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Crystallization-dependent magnetic properties of $Mn_{1.56}Co_{0.96}Ni_{0.48}O_4$ thin films

Y.Q. Gao [a], Z.M. Huang [a,*], Y. Hou [a], J. Wu [a], Z.Q. Li [b], J.H. Chu [a]

[a] National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Science, Yu Tian Road 500, Shanghai 200083, China
[b] Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparing Technology, Institute of Advanced Materials Physics, Faculty of Science, Tianjin University, Tianjin 300072, China

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ABSTRACT

The effects of magnetic property dependence of the $Mn_{1.56}Co_{0.96}Ni_{0.48}O_4$ (MCN) films on crystallization are investigated in the growth temperature of 450–750 °C. With the growth temperature increase, both the crystalline quality and the grain size improve. The MCN films exhibit paramagnetic to ferromagnetic transition and the paramagnetic parts fit to the modified Curie–Weiss law. The ferromagnetic couplings of the magnetic ions in the MCN films enhance at elevated growth temperature. The saturation magnetization at 5 K increases with increasing growth temperature, but coercive field decreases monotonously. The magnetic properties of the MCN films strongly depend on their microstructures.

1. Introduction

Transition metal oxides of spinel oxides are generally represented by the formula AB_2O_4 (A = Zn, Fe, Co, Ni, Mn, Mg, Cd, etc; B = Co, Fe, Cr, Al, Ga, Mn, etc), where A and B represent divalent and trivalent cations, respectively [1]. Magnetic moments in each of A (tetrahedrally) and B (octahedrally) sublattices are aligned [2]. Among them, spinel ferrites like $Zn_xFe_{1-x}O_4$, $Fe_{3-x}Mn_xO_4$, and $NiFe_2O_4$ exhibit a rich variety of electrical and magnetic properties even at room temperature and are regarded as candidates for application in functional spintronics devices [3–5]. Due to their interesting, versatile, and tunable properties magnetite thin films and heterostructures became the focus of recent research activities [6]. Mn–Co–Ni-oxide is typical spinel structure based on the well known $NiMn_2O_4$. It shows both high Curie temperature (T_c) and semiconductor property [7]. The combination of spinel ferrites with Mn–Co–Ni-oxide films in multifunctional heterostructures maybe particularly appealing. The structure and electrical properties of this kind of materials have been studied extensively; however, few works deal with magnetic studies. Peña et al. undertook systematic studies in the magnetic properties of $NiMn_{2-x}Co_xO_4$ spinel oxides by changing Co doping concentrations, however, which were limited in bulk form [8]. Traditionally, these samples were commonly prepared from oxide powders by solid state sintering method at high temperature (~1050–1200 °C). There are often problems with poor stability and reproducibility due to high porosity and incomplete intergranular contact. However, the materials fabricated in film form would be much better than that in bulk form for its development in the modern electronic devices.

Recently, Huang and co-workers have prepared high quality $Mn_{1.56}Co_{0.96}Ni_{0.48}O_4$ (MCN) films by chemical solution deposition method at a low crystallization temperature of 600 °C [9,10]. In this paper, we find a way to adjust the magnetic properties of the MCN thin films by crystallization effect.

2. Experiments

The MCN films in this study were prepared by the starting materials of the manganese acetate $Mn(CH_3CO_2)_2{\cdot}4(H_2O)$, cobalt acetate $Co(CH_3CO_2)_2{\cdot}4(H_2O)$, and nickel acetate $Ni(CH_3CO_2)_2{\cdot}4(H_2O)$. The three acetates with an atom rate Mn:Co:Ni = 52:32:16 were dissolved in glacial acetic acid. Then the mixture was filtered through 0.2 μm syringe filters to remove dust and impurities. The stock solution was wine red, clear, and transparent. The MCN films were deposited on Al_2O_3 substrate by spin coating of the solution at 4000 rpm for 20 s. After coating each layer, the wet films were dried at 250 °C to remove residual organic, following sintering at different growth temperatures (450 °C, 550 °C, 650 °C and 750 °C) by rapid thermal process (RTP) for 5 min. The deposition

* Corresponding author. Tel.: +86 21 65420850; fax: +86 21 65830734.
E-mail address: zmhuang8@yahoo.com (Z.M. Huang).

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and heat-treatment procedure was then repeated for ten times to obtain a desired film thickness.

The phase analysis and the structure of the samples were identified by X-ray diffraction (XRD) using a Rigaku D/MAX-2550 X-ray diffractometer at room temperature. The surface morphology and the thickness of the films were measured by the scanning electron microscopy (SEM). Magnetic measurements were made at field cooling (FC) mode from 305 K to 5 K under 1000 Oe using a vibrating sample magnetometer (VSM) which is equipped in a physical properties measurement system (PPMS-6000, Quantum Design). Samples were cut into rectangles (less than 10 mm × 3 mm) so that the surface area size could be calculated.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the MCN films at growth temperature 450 °C [MCN(450)], 550 °C [MCN(550)], 650 °C [MCN(650)] and 750 °C [MCN(750)]. From the X-ray diffraction patterns of the thin films, we can see that the crystallization of the films strongly depends on the growth temperatures. It is obvious that not only the (3 1 1) peak intensity

