Improved properties of epitaxial $YNi_xMn_{1-x}O_3$ films by annealing under high magnetic fields

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The effect of annealing under a magnetic field on the microstructure and properties of $YNi_xMn_{1-x}O_3$ ($x=0.33$ and 0.5) films has been investigated. It is found that the ferromagnetic transition temperature is significantly enhanced after postannealing in the presence of an 8 T magnetic field. Characterization study shows that the microstructure is affected, obtaining larger grains of uniform size when films are annealed under a magnetic field. The improvement in the ordering temperature of all films is interpreted in terms of the grain growth caused by the magnetic field driving force for boundary motion where the exchange coupling is high. © *2006 American Institute of Physics*.
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$YMnO_3$ is a ferroelectric, antiferromagnetic compound of hexagonal structure. The substitution of Ni^{2+} for Mn^{3+} leads to a phase transition from hexagonal towards an orthorhombic perovskite phase for Ni amounts larger than 20 at. %; at the other end, the solid solution is limited to a maximum of 50 at. % Ni, which means that Ni adopts a stable divalent state.[1] The magnetic properties of the $YNi_xMn_{1-x}O_3$ solid solution change with the Ni content, evolving from an antiferromagnetic behavior at low nickel concentration to ferromagnetism at high nickel content, the threshold value being the critical concentration $x(\mathrm{Ni})=1/3$.[2] It becomes then interesting to investigate such system in thin-film form since epitaxial growth may improve the conducting properties and eventually, disable the phase segregation which may appear at the frontier of antiferromagnetism and ferromagnetism. Recently, we have grown epitaxial $Y(Ni,Mn)O_3$ (YNMO) thin films on $SrTiO_3$ substrates by pulsed laser-ablated deposition techniques and investigated the magnetic and microstructural properties.[3]

On the other hand, high magnetic fields are known to modify the microstructure of materials during their fabrication process. In most cases, a weak paramagnetic magnetization is usually coupled to a strong field to orientate anisotropic grains.[4–6] It has been reported that the microstructure and magnetic properties of manganite films are sensitive to preparation and annealing conditions.[7,8] Stronger effects or unknown effects are expected if applying a high magnetic field during YNMO postdeposition annealing, a process which we will refer hereafter as "magnetic annealing." In the present work, we have investigated the effect of such magnetic annealing on thin films of $YNi_xMn_{1-x}O_3$ grown on $SrTiO_3$ substrates. For this, we have chosen two characteristic compositions, $x=0.33$ and 0.5, because they better characterize the magnetic and electrical behaviors of this series, as exposed above. In the course of our investigations we have found that magnetic field annealing effectively promotes the ordering temperature of YNMO films.

Thin films of YNMO were grown using pulsed laser deposition. Deposition was performed from targets with stoichiometric composition of $YNi_xMn_{1-x}O_3$ ($x=0.33$ and 0.5). Films were synthesized on $SrTiO_3$ (100) substrates (cubic, $a=3.905$ Å). A detailed description of the deposition system is mentioned elsewhere.[9] Then, the samples were annealed with a flowing oxygen gas in an electrical furnace, which was installed in the room temperature bore of a cryogen-free superconducting magnet.[10] A magnetic field of 8 T was applied during annealing. The annealing temperature was 850 °C; the annealing time was 2–10 h. In order to evaluate the effect of the magnetic field, the samples were annealed under the same conditions but without any magnetic field. The direction of the magnetic field was perpendicular to the film plane.

XRD patterns of YNMO films ($x=0.5$ and 0.33) from the as grown to different annealings are shown in Fig. 1. For the as-deposited films, only $00l$ diffraction peaks of the phase are present evidencing an oriented film with the c axis perpendicular to the surface of the substrate. XRD patterns of nonfield and magnetic field annealed films were similar to that of as-deposited films. However, there is a significant increase in the intensity of diffraction peaks as the samples were annealed, especially in the case of magnetic field annealing. Crystalline quality of the films was analyzed using the measured full width at half maximum (FWHM) of the rocking curves. X-ray rocking curves of the (004) peak show that the crystalline mosaic spread decreases with different annealings for both $x=0.33$ and 0.5 films. As for the $x=0.33$ films, values of FWHM are 1.02°, 0.32°, and 0.25° for the as grown, nonfield, and magnetic field annealing states, respectively. This compares with a change of 1.16° to 1.1°, and to 0.8° for the $x=0.5$ films from the as grown, to nonfield, and to magnetic annealing states. These results suggest that the crystalline quality is significantly improved by application of the external field in comparison with the as-grown ones. It is also clear that magnetic field annealing is much more effective in enhancing the crystallinity of the films compared to nonfield heat treatments.

