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Effect of oxygen vacancy induced by pulsed magnetic field on the room-temperature ferromagnetic Ni-doped ZnO synthesized by hydrothermal method

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ABSTRACT

Room temperature ferromagnetic 2% Ni doped ZnO rods were synthesized by high pulsed magnetic field-assisted hydrothermal method. A detailed study on the effect of high pulsed magnetic field on morphology, structural and magnetic properties of the ZnO rods has been carried out systematically by varying the intensity of field from 0 to 4 T. X-ray diffraction, Energy-dispersive spectroscopy measurements, and Raman spectra analysis suggest that all the samples have hexagonal wurtzite structure without detectable impurity. Field emission scanning electron microscopy images indicate that the particle size of samples decrease with increasing intensity of field. High resolution transmission electron microscopy observation ensures that the Ni ions addition do not change the wurtzite host matrix. X-ray photoelectron spectroscopy confirms the incorporation of Ni elements as divalent state and the dominant presence of oxygen vacancies in samples fabricated under 4 T pulsed magnetic field. Hysteresis loops demonstrate that the saturation magnetization increased regularly with the mounting magnetic field. On the framework of bound magnetic polaron model, the rising content of oxygen vacancies, as donor defect, lead to the stronger ferromagnetism in samples with pulsed magnetic field. Our findings provide a new insight for tuning the defect density by precisely controlling the intensity of field in order to get the desired magnetic behavior at room temperature.

1. Introduction

Over the past ten years or so, the research on ferromagnetism in diluted magnetic semiconductors (DMSs) and diluted magnetic oxides (DMOs) has attracted intense attention for potential new applications in spin-based information-processing technologies [1–5]. One significant challenge to promote these practical applications of DMSs materials is the preparation of intrinsic ferromagnetic DMSs with Curie temperature (T_C) above room-temperature. Despite the many investigations, the origin and control of ferromagnetism in DMSs is arguably the most controversial research in materials science and condensed-matter physics [6]. Thus a detailed understanding of ferromagnetism in DMSs is extreme necessary for device applications. Since the predication of high temperature ferromagnetism by Ditel et al. [7] and Sato et al. [8] in transition metals (TM, such as Mn, V, Cr, Fe, Co and Ni)) doped ZnO, enormous efforts have been mounted, encompassing both experimental and theoretical research, toward understanding the underlying origin of ferromagnetism in TM-doped ZnO. Among the TM elements, nickel (Ni) is the most efficient dopant to improve and tune the optical, electrical and magnetic properties of ZnO semiconductor due to its similar ionic radius, abundant electronic states and the divalent state. The intrinsic ferromagnetism was observed in the Ni-doped ZnO samples prepared by the sol–gel and hydrothermal method [9]. However, Yin et al. [10] found that Ni-doped ZnO films synthesized by rf magnetron sputtering were paramagnetism at room temperature. The origin of room temperature ferromagnetism (RTFM) of Ni-doped ZnO is still controversial.

Recently, the role of defect on the ferromagnetism has been reminded to explain the sensitive of ferromagnetic property about the preparation method of DMSs. The defect physics of ZnO is quite complex. According to the bound magnetic polarons (BMP) model

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proposed by J.M.D Coey et al. [11], the magnetic exchange interaction between oxygen vacancy and transition-metal ions makes all spins align to the same direction around the defect. Ferromagnetism achieves while these BMPs overlap. It is well known that p-type TM-doped ZnO DMS is difficult to obtain, because of the high formation energy of oxygen interstitials (O_i), zinc vacancies (V_{Zn}) and oxygen antisite defect (O_{Zn}) as acceptors in ZnO. However, oxygen vacancies (V_O), as donor defect, are easier to form in the natural ZnO to induce n-type conductivity.

This work focuses on the investigation of the oxygen vacancy induced RTFM in Ni-doped ZnO nanorods by introducing pulsed magnetic field during the hydrothermal process. The correlations between room temperature ferromagnetism and high pulsed magnetic field were established based on the analysis of the crystal structure, morphology and magnetic properties of 2% Ni (at%, nominal composition)-doped ZnO DMS synthesized by hydrothermal method.

2. Experimental details

Ammonia buffer solution was slowly dropped into the zinc acetate solution and stirred for 0.5 h. Then, nickel acetate solution was added into the precipitation state mixture followed by stirring for 0.5 h. The whole mixture was then transferred into Teflon-lined titanium alloy autoclave, and maintained at 200 °C for 4 h under 0, 1, 2, 3 and 4 T (Tesla) pulsed magnetic field. Finally, the reacted products were washed with deionized water repeatedly and dried in vacuum drying oven at 80 °C for 10 h. The samples were collected and hereafter named as 0 T, 1 T, 2 T, 3 T and 4 T samples according the intensity of magnetic field during the fabrication process, respectively.

