

Magnetic properties of manganese ferrite films grown at atomic scale

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Manganese ferrite is a partial inverse spinel which, when prepared by conventional growth techniques, has ~20% of the Mn^{2+} ions on the octahedral sublattice. Here we describe a layer-by-layer growth scheme at atomic scale by which the percentage of Mn^{2+} ions on the octahedral sublattice can be artificially controlled. Manganese ferrite films grown by this technique exhibits different degrees of cation inversion when grown on {100} and {111} MgO substrates. It was observed that saturation magnetization varied in a wide range of values depending on chemical composition and oxygen pressure. Although bulk manganese ferrite was low anisotropy magnetic material, uniaxial anisotropy was observed at room temperature in the films deposited on {100} MgO substrates, and its magnitude and direction sensitively depended on chemical composition and oxygen pressure during deposition. © 2005 American Institute of Physics.

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INTRODUCTION

Manganese ferrite is a partial inverse spinel ferrite, where about 20% of the Mn^{2+} ions are on the B sites (or octahedrally coordinated sites) and the rest reside on the A sites (or tetrahedrally coordinated sites).¹ The remaining A and B sites are occupied by the Fe^{3+} cations. Since the cation type, occupancy, and valence determine the magnetic and electronic properties of this important class of materials, there have been many studies attempting to explain the role of distribution of magnetic ions.² These previous studies reveal that at high temperatures (>900 °C) magnetic ions or nonmagnetic substitutions have sufficient thermal energy to migrate from site to site. Since the growth of spinels by conventional means usually exceeds 900 °C, migration between sites is governed by thermodynamics.

An interesting feature of spinels is that for growth along the <111> and <100> directions the A-site and B-site polyhedral form parallel “sheets.”³ This stacking arrangement of polyhedral presents an opportunity to grow spinel ferrites in a layer-by-layer method, where a *layer* is defined as a layer of polyhedral in same symmetry. This implies that if the deposition of the *layers* can be achieved at temperatures below 900 °C, it may be possible to overcome the thermodynamic equilibrium and impose external control over the distribution of magnetic ions. The fundamental issue that we discuss here is whether one can control the degree of cation inversion in spinel ferrites using this layer-by-layer growth

method and its impacts on the fundamental magnetic properties (saturation magnetization and anisotropy) of the manganese ferrite films that were well-studied.⁴

EXPERIMENTS AND RESULTS

Deposition technique

The artificial films of manganese ferrite were deposited from *separate binary oxide targets* of MnO and Fe_2O_3 . Alternate layers of MnO and Fe_2O_3 were deposited sequentially to produce films whose crystal structure and composition were similar to that of bulk manganese ferrite. Specifically, targets of MnO and Fe_2O_3 were mounted on a target rotator driven by a servomotor and synchronized with the trigger of the pulsed excimer laser (KrF $\lambda=248$ nm). In each deposition cycle, the ratio of laser pulses incident upon the MnO target to those upon the Fe_2O_3 target varied from 1:10 to 6:10 and 4:8. The energy of each laser pulse was fixed at 400 mJ, and the typical duration of a pulse was 50 ns. The deposition was carried out in a pure oxygen background of 1 to 50 mTorr. There were 1000 deposition cycles for each film resulting in a thickness ranging from 0.53 to 0.86 μm , measured by a step profilometer. The substrates of MgO, both <111> and <100> orientation, were mounted on the substrate heater using silver paste and heated to 700 °C during deposition. Deposition on {111} MgO substrates simulated the normal spinel structure, where A and B sites were parallel to each other along the <111> direction. If, for example, Mn^{2+} ions occupy A sites and Fe^{3+} ions B sites, it would simulate a normal spinel structure. Alternatively, deposition on {100}