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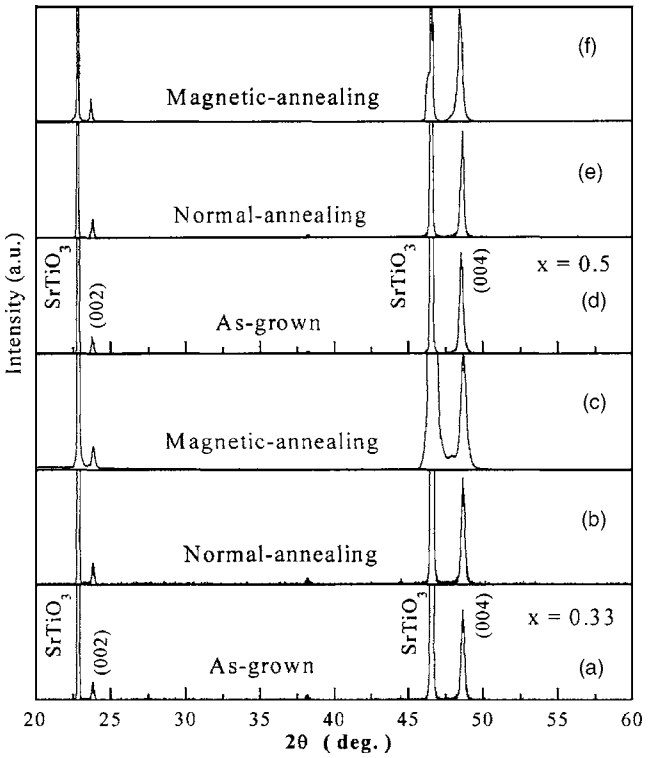

FIG. 1. XRD patterns of $YNi_xMn_{1-x}O_3$ films subjected to different annealing conditions. For $x=0.33$: (a) as gown, (b) nonfield annealing, and (c) magnetic field annealing. For $x=0.5$: (d) as gown, (e) nonfield annealing, and (f) magnetic field annealing. Note that two small peaks at $2\theta=38.286°$ and $44.423°$ were contributed by the sample holder.

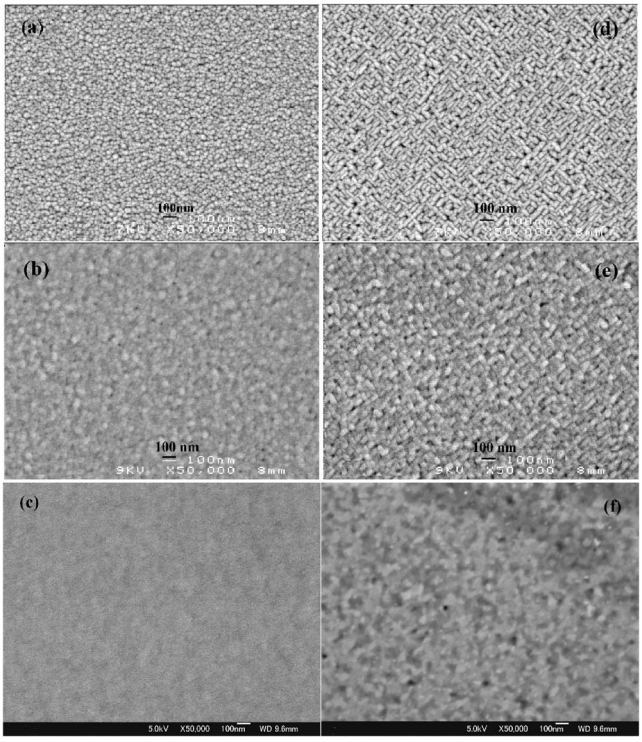

FIG. 2. Images of typical areas of $YNi_xMn_{1-x}O_3$ films. For $x=0.33$: (a) as gown, (b) nonfield annealing, and (c) magnetic field annealing. For $x=0.5$: (d) as gown, (e) nonfield annealing, and (f) magnetic field annealing.

