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Research Article

Effects of Temperature on the Microstructure and Magnetic Property of Cr-Doped ZnO DMS Prepared by Hydrothermal Route Assisted by Pulsed Magnetic Fields

Shiwei Wang, Min Zhong, Cong Liu, Ying Li, Mingyuan Zhu, Hongming Jin, and Yemin Hu

Laboratory for Microstructures/School of Materials Science and Engineering, Shanghai University, 149 Yanchang Road, Shanghai 200072, China

Correspondence should be addressed to Yemin Hu; huyemin@shu.edu.cn

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In the present work, Cr-doped ZnO diluted magnetic semiconductor was synthesized by hydrothermal method under pulsed magnetic fields. The samples were characterized by XRD, SEM, VSM, Raman, and XPS techniques. Results demonstrated that Zn ions in the ZnO crystal lattice were partially displaced by Chromium (III) ions. All samples show room temperature ferromagnetism which was enhanced by pulsed magnetic fields. The mechanism of ferromagnetism of Cr-doped ZnO particles was discussed.

1. Introduction

Over the past few decades, diluted magnetic semiconductors (DMSs) have been attracted considerable interests due to their versatile potential applications in spin electronic devices, such as spin field-effect transistors; nonvolatile memory devices; and quantum computer [1–7]. Zinc oxide has been considered as one of the promising DMS candidates for its superior semiconductor performance [8]. It also possesses outstanding piezoelectric property and excellent chemical stability [9, 10]. Since the study of Dietl et al. [1] predicted that the Curie temperature (Tc) of TMs-doped ZnO DMS could be above room temperature (RT), and furthermore Sato and Katayama-Yoshida [11] predicted that ZnO-doped with Cr, V, Fe, Ni, and Co could be RT ferromagnetic (FM), TMs-doped ZnO DMSs have been extensively investigated. A challenge for the application of ZnO DMSs is to enhance their room temperature magnetic property. Our group recently has successfully developed a novel hydrothermal method under high magnetic field to prepare a series of transition metal ions (Cr^{3+}, Mn^{2+}, and Co^{2+})-doped ZnO DMSs [12–14]. Magnetic cations-doped ZnO synthesized under high magnetic field shows better FM behavior. It is believed that the magnetic field provided an external energy to facilitate metal ions migrating into the ZnO lattice and caused more lattice defects. The hybridization effect between the metal ions and lattice defects changed the magnetic property of DMSs.

Among the doping elements, Cr draws the most attention [15, 16]. Currently, many methods have been reported to fabricate Cr-doped ZnO DMSs [17–21], such as vapors phase growth, thermal decomposition, seed-mediated, and reverse micelle. However, in some reports, the results are opposite even the samples were prepared in the same way, for example, some samples exhibited paramagnetic (PM), but some exhibited FM. It indicates that the magnetic performance of ZnO DMSs is very sensitive to the reaction conditions. Therefore, the present work is to introduce an external high magnetic field and well control the chemical reaction conditions to enhance the magnetic property of DMSs. We intend to investigate the effects of the magnetic field together with the reaction temperature on the microstructure, morphology, and magnetic properties of Cr-doped ZnO DMS prepared by hydrothermal method under high pulsed magnetic fields.

2. Experimental

Zinc chloride ($ZnCl_2$), chromic chloride ($CrCl_3{\cdot}6H_2O$), aqueous ammonium ($NH_3{\cdot}H_2O$), and ammonium chloride (NH_4Cl) were of used. All chemical reagents were analytical