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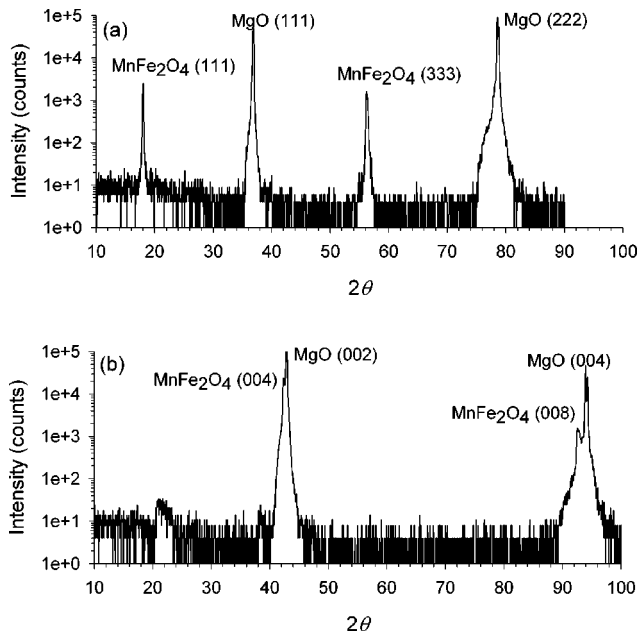


FIG. 1. X-ray diffraction of artificial manganese ferrite films on both $\{111\}$ and $\{100\}$ MgO substrates using $\text{Cu-K}\alpha$ line.

MgO substrate would simulate a partial inverse spinel ferrite structure. Here the MnO and Fe_2O_3 layer thickness need to be readjusted, if one wishes to pursue pure normal or inverse structures. Films deposited by sequential deposition from the two targets on either $\{111\}$ or $\{100\}$ MgO substrate are henceforth referred to as *artificial* ferrite films.

Structure and cation distribution

X-ray diffraction (XRD) and extended x-ray absorption fine structure (EXFAS) measurements were performed on artificial films. In Fig. 1, XRD data are shown for the artificial films grown on $\{111\}$ and $\{100\}$ MgO substrates. The XRD results reveal peaks indexed to (n,n,n) of artificial ferrite films on the $\{111\}$ oriented MgO substrate and $(0,0,4n)$ on the $\{100\}$ oriented MgO substrates, indicating that the films were epitaxially grown. No phase other than spinel was observed.

EXAFS measurements, following the procedure of Ref. 5, revealed the degree of cation inversion (δ) of the $\{111\}$ and $\{100\}$ artificial films as 0.1756 and 0.3195, respectively. δ is defined as the percentage of Mn cations on B sites.⁶ These films were prepared with a MnO-to- Fe_2O_3 ratio of 4:10 and an oxygen pressure of 1 mtorr. It was observed that the degree of cation inversion depended on oxygen pressure during deposition. For example, at 50 mtorr, there were about 66% of Mn cations on B sites. The oxygen parameter (u) of $\{100\}$ films was also measured by EXAFS. The measured u was 0.012 to $0.022(\pm 1 \times 10^{-3})$ larger than the bulk value of 0.3846 and increased with oxygen pressure during deposition, which was a significant deviation from the bulk value.

Saturation magnetization and uniaxial magnetic anisotropy field

The saturation magnetization ($4\pi M_S$) and uniaxial magnetic anisotropy field (H_u) at room temperature were mea-

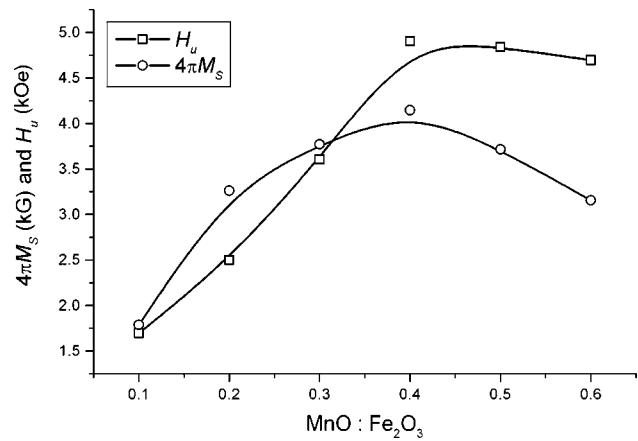


FIG. 2. Saturation magnetization and magnetic anisotropy field as a function of the shot ratio of MnO to Fe_2O_3 .

sured by vibrating sample magnetometer and (FMR). Although the magnetic anisotropy in bulk manganese ferrite materials was small, uniaxial anisotropy was observed in the films deposited on $\{100\}$ MgO substrates but not on $\{111\}$ substrates. It was observed that the saturation magnetization and uniaxial magnetic anisotropy field sensitively depended on the chemical composition (MnO-to- Fe_2O_3 ratio) and oxygen pressure during deposition (p_{O_2}).

