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The effect of growth temperature of seed layer on the structural and optical properties of ZnO nanorods

Khyati Gautam [a,*], Inderpreet Singh [b], P.K. Bhatnagar [a], Koteswara Rao Peta [a]

[a] Department of Electronic Science, University of Delhi South Campus, Benito Juarej Road, New Delhi 110021, India
[b] Department of Electronics, SGTB Khalsa College, University of Delhi, Delhi 110007, India

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ABSTRACT

The structural and optical properties of ZnO nanorods are investigated as a function of growth temperature of the seed layer. The seed layer comprising of ZnO nanocrystallites is grown on ITO substrates at five different temperatures (150–550 °C) and the nanorods are grown on the seed layer by the facile hydrothermal method. The seed layer grown at 350 °C is observed to be uniformly textured with c-axis orientation leading to the synthesis of vertically aligned nanorods with smaller diameter. The HR-TEM analysis and the intense peak along (002) direction in the XRD spectra of this sample implied that the nanorods possess c-axis orientation. An enhanced UV emission is also observed in the photoluminescence spectra of this sample. The diversity in the morphology and orientation of the seeds at different temperatures has been explained by the growth kinetics of the ZnO nanocrystallites.

1. Introduction

Zinc oxide with its unique combination of wide bandgap (3.37 eV) and high exciton binding energy (60 meV) has drawn considerable attention of the researchers over the years. It possesses a family of nanostructures such as nanorods, nanotubes, nanoflowers, nanohelix etc. among which, ZnO nanorods are of particular interest because of their quasi 1-D structure, enhanced charge injection efficiency and improved emission that provides tremendous opportunity for their application in optoelectronic devices [1–6]. The performance of these devices depends majorly on the distribution and alignment of the nanorods over the substrate. If the distribution is homogeneous, then the optical and electrical contribution of the nanorods will be uniform throughout the device structure. Also, if the alignment of the nanorods is vertical, it enhances the charge injection across the device.

ZnO nanorods grown by gas-phase synthesis technique (chemical vapor deposition (CVD) [7], metal organic chemical vapor deposition (MOCVD) [8] vapor-liquid-solid (VLS) [9] and pulsed laser deposition (PLD) [10] are reported to be perfectly aligned, homogeneously distributed with high crystallinity. But these methods require high processing temperature and also their development cost is very high. On the other side, liquid phase synthesis (involving the hydrothermal method and electrochemical method) is simple and requires low temperature and therefore has become popular among the researchers for large scale production [4,11–13]. However, the main challenge for researchers in the liquid phase synthesis is to reduce the defects, which are inherently introduced in the structure due to the growth technique. Many research groups are working

* Corresponding author.
E-mail address: khyati34@gmail.com (K. Gautam).

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towards obtaining good quality nanorods using hydrothermal method with minimal defects by controlling the growth parameters such as temperature, precursor concentration, pH value, growth time and the nature of the substrate.

Recently, it has been observed that by depositing a seed layer comprising of ZnO nanocrystals over the substrate, the nanorods parameters, namely their alignment, diameter, density, crystallinity and photoluminescence (PL) can be precisely controlled [14–18]. It has been shown by Song et al. [14]. that the morphology of the ZnO nanorods is strongly dominated by the thickness and the crystal size of the seed layer. Ghayour et al. [15]. have described the effect of seed layer thickness on the alignment and diameter of the nanorods. They revealed that the alignment of nanorods depends on the crystallinity, grain size and RMS roughness of the seed layer. Wu et al. [16]. have proposed a molecule adsorption stabilization mechanism to explain the seed orientation. They concluded that the verticality of the nanorods array depends heavily on the seed orientation. It has been shown by Guillemin et. al. [17] that the growth of ZnO nanowires is limited by the mass transport of chemical precursors in solution, leading to the inverse relationship of their average diameter and length with their density. They concluded that the vertical alignment of ZnO nanowires and their density increases, when the seed layer texture is strengthened along the c-axis. In their recent publication [18] they have suggested an alternative approach for the formation of ZnO nanowire arrays with high structural and optical quality. It is based on the spontaneous transformation of a ZnO thin film into ZnO nanowires through simple annealing. The precursor concentration of the solution of ZnO seed layer is also found to affect the residual stress in the nanorods grown on these seeds.

