



Structural and photoluminescence properties of aligned Sb-doped ZnO nanocolumns synthesized by the hydrothermal method

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ABSTRACT

Aligned Sb-doped ZnO nanocolumns were synthesized by a simple hydrothermal method. Based on the analyses of the X-ray diffraction and photoluminescence result, it could be confirmed that the Sb has successfully doped in the ZnO crystal lattices to form an acceptor energy level. At 85 K, the recombination of the acceptor-bound exciton was predominant in PL spectrum, which was attributed to the transition of the ($\text{Sb}_{\text{Zn}}\text{-}2\text{V}_{\text{Zn}}$) complex bound exciton. The acceptor binding energy had been calculated to be 123 meV.

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1. Introduction

One-dimensional (1D) materials such as nanowires, nanotubes, and nanorods have drawn great attention in recent years [1,2]. Among them, ZnO has been widely studied because of its large exciton binding energy (60 meV) and large band gap energy (3.37 eV), which make ZnO have a potential applications in nanodevices [3,4]. To realize nanodevices, p-type ZnO is essential. Many dopants, such as N, P, As, Li, have been used to fabricate p-ZnO thin films and nanostructures. But there is no repeatable and wide-accepted method to overcome the p-type doping difficulty for ZnO. Recently, Limpitjumnong et al. proposed a model for the large-size-mismatch group-V dopants in ZnO based on a first-principles calculation [5]. It has been predicted that Sb would occupy the Zn site and simultaneously induce two Zn vacancies to form a complex ($\text{Sb}_{\text{Zn}}\text{-}2\text{V}_{\text{Zn}}$) serving as an acceptor. Based on this theory, many groups fabricated Sb-doped p-type ZnO thin films by using chemical vapor deposition [6], pulsed-laser deposition [7], and molecular beam epitaxy [8] methods.

In this paper we tried to synthesize Sb-doped ZnO nanocolumns by a hydrothermal method and to study the effects of doping on the structure and optical properties in ZnO nanostructures. Because ZnO nanorods fabricated by the hydrothermal method were almost single crystalline, we could understand the essential physical aspect for ZnO

doping. There were already some reports about the N, P, As, Sb-doped ZnO nanostructures by using the vapor deposition and diffusion methods. But there were few reports about the doping in ZnO by the hydrothermal method.

2. Experimental details

Before the growth of ZnO nanorods, ZnO film with the thickness of 100 nm and (002) orientation was deposited onto the Si substrate by the magnetron sputtering. 0.01 M zinc acetate [$\text{Zn}(\text{Ac})_2 \cdot \text{H}_2\text{O}$], 0.01 M hexamethylenetetramine, and 0.0005 M SbCl_3 were dissolved in a mixed solvent of ethanol and water (18.2 MΩ cm) in a 4:1 volume ratio to form a 50.0 ml solution. Then 30 ml of this mixture were transferred to a Teflon-lined stainless autoclave of 50 ml capacity. The as-grown ZnO film/Si substrate was put into the solution. The tank was conducted in an electric oven at 90 °C for 24 h. After reaction, the sample was washed by deionized water and dried in air at 60 °C for 2 h. For comparison, undoped ZnO nanorods were also grown followed the procedure proposed by Vayssieres [9].

The sample was investigated by a field-emission scanning electron microscopy (FESEM, Hitachi-4800), attach to energy-dispersive X-ray spectroscopy (EDX, GENE SIS 2000 XMS 60 S, EDAX, Inc.) operated at 10 kV for Fig. 1(a), and 15 kV for Fig. 1(b). The structure of the samples were determined by X-ray diffraction (XRD, D/max-RA) using a $\text{CuK}\alpha$ radiation. Photoluminescence (PL, LABRAM-UV Jobin Yvon) measurements were performed using a He–Cd laser line of 325 nm as the excitation source.