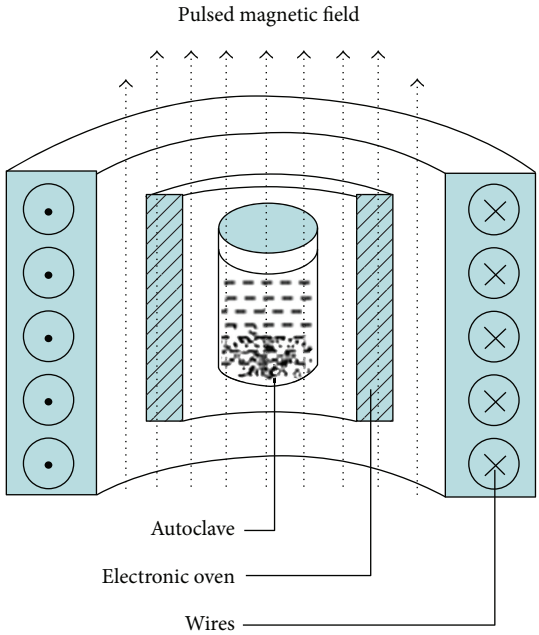

Figure 1: The schematic diagram of pulsed magnetic fields assisting hydrothermal system.

grade without any further purification. A 6 mL 2 M zinc chloride solution; 6 mL 0.04 M chromic chloride solution; and 8 mL of buffer solution (pH = 10.0, NH_3/NH_4Cl (aq)) were mixed sequentially. The nominal content of Cr ions in ZnO was about 2 at%. After stirring for 1 h, the mixture was transferred into a 25.0 mL Teflon-lined titanium alloy autolave. The autoclaves were placed in an electric oven and heated at 100–180°C range of temperature for 4 hours with or without pulsed magnetic fields (4 T). The experimental setup is illustrated as in Figure 1. The mixture was then filtrated, and the solid product was washed twice with distilled water and once with absolute ethanol. It was then dried in 80°C air for 8 h. Samples prepared under 4 T pulsed magnetic fields at N°C were referred to as S-N°C-4 T and those without pulsed magnetic fields as S-N°C-0 T. Pure ZnO was prepared with the similar process at 180°C.

The microstructure of the samples were characterized by X-ray diffraction meter (XRD, D/max 2550 V, Rigaku, Cu Kα, λ = 0.15406 nm). The morphologies of above-prepared samples were observed by scanning electron microscopy (SEM, JSM-6700F, JEOL). The magnetic hysteresis loops of the specimens were estimated by vibrating sample magnetometer (VSM, Lakeshore 7407). Raman scattering (RS, inVia plus, Renishaw) was used to record the information about the crystal defect and change of free carriers in the samples. The valence state of element was analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250).

3. Results and Discussions

Figure 2 shows XRD patterns of Cr-doped ZnO particles prepared at different reaction temperature with and without pulsed magnetic fields. For all samples, all diffraction peaks

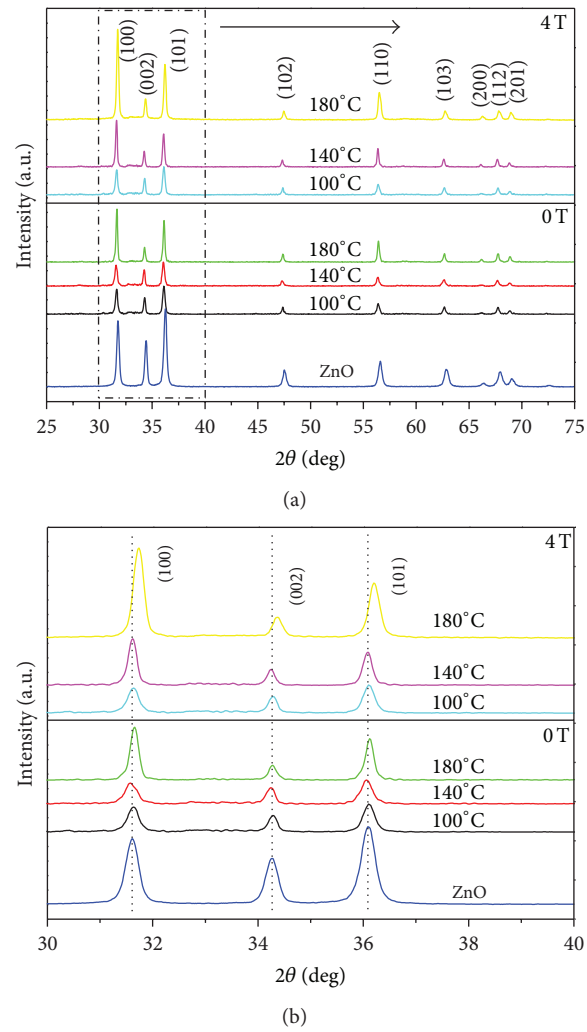

Figure 2: The XRD patterns of the samples.

