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SCIENCE DIRECT
Journal of the European Ceramic Society 25 (2005) 2147–2150
ECERS
www.elsevier.com/locate/jeurceramsoc

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

Yanwei Ma[a,b,∗], M. Guilloux-Viry[b], P. Barahona[b,1], O. Peña[b], C. Moure[c]

[a] Institute of Electrical Engineering, Chinese Academy of Sciences, Beijing 100080, China
[b] LCSIM, UMR 6511, CNRS, Université de Rennes 1, Institut de Chimie de Rennes, 35042 Rennes Cedex, France
[c] Instituto de Ceramica y Vidrio, CSIC, 28049 Madrid, Spain

Available online 30 March 2005

Abstract

Epitaxially *c*-axis oriented thin films of $YNi_xMn_{1-x}O_3$ (YNMO), $x = 0.33$ and 0.5, were grown on (1 0 0) $SrTiO_3$ substrates by pulsed laser-ablated deposition technique. High temperature oxygen annealing shows a large improvement in the ferromagnetic transition temperature T_c for the film with x(Ni) = 0.33 while only a slight increase in T_c occurs for the x(Ni) = 0.5 film. We suggest that such increase in T_c is largely associated with microstructural changes induced by the thermal annealing. In order to optimize the magnetic properties of the 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

1. Introduction

Research on thin films of manganese oxides $RE_{1-x}A_xMnO_3$, where RE is a rare-earth element 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 a divalent transition element (e.g., Cu^{2+}, Co^{2+}, Ni^{2+}, ...). Concerning this type of substitution in the solid solution $Y(Ni,Mn)O_3$, we have recently grown thin films and reported the effect of Ni substitution for Mn on the structural and magnetic properties of the Y-based manganite system $YNi_xMn_{1-x}O_3$ ($0 \le x \le 0.5$).[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, because of strain effects due to the substrate or because of oxygen deficiencies in a thin film, it is often difficult to reach the same properties as in the bulk. In the early studies of manganese oxides films, a post-deposition anneal in oxygen at high temperature was critical to achieve better physical properties.[3] In this paper, we investigate the effect of post-deposition heat treatments on thin films of $Y(Ni,Mn)O_3$ grown on $SrTiO_3$ substrates. We then compare the properties of the as-grown films with those of the post-annealed ones under oxygen.

2. Experimental

$YNi_xMn_{1-x}O_3$ (YNMO) films ($x = 0.33$ and 0.5) were grown in situ on (1 0 0) $SrTiO_3$ (STO) substrates using a pulsed laser ablation deposition (PLD) 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 an oxygen pressure of about 0.6 mbar were

∗ Corresponding author. Tel.: +86 10 62528719; fax: +86 10 62542034. *E-mail address:* ywma@mail.iee.ac.cn (Y. Ma).
[1] Present address: Chemistry Department, Faculty of Sciences, Universidad de Chile, Santiago, Chile.

0955-2219/$ – see front matter
doi:10.1016/j.jeurceramsoc.2005.03.061

used during the deposition. The films were then 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 structural, microstructural and magnetic properties, the films were subjected to post-deposition annealing under oxygen atmosphere at 850 °C for 10 h.

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.

3. Results and discussion

Fig. 1 shows the typical X-ray θ–2θ scans recorded for the YNMO films, without annealing and after annealing. From this figure, it is clear that all films are single-phased presenting (0 0 *l*) peaks with $l = 2$ and 4. The presence of only sharp (0 0 *l*) peaks indicates a highly textured growth on the (1 0 0) STO substrate, for all films. The out-of-plane lattice parameter (2*c*) for the *x*(Ni) = 0.5 films with no annealing and after annealing was found to be 7.492 and 7.478 Å, respectively (according to the diffraction angle of the (0 0 4) peak). We speculate that the decrease in the lattice constant may be related to the increase in quantity of Mn^{4+} ions, which have a smaller radius in comparison with the Mn^{3+} ions. The same was found to be the case for *x*(Ni) = 0.33. The crystalline quality of the films was analyzed using the full-width-at-half-maximum (FWHM) of the rocking curves. The rocking curve FWHM of the (0 0 4) peak shows that the crystalline mosaic spread for the *x*(Ni) = 0.33 film decreases greatly with annealing, with values of 1.02 and 0.3°, for the as-grown and the post-annealed (850 °C/10 h) films, respectively. By contrast, the rocking curve of the (0 0 4) peak for the *x*(Ni) = 0.5 film remains almost unchanged (1.16°).