In the present work, ZnO nanorods have been synthesized on ZnO seed layers that are grown at different temperatures, i.e. 150 °C to 550 °C. The effect of different growth temperatures of seed layer on the morphological and optical properties of the as-grown ZnO nanorods has been investigated. The seed layer was synthesized by thermal decomposition of zinc acetate dihydrate in ethanol and the nanorods were grown over the seed layer by the facile hydrothermal method. The structural and optical properties of the nanorods were found to be strongly affected by the growth temperature of the seed layer.

2. Material and methods

The chemicals used for synthesizing ZnO seeds and nanorods viz. zinc acetate dihydrate, zinc nitrate hexahydrate and hexamethylenetetramine were commercially procured from Fisher Scientific. These constituents along with organic solvents and DI water were used to synthesize ZnO seed layer and nanorods as mentioned below.

2.1. Synthesis of ZnO seed layer

For ZnO seed layer, a solution of 0.005 M zinc acetate dihydrate was prepared in ethanol. The solution was then kept in an ultrasonicator for ~1 h for homogenization. Subsequently, an ITO coated glass substrate was taken and the so obtained solution was drop cast over it. It was then allowed to dry in the air and the process was repeated three times to ensure proper coating of the solution throughout the substrate. Five different substrates were obtained in this manner and were heated to five different temperatures, i.e. 150 °C, 250 °C, 350 °C, 450 °C and 550 °C (Sample A-E) in a muffle furnace for 20 min to prepare ZnO seed layer. These substrates coated with a seed layer of ZnO nanocrystals were further used to grow ZnOnanorods over them.

2.2. Synthesis of ZnO nanorods

For this purpose, an equimolar solution of 0.025 M of Zinc nitrate hexahydrate and hexamethylenetetramine in DI water was taken. This solution was homogenized by ultrasonication for ~1 h. After this, the solution was transferred to a petri dish and the ITO substrate already coated with the seed layer was immersed into the solution. The solution was then kept in an oven for 5 h at 90 °C. Subsequently, the substrate was taken out of the solution and then washed in DI water. Afterwards, the sample was again annealed to 100 °C for 10 min to completely remove the moisture. The same process was repeated for all the five samples.

The structural properties of the seeds and nanorods were studied using Scanning Electron Microscope (SEM) (JEOL JSM 6610LV), X-ray diffraction (XRD) (Bruker D8 X-ray Diffractometer with CuKα source (λ~ 1.5406 Å)) and High Resolution Transmission Electron Microscope (HR-TEM) (FeiTecnai G2 STWIN HRTEM 200 kV). For optical characterization, the PL spectra of the samples were studied using Shimadzu spectrofluorophotometer model RF-5301 PC.

3. Results and discussion

The SEM images of the nanorods grown on different seed layers are shown in Fig. 1(a). It is found that the ZnOnanorods grown on the sample A, D and E are randomly aligned while the nanorods in samples B and C showed selective growth behavior. The nanorods in both these samples are found to be vertically aligned with narrow diameters. Between the two, the nanorods in sample C are found to exhibit improved alignment and high density over the substrate.

To verify the orientation of the as-grown nanorods, XRD measurements were done (Fig. 2). The presence of significant peaks along (100), (002) and (101) directions in the XRD spectrum of sample A indicates the polycrystalline nature of these nanorods. It also confirms the random growth of nanorods for this sample. As expected, for samples B and C, intense peaks are observed along (002) direction, which is an indication of the improved crystallinity. This ensures the preferential growth of