Annealing effects on microstructure and properties of $Y(Ni, Mn)O_3$ thin films

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Abstract

Epitaxially c-axis oriented thin films of $Y(Ni,Mn)O_3$ (YNMO) were grown on (100) $SrTiO_3$ substrates by pulsed laser-ablated deposition technique. High temperature oxygen annealing shows a much improvement in the transition temperature for $x = 0.33$ film while only a slight increase in Tc for $x = 0.5$ film. We suggest that the increase in Tc may be largely associated with microstructural changes induced by thermal annealing. In order to optimize the magnetic properties of YNMO films, it is necessary to control the initial growth conditions so as to have a microstructure of well-connected grains of uniform size.

Keywords: films, magnetic properties, perovskites.

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Introduction

Research on thin films of manganese oxides $RE_{1-x}A_xMnO_3$, where RE is a rare earth and A is an alkali earth element, has become one of the attractive topics over the last decade for many researchers in the field of condensed matter physics. Indeed, manganite films appear to be rather good candidates for potential applications due to the large change exhibited in electrical resistance when an external magnetic field is applied. On the other hand, there are only a few reports on doping the Mn-site of the $REMnO_3$ perovskite, in which manganese can be partially substituted by divalent transition elements (e.g., Cu^{2+}, Co^{2+}, Ni^{2+}…). Recently, concerning this type of substitution in the solid solution $Y(Ni,Mn)O_3$, we have successfully grown thin films, and reported the effect of Ni substitution for Mn on the structural and magnetic properties of the Y-based manganite system $YNi_xMn_{1-x}O_3$ [1, 2]. It is well known that the properties of epitaxial thin films are closer to the intrinsic properties than those of bulk ceramics. However, due to the strain effect of the substrate or because of oxygen deficiency in a thin film, it is often difficult to reach the same properties as the bulk. In the early studies of manganese oxides films, a post deposition anneal in oxygen at high temperatures was critical for achieving better physical properties [3]. In this paper, we investigate the effect of post deposition heat treatments in thin films of $Y(Ni, Mn)O_3$ grown on $SrTiO_3$ substrates. We then compare the properties of as-grown films and post annealed ones under oxygen.

Experimental

$YNi_xMn_{1-x}O_3$ (YNMO) films were grown *in situ* on (100) $SrTiO_3$ (STO) substrates using a pulsed laser ablation system. A detailed description of the deposition system is mentioned elsewhere [4]. In brief, a 248 nm KrF pulsed laser with 5 Hz repetition rate and 2 J/cm^2 energy density was used. A substrate temperature of 740 °C and oxygen pressure of about 0.6 mbar were used during the deposition of the films. Following the deposition, the films were cooled down to room temperature at a rate of about 35 °C/min in 200 Torr of oxygen. After the initial characterization to check their properties, the films were subjected to post deposition annealing in oxygen at 850 °C for 10 hrs.

The films were characterized using scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX), and x-ray diffraction (XRD) measurements (Brüker AXS D8 Discover). The magnetization of the thin films was measured using a superconducting quantum interference device (SQUID) magnetometer (MPMS-XL5, Quantum Design). The applied fields were in the film plane.

Results and discussion

Figure 1 shows the typical x-ray $\theta/2\theta$ scans recorded for YNMO films, with no annealing and after annealing. From the figure it is clear that all the films have single phase with $(00l)$ peaks with $l = 2$ and 4. The presence of only sharp $(00l)$ peaks indicates the highly textured growth of all the films on (100) STO substrate. The out-of-plane lattice parameters (2*c*) for the x = 0.5 films with no annealing and annealing were found to be 7.492 and 7.478 Å, respectively (according to the diffraction angle of (004) peak). We speculate that the decrease in lattice constant may be related to the increase of Mn^{4+} ions which have a smaller radius in comparison with Mn^{3+} ions. The same was found to be the case for x = 0.33. Crystalline quality of the films was analyzed using the measured full width at half maximum (FWHM) of the rocking curves. The rocking curve FWHM of the (004) peak shows that the crystalline mosaic spread decreases greatly with annealing for the x = 0.33 film, with values decreasing from 1.02° to 0.3°. By contrast, the rocking curve of (004) for the x = 0.5 film remains almost unchanged (1.16°).