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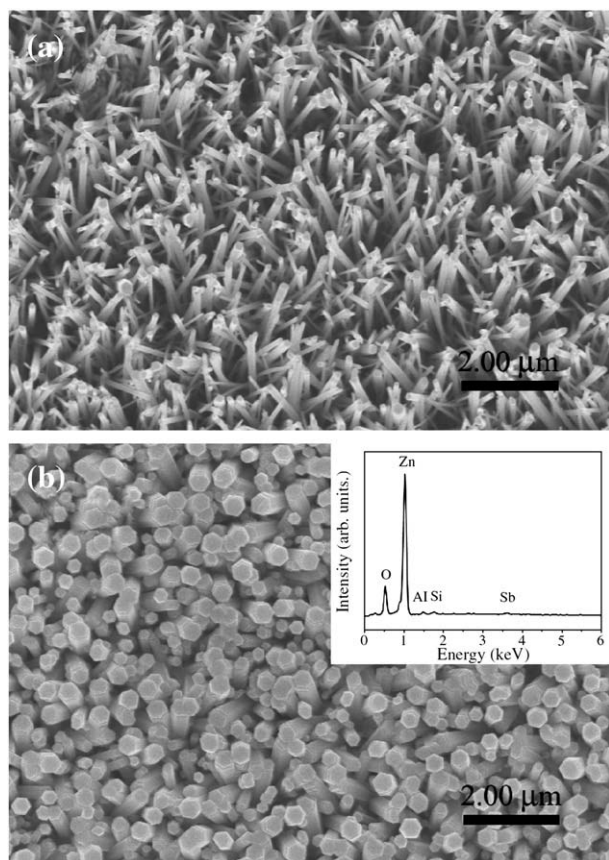


Fig. 1. (a) SEM image of undoped ZnO nanorods, (b) Sb-doped ZnO nanocolumns, the inset shows the EDS spectrum of Sb-doped ZnO nanocolumns.

3. Results and discussion

The morphologies of the as-grown undoped ZnO nanorods and Sb-doped ZnO nanocolumns were investigated using SEM. As shown in Fig. 1(a), quasi-aligned undoped ZnO nanorods with well-defined facets on the coated Si substrate. The nanorods have typical diameters of about 100 nm with lengths of a few micrometers. Fig. 1(b) shows rough and uniform Sb-doped ZnO nanocolumns. The diameters of the nanocolumns range in 250–500 nm and their lengths range in 1–2 μm. From the insert of Fig. 1(b), the EDS analysis indicates that there are only zinc, oxygen and antimony elements in the nanocolumns. And the Sb concentration in nanocolumns is about 1 atom%, revealing the possibility of incorporation of antimony entering into the ZnO nanocolumns. The containing Al in the sample originates from substrate aluminum tray.

Because the measured concentrations are near the detection limit of the EDS equipment, the structural properties of the nanocolumns were further characterized by XRD to verify the presence of Sb dopant in the ZnO structures. Fig. 2 shows the XRD pattern of Sb-doped ZnO nanocolumns and undoped ZnO nanorods. For each sample, all diffractive peaks can be indexed to hexagonal wurtzite ZnO, and no diffraction peaks from any other minerals were observed. The ZnO (002) diffraction peak is dominant demonstrates that the samples have a preferred orientation along the *c*-axis direction. Compared with undoped ZnO, the peak intensities of (002) diffraction peak of Sb-doped ZnO nanocolumns is decreased, and shifts to the small-angle side (as shown in the insert of Fig. 2), which is caused by substitutional Sb ion sits in the Zn site of the lattice and forms $\text{Sb}_{\text{Zn}}-2\text{V}_{\text{Zn}}$ [5,10]. This result suggests that the Sb has been doped into the ZnO lattice, which is in agreement with the EDS analysis.