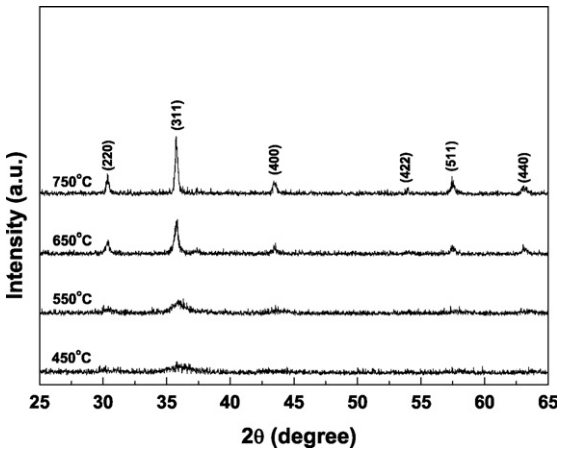

Fig. 1. XRD patterns of the MCN films under growth temperatures of 450 °C, 550 °C, 650 °C and 750 °C.

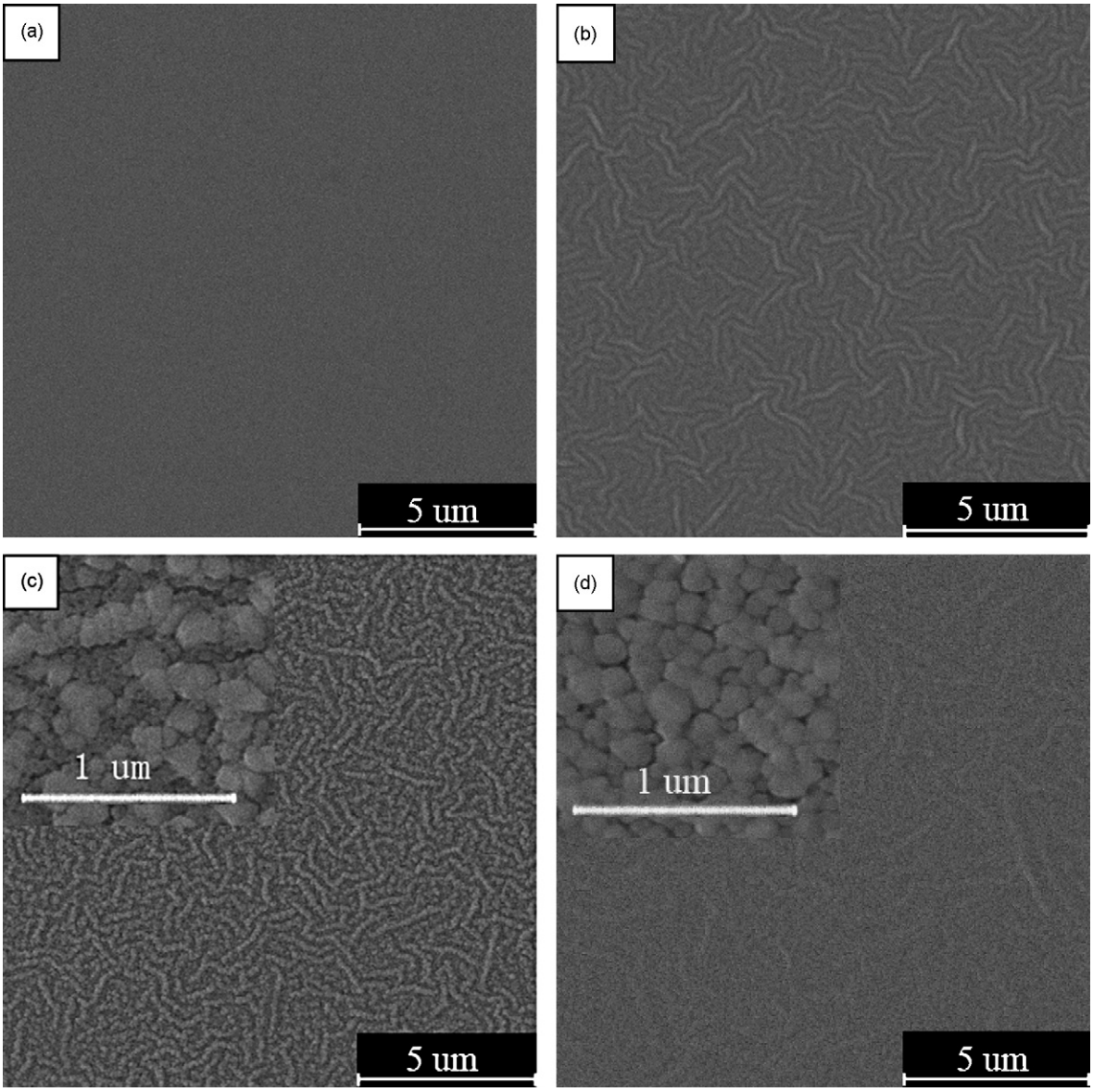

Fig. 2. SEM images of the MCN films under growth temperatures of (a) 450 °C, (b) 550 °C, (c) 650 °C and (d) 750 °C.