correspond well to the hexagonal wurtzite ZnO crystal structure (space group $P6_3mc$; JCPDS card number 36-1451). No other phases or impurities were found in the crystals. Compared with pure ZnO, main peaks of Cr-doped ZnO shifted slightly to higher angles. It indicated that the distortion in the lattice was brought by Cr doping into the ZnO crystal lattice. As the radius of Cr^{3+} ions (0.63 Å) is smaller than that of Zn^{2+} ions (0.74 Å), the lattice volume of Cr^{3+}-doped ZnO would be decreased. The higher the content of Cr^{3+} in ZnO is, the smaller the lattice constants are, and the greater the distortion of ZnO crystal lattice will be. It was observed in Figure 2(b) that both higher reaction temperature and pulsed magnetic fields resulted in enhanced shifts of the main peaks of Cr-doped ZnO. These phenomena demonstrated that a combination of high reaction temperature and pulsed magnetic fields were favorable for Cr^{3+} incorporated ZnO.

The morphologies of Cr-doped ZnO DMS are shown in Figure 3. Table 1 gave the average sizes of the samples. The sizes of sample S-100°C-0 T were about 50–100 nm in diameter and 1–3 μm in length. For sample S-100°C-4 T, the diameter and length increased to about 100–150 nm and

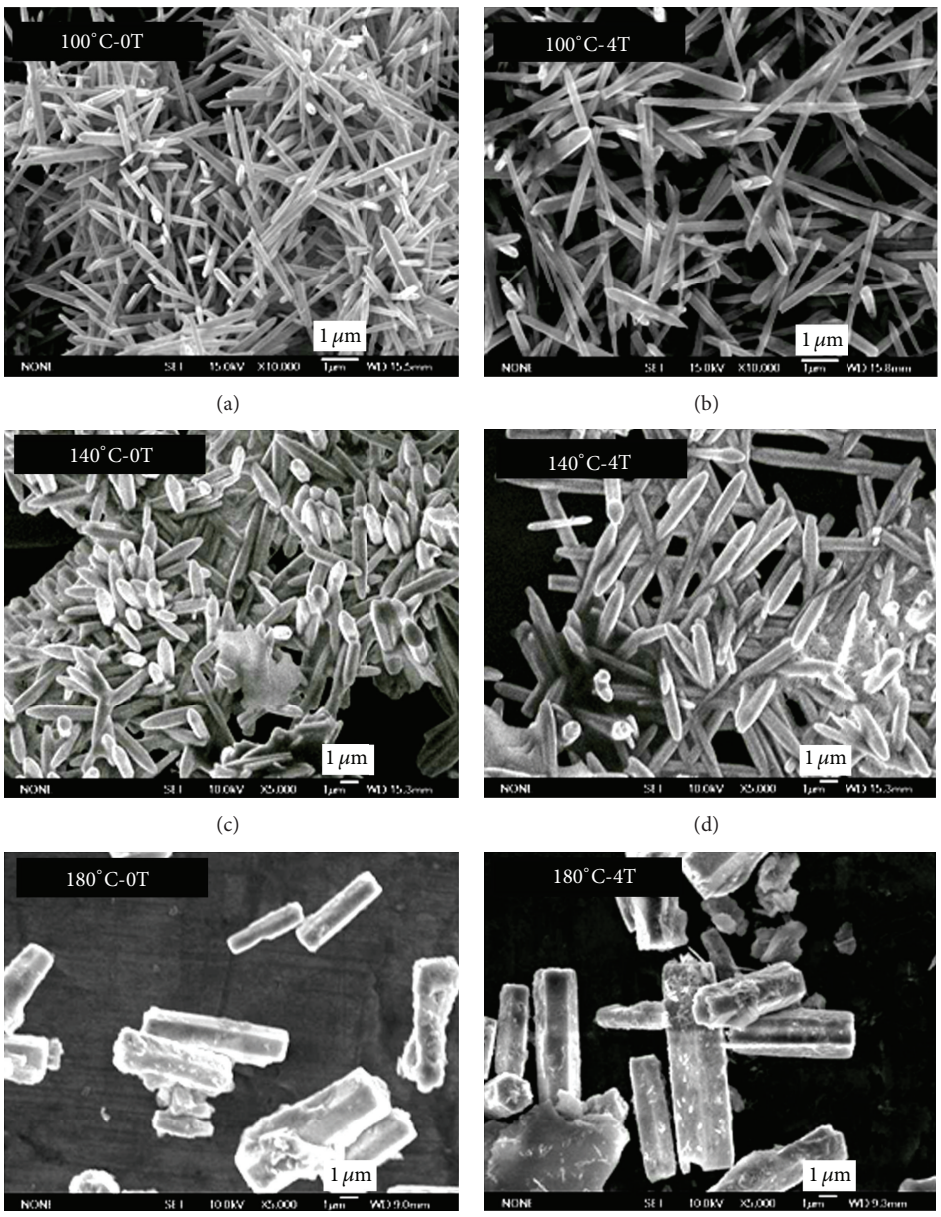

Figure 3: The SEM images of the samples: (a) 100°C-0 T, (b) 100°C-4 T, (c) 140°C-0 T, (d) 140°C-4 T, (e) 180°C-0 T, and (f) 180°C-4 T.