Figure 2 shows the dc magnetization taken under a magnetic field of 100 Oe for the as-grown and annealed films of both x = 0.33 and 0.5. For $Y(Ni,Mn)O_3$ system, our previous work indicated a spin-glass characteristic in the x = 0.33, while a cluster glass-like behavior was observed for x = 0.5 [1]. The Tc for the as-grown x = 0.5 film is about 85 K compared to that of its bulk at ~80 K. The difference in Tc is attributed to the type of strain developed between the film and the substrate. Further, x = 0.5 films subjected to annealing show little effect on the transition temperature, only a slight increase of the magnetization. Contrary to this, the transition temperature Tc value for x = 0.33 is increased from about 60K to 70K after annealing. At the same time, the spin canting-like transition temperature increases from about 32 K to 37 K. The increase of the transition temperature under annealing is not surprising since this treatment can lead to the increase of the oxygen content of the films and optimizes the ratio Mn^{3+}/Mn^{4+}. At the same time, it makes the thin film to become more homogeneous. In other words, oxygen incorporation not only results in the optimal doping level but also increases the strength of the Mn-O bond due to saturation of anion defect sites, hence higher Tc [3, 5]. However, it is surprising that the oxygen annealing effects on the x = 0.5 films are not obvious. This may be related to the thermal effect of annealing. It is well known that annealing at high temperatures also causes grain growth which would relieve the structural strain induced by lattice mismatch and also create microstructural change.

In order to investigate the relation between magnetic properties and microstructure, we carried out SEM observations for all the films. Figure 3 displays the SEM images of as-grown and oxygen-annealed YNMO films for x = 0.33 and 0.5. For x = 0.33, the surface of the as-grown film is covered with spherical grains with an average lateral size of 30 nm, while the average grain size of the post-annealed films are in the range of 60-90 nm, about two or three times larger than those of the as-grown film, and the boundaries between grains become blurred. In addition, the surface roughness of the annealed film is substantially reduced compared to the as-grown one. SEM images reveal that both the as-grown and annealed films are dense, pore free.

Conversely, for x = 0.5, the as-grown film consists of in-plane oriented longitudinal islands and there is a wide distribution of grain size with an average grain size of 60 nm. The grains of annealed film were found to be slightly larger with an average grain size of 80 nm. Unlike the x = 0.33 films, the islands showed poor connectivity with some pores between islands. After annealing, although the grain connectivity was improved, a broader distribution of grain sizes persisted.

The structural and microstructural measurements explain the observed changes in magnetic properties with annealing. Upon annealing, grain growth occurred by diffusion, so that the grain size is enlarged and the surface roughness is diminished. These diffusive processes also led to strain relaxation between the substrate and film. This improvement in microstructure led to an increase in the transition temperature, despite only a slight increase in Tc for x =0.5 films. However, the rate at which Tc increased was not the same for both x = 0.33 and 0.5 films, the results may be again explained by the following reasons. The better crystalline quality and good grain coupling can lead to the better physical properties [5]. The initial microstructure predetermines the nature of the final microstructure. Clearly, from SEM, the as-grown x = 0.5 film showed poorer grain connectivity and a broader grain size distribution than the as-grown x = 0.33 film. Further, the sharpening of rocking curves for x = 0.33 films suggests a much decreased crystalline mosaic spread, as described above. Hence for the x = 0.33 film, the well-connected grains and much improved order in the structure with annealing lead to higher magnetic transition temperature Tc. For the x = 0.5 film, some pores persisted upon annealing and there was almost no change in crystalline mosaicity. This indicates that the Tc of the as-grown film for x = 0.5 is stable, and may be close to its intrinsic maximum value. Thus, Tc rose only a little with annealing because the improvement in structural ordering and crystallinity with annealing was small.

Conclusions

We have investigated the effects of oxygen annealing on the structural and magnetic properties of $Y(Ni,Mn)O_3$ thin films grown by pulsed laser deposition on STO substrates. We found that upgraded magnetic properties resulted from improved crystallinity which occurred as a result of grain growth. We have demonstrated that it is necessary to control the initial growth conditions so as to have a microstructure of well-connected grains of uniform size, to optimize magnetic properties of YNMO films.