SEM observations further demonstrate that magnetic field annealing has an effect on the microstructural evolution. Figure 2 shows the morphology of as-grown, nonfield, and field-annealed YNMO films for $x=0.33$ and 0.5. After the thermal treatment, the grain shape seems similar to that of as-grown films, but the grain size is largely increased and the boundaries between grains become blurred. Clearly, upon the magnetic annealing, the grains in the YNMO films were significantly enlarged and the grain boundary density was consequently reduced. In the case of $x=0.5$, the as-grown film consists of in-plane oriented longitudinal islands with an average grain size of 60 nm [Fig. 2(d)]. However, the films subjected to magnetic field annealing show significant increase in the grain size (up to 145 nm), more than two times larger than that of the as-grown film while slight increment of grain size was observed in the nonfield annealed films [Fig. 2(e)]. Similarly, for $x=0.33$, the films annealed in the field also show remarkable enhancement in the grain size [108 nm, Fig. 2(c)] compared to the as-deposited film [spherical grains with an average grain size of 30 nm, Fig. 2(a)]. The average grain sizes for all the films are summarized in Table I. Clearly, magnetic annealing of the YNMO film results not only in grain growth which reduces the density of grain boundaries but also in an improvement in the film crystallinity, as supported by the XRD measurements, thus increasing the exchange coupling. Therefore, enhanced magnetic properties are expected after magnetic annealing.

The ZFC/FC magnetization of as-grown and magnetic annealed YNMO films is shown in Fig. 3. As-grown films of $x=0.5$, typically, have a ferromagnetic transition temperature $T_C \sim 85$ K; magnetic annealing raises T_C to about 93 K. In $x=0.33$ films, the as-grown T_C is ~ 60 K. Magnetic annealing causes a dramatic improvement in the properties of YNMO films. As shown in Fig. 3(a), in annealed films we observe $T_C \sim 80$ K, that is, an increase of T_C by ~ 20 K is achieved, bringing the transition in this composition approximately equal to the transition temperature of $x=0.5$ as-grown films. At the same time, the spin cantinglike transition T_{max} (defined at the maximum value of the ZFC magnetization) increases from about 42 to 48 K. Along with the enhanced T_C, dc magnetization measurements at low fields (as exemplified in Fig. 3) indicate a remarkable increase in the field-cooling magnetic moment in all the samples after magnetic annealing. This increase of the total magnetic moments strongly suggests an increase in the ferromagnetic (FM) moments due to magnetic annealing. These clearly show that the magnetic annealing is helpful to improve the magnetic properties of YNMO films.

The effect of magnetic field annealing is further demonstrated by the field dependence of magnetization measurements for $x=0.33$ and 0.5 films at 5 K as shown in Fig. 4. As for the $x=0.5$ film subjected to magnetic annealing, the magnetization not only is much larger but also saturates more easily than that of as-grown samples indicating a more typical FM character. Similarly, magnetically annealed films of $x=0.33$ show also a considerable increase of the magnetization. However, magnetic annealing hardly changes the coer-

TABLE I. Transition temperature (T_C) and average grain size of $x=0.33$ and 0.5 films of as grown, nonfield annealing, and magnetic field annealing.

	As grown		Nonfield annealing		Magnetic field annealing	
Films	T_C (K)	Grain size (nm)	T_C (K)	Grain size (nm)	T_C (K)	Grain size (nm)
$x=0.33$	60	30	70	75	80	108
$x=0.5$	85	60	85.5	80	93	145

