Research Article

Effect of Annealing on the Structure and Photoluminescence of Eu-Doped ZnO Nanorod Ordered Array Thin Films

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Eu-doped ZnO nanorod ordered array thin films were synthesized on glass substrates with a ZnO seed layer via hydrothermal method. XRD reveals that the (002) diffraction peak of films annealed in hydrogen is sharper than that annealed in air. SEM reveals that the nanorods of films annealed in hydrogen are shortened and widened. TEM results demonstrate that the nanorods are single crystalline and the lattice spacing of 0.52 nm agrees with the d spacing of (001) crystal planes along c -axis. Room temperature photoluminescence (PL) reveals that the PL of films annealed in hydrogen is the strongest and shifts to lower wavenumber. The point defect of Eu-doped ZnO nanorod array thin film is transferred from O_i to O_{Zn} by annealing in hydrogen.

1. Introduction

Zinc oxide is an important member in the II–VI family with a wide band gap (3.37 eV) and a large excitonic binding energy (60 meV) [1–5]. Furthermore, ZnO is one of the environmental friendly materials, and the impurity-doped ZnO nanocrystals emitting visible light are expected to be appropriate materials for flat panel displays, florescence labels for biological imaging, and so on [6]. High quality II–VI semiconductor nanocrystals also become materials for doping of optically active impurities. The II–VI semiconductor nanocrystals doped with luminescence centers exhibit efficient luminescence even at room temperature [7–9].

Rare-earth ions are unique dopants, because they are optically and magnetically active in the semiconductor host crystals [10]. It is anticipated that in impurity-doped ZnO, strong interactions between the quantum-confined carriers and localized electrons on impurities will produce efficient photoluminescence (PL) [11, 12]. Eu is an attractive dopant for red emission in the range of 540–665 nm and the Eu-related luminescence lines are found to be a strong function

of the structural quality and thermal cycling in the case of GaN [13].

In addition, nanorod thin films have some interesting properties. Among various synthesis methods, the hydrothermal method is attractive through which ZnO nanorods can be fabricated at low cost [14]. Despite various ZnO nanostructures that have been produced, few work has been executed on the synthesis of rod-like Eu-doped ZnO array thin films. In our work, via a low-temperature (70°C) hydrothermal synthesis, we present a nontoxic, large-scale, and low-cost method of preparing morphology-controlled Eu-doped nanorod ZnO array thin films on glass substrates with ZnO seed layer, and the effects of annealing atmosphere and Eu-doping on crystalline orientation and luminescence of the ZnO : Eu films are also investigated.

2. Experimental Details

2.1. Preparation of ZnO Seed Layer. The ZnO seed layer was prepared on glass substrates by the sol-gel spin-coating method. Zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] was used as

FIGURE 1: X-ray diffraction patterns of the Eu-doped nanorod ZnO array thin films.

FIGURE 2: Secondary electronic microscopy micrographs of Eu-doped ZnO nanorod array thin films: (a) unannealed, (b) annealed in air, (c) annealed in hydrogen.

FIGURE 3: Low-resolution cross-sectional TEM image of the ZnO nanorods: (a) unannealed, (b) annealed in air, (c) annealed in hydrogen.

a basic chemical. Ethylene glycol monomethyl ether ($C_3H_8O_2$) and ethanolamine (C_2H_7NO) were used as solvent and stabilizer, respectively. The molar ratio of ethanolamine to zinc acetate was 1 : 1 and the concentration of the solution was 0.8 mol/L. The obtained mixture was stirred at 60°C for 4 h to yield a clear and homogeneous solution, which then served as the coating source after being cooled down to room temperature. The glass substrates were first cleaned in detergent, then in methanol and acetone using an ultrasonic cleaner, for 30 min each. Finally, the glass substrates were rinsed with deionized water and dried in oven. The coating solution was then dropped onto the glass substrate, which was rotated at 3000 rpm for 30 sec using KW-4A spin coater. After spin coating, the films were dried at 350°C for 20 min in a furnace to evaporate the solvent and remove organic residuals. This coating/drying procedure was repeated for three times before the films were inserted into a tube furnace and annealed at 550°C for 2 h in air.

2.2. Film Growth by Hydrothermal Method. At room temperature, diluted ammonia solution was dripped into the zinc nitrate solution under stirring, and requisite Eu_2O_3 was dissolved into dilute HNO_3 . By mixing the above two solutions, we obtain one with Au-Zn molar ratio of 1 : 50, in which zinc nitrate was 0.54 g and the volume of solution was 40 mL. The glass substrates with the seed layer were immersed into the teflon lined stainless steel autoclaves filled with the resultant solution, and then the sealed vessels were put in the oven for heating at 70°C for 5 h. The grown films were rinsed with deionized water and dried in the air.