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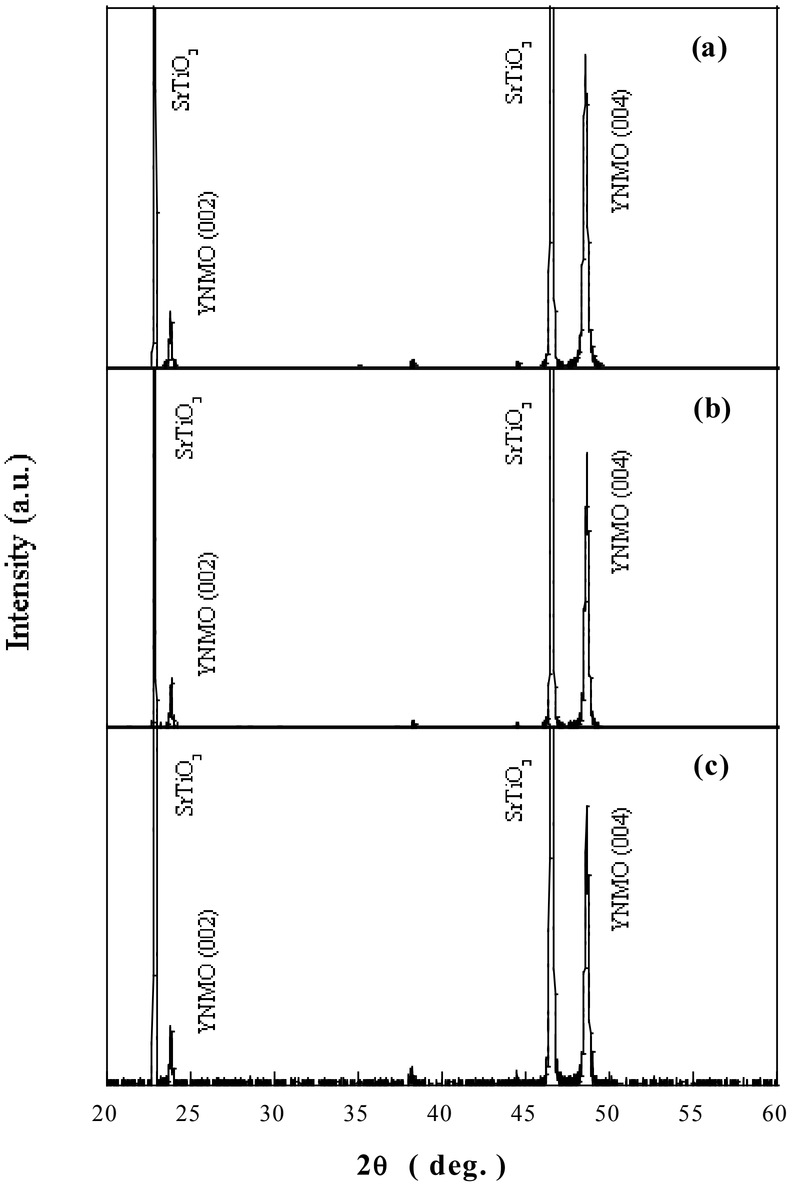
Captions

Figure 1	XRD patterns of YNMO films, (a) as-grown, (b) $x = 0.33$, after annealing, and (c) $x = 0.5$, after annealing. Note: two small peaks of $2\theta = 38.2°$ and 44.4° were contributed from the sample holder.
Figure 2	Variation of dc magnetization with temperature for the following films (a) $x = 0.33$, (b) $x = 0.5$. The inset shows the enlarged view near the transition temperatures.
Figure 3	SEM images of typical areas of YNMO films: (a) $x = 0.33$, as-grown; (b) $x = 0.33$, after annealing; (c) $x = 0.5$, as-grown; (d) $x = 0.5$, after annealing.



Intensity (a.u.)
(a)
(b)
(c)
SrTiO3
YNMO (002)
SrTiO3
YNMO (004)
20
25
30
35
40
45
50
55
60
2θ (deg.)

Fig. 1 Ma et al.

