on the morphological, structural, optical and electrical properties of ZnO nanorods.

2. Materials and methods

2.1. Materials

Zinc acetate dihydrate (ZAD) (Zn $(CH_3COO)_2 \cdot H_2O$, Merck 99.9%), monoethanolamine (MEA) ($HOCH_2CH_2NH_2$, Merck 99.9%), 2-propanol (IPA), zinc nitrate hexahydrate ((ZNH), $(Zn(NO_3)_2 \cdot 6H_2O)$, Sigma-Aldrich) and hexamethylenetetramine (HMTA), ($C_6H_{12}N_4$, Sigma-

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Aldrich) of analytical grade chemicals were used without further purification.

2.2. Preparation of ZnO nanorods

The seed solution was prepared by a simple sol gel technique. In this procedure, 3.16 g of ZAD was dissolved in 15 ml of IPA (0.9 M). MEA (0.86 ml) which acts as a stabilizer was added drop wise to this solution to obtain a clear solution. The molar ratio of ZAD and MEA was maintained at 1:1. The above solution was stirred at 70 °C for 1 h and aged overnight to yield a homogeneous mixture.

A microscope slide glass substrate (2 cm × 2 cm) was taken and cleaned using chromic acid solution and rinsed in de-ionized (DI) water. Further, the glass substrate was ultrasonically cleaned using acetone for 10 min followed by rinsing in DI water and drying at 50 °C.

Deposition of seed layer was carried out by spin coating using the prepared solution on the cleaned glass substrate at 3000 rpm for 30 s. And this substrate was heat treated at 300 °C in air for 10 min. This deposition procedure was repeated for five times over the same substrate and the ZnO seed layer was annealed at 300 °C in air for 1 h, so as to obtain a uniform seed layer of about 1.5 μm thick.

A solution containing zinc nitrate hexahydrate (1.484 g) and hexamethylenetetramine (0.70 g) with the molar ratio of 1:1 was prepared using 50 ml distilled water and poured inside a Teflon-lined autoclave. The ZnO seed layer coated substrate was kept inside the autoclave in vertical position such that it was completely immersed in the solution. The autoclave was sealed and maintained at 90 °C for 3 h in a hot air oven. Then the obtained film was washed with de-ionized water to remove any residual materials and then annealed in air at 350 °C, 450 °C and 550 °C for 1 h. As grown sample was characterized to distinguish the effect of annealing temperature on the properties of ZnO nanorods. For electrical characterization, interdigitated electrode (IDE) structures were fabricated by depositing gold through a shadow mask over the synthesized ZnO nanorods by thermal evaporation method. The schematic illustration of the preparation of ZnO nanorods and IDE structure is shown in Fig. 1.

2.3. Characterization

The surface morphology and elemental analysis of ZnO nanorods were examined using field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX) using FEI Quanta FEG 200. XRD pattern of all the synthesized samples were obtained by PANalytical's X'Pert Pro with CuKα radiation (λ = 1.5406 Å). Photoluminescence (PL) was recorded using Jasco Spectrofluorometer FP-8600 with He–Cd laser (λ = 325 nm) as excitation source. Optical absorption measurements were carried out using SHIMADZU UV–vis–spectrophotometer. I–V measurements were performed using Electrochemical Impedance Spectrometer SP-3000.

3. Results and discussion

3.1. Morphological analysis

Fig. 2 shows FESEM images of the (a) ZnO seed layer, (b) as grown sample, (c) sample annealed at 350 °C, (d) sample annealed at 450 °C and (e) sample annealed at 550 °C and they reveal the formation of ZnO nanorods. The FESEM image of the ZnO seed layer (1.5 μm thick) shows the average particle size of about 24.8 nm. The average diameter of the nanorods is found to increase from ~200 nm (350 °C) to ~500 nm

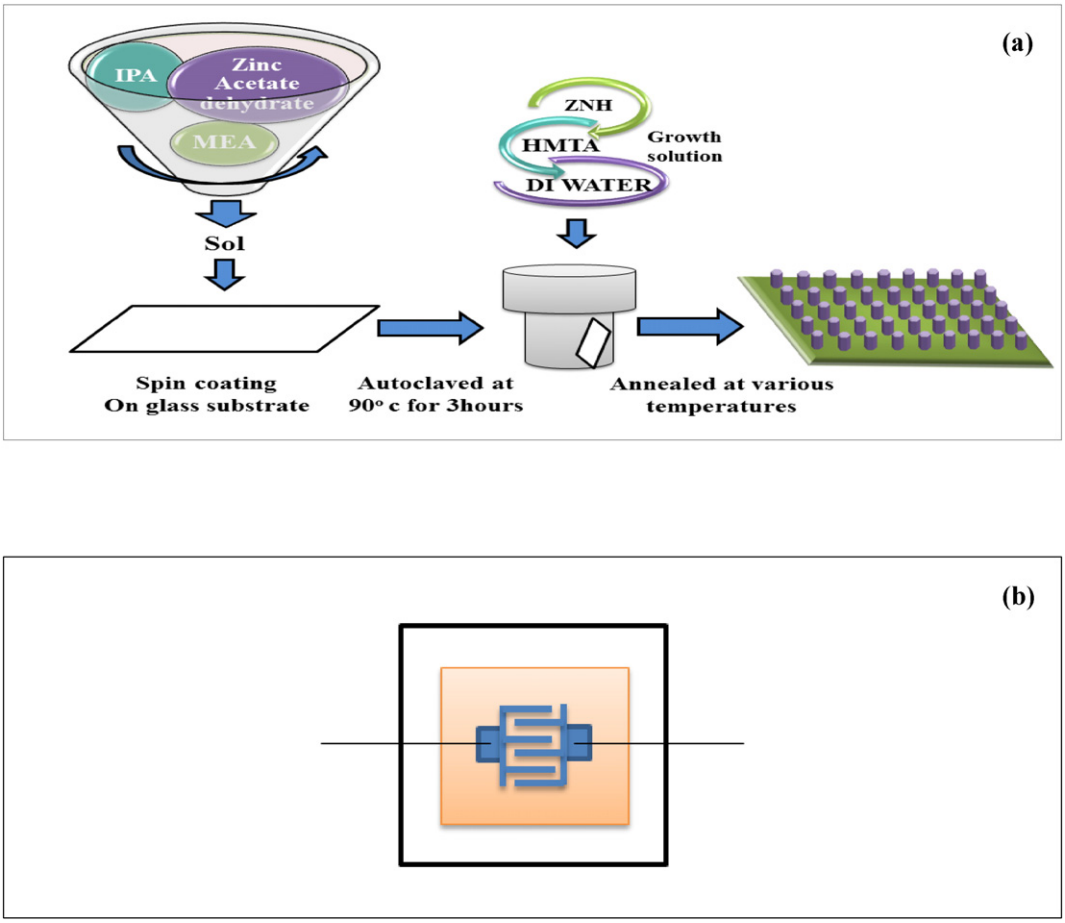

Fig. 1. Graphical representation of (a) preparation of ZnO nanorods by hydrothermal process and (b) interdigited electrode.