In our previous work on the $YNi_xMn_{1-x}O_3$ system, we observed a spin-glass characteristic for $x = 0.33$, while a cluster glass-like behavior was suggested for $x = 0.5$.[1] Fig. 2 shows the zero-field-cooled/field-cooled (ZFC/FC) magnetization measured under an applied field of 100 Oe, for the as-grown and annealed films of both *x*(Ni) = 0.33 and 0.5. The transition temperature T_c for the as-grown *x*(Ni) = 0.5 film is about 85 K compared to that of bulk samples ($T_c^{bulk} \sim 80$ K). This difference in T_c is attributed to the type of strain developed between the film and the substrate. Further, the $x = 0.5$ films subjected to annealing show little or no effect on the transition temperature; only a slight increase of the magnetization is observed (inset, Fig. 2b). Contrary to this, the transition temperature

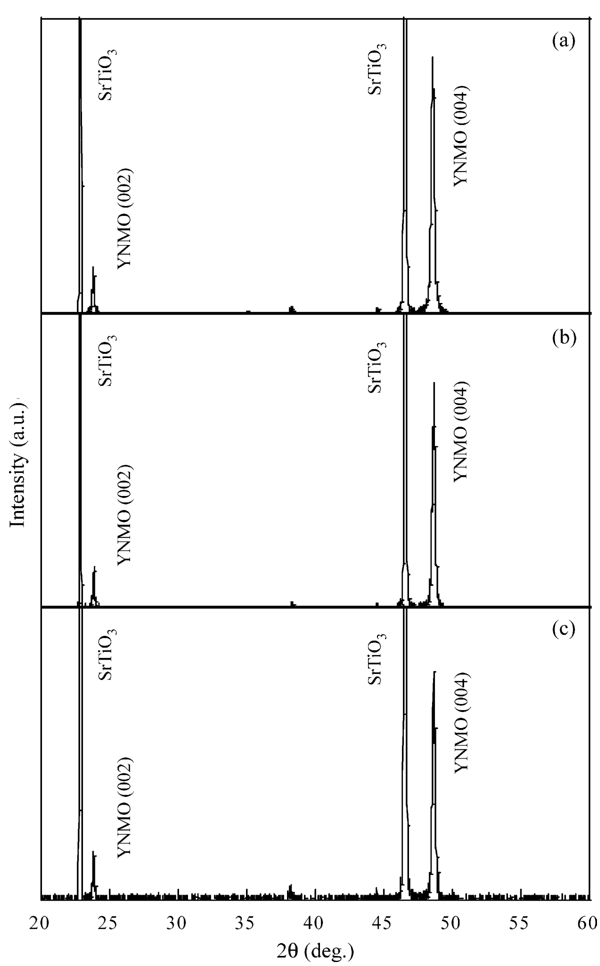

Fig. 1. XRD patterns of $YNi_xMn_{1-x}O_3$ films, (a) typical as-grown film, (b) $x = 0.33$ after annealing, and (c) $x = 0.5$ after annealing. Note: two small peaks at $2\theta = 38.2$ and 44.4° are due to the sample holder.

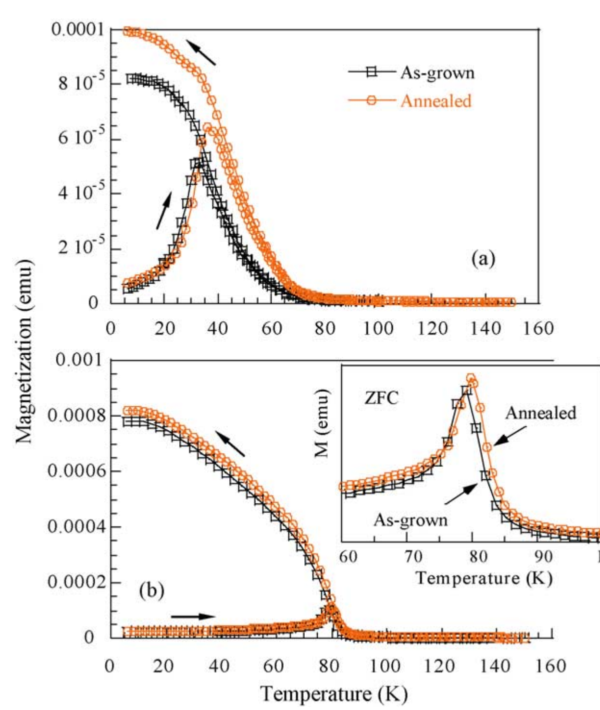

Fig. 2. Thermal variation of the ZFC/FC magnetization for the following $YNi_xMn_{1-x}O_3$ films: (a) $x = 0.33$ and (b) $x = 0.5$. The inset shows the enlarged view near the transition temperature.