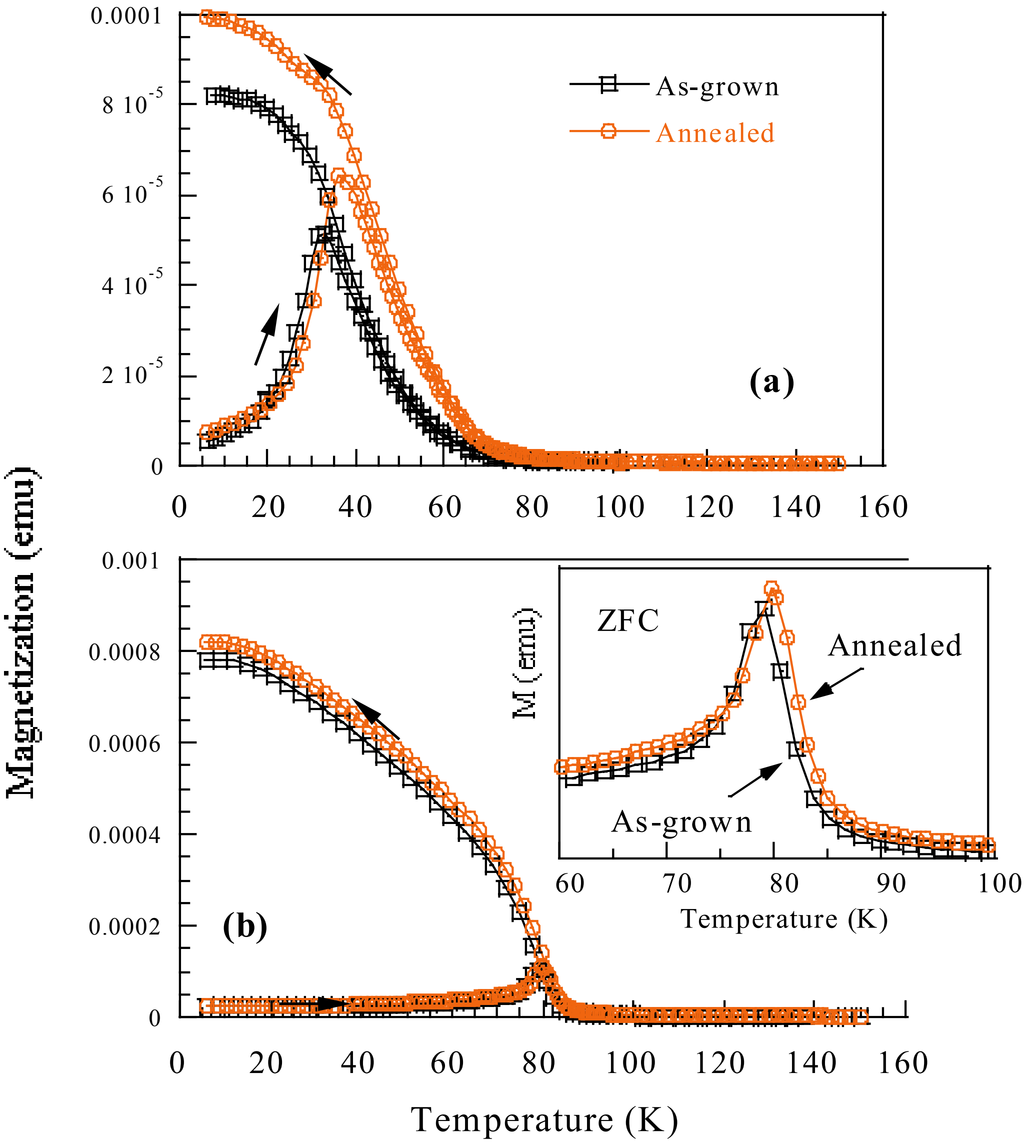

0.0001
8 10-5
6 10-5
4 10-5
2 10-5
0
0
20
40
60
80
100
120
140
160
As-grown
Annealed
(a)
Magnetization (emu)
0.001
0.0008
0.0006
0.0004
0.0002
0
0
20
40
60
80
100
120
140
160
(b)
Temperature (K)
ZFC
Annealed
As-grown
M (emu)
60
70
80
90
100
Temperature (K)

Fig. 2 Ma et al.

