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Effect of thermal treatment on room-temperature ferromagnetism in Co-doped ZnO powders

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ABSTRACT

The Co-doped ZnO powders were synthesized by sol–gel method, and treated at different temperatures (673–873 K) in the presence or absence of NH_3 atmosphere for 0.5 and 2 h, respectively. X-ray diffraction (XRD) and vibrating sample magnetometer (VSM) show that better crystal structure can cause larger ferromagnetism and the second phase (Co_3O_4) is the reason for saturation magnetization decrease of the sample sintered at higher temperature in air. XPS and nuclear magnetic resonance (NMR) prove the existence of Co^{2+} ions in the $Zn_{0.9}Co_{0.1}O$ and the absence of Co clusters, indicating intrinsic ferromagnetism of the samples treated in air. However, strong ferromagnetism of the samples annealed in NH_3 is ascribed to cobalt nitride formed during annealing.

1. Introduction

Most recently, diluted magnetic semiconductor (DMS) has attracted extensive attention because of its potential application prospect. Specially, ZnO-based DMSs with broad band gap (3.3 eV) have become one of the most important candidates for high Tc ferromagnetism. Up to now, most of the studies focused on the films fabricated by physical methods, such as PLD, but few of them on Co-doped ZnO powders fabricated by chemical methods [1–3]. Although some reports were about the effects of temperature on the magnetic property of ZnO-based DMSs [4,5], the results from different groups are scattered, and few explanations were given. In this paper, we report the magnetic property of $Zn_{0.9}Co_{0.1}O$ powder fabricated by chemical method [6] and explore the effect of annealing condition (temperature and NH_3 atmosphere) on structure and magnetic property.

2. Experiments

Zinc acetate, cobalt acetate and citric acid in appropriate proportions were dissolved in distilled water; the resulting solution obtained by durative stirring at 353 K for 4 h was dried at 453 K to form a dark precursor. Then the precursors were treated at a different temperature, Ts, in the absence or presence of NH_3 gas for 0.5 and 2 h, respectively. In this paper, much attention has been paid to the influence of treating conditions, especially NH_3 atmosphere, on structure and the formation of magnetic semiconductor.

The crystal structure and magnetic property of powders were characterized using X-ray diffraction (XRD, Philips X'pert Pro) and a vibrating sample magnetometer (VSM, Lakeshore7304). XPS studies were performed using PHI 5702 XPS/AES system to identify the valence state of Co. In order to exclude Co clusters, zero field ^{59}Co spin echo nuclear magnetic resonance (NMR) spectrum has been recorded at 6 K using a Tecmag spin echo NMR spectrometer with digital quadrature detection.

3. Results and discussion

Fig. 1(a) shows XRD patterns of Co-doped ZnO powder samples sintered in air for 0.5 h. It is clear that all the samples have hexagonal wurtzite structure. The weak peak intensity and the large linewidth imply the poor crystallinity when the sample was sintered at 673 K and the crystallinity becomes better with increasing T_s when $T_s < 723$ K. However, Co oxides (Co_3O_4) appear

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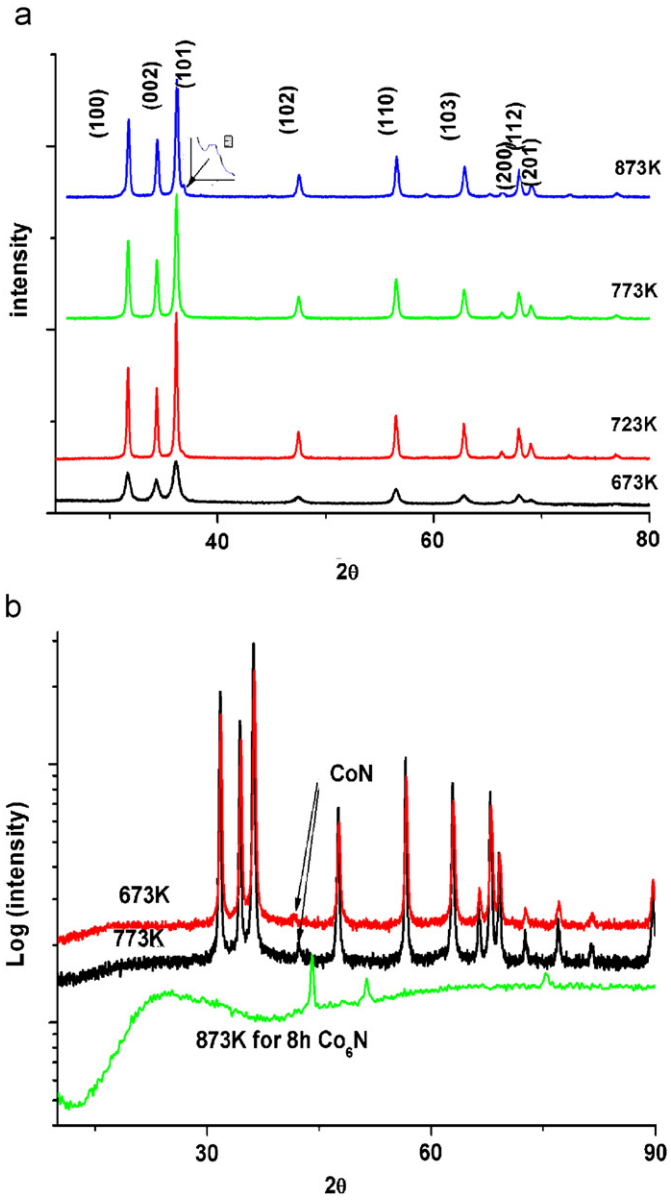

Fig. 1. XRD patterns of powder samples treated (a) in air for 0.5 h (the arrow is marker of Co_3O_4) and (b) in NH_3 gas at different temperatures for 2 h.