In order to examine the changes of optical properties for Sb-doped ZnO, the room temperature PL measurement was performed. Fig. 3

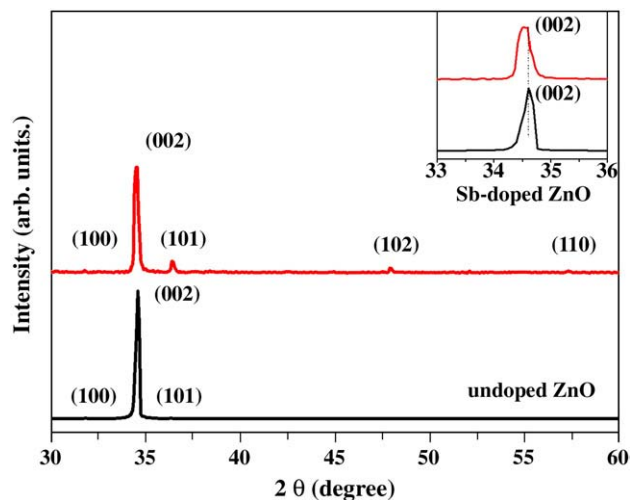


Fig. 2. XRD pattern of the undoped ZnO nanorods and Sb-doped ZnO nanocolumns. The inset shows the amplified spectra for (002) diffractive peaks.

shows room temperature PL spectra of undoped ZnO and Sb-doped ZnO. The PL spectrum of the undoped ZnO shows an exciton emission at 377 nm and a weak deep level emission in the visible region, which is attributed to the defect related emission in ZnO. For the Sb-doped ZnO, the intensity of exciton emission located at 379 nm decreased distinctly. However, the intensity of deep level emission increased due to more defects introduced by Sb [11].

To further confirm the Sb doping in the ZnO crystal lattices and form an acceptor energy level, the low-temperature PL measurements of undoped and Sb-doped ZnO were carried out at 85 K, as shown in Fig. 4(a). The PL spectrum of the undoped ZnO nanorods shows a strong near-band-edge emission located at 3.365 eV, which is assigned to the transition of neutral donor-bound exciton (D^0X) [12]. Because this emission peak was too strong, so other emission peaks were covered, such as FX and FX-1LO. And the peak at 3.231 eV is FX-2LO. For Sb-doped ZnO nanocolumns, the PL spectrum shows that well-resolved emissions located at 3.356, 3.314 and 3.242 eV. The peak at 3.356 eV accords well with the neutral acceptor-bound exciton (A^0X) emission in ZnO [13]. This peak is also observed in Sb-doped ZnO films and nanowires. Therefore, it is attributed to the A^0X emission. The peak at 3.242 eV showed a small blue shifts during the temperature increase (shown in Fig. 4(b)), which are typical characteristic of donor–acceptor pair (DAP) emission. Therefore, the

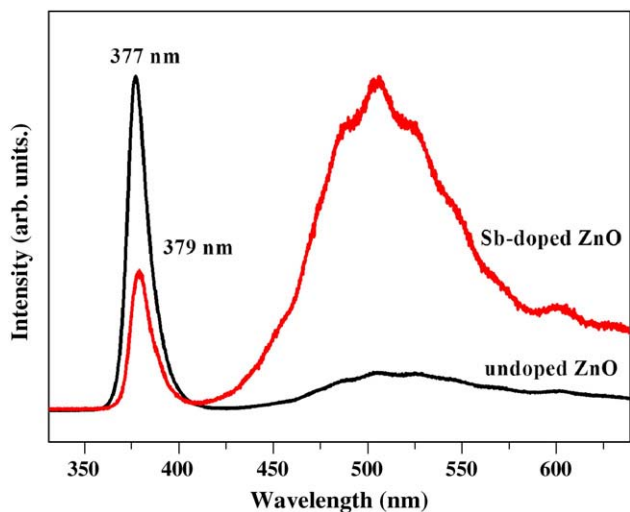


Fig. 3. Room temperature PL spectrum of the undoped ZnO nanorods and Sb-doped ZnO nanocolumns.