T_c for x(Ni) = 0.33 increases from about 60 to 70 K after annealing under oxygen at 850 °C. At the same time, the spin canting-like transition T_{max} (defined at the maximum value of the ZFC magnetization) increases from about 32 to 37 K (Fig. 2a). Such an increase of the transition temperatures T_c and T_{max} under annealing is not surprising since the post-deposition annealing treatment can lead to an increase of the oxygen content of the films, optimizing the ratio Mn^{3+}/Mn^{4+}. At the same time, it makes the film to become more homogeneous. In other words, oxygen incorporation not only results in an optimal doping level but it also increases the strength of the Mn–O bond due to the saturation of anion-defect sites, hence leading to a higher T_c.[3,5] However, it may appear surprising that the oxygen annealing of the x = 0.5 films could be less obvious. This may be related to the thermal effect of annealing. Indeed, it is well known that high temperature treatment also causes grain growth which would relieve the structural strain induced by the lattice mismatch and also may create microstructural changes.

In order to investigate the relation between magnetic properties and microstructure, we carried out SEM observations for all films. Fig. 3 displays the SEM images of as-grown and oxygen-annealed YNMO films for x(Ni) = 0.33 and 0.5. For x = 0.33, the surface of the as-grown film is formed of spherical grains of 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. Also, the boundaries between grains become blurred. SEM images reveal that both the as-grown and annealed films are dense, pore free. The surface roughness, as evaluated from atomic force microscopy (AFM) observations of the rms height of the thin film, is of the order of 11 nm.

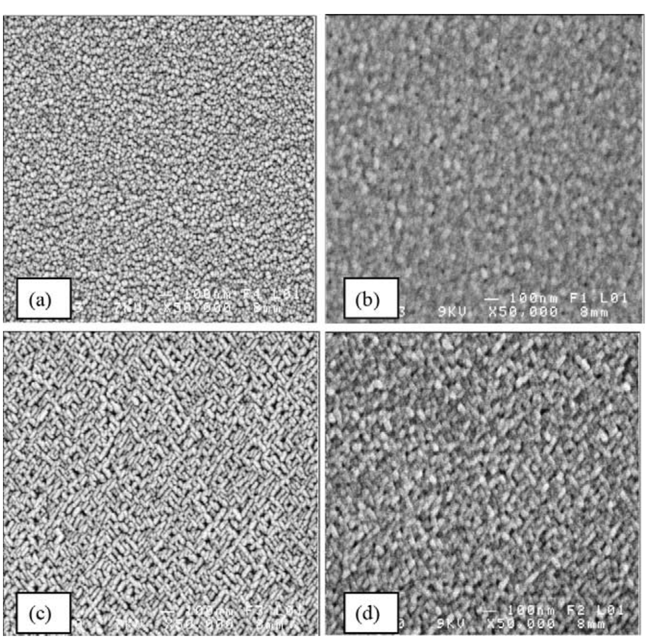

Fig. 3. SEM images of typical areas of $YNi_xMn_{1-x}O_3$ films: (a) x = 0.33, as-grown; (b) x = 0.33, after annealing; (c) x = 0.5, as-grown; and (d) x = 0.5, after annealing.

Conversely, for x(Ni) = 0.5, the as-grown film consists of in-plane islands oriented longitudinally, showing a wide distribution of grains of average size of 60 nm. After annealing, the grains were found to be slightly larger with an average size of 80 nm. Unlike the x(Ni) = 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 easily explain the observed changes in the magnetic properties with annealing. Upon annealing, grain growth occurs by diffusion, so that the grain size is increased and the surface roughness is diminished. These diffusive processes also lead to strain relaxation between the substrate and the film. This improvement of the microstructure leads to an increase of the transition temperature, even though the increase in T_c for the x = 0.5 films is very small compared to the rate of increase in the x = 0.33 films. Results may be explained as follows. Since a better crystalline quality and a good grain coupling lead to better physical properties,[5] it is good to know how the initial microstructure predetermines the nature of the final microstructure. Clearly, from SEM observations, the as-grown x(Ni) = 0.5 film showed poorer grain connectivity and a broader grain size distribution than the as-grown x(Ni) = 0.33 film. Further, the sharpness of the rocking curves for the x = 0.33 films suggests a minor crystalline mosaic spread, as described above. Hence for the x = 0.33 film, the well-connected grains and a much improved order in the structure after annealing should lead to a higher magnetic transition temperature T_c, as observed. For the x = 0.5 film, some pores persisted and there was almost no change in the crystalline mosaicity. This indicates that the T_c of the as-grown film for x = 0.5 is stable, and may be close to its intrinsic maximum value, leading to a very small change in T_c and not very significant changes of the structural ordering and crystallinity with annealing.

4. 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, in order to optimize the magnetic properties of the YNMO films, it is necessary to control the initial growth conditions so as to have a microstructure of well-connected grains of uniform size.

Acknowledgments

Authors thank M. Bahout and T. Guizouarn for technical assistance during magnetic measurements. Financial support from Region Bretagne is greatly acknowledged.

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