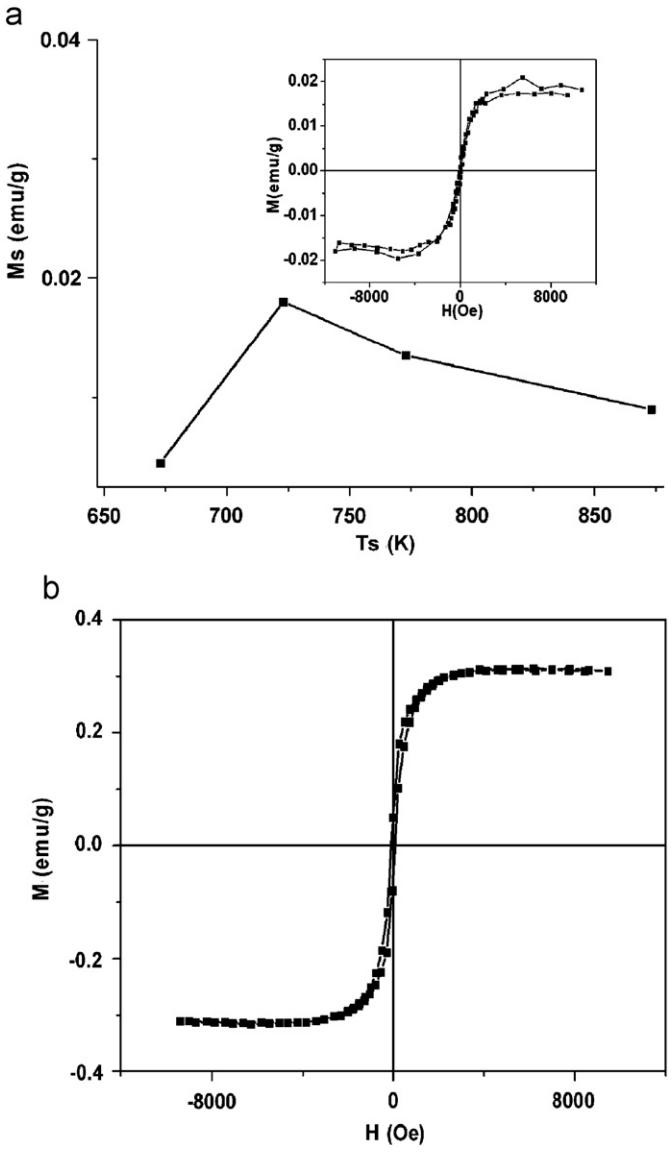

Fig. 2. (a) Sintered temperature dependence of the ferromagnetism of different samples, the inset is the magnetic hysteresis loop of the sample sintered at 723 K in the absence of NH_3 ambiance for 0.5 h and (b) hysteresis loops of the samples sintered in NH_3 at 773 K for 2 h.

when the T_s rises up to be higher than 873 K. In Fig. 1(a), all diffraction peaks shift toward the low-angle side compared to those of pure ZnO, due to the strain produced by the organisms rapid combustion. With increasing T_s, all peaks move toward the higher angles, reaching those of pure ZnO. This can be understood by H.P. He's paper [7] in which the strains formed during the growth in the samples were released due to anneal. In addition, the strain release is why the coercive field (H_c) decreases with T_s when $T_s < 773$ K (from 48 Oe for the sample sintered at 673 K to 38 Oe at 773 K), which is different from other reports [5] in which H_c increases first, then decreases and is around 250 Oe. However, CoN occurs when the sample is annealed in NH_3 atmosphere at 673 K for 2 h, and only Co_6N exists at 873 K for 8 h, as shown in the inset of Fig. 1(b).

The inset of Fig. 2(a) shows the magnetic hysteresis loop of the sample sintered at 723 K in the absence of NH_3 ambiance. (The paramagnetic contributions from the sample holder, the sample and diamagnetic contributions from Si substrate have been subtracted from the data). It is seen that the sample is ferromagnetic at room temperature, and ferromagnetism increases with increasing T_s when $T_s < 723$ K, reaches a maximum at $T_s = 723$ K, then decreases with T_s, as shown in Fig. 2(a). Combined with the above XRD results, we suppose that the better sample's crystal structure is responsible for the increase of the ferromagnetism when $T_s < 723$ K, while the decrease in ferromagnetism as $T_s > 723$ K is ascribed to the presence of Co_3O_4 phase (antiferromagnetism). Since the monotone enhancement of magnetization has not been observed when T_s is between 673 and 873 K, and transition temperature T_N of Co_3O_4 is 33 K, the RT-ferromagnetism is not contributed by Co oxides. Some groups have obtained similar results in DMS system [4,5,8,9]. Xavier Mathew [8] and Punnoose et al. [9] think that the ferromagnetism decrease is because of a systematic surface diffusion of the doped magnetic ions with temperature. In this paper, the second phase (Co_3O_4) is the reason, just like the description in Ref. [4]. The hysteresis loops of the sample annealed in NH_3 at 773 K for 2 h are