Table 1: Average size of the samples.

Field (T)	Sizes parameters (length, diameter)		
	100°C	140°C	180°C
0	1–3 μm, 50–100 nm	5 μm, 700 nm	7 μm, 1 μm
4	4 μm, 100–150 nm	6 μm, 800 nm	8 μm, 1.5 μm

4 μm, respectively. ZnO particles prepared at 140°C were larger than those prepared at 100°C. The sizes of sample S-140°C-4 T were larger and more uniform than sample S-140°C-0 T. When reaction temperature was raised to 180°C, the sizes of ZnO particles became much larger, especially their diameters. It could be concluded that pulsed magnetic fields accelerated the growing of ZnO particles, by supplying additional energy to the particle crystalizing process.

Figure 4 shows the magnetic hysteresis loops (M-H) of Cr-doped ZnO DMS measured at room temperature. All samples exhibited room temperature ferromagnetism. The saturation magnetizations (Ms) of the samples varied in the range of 0.0227–0.0716 emu/g, as listed in Table 2. Δ represented the difference of Ms of two of the samples, prepared at the same reaction temperature with and without pulsed magnetic fields, respectively. Ms increased with reaction temperature increased from 100°C to 180°C. For the samples of the same reaction temperature, the Ms of the samples prepared under 4T pulsed magnetic fields were higher than that of the samples under no pulsed magnetic fields.

