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Investigation of ZnO nanorods synthesized by a solvothermal method, using Al-doped ZnO seed films

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ABSTRACT

ZnO nanorods were successfully grown on common glass substrates using a simple solvothermal method via the precursors of zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and Hexamethylenetetramine ($C_6H_{12}N_4$) with equal molar concentration at 0.01 mol/l, 0.025 mol/l, 0.05 mol/l, and 0.075 mol/l. The ZnO nanorods were characterized by X-ray diffraction (XRD), Scanning electron microscopy, UV–Vis absorption spectrophotometer and photoluminescence (PL) spectrometer. XRD results indicated that all the ZnO nanorods were preferentially grown along [0001] direction (*c*-axis). With an increase of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ concentration, the diffraction intensity of ZnO nanorod along *c*-axis also increased. Scanning electron microscopy images showed that the well-faceted hexagonal ZnO nanorods were grown vertically from the common glass substrates. In addition, with the increase of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ concentration, the exciton band of ZnO nanorods determined by UV–Vis absorption spectra gradually became narrow and the intensity of exciton band also remarkably augmented. Photoluminescence spectra showed that with the increase of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ concentration, the position of emission peak of ZnO nanorod blue-shifts towards shorter wavelength in UV region and the luminescence intensity remarkably enhances in visible emission range (470–630 nm).

1. Introduction

One-dimensional semiconductor nanomaterials have attracted much attention in recent years due to their novel optical, electrical and mechanical properties [1]. Among various one-dimensional semiconductor nanomaterials, Zinc oxide (ZnO) nanorods are the most frequently studied and can be used in nanogenerator [2], rectifying diodes [3], sensors [4], and electron emitters [5] because of their wide direct bandgap of 3.37 eV and large excitation binding energy of 60 meV at room temperature. As a result, searching a new methodology to synthesize aligned ZnO nanorods array is of great importance for both fundamental study and practical application. Up to now, various methods such as pulsed laser deposition (PLD) [6], chemical bath deposition (CBD) [7], sol–gel [8], spray pyrolysis (SP) [9], electrochemical deposition (ECD) [10], hydrothermal (HT) [11], etc. have been utilized to fabricate ZnO nanorods. Among these methods, the hydrothermal method offers advantages of being environmental friendly, large area deposition, low synthesis temperature, and low production cost. As we know, both a surfactant or organic solvent-assisted and a surfactant-free hydrothermal method have ever been applied to fabricate the ZnO nanorods. The existed findings demonstrate that the synthesis temperature of ZnO nanorods grown by a surfactant or organic solvent-assisted hydrothermal method is less than that of ZnO nanorod grown by a surfactant-free hydrothermal method, and the former is at 90 °C and the latter is at 110 °C, 180 ° or 200 °C [12–15]. Consequently, it will be a good choice for synthesizing ZnO nanorods via a surfactant or organic solvent-assisted hydrothermal method.

Recently, the dependence of well-oriented hexagonal ZnO nanorods synthesized by a sol–gel method on the volume ratios of precursor solutions under the equimolar concentration of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and Hexamethylenetetramine ($C_6H_{12}N_4$) aqueous solutions has been reported [8]. However, in this study, we report the dependence of the hexagonal ZnO nanorods array synthesized via a solvothermal method on the molar concentrations of Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and Hexamethylenetetramine ($C_6H_{12}N_4$) precursor solutions. The crystalline structures and surface morphologies of ZnO nanorods were measured by XRD and SEM. The optical performances of the ZnO nanorods were characterized by a UV–Vis absorption spectra spectrophotometer and a photoluminescence (PL) spectrometer.

2. Experimental details

All chemicals were reagent grade and used without further purification. Common glass plates were used as substrates and were cleaned to remove contaminants by standard procedures prior to use. ZnO nanorod array films were coated on a common glass substrate by a two-step method. A thin Al-doped ZnO seed

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buffer layer was first deposited via a sol–gel method, A ZnO nanorod array film was then grown in a solvothermal method. In detail, Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), Ethylene glycol menomethyl ether ($C_3H_8O_2$), ethanolamine (C_2H_7NO) and aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$) were used to synthesize Al-doped ZnO precursors. 4.6094 g $Zn(CH_3COO)_2{\cdot}2H_2O$ in weight was dissolved into $C_3H_8O_2$ solvent at room temperature. Then 1.2827 g C_2H_7NO in weight was added as a sol stabilizer. The concentration ratio of $Zn(CH_3COO)_2{\cdot}2H_2O$ and C_2H_7NO was kept at 1:1. The formed mixture was stirred at 60 °C for 1 h in a water bath, and then 0.1182 g $Al(NO_3)_3{\cdot}9H_2O$ in weight was added into the mixture solutions and stirred for 1 h to form a transparent homogeneous mixture. After 24 h aging at room temperature, the finally formed Al-doped ZnO precursor was firstly deposited onto the common glass substrate by a spin coating with a rotation speed of 800 rpm for 30 s, annealed on a hotplate at 300 °C for 10 min, followed by annealing at 500 °C for 2 min. The two step annealing process utilized in this study aims to improve the crystal quality of Al-doped ZnO buffer layer [16]. Subjected to the above procedure, a Al-doped ZnO seed layer of almost 86 nm thickness was finally formed on the common glass substrate.

Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and Hexamethylenetetramine ($C_6H_{12}N_4$) reagents were separately dissolved into deionized water at room temperature in an equal molar concentration. The concentrations of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ aqueous solutions were adjusted at 0.01 mol/l, 0.025 mol/l, 0.05 mol/l, and 0.075 mol/l, respectively. After uniformly stirred, we mixed and continuously agitated them for 30 min. And then, we transferred them into four Teflon-line autoclaves. Four identical glass substrates coated with Al-doped ZnO seed layer were loaded on Teflon holder in autoclave, respectively. The seeded surface was facing to bottom of container and the holder was immersed into the reagent solution. The container was then covered using a commercially fabricated Teflon lead to avoid the evaporation. During the ZnO nanorod growth, these four Teflon-line autoclaves were placed into an electric oven at a temperature of 90 °C. After keeping temperature at 90 °C for 3 h, the vessels were cooled down to room temperature naturally. The products on substrate were washed with deionized water and ethanol for several times and dried them in an electric oven at a temperature of 90 °C for 2 h. It is worth noting that the formation process for the hexagonal ZnO nanorod using a hydrothermal method in this study can be expressed as follows [17]:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \rightarrow OH^- + NH_4^+ \quad (2)$$

$$2OH^- + Zn^{2+} \rightarrow ZnO_{(s)} + H_2O \quad (3)$$

The crystalline and nanostructure properties of ZnO nanorod films synthesized in this study were investigated by θ–2θ method of XRD with a Cu Kα_1 (λ = 0.15406 nm) source at 40 kV and 30 mA using a multi-purpose XRD system (D/MAX-RB). The morphologies of the ZnO nanorod films were also analyzed by a scanning electron microscope (SEM, JSM-5900). SEM photographs for the ZnO nanorod films were recorded at 15 kV from samples covered with a gold thin film. The optical properties and crystal defects of the ZnO nanorod films were obtained through room temperature photoluminescence using an excitation wavelength of 325 nm via a Horiba Jobin Yvon FL3-221 spectrometer. The UV–Vis absorption spectrum was investigated on a UV2102PCS UV–Vis spectrophotometer.

3. Results and discussion

The crystalline of the ZnO nanorods was investigated using XRD pattern. Fig. 1 shows the XRD pattern of the ZnO nanorods synthesized by the precursors of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ with equal molar concentration at 0.01 mol/l, 0.025 mol/l, 0.05 mol/l, and 0.075 mol/l, respectively. All of the diffraction peaks can be indexed within experimental error as hexagonal ZnO phase (wurtzite structure) by comparison with the data from the Joint Committee on Powder Diffraction Standardards (JCPDS) card for ZnO (JCPDS 89-1397) [8]. The clear and narrow diffraction peaks in Fig. 1 indicate that all the ZnO nanorods have a good crystalline and size. No characteristic peaks from other impurities are detected. For ZnO nanorod synthesized from the precursors of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ with equal molar concentration at 0.01 mol/l, only the diffraction peak of (002) is detected. For ZnO nanorod synthesized from the precursors of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ with equal molar concentration at 0.025 mol/l, the sharp diffraction peaks of (002) , (101) and the faint diffraction peak of (103) arise up. For the ZnO nanorod synthesized from the precursors of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ with equal molar concentration at 0.05 mol/l, only the strongest diffraction peaks of (002) and the faint diffraction peak of (103) are detected. For the ZnO nanorod synthesized from the precursor of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ with equal molar concentration at 0.075 mol/l, Diffractions from (100), (002), (101), and (102) and (103) planes of ZnO nanorod appear in XRD pattern. It is well-noted that the (002) diffraction peak dominates the spectra of all the ZnO nanorod synthesized in this study and the other diffraction peaks are weak, suggesting that the well aligned [0001]-oriented ZnO nanorods have been achieved, which is in good consistent with the SEM images.

Fig. 2a–d shows the SEM images of the ZnO nano-rods synthesized from the precursors of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ with equal molar concentration at 0.01 mol/l, 0.025 mol/l, 0.05 mol/l, and 0.075 mol/l, respectively. The plain-view images in Fig. 2a–d shows that ZnO nanorods had grown at high density across the glass substrate. As the precursor concentration increases, the formed ZnO nanorod density also increases. For the ZnO nanorods synthesized from the precursors of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ with equal molar concentration above 0.025 mol/l, a clear well-faceted hexagonal rods had arisen. Such a hexagonal crystal structure was described by Laudise and Ballman, who reported that ZnO prefers to grow along the [0001] direction [18]. In addition, with an increase of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ concentration, the formed ZnO nanorods also gradually become large in width. The cross-section images of ZnO nanorod arrays synthesized from the precursors of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ with equal molar concentration at 0.025 mol/l is shown in Fig. 2e. It is obvious that the nanorods grow vertically from the common glass substrates.

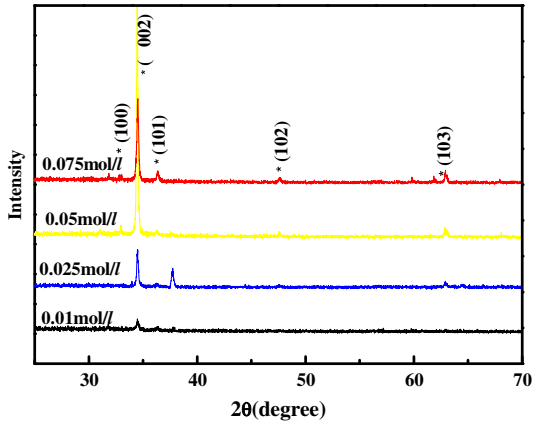

Fig. 1. XRD patterns of ZnO nanorod films synthesized from the precursors of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $C_6H_{12}N_4$ with equal molar concentration at 0.01 mol/l, 0.025 mol/l, 0.05 mol/l, and 0.075 mol/l, respectively.