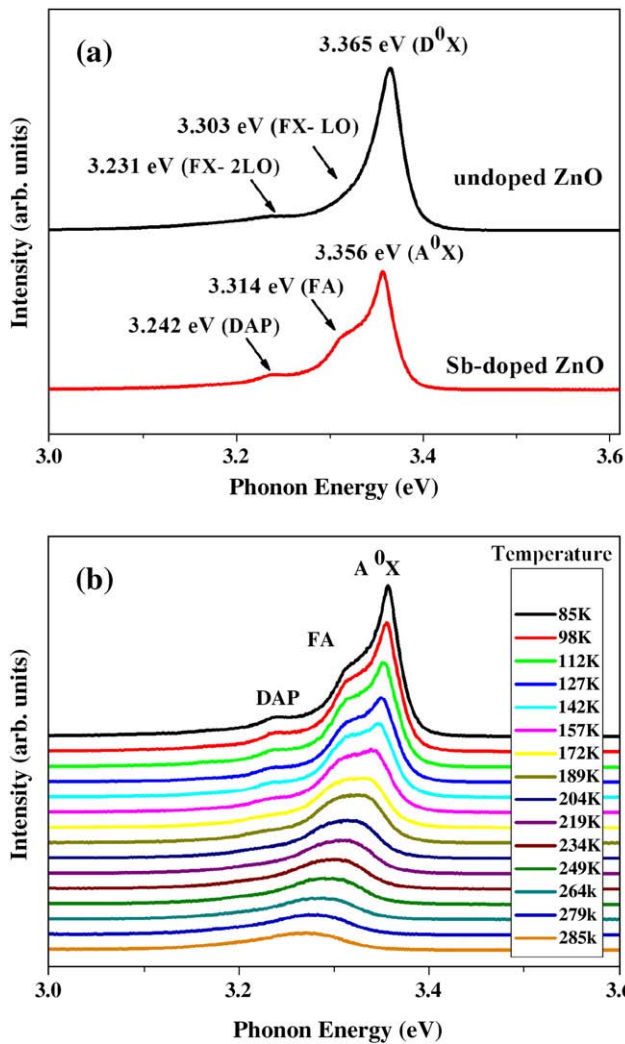


Fig. 4. (a) The low-temperature PL spectra of undoped ZnO nanorods and Sb-doped ZnO nanocolumns. (b) The temperature-dependence PL spectra of Sb-doped ZnO nanocolumns.

3.242 eV peak is attributed to the DAP emission, and the 3.314 eV peak to free electron to the acceptor transition (FA).

The acceptor binding energy of E_A in ZnO can be estimated by the following formula [14].

$$E_A = E_{\text{gap}} - E_{\text{FA}} + \frac{k_B T}{2}$$

where $E_{\text{FA}} = 3.314$ eV, k_B is the Boltzmann constant, and T is the temperature. With an intrinsic band gap of $E_{\text{gap}} = 3.437$ eV [15], the acceptor binding energy of E_A can be calculated to be about 123 meV, which is similar to the value of Sb-doped ZnO film [16].

4. Conclusions

In conclusion, we used hydrothermal method to synthesize the reproducible Sb-doped ZnO nanocolumns. The XRD pattern showed ZnO with a hexagonal wurtzite structure oriented in the c -axis direction. The optical properties of Sb-doped ZnO nanocolumns were characterized by low-temperature and temperature-dependence PL spectra. The PL spectra at 85 K, the peaks position and linewidth of Sb-doped ZnO nanocolumns were obviously different to the undoped ZnO nanorods. Compared to the undoped ZnO nanorods temperature-dependence PL spectra, the peaks at 3.356 eV (A^0X), 3.310 eV (FA) and 3.241 eV (DAP) were attributed to antimony-related complex acceptor transitions and its binding energy was calculated to be 123 meV. Based on the results of PL spectra, we can reach the conclusion that Sb-doped ZnO nanocolumns might be a p-type conductivity, which would provide a method of preparation of ZnO homojunctions LED.

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