Effects of ZnO Seed Layers Prepared with Various Precursor Concentrations on Structural and Defect Emission Properties of ZnO Nanorods Grown by Hydrothermal Method

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Abstract: ZnO nanorods were grown by a hydrothermal method on ZnO seed layers that had previously been prepared from solutions containing various precursor concentrations. The effects of the ZnO seed layers prepared with various precursor concentrations on the structural and defect emissions of the ZnO nanorods were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), and photoluminescence (PL) spectroscopy. The surface morphology of the ZnO seed layers changed with an increasing precursor concentration, and the diameters and densities of the ZnO nanorods depended on the morphologies of the ZnO seed layers. The ZnO seed layers prepared with various precursor concentrations affected the residual stress in the nanorods grown on the seed layers, the intensity and full widths at half maximum of the 2-theta angle in the XRD spectra for the nanorods, and the intensity and position of the defect emission peak in deep-level emission (DLE) PL spectra for the ZnO nanorods.

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1. INTRODUCTION

Zinc oxide (ZnO) is one of the most promising semiconductors in the field of optoelectronics. The wide direct band gap (3.37 eV) and high exciton binding energy (60 meV) it exhibits at room temperature (RT) [1] make it an excellent candidate for applications such as short-wavelength light-emitting diodes [2], field-emission devices [3], solar cells [4], and chemical sensors [5]. In recent years, one-dimensional (1-D) nanostructure materials have been of great interest in scientific research because of their unique chemical and physical properties. Various 1-D nanostructures, such as nanowires [6], nanorods [7], nanobelts [8], nanotubes [9], nanoneedles [10], and soccer balls [11] have previously been reported for ZnO. The 1-D nanostructure has been synthesized using thermal evaporation [12], vapor phase transport [13], chemical vapor deposition [14], and hydrothermal methods [15]. Among the various methods of synthesizing 1-D nanostructures, hydrothermal methods are the most convenient and economical for growing well-ordered ZnO nanostructures such as nanorods and nanowires [16]. In general, growing ZnO nanorods with a hydrothermal method requires the deposition of ZnO seed layers. It is the most critical step, so the effects of the seed layers on the growth of ZnO nanorods have previously been studied in detail [17-21].

In addition to ultraviolet (UV) excitonic emission peak, ZnO commonly exhibits visible luminescence at various emission wavelengths because of the intrinsic or extrinsic defects of ZnO [22]. Thus, it is necessary to decrease the concentrations of defects and impurities in order to produce high-quality ZnO thin films and nanostructures. It is still challenging to synthesize ZnO with decreased concentrations of defects and impurities, which either are formed during growth or are intentionally induced by doping [12]. In this study, various precursor concentrations ranging from 0.4 to 1.0 M were used in sol-gel spin-coating to deposit ZnO
seed layers onto Si (100) substrates in order to decrease the concentrations of defects and impurities in ZnO nanorods. The ZnO nanorods were then grown using the hydrothermal method on the ZnO seed layers. The effects of the seed layers prepared with various precursor concentrations on the structural and defect emission properties of the ZnO nanorods were investigated.

2. EXPERIMENTAL PROCEDURES

The ZnO seed layers were deposited using sol-gel spin-coating onto p-type Si (100) substrates. The precursor solutions were prepared by dissolving 0.6 M zinc acetate dihydrate [Zn(CH$_3$OO)$_2$·2H$_2$O] in 0.6 M 2-methoxyethanol as a solvent with monoethanolamine (MEA) added to stabilize the sol-gel. The molar ratio of MEA to zinc acetate was maintained at 1:1, and the concentration of zinc acetate was varied from 0.4 to 1.0 M. The mixed solution was then stirred at 60 °C for 2 h until a clear and homogeneous solution was obtained. The clear solution was retained at RT for 24 h. The solution was spin-coated onto Si substrates that were then rotated at 3000 rpm for 20 s. After the ZnO seed layers were deposited by spin-coating, they were pre-heated at 300 °C for 10 min to evaporate the solvent and to remove the residual organic materials. The ZnO seed layers were then cooled at a rate of 5 °C/min to prevent the formation of cracks. Coating and pre-heating were each repeated three times, and the ZnO seed layers were then post-heated in a furnace at 550 °C in air for 1 h.

The hydrothermal method was then used to grow ZnO nanorods on the ZnO seed layers. The ZnO seed layers were rinsed with deionized (DI) water and were transferred into a Teflon-lined autoclave containing an aqueous solution of 0.3 M zinc nitrate hexahydrate [Zn(NO$_3$)$_2$·6H$_2$O] and 0.3 M hexamethylenetetramine [C$_6$H$_{12}$N$_4$]. The growth temperature was maintained at 140 °C for 2 h. After completion of the reaction, the substrate was thoroughly rinsed with DI water and was blow-dried with ultra-high-purity (99.9999%) nitrogen gas to remove any residual salts and organic materials. The structural and defect emission properties of the ZnO nanorods grown on the ZnO seed layers prepared with various precursor concentrations were then investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD) spectroscopy, and photoluminescence (PL) spectroscopy.

3. RESULTS AND DISCUSSION

Figures 1(a)-(d) show the SEM images of the ZnO seed