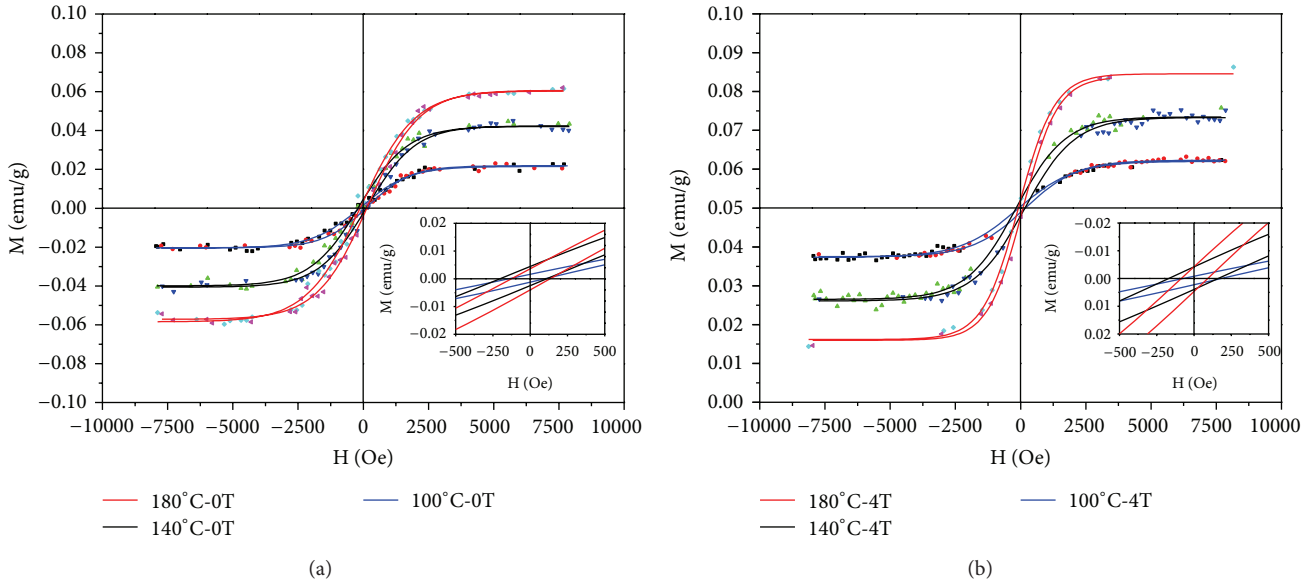

Figure 4: The magnetic hysteresis loops of the Cr-doped ZnO particles: (a) 0 T and (b) 4 T.

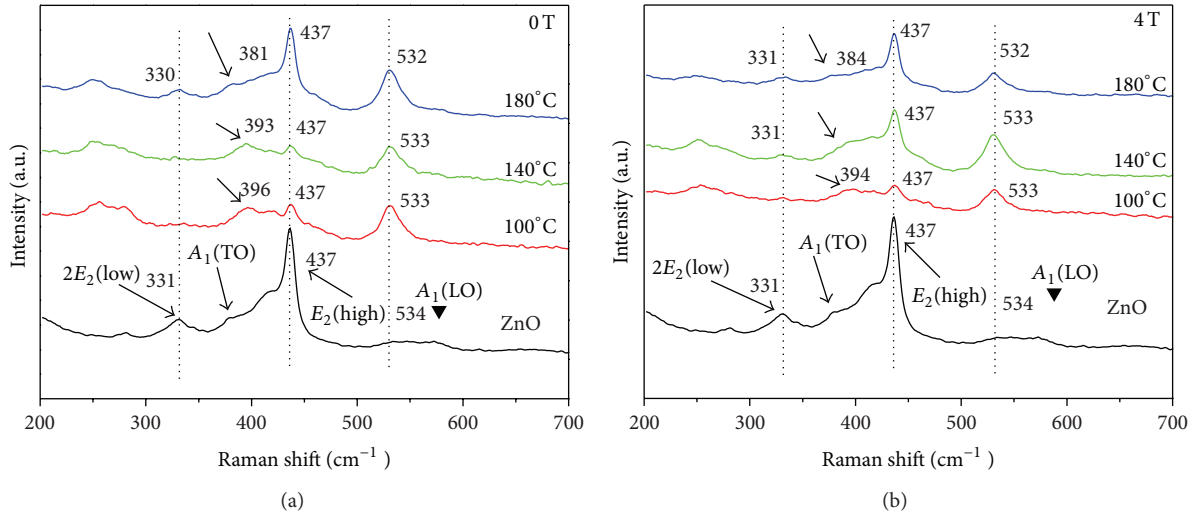

Figure 5: The Raman spectra of the samples.

The results indicated that pulsed magnetic fields do enhance the ferromagnetic properties of Cr-doped ZnO DMS. As mentioned before, both higher reaction temperature and applying pulsed magnetic fields affect the hydrothermal fabrication process of Cr-doped ZnO DMS, more Cr^{3+} ions were incorporated into ZnO lattice. Here M-H loops demonstrated that the more the Cr^{3+} ions-doped into ZnO, the stronger the room temperature ferromagnetism of ZnO DMS. According to the BMP model, the occurrence of strong electronic coupling between bound polarons and Cr^{3+} ions would form bound magnetic polarons [22], which was suggested to play an important role in the ferromagnetic origin of Cr-doped ZnO DMS [23, 24].