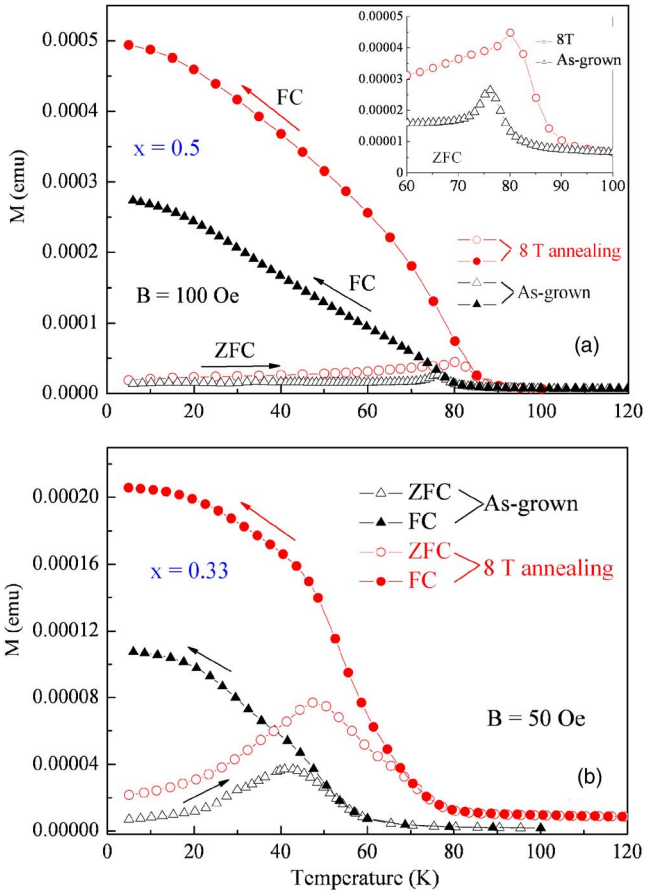

FIG. 3. (Color online) Thermal variation of the ZFC/FC magnetization for the following $YNi_xMn_{1-x}O_3$ films: (a) $x=0.33$ and (b) $x=0.5$. The inset shows the enlarged view near the transition temperature. Note that the as-grown sample was measured and then subsequently magnetically annealed to give the "magnetically annealed" sample.

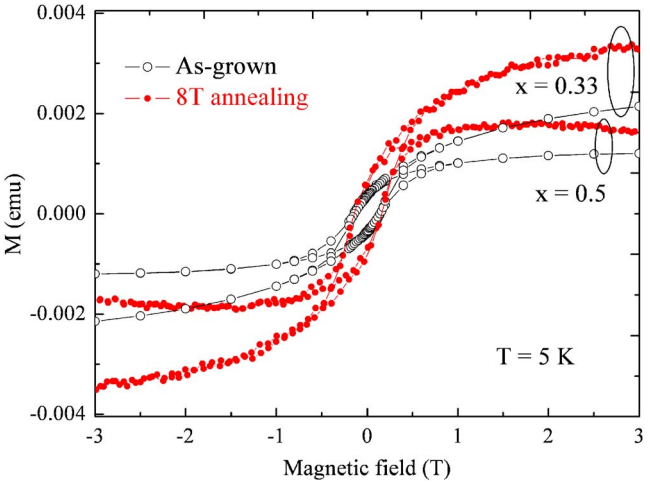

FIG. 4. (Color online) Hysteresis loops, up to 3 T, measured at 5 K on $YNi_xMn_{1-x}O_3$ films of $x=0.33$ and $x=0.5$. Note that the as-grown sample was measured and then subsequently magnetically annealed to give the magnetically annealed sample.

cive field, keeping a value of the order of 1500 Oe for both $x=0.5$ and 0.33 films.

From the above results, not only is the crystallinity improved but also the grain size is increased when the magnetic field is applied to annealing process for YNMO films. It is also recognized that the larger the grain, the lower the density of the grain boundaries. Thus the exchange coupling between grains is enhanced and hence the T_C improvement. As reported earlier, T_C decreases when the grain size decreases, eventually giving rise to superparamagnetic particles without a distinct T_C when the particle size is very small.[11–13] The fact also corroborated by the results of Nam *et al.*[14] They found that the better crystalline quality and good grain coupling can lead to the better physical properties. Clearly, our observation of T_C enhancement by magnetic annealing is in good agreement with this viewpoint. Therefore, the mechanism operating to achieve such improvement of magnetic properties is closely related to better crystallinity and reduction of grain boundaries caused by magnetic annealing.

The question now is how does the magnetic field influence the grain growth and grain boundary by magnetic sintering? It has been found[15,16] that an applied magnetic field during annealing can play a significant role even when the material is in its paramagnetic state above the Curie point, as pointed out by Tsurekawa *et al.* in iron samples.[15] In our case, YNMO is in its paramagnetic state at 850 °C. Applying a magnetic field forces the magnetic moments to align in the direction of the external field, in a much more efficient way than a random disorientation due to thermal motion. This magnetic ordering together with magnetocrystalline anisotropy provides a driving force for grain boundary migration that greatly contributes to the grain growth.[17] As a consequence, grains become larger, and crystallinity is enhanced, making the exchange-coupled adjacent grains crystallographically coherent, thus improving the magnetic properties of the YNMO films.

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