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Room temperature ferromagnetic properties of ZnFeO thin films prepared by thermal oxidation of ZnFeS thin films

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ABSTRACT

Room temperature ferromagnetism is observed in ZnFeO thin films with different Fe content prepared by thermal oxidation of ZnFeS thin films. ZnFeS thin films were grown on c-plane sapphire substrate by low-pressure metalorganic chemical vapor deposition (LP-MOCVD) equipment. The X-ray diffraction (XRD) patterns indicated that a transformation from ZnFeS to ZnFeO has taken place at optimum annealing temperature of 800 °C, and the $d(0\,0\,2)$ values were gradually enlarged with increasing Fe content and it further indicates Fe atoms substituting for Zn atoms in the lattice. The images of field-emission scanning electron microscope (SEM) of ZnFeO thin films show that the grain size increases with increasing Fe content. It was found that the ZnFeO thin films were ferromagnetic above room temperature.

1. Introduction

Diluted magnetic semiconductors (DMSs) have been of much interest and studied actively in recent years because of the possibility of incorporating the magnetic degrees of freedom in traditional semiconductors [1,2]. Ferromagnetic DMSs have been proposed as pivotal contents in a new category of spin electronics (spintronics) devices that aim to control electron spin currents as well as charge currents to increase data processing speeds, reduce power consumption, reduce hardware dimensions, and possibly introduce new functionalities to semiconductor information processing technologies [3]. A key requirement in realizing most devices based on spins in solids is that the host material be ferromagnetic above room temperature. Dietl et al. suggested ZnO and GaN as candidate having a high Curie temperature (T_c) and a large magnetization [4]. Because II–VI type materials are known to support greater doping than III–V materials [5]. Therefore, further investigation on the feasibility of ZnO-based DMS is of great interest. Recently, some groups were reported room temperature ferromagnetism in the ZnO-based DMS, such as in Mn-doped [6,7], Co-doped [8,9], Ni-doped [10], and Cr-doped [11] ZnO films, but there are few reports on the ZnFeO DMS.

In this work, ZnFeO thin films with room temperature ferromagnetism were prepared by thermal oxidation of ZnFeS thin films. The crystal structure, surface morphology and magnetic property of the ZnFeO films with different Fe content were investigated.

2. Experimental

ZnFeS samples with thickness about 200 nm were grown on c-plane sapphire substrates by LP-MOCVD. Ironpentacarbonyl ($Fe(CO)_5$), dimethylzinc (DMZn) and H_2S were used as reaction precursors. The details of the sample preparation can be found elsewhere [12]. After deposition, thermal oxidation of the ZnFeS films was carried out in an oxygen ambient with a atmospheric pressure at different temperature in range of 500–900 °C for 1 h. Structures and crystalline quality of the obtained ZnFeO thin films are analyzed by X-ray diffraction (XRD) on a Rigaku O/max-RA X-ray system in θ–2θ configuration. The ZnFeO samples were measured by the energy dispersive X-ray detector (EDX) to determinate the Fe contents composition. Surface morphology of samples was examined using a field-emission scanning electron microscope (FE-SEM). Magnetic characteristics are studied using a vibrating sample magnetometer (VSM) (Lake Shore Company) at room temperature.

3. Results and discussion

In order to obtain optimum thermal oxidation temperature, the XRD of scans was performed. Fig. 1 shows the XRD patterns of ZnFeS thin films annealed at different temperatures ranging from 500 to 900 °C. The XRD pattern of as-grown ZnFeS thin film shows that high oriented ZnFeS thin films with the hexagonal structure were obtained, shown in Ref. [12]. When the thin films are annealed at 500 °C, only consists of ZnFeS (0 0 2) diffraction peak was obtained in the XRD patterns. For the annealing temperature of 550 °C, ZnFeO

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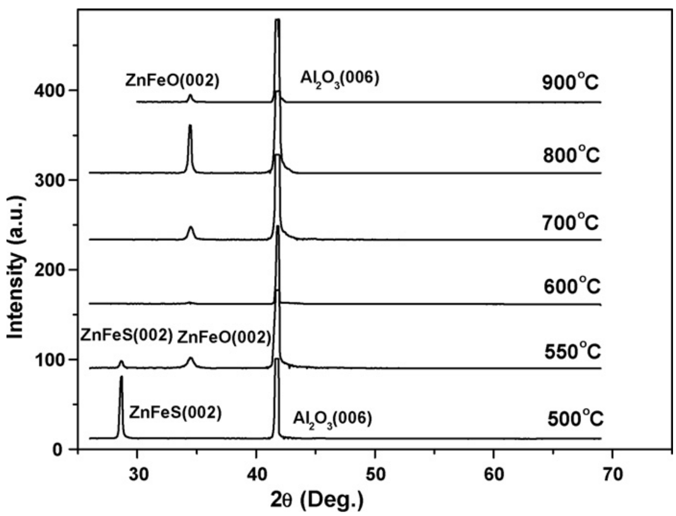

Fig. 1. The XRD patterns of the ZnFeS thin films at different annealing temperatures (500–900 °C).

(0 0 2) diffraction peak is clearly observed. This indicates the ZnFeS begins a transformation to ZnFeO from a mixed diffraction pattern of ZnFeS and ZnFeO. When annealing temperature was higher than 600 °C, only consists of ZnFeO (0 0 2) diffraction peaks was obtained in XRD pattern, which indicated that the ZnFeS fully transforms into ZnFeO with hexagonal wurtzite structure. The full-width at half maximum (FWHM) of ZnFeO (0 0 2) diffraction peaks were 0.53°, 0.50°, 0.41°, 0.24° and 0.30° for the samples annealed at 550, 600, 700, 800 and 900 °C, respectively. This shows the optimized growth temperature of about 800 °C.