2.3. Characterization. The crystal graphic interpretations were performed on an X'Pert Pro XRD system with X-ray Mirror PFX at an operation voltage of 40 kV and a current of 40 mA, in which $\text{Cu K}\alpha$ ($\lambda = 0.154059 \text{ nm}$) was used and scanned in a 2θ range from 15° to 80° . Surface morphology and thickness of the film were studied via an FEI-SIRION

FIGURE 4: High-resolution TEM image of the ZnO array thin films together with the corresponding SAED pattern (inset): (a) unannealed, (b) annealed in air, (c) annealed in hydrogen.

scanning electron microscope (SEM). Transmission electron microscope (TEM) micrographs and selected-area electron diffraction (SAED) patterns were obtained on a PHILIPS-CM200 and JEM-2010 type TEM. The PL spectra were recorded from 330 to 800 nm at room temperature by a 325 nm excitation from Xe lamp (F-4500 Fluorescence Spectrophotometer).

3. Results and Discussion

3.1. Structure and Surface Morphology. Figure 1 shows the XRD patterns of the samples deposited on glass substrate with ZnO seed layer by hydrothermal synthesis under different annealing atmosphere. All the diffraction peaks can be indexed to a hexagonal wurtzite ZnO structure ($a = 0.325$ nm, $c = 0.521$ nm) and no peaks are detected from any

impurities. The (002) reflection sharpens up distinctly, indicating the c -axis of ZnO nanocrystals is oriented perpendicular to the plane of the ZnO seed layer. It can be also seen that the (002) diffraction peak is the strongest when the film is not annealed, and that which annealed in hydrogen is the second, while that annealed in air is the last. These results indicate that the prepared ZnO using the present method is highly crystallized.

Furthermore, in our experimental condition, a novel one-dimensional nanorod array thin film of ZnO was synthesized. The SEM micrographs of Eu doped ZnO nanorod array thin films are shown in Figure 2, in which Figures 2(a), 2(b), and 2(c) represent unannealed, annealed in air, and annealed in hydrogen of samples, respectively. From these pictures, it can be seen that nanorods are grown vertically oriented with seed layer. Notably, when the films were

FIGURE 5: PL spectra of Eu-doped ZnO nanorod array thin films.

annealed in hydrogen, the nanorods become shorter and wider. In addition, the typical EDS pattern of the nanorod indicates that the film consists of Zn, O, and Eu, and the molar ratio of Zn, O, and Eu is 48:0.4:51.6. The results reveal that the Eu atom might be doped into the nanorod in the form of substitution.

To characterize the crystallinity of the ZnO nanorods by TEM, we remove the products from the seed layer by ultrasonication in the ethanol. Figure 3 displays the TEM images of Eu doped ZnO nanorod array thin films. Among them, Figures 3(a), 3(b), and 3(c) denote the samples which are unannealed, annealed in air, and annealed in hydrogen, respectively. Those figures show that ZnO nanorods are straightforward with nonuniform diameter along their axis, and the ZnO nanorods are the widest when the films were annealed in hydrogen.

In Figure 4, we display the high-resolution TEM images and the corresponding SAED pattern of Eu doped ZnO nanorod array thin films. In a similar way, Figures 4(a), 4(b), and 4(c) denote the samples which are unannealed, annealed in air, and annealed in hydrogen, respectively. Those images further confirm that the nanorods are single crystalline and the obtained lattice spacing of 0.52 nm agrees with the d spacing of (001) crystal planes along c -axis, which is also supported by SAED patterns (inset in Figure 4).

3.2. PL Spectra. Figure 5 shows the PL spectra of the Eu-doped ZnO nanorod array thin films. We detected that the unannealed films have emission at 400, and 560 nm, the films annealed in air have emission at 400 nm, and the films annealed in hydrogen have emission at 390, and 520 nm. Furthermore, the figure confirms that the PL of films annealed in hydrogen is the strongest and shifts to lower wavenumber. Srikanth and Clarke assigned the UV emission at ~ 395 nm to a shallow donor [15], and the nature of the shallow donor might be the complex defect of Zn_i [16].

The peak at ~ 520 nm remains controversial and is more preferably attributed to O_{Zn} [17, 18]. The origin of yellow and orange luminescence (>540 nm) is ascribed to O_i [19]. The above analysis verifies our assumption that the films unannealed have point defect O_i , and the films annealed in hydrogen have point defect O_{Zn} . In a word, the point defect of Eu-doped ZnO nanorod array thin film is transferred from O_i to O_{Zn} by annealing in hydrogen.

4. Conclusions

In summary, we present the fabrication of the Eu-doped ZnO nanorod ordered array thin films via hydrothermal method. Test results demonstrate that the (002) diffraction peak of films annealed in hydrogen is sharper than that annealed in air, and the nanorods of films annealed in hydrogen become shorter and wider. TEM results further demonstrate that the nanorods are single crystalline and the obtained lattice spacing of 0.52 nm agrees with the d spacing of (001) crystal planes along c -axis. Room temperature photoluminescence reveals that the PL of films annealed in hydrogen is the strongest and shifts to lower wavenumber. The point defect of Eu-doped ZnO nanorod array thin film is transferred from O_i to O_{Zn} by annealing in hydrogen.

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