The microstructure of the samples was determined by X-ray diffraction (XRD, D/MAX) with Cu Kα radiation (λ = 1.5406 Å), field emission scanning electron microscopy (FESEM, JSM-6700F Cold) and high resolution transmission electron microscopy (HRTEM, JEM-2010F). The Energy-dispersive spectroscopy (EDS, INCA Oxford) attached to TEM and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) were used to determine the presence of Zn, Ni and O in the powder samples. Raman scattering spectra (Raman, INVIA) 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).

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of the samples synthesized in magnetic field of 0, 1, 2, 3 and 4 T and the enlarged diffraction from 30 to 40°. All the XRD peaks of as-prepared 0–4 T samples in this figure can be indexed to the hexagonal wurtzite ZnO (JCPDS card no. 36-1451) with $P6_3mc$ space group. The sharp and intense XRD diffraction peaks of all the samples show their high crystallization characteristics. The structure is not disturbed by dopant and pulsed magnetic field. Neither Ni metal nor its oxide phases were observed within the detection limit of XRD. The enlarged diffraction peaks from 30° to 40° given in Fig. 1(b) show that the peak position shift to the larger angles for the samples prepared with pulsed magnetic field. According to the Bragg equation ($2d\sin\theta = n\lambda$), the peak positions would move to larger diffraction angles when the interplanar spacing become smaller. These shifts agree with that the ion radius of Ni^{2+} (0.69 Å) is less than that of Zn^{2+} (0.74 Å). That is, Ni ions were incorporated into ZnO lattice sites without any detectable secondary phases. In view of the sensitivity of XRD, XPS measurements were discussed later.

3.2. FESEM, HRTEM and EDS measurements

Fig. 2 gives the FESEM images of as-synthesized Ni-doped ZnO with (a) 0 T, (b) 1 T, (c) 2 T, (d) 3 T and (e) 4 T field, respectively. Fig. 2(f) shows the relationship between intensity of pulsed magnetic field and crystal size estimated from SEM images. It can be clearly seen that hexagonal rod-like ZnO was formed for all the samples. Interestingly, the average length and width as displayed in the inset of Fig. 2(f) of crystal decrease obviously with the enhancement of magnetic field. Chu et al. [12] analyzed this phenomenon from the magnetization energy of nanocrystal. The value of the magnetic energy can be illustrated by $U = -\chi B^2/[2\mu_0(1+N\chi)^2]$, where N is the demagnetization factor, and χ is the magnetic susceptibility. For ZnO, U_c is larger than $U_{a,b}$ ($\chi_c<\chi_{a,b}$), so c-axis needs more magnetization energy and is less stable in magnetic field during crystal growth process. Therefore, the growth rate along c-axis is suppressed and the average length of rods significantly decreases. More than that, both length and width of ZnO hexagonal rods decreased apparently with the mounting value of magnetic field. Actually, it can be concluded from crystallography more easily. Taking the characteristic of high pulsed magnetic field into consideration, strong vibrations induce by pulsed magnetic field will provide the flow of the solution and an indirect rotation effect during the preparation process. These influences will increase the nucleation rate and suppress the crystal growth. Thus, the crystal size declines with the increasing intensity of field as shown in Fig. 2(f).

The HRTEM images of 2%Ni-doped ZnO samples prepared under 0 T and 4 T pulsed magnetic field are showed in Fig. 3(a) and (b), respectively. And the corresponding low magnification TEM images and Fast Fourier Transform (FFT) patterns of the selected area along $[21\bar{3}0]$ and $[12\bar{3}0]$ zone axes were inserted. EDS analysis confirms the composition of ZnO with the existence of Zn, O and Ni ions in the samples. It can be seen that both of the samples are single crystals and no cluster or other phase is found. Well-resolved lattices with a measure interplanar spacing of 0.26 nm is showed in 0 T and 4 T samples, which is consistent with the standard distance between (0002) crystal planes of ZnO. The hexagonal wurtzite structure was not changed by the incorporation of 2% Ni and 4 T pulsed magnetic field, which agrees well with the XRD results. Considering the EDS analysis, Ni ions did dope into ZnO matrix without any secondary phase.

3.3. XPS results

To give more direct evidence of the substitutional effects of Ni, XPS measurement was employed to investigate the electronic and chemical states of the host and dopant elements. The results are shown in Fig. 4 and all data are corrected with respect to the standard peak of C 1s at 284.6 eV. The typical XPS survey spectra of 2% Ni doped ZnO with and without field are showed in Fig. 4(a). No extra peaks corresponding to any other impurity atoms were detected and Ni elements exist in the samples obviously. The analyzed XPS core level high-resolution spectra of Ni 2p and O 1s are shown in Fig. 4(b–d), respectively, in which overlapped band were deconvoluted into separate peaks by Gaussian fitting using XPS peakfit software.

The high-resolution Ni 2p spectra of samples with and without pulse magnetic field processing are shown in Fig. 4(b), corresponding satellite structure labeled as 'sat' are also clearly observed in this figure. The peaks of Ni $2p_{3/2}$ and Ni $2p_{1/2}$ core levels are found to be centered at 856.0 eV, 873.9 eV for 0 T and 855.9 eV, 873.6 eV for 4 T, respectively, whereas the corresponding satellite