Fig. 2 shows the XRD patterns of ZnFeO with different Fe content at annealing temperature of 800 °C. The compositions of ZnFeO with different Fe content measured by the EDX are listed in Table 1. The only (0 0 2) diffraction peak of samples (A–D) can be observed in Fig. 2, indicating that the ZnFeO samples have better oriented crystal. When Fe content was 0.32, the XRD of sample E appeared mixed diffraction pattern of ZnFeO (0 0 2), Fe_2O_3 (0 0 6) and (2 0 2). Furthermore, the dependence of the *c*-axis lattice constants [*d*(0 0 2) values] of ZnFeO samples (A–E) on the Fe molar content is shown in Fig. 3 for clarity. In Fig. 3, it is clear that the *d*(0 0 2) values increased almost linearly as a function of the Fe content below 0.25, this phenomenon is usually considered that relates to the lattice spacing to be changed. The lattice spacing was gradually enlarged with increasing Fe content and it further indicates Fe atoms substituting for Zn atoms in the lattice. Moreover, regarding this curve, it seems that the limit of the solution is close to 0.25, since for higher Fe content, the lattice parameter does not change [13,14].

Table 1
The compositions of ZnFeO with different Fe content measured by the energy dispersive X-ray detector (EDX)

Samples	Fe content
A	0
B	0.05
C	0.12
D	0.25
E	0.32

Fig. 4 shows FE-SEM image of ZnFeO samples (A–D) at annealing temperature of 800 °C. In Fig. 4, it can be seen that the surfaces of samples are smooth, and mean grain size is uniform. In addition, the grain size grown up with the increase in Fe content. This effect is also observed in other doped ceramics systems [15,16] as a consequence of some heterogeneity in the additive distribution in the grain boundaries, which may result in different grain boundary mobilities due to the influence of the dopant on the grain boundary transport [17].

In order to investigate magnetic characteristics of ZnFeO thin films with different Fe content, the VSM was performed. Fig. 5 presents the *M*–*H* curves of samples C, and D measured by the VSM at room temperature. We can see that the ZnFeO thin films are ferromagnetic and the Curie temperature T_c should be higher than room temperature. The sample B did not obtain the *M*–*H* curve at room temperature. This may be due to that the magnetic signal of sample B with relatively small magnetic elements is difficult to separate from the noise single in the process of testing. The saturation magnetizations (M_s) and coercivity (H_c) of samples C, and D are 12 and 21 emu cm^3, 290 and 127 Oe, respectively. By simple comparison, it can be seen that sample D has the lowest H_c but the highest M_s among the three samples. This is in agreement with the SEM observation that the sample D has larger grain size. Since the ferromagnetic coupling is strongly dependent on the exchange interaction between neighboring magnetic ions, decrease of the grain size (or domain) can even change a system from a ferromagnetic state to a paramagnetic state. Thus, samples with larger grains

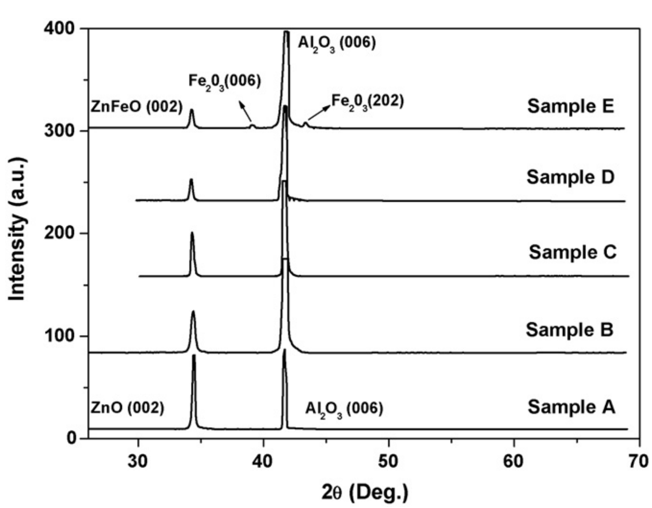

Fig. 2. The XRD pattern of ZnFeO with different Fe content at annealing temperature 800 °C.

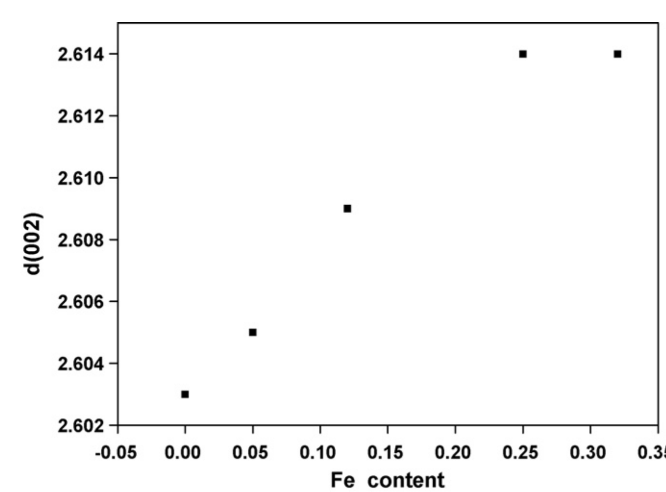

Fig. 3. Evolution of the *c*-axis lattice constants [*d*(0 0 2) values] of ZnFeO samples (A–E) as a function of the Fe molar content.