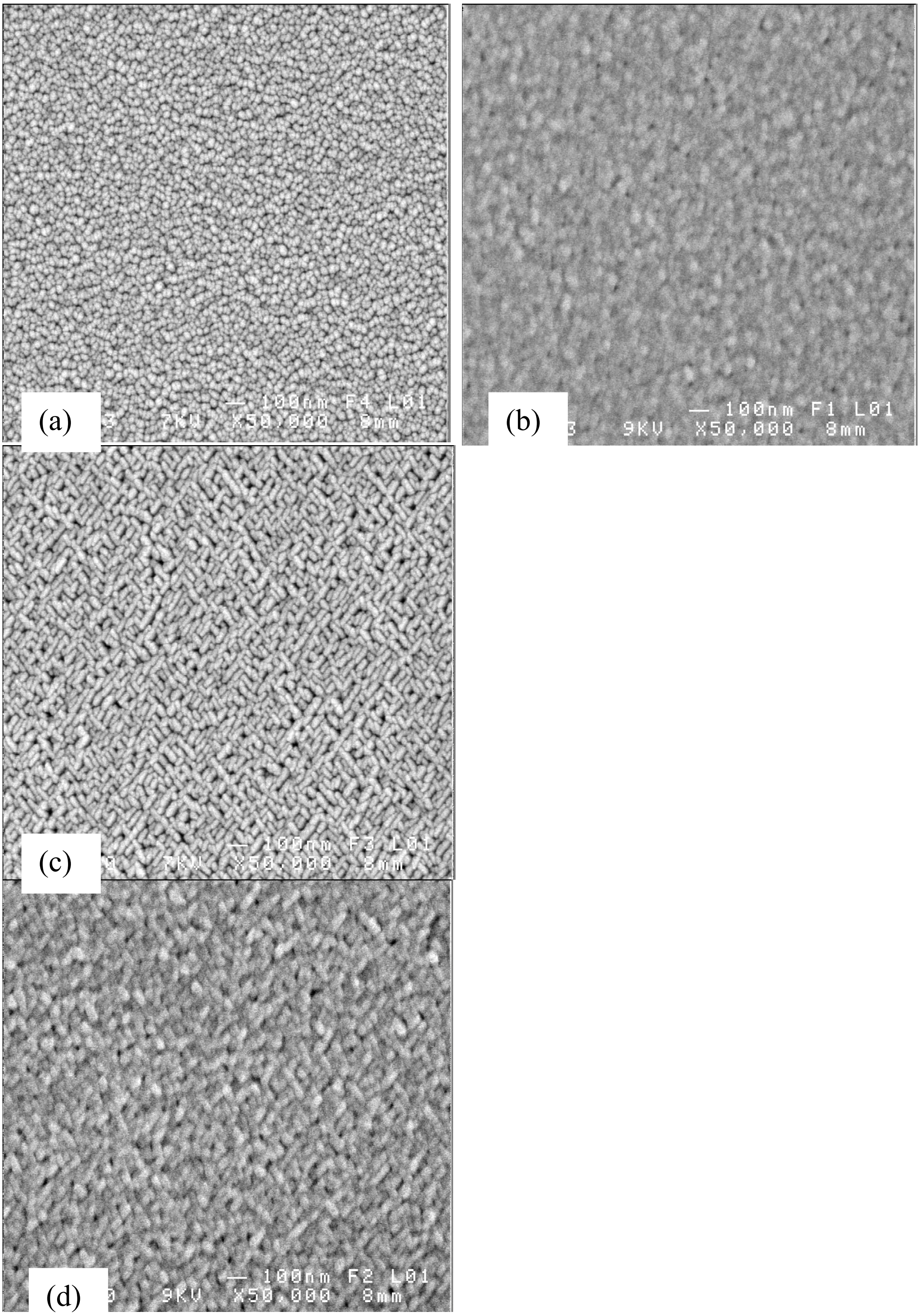

(a)
— 100nm F4 L01
3 7KV X50,000 8mm
(b)
— 100nm F1 L01
3 9KV X50,000 8mm
(c)
— 100nm F3 L01
0 7KV X50,000 8mm
(d)
— 100nm F2 L01
0 9KV X50,000 8mm

Fig. 3 Ma et al.