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Room temperature ferromagnetic Cr–Ni codoped ZnO diluted magnetic semiconductors synthesized by hydrothermal method under high pulsed magnetic field

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Abstract

Pulse magnetic field-assisted hydrothermal method was used for the preparation of Cr–Ni codoped ZnO diluted magnetic semiconductors. XRD analysis reveals that all the samples have hexagonal wurtzite structure. HRTEM, EDS measurements and XPS results ensure that the divalent Cr and Ni ions have incorporated in the wurtzite host matrix without any detectable impurity phase formed. *M–H* and ZFC/FC curves of the samples reveal the enhancement of ferromagnetism resulted from the magnetic field processing. XPS measurement and Raman scattering spectra indicate that the content of oxygen vacancies in the sample increases with pulse magnetic field processing. According to the bound magnetic polaron model, this may be the reason for the sample with magnetic field processing having better ferromagnetism than that without field processing.

Keywords: ZnO; Diluted magnetic semiconductor; Hydrothermal method; Ferromagnetism; Pulsed magnetic field

1. Introduction

Over the past decade, diluted magnetic semiconductors (DMSs), which refers to the cationic site of the host semiconducting lattice partially substituted by transition-metal (TM) element, have attracted considerable attention of scientific community due to their potential applications in spin electronics and magnetic devices [1–3]. Owing to the combined effect of magnetic and semiconducting behaviors, diluted magnetic semiconductors which the spin degree of freedom is added to charge, exhibit interesting properties such as magnetic, opto-electronic, magneto-electronic, magneto-optical and spintronic [4]. The crucial challenge for practical application of the DMSs materials is the achievement of ferromagnetic DMSs with Curie temperature (T_C) above room-temperature. Dietl et al. [5] predicted that the T_C of a p-type ZnO semiconductor doped with 5% Mn would be higher than the room temperature. In addition, Sato and Katayama-Yoshida [6] theoretically demonstrated that ZnO doped with TM atoms such as V, Cr, Fe, Co, and Ni exhibit ferromagnetic stability using first-principle calculations.

Lately, ZnO semiconductor doped with TM to achieve ferromagnetism at room temperature becomes one of the most extensively studies of DMSs materials. Recent computational results calculated by the first-principles method based on the density functional theory (DFT) showed that codoping in ZnO could change the antiferromagnetic interaction into ferromagnetism due to hybridization [7]. So far, many experimental results about codoping have been reported. Singhal et al. [8] reported that the codoping Mn and Co into ZnO enhanced the ferromagnetic ordering. Also, Aljawfi et al. [9] suggested that

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Cr/Co codoped ZnO nanoparticles improved the ferromagnetism with increasing Cr doping. And Yan et al. [10] reported the same tendency in Zn(Co)O thin films as increasing Cr dopant. These studies indicate that codoping would be a potential approach to enhance ferromagnetism in TM-doped ZnO. Thus, in our current studies, chromium (Cr) and nickel (Ni) were chosen as the dopants among TM elements.

There are many ways to synthesize TM-doped ZnO, which could be chemical vapor deposition, physical vapor deposition, solid state reaction, hydrothermal, sol–gel, etc. [11–15]. Among these methods, hydrothermal method becomes the most efficient choice for its advantages of easy control and uniform products [16]. In addition, the magnetic field has been applied as an effective way to influence the hydrothermal growth, morphology and the properties of nanomaterial, such as Cr-doped ZnO [17], Fe_3O_4 nanowires [18], Co_3O_4 nanocubes/nanospheres [19] and so on. In these papers, it can be found that an external magnetic field influences significantly the growth behavior and the exchange interactions between the spins in the nanoparticles during the hydrothermal process. In view of this, the effect of pulsed magnetic field on the ferromagnetism of Cr–Ni codoped ZnO diluted magnetic semiconductor is really to be expected.

In this paper, 1 at% Cr and 1 at% Ni codoped ZnO was synthesized by hydrothermal method with 4 Tesla (T) pulsed magnetic field. The effects of pulsed magnetic field on the structure, morphology and magnetic properties were investigated by several techniques.