Raman scattering is a versatile technique for detecting the defects and lattice disorder in the host lattice [25]. Figure 5 illustrates the unpolarized Raman spectra of the Cr-doped and pure ZnO samples in the range 200–700 cm^{-1} at room temperature. The spectra revealed standard phonon modes at 331, 381, 437, and 534 cm^{-1} of pure ZnO [26, 27]. For the Cr^{+3}-doped samples, there was a shift towards the low-frequency, depending on the structural disorder and crystal

Table 2: The saturation magnetizations of the samples.

	Ms (emu/g)		
	100°C	140°C	180°C
0 T	0.0227	0.0418	0.0592
4 T	0.0279	0.0515	0.0716
Δ	0.0052	0.0097	0.0124

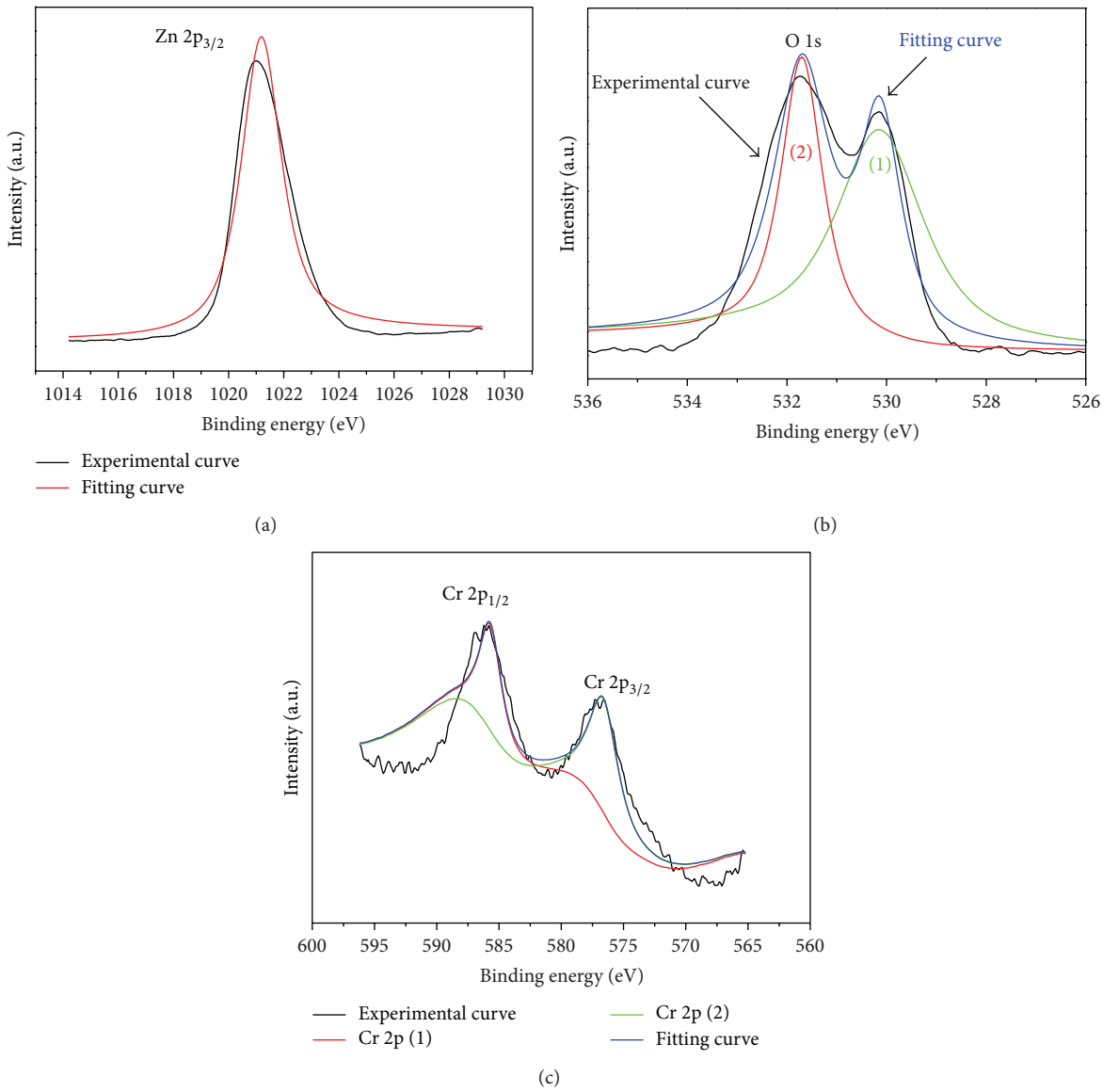

FIGURE 6: XPS spectrum of Cr-doped ZnO DMS.

