Synthesis, Structure and Photoluminescence of Ni-doped ZnO Rods via Hydrothermal Technique

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Abstract. Zn₁ₓNiₓO rods with x=0, 0.005, 0.01, and 0.03 were synthesized by a simple hydrothermal technique and characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and photoluminescence (PL). The results show that all the as-synthesized samples are hexagonal wurtzite structure and display rod-like shape except the sample with x=0.03 contains a small amount of hexagonal Ni(OH)₂. The room-temperature PL spectra of the Ni-doped ZnO rods exhibit a strong blue emission at 440nm, two weak should emission bands centered at 410nm and 467nm and a weak broad yellow emission centered at 550nm. The intrinsic defects increase with the introduction of Ni.

Introduction

Zinc oxide (ZnO) is one of the most promising materials for optoelectronic applications due to its wide direct band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature [1]. Moreover, diluted magnetic semiconductors (DMSs), formed by partial replacement of the cations of the nonmagnetic semiconductors by magnetic rare earth or transition-metal ions, have attracted considerable research interest in recent years due to their great potential applications in spintronic devices [2]. Particularly, transition-metal-doped ZnO DMSs have been extensively investigated since Dietl et al. [3] and Sato et al. [4] predicted the existence of room temperature ferromagnetism in transition-metal-doped ZnO. Combining the excellent optical properties with room temperature ferromagnetism, many magnetic-optic devices could be made from transition-metal-doped ZnO. Up to now, some groups have demonstrated intrinsic room temperature ferromagnetism, as predicted theoretically, in Ni-doped ZnO films [5], nanorods [6] and rod arrays [7]. However, the optical properties of Ni-doped ZnO micrometer or sub-micrometer rods are rarely reported. As far as the methods for preparing transition metal-doped ZnO are concerned, the hydrothermal technique has several clear advantages: a high reaction rate, good dispersion in liquid, almost pollution free, low cost, simplicity, and energy conservation [8]. More importantly, doping during the hydrothermal process is very simple and typically involves mixing the precursors in appropriate ratio [9].

In this paper, Ni-doped ZnO rods were synthesized by a simple hydrothermal method. The morphological, structural and optical properties of the Ni-doped ZnO rods were investigated by FESEM, XRD and PL spectrometry, respectively.

Experimental

Ni-doped ZnO rods were synthesized by a simple hydrothermal method. Zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O], nickel acetate tetrahydrate [Ni(CH₃COO)₂·4H₂O] and sodium hydroxide (NaOH) were used as raw materials. All chemicals were analytical grade and used without further purification. Stoichiometric amount of Zn(CH₃COO)₂·2H₂O and Ni(CH₃COO)₂·4H₂O according to the chemical formula Zn₁ₓNiₓO (x=0, 0.005, 0.01, 0.03) were dissolved in deionized water to form a 0.2 M ([Zn²⁺]+[Ni²⁺])= 0.2 M cation aqueous solution, then equal volume of 3.6 M NaOH aqueous solution was slowly dripped into above solution at room temperature under magnetic stirring, and a
mixed solution was formed. Subsequently, 35 ml of the mixed solution was transferred into a Teflon-lined stainless autoclave of 50 ml capacity. The tank was conducted in an electric oven at 200°C for 12 h. When the Teflon-lined autoclave was cooled naturally to room temperature, the products were collected and washed with Milli-Q water and absolute ethanol for several times, and dried in air at 60°C for 10 h.

The crystal morphology and structure of the obtained samples were characterized by field-emission scanning electron microscopy (FESEM, JEOL JSM-6390A) and X-ray diffraction (XRD, XRD-7000S) with CuKα radiation of 1.54 Å. Photoluminescence (PL) measurement was carried out on a fluorescence spectrophotometer (F-4500) using a Xe lamp as the excitation source at room-temperature.

**Results and Discussion**

Fig. 1 shows the XRD patterns of Zn$_{1-x}$Ni$_x$O samples. For the samples with $x=0$, 0.005, 0.01, all the observed diffraction peaks can be indexed to hexagonal wurtzite structure of ZnO (JCPDS 36-1451) and no characteristic peaks from secondary phase are found, which reveal the Ni ions successfully occupy Zn sites without changing the wurtzite structure of ZnO. For the samples with $x=0.03$, secondary phase of hexagonal Ni(OH)$_2$ is detected besides the main phase of hexagonal wurtzite structure. Compared to undoped ZnO, all the XRD peaks of hexagonal wurtzite structure shift to high angle with the increment of Ni doping concentrations, which possibly because the radius of Ni$^{2+}$ (0.69Å) is slightly less than that of Zn$^{2+}$ (0.74Å) [10].

![Figure 1. XRD patterns of Zn$_{1-x}$Ni$_x$O.](image1.png)

![Figure 2. FESEM images of Zn$_{1-x}$Ni$_x$O.](image2.png)
The FESEM images of Zn$_{1-x}$Ni$_x$O are shown in Fig. 2. It can be clearly observed that each sample consists of large numbers of straight rods with smooth surface except a layer of floc on the surface of the sample with $x=0.03$, which may be related to the precipitated Ni(OH)$_2$. For undoped ZnO, the average diameter and length of the rods are about 0.8 $\mu$m and 10 $\mu$m. The rods grow thick or long with the increment of Ni doping concentrations. For the sample with $x=0.03$, some rods reach to 2 $\mu$m and 20 $\mu$m in diameter and length. It is obvious that the dopant Ni has an effect on the growth of samples.

![Room-temperature PL spectra of Zn$_{1-x}$Ni$_x$O.](image)

Fig. 3 shows the PL spectra of Zn$_{1-x}$Ni$_x$O measured with an excitation wavelength of 325nm at room temperature. Four visible emission bands including a strong blue emission at 440nm, a weak shoulder violet emission at 410nm, a weak shoulder blue emission at 467nm and a weak broad yellow emission centered at 565nm can be observed in undoped ZnO. It is generally accepted that the origin of the visible emission of ZnO is attributed to native defects such as vacancies and interstitials of oxygen and zinc [11] and the UV emission originates from the recombination of free excitons corresponding to near-band-edge emission of ZnO [12], which is not be observed in all the samples. In this case, the strong blue emission is considered to be the result of radiative recombination of photo-generated holes with singularly ionized oxygen vacancies [13]. The weak violet emission is ascribed to zinc vacancies [14]. The weak blue emission at 467nm arises from oxygen vacancies [15]. The yellow luminescence is attributed to interstitial oxygen defects [16]. In contrast with undoped ZnO, a blue shift occurs from 565 nm to 550 nm with the introduction of Ni, which may be result from inner stress, and the intensities of all the emission peaks increase with the Ni doping concentrations increasing. It is concluded that oxygen vacancies, zinc vacancies and oxygen interstitials are contained in all the samples and increase with the Ni doping concentrations increasing. However, a number of intrinsic defects will lead to the annihilation of exciton [17], so all the samples exhibit no UV emission which is closely relative to free excitons.

**Summary**

In summary, Ni-doped ZnO rods have been synthesized at 200°C by a simple hydrothermal technique. The room-temperature PL spectra of the Ni-doped ZnO rods show a strong blue emission at 440nm, two weak should emission bands centered at 410nm and 467nm and a weak broad yellow emission centered at 550nm. The intrinsic defects increase with the introduction of Ni.

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References