2. Experimental

2.1. Procedure

Potassium hydroxide solution (1.33 M) was slowly dropped into the zinc acetate solution (1.00 M) and stirred for 0.5 h. Then, chromium chloride solution (0.01 M), and nickel acetate solution (0.01 M) were slowly dropped into the precipitated mixture followed by stirring for 0.5 h. The whole mixture was then transferred into a Teflon-lined titanium alloy autoclave, which was maintained at 200 °C for 4 h under 4 T pulsed magnetic field. Finally, the reacted products were washed with deionized water repeatedly and dried at 80 °C for 10 h. As a contrast, another sample was synthesized in the same conditions but without external field. The samples were hereafter named as ZnO–Cr–Ni-4 T and ZnO–Cr–Ni-0 T for the reaction process with and without magnetic field, respectively. Similarly the sample of pure ZnO synthesized by the same method without magnetic field and any dopants was named as ZnO.

2.2. Materials characterization

The microstructure of the samples was determined by X-ray diffraction (XRD, D/MAX) with Cu Kα radiation ($\lambda = 1.5406$ Å), field emission scanning electron microscopy (JSM-6700F Cold FESEM) and high resolution transmission electron microscopy (JEM-2010F HRTEM). The X-ray diffraction patterns were analyzed by XPERT Plus program using Rietveld whole profile fitting method. The TEM (JEM-2010F) attached to energy-dispersive spectroscopy (EDS, INCA, Oxford) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) were used to determine the presence of Zn, Cr, Ni, and O in the powder samples. Raman scattering spectra of the samples were measured with a Renishaw Invia Confocal micro-Raman System using 785 nm line as excitation source. Magnetic properties of the samples were measured by the vibrating sample magnetometer (VSM, Lakeshore 7404). Temperature dependent magnetization curves, during zero field cooling (ZFC) and field cooling (FC), were carried out by Physical Property Measurement System (PPMS-9, Quantum Design).

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of ZnO–Cr–Ni-4 T and ZnO–Cr–Ni-0 T samples. Using XPERT Plus program, the crystal structure was refined by Rietveld's profile technique in the hexagonal structure with $P6_3mc$ space group. The Reitveld refined patterns and curves giving the difference between the experimentally observed patterns and the computationally refined patterns are showed in Fig. 1. It can be seen that all the diffraction peaks are sharp and in agreement with the standard peaks of pure ZnO (JCPDS no. 36-1451). All the investigated samples are hexagonal wurtzite structure. And the structure is not disturbed by codoping and magnetic field. Further, using the refined patterns, the unit cell parameters (a, b, c) along with the agreement factors (Rexp, R, S) were calculated and represented in Table 1. The obtained unit cell parameters are in very good agreement with the wurtzite ZnO structure ($a = b = 3.249$ Å and $c = 5.206$ Å). It indicates that there are not any detectable other phases related to either Cr or Ni in both samples except ZnO phase. In view of the argument that XRD may not be a very reliable technique to catch tiny

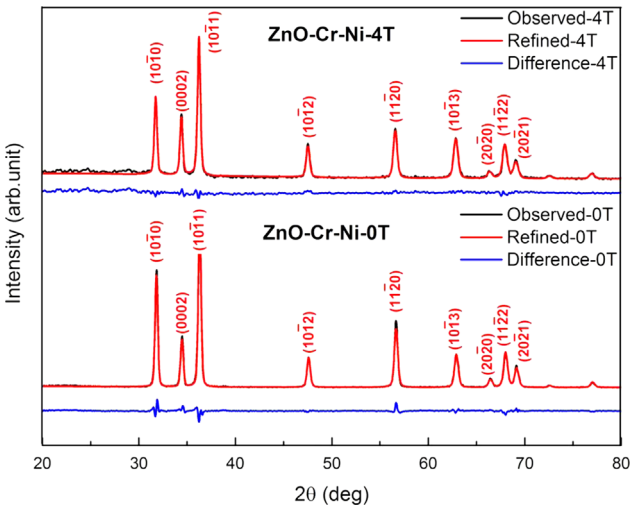

Fig. 1. X-ray diffraction and Rietveld refined patterns of Zn–Cr–Ni-0 T and ZnO–Cr–Ni-4 T.