defects of the samples. The zone-center optical phonons of the wurtzite structure of ZnO could be classified according to the following irreducible representations:

$$\Gamma_{\text{opt}} = 1A_1 + 2B_1 + 1E_1 + 2E_2. \quad (1)$$

The B_1 modes were silent in Raman scattering, whereas A_1 and E_1 modes were polar and hence exhibit different frequencies for the transverse-optical (TO) and longitudinal-optical (LO) phonons [28]. The nonpolar E_2 modes have two frequencies, namely, E_2 (high) and E_2 (low), associated with the motion of oxygen (O) atoms and zinc (Zn) sublattice, respectively [29]. For all the samples, the sharpest and strongest peak at 437 cm^{-1} could be assigned to E_2 (high), which was the strongest mode in wurtzite crystal structure. The peaks at 331 and 380 cm^{-1} were assigned to the second-order vibration mode and A_1 (TO) mode, respectively. The peak at 437 cm^{-1} was sensitive to the crystal stress, while the peak at 580 cm^{-1} was sensitive to the change of free carrier concentration [25, 30]. As Wang et al. [31] reported that the intensity of A_1 (LO) mode decreased with the increase in carrier concentration. In the present work, the A_1 (LO) modes of all the Cr-doping ZnO samples disappeared, which indicated the increase of free carrier induced by Cr doping. Kittilstved et al. [32] suggested that defect-bound carriers such as point defects hybridization with magnetic dopants would induce ferromagnetism in transition metal (TM) ions-doped ZnO DMS. In this study, it was found that pulsed magnetic fields induced Cr^{3+} ions substitute into the ZnO crystal lattice. Since more defects were introduced into the crystal lattice under pulsed magnetic fields, it resulted in the more hybridization between the defects and Cr dopants, which may be responsible for the result of room temperature

ferromagnetism and the enhancement of saturation magnetization of the pulsed magnetic fields processed Cr-doped ZnO DMS.

In order to investigate the chemical state of the host and dopant elements, the XPS studies were undertaken. XPS analysis shows the presence of Zn, Cr, and O elements in Cr-doped ZnO. The overlapped bands were resolved into separated peaks by using XPS PEAK41 software. The Zn $2p_{3/2}$, O 1s, Cr $2p_{3/2}$, and Cr $2p_{1/2}$ XPS spectral regions of the Cr-doped ZnO DMS prepared at 100°C without pulsed magnetic fields were shown in Figure 6. Based on the Gauss fitting, the Cr $2p_{3/2}$ peak position was at 576.6 eV in the Cr-doped ZnO nanoparticle. It was clearly different from 574.2 eV of Cr metal and 576.0 eV of Cr^{2+}, but quite close to the peak position of Cr $2p_{3/2}$ (576.7 eV) in Cr_2O_3 [33]. It suggested that Cr^{+3} ions were actually the incorporated dopants.

4. Conclusions

Cr-doped ZnO DMSs were prepared by the hydrothermal method at different temperature under pulsed magnetic fields. All samples kept the hexagonal wurtzite structure and possessed room temperature ferromagnetism. High reaction temperature and pulsed magnetic fields both promoted higher Cr^{+3} ions incorporation. The crystals grew bigger as the temperature rose and pulsed magnetic fields were applied. Both higher reaction temperature and applying pulsed magnetic fields enhanced the magnetic property of Cr-doped ZnO DMS. The ferromagnetism may be results of free carrier induced by Cr doping. It was demonstrated that the Zn^{+2} ions were displaced by the Cr^{+3} ions in the doping process.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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