As the MnO-to- Fe_2O_3 ratio was varied from 1:10 to 6:10, the chemical composition of the films varied from iron-rich to manganese-rich, which significantly affected the saturation magnetization and magnetic anisotropy field of the films. In order to isolate the effects of chemical composition on the magnetic properties of the artificial films, we compared the magnetic properties of the films deposited with $p_{\text{O}_2}=1$ mtorr. The maximal saturation magnetization (~ 4.2 kG) and uniaxial magnetic anisotropy field (~ 5.0 kOe) was achieved when the MnO-to- Fe_2O_3 ratio was about 4:10 (Fig. 2). The saturation magnetization at this ratio was also close to the bulk value. Auger spectroscopy measurement showed that this ratio was corresponding to the stoichiometry composition of manganese ferrite (MnFe_2O_4). The saturation magnetization curve was almost symmetric about the ratio of 4:10, since Fe^{2+} in iron-rich side and Mn^{3+} in manganese-rich had the same magnetic moment of about $4 \mu_B$. However, the uniaxial magnetic anisotropy curve was obviously asymmetric about the ratio of 4:10. The anisotropy dropped fast in the iron-rich side and quite slow in the manganese-rich side.

It was observed that oxygen pressure during deposition (p_{O_2}) also affected the magnetic properties of the artificial films (Fig. 3). As oxygen pressure increased in the low-pressure region (<10 mtorr), the saturation magnetization decreased from 4.2 to 2.6 kG. In the high-pressure region (>10 mtorr), the saturation magnetization varied slowly (from 2.6 to 3.1 kG). The uniaxial magnetic anisotropy field showed a sensitive dependence on oxygen pressure during deposition. In the low-pressure region, it decreased quickly from 5.0 to -0.5 kOe. Here, a positive value suggested that the film plane was the magnetic preferential plane and the negative one suggest that the norm of the film plane was the magnetic preferential direction. The transition oxygen pres-

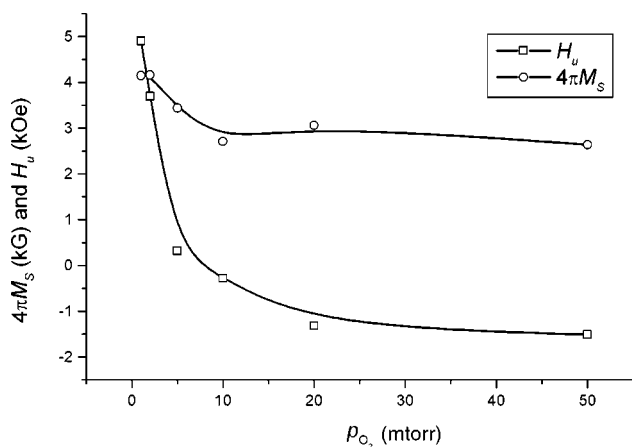


FIG. 3. Saturation magnetization and magnetic anisotropy field as a function of the oxygen pressure during deposition.

sure from an easy plane to easy axis anisotropy occurred at about 8 mtorr. In the high-pressure region, the uniaxial magnetic anisotropy field dropped slowly from -0.5 to -1.5 kOe.

DISCUSSION AND CONCLUSION

The experimental results were self-clear to show the power and flexibility of the deposition technique introduced here. By varying the MnO-to-Fe₂O₃ ratio and oxygen pressure, it was possible to tune the fundamental magnetic properties of the artificial films in a wide range. This merit to ferrite should be as important as the doping technique to semiconductors in the sense of processing.

The oxygen pressure during deposition played a key role, since it affected cation distribution, oxygen parameter, saturation magnetization, and uniaxial magnetic anisotropy. Plotting cation distribution, oxygen parameter, and uniaxial magnetic anisotropy field as a function of oxygen pressure during deposition, we observed a correlation between these quantities.

The oxygen pressure during deposition affected saturation magnetization and cation distribution through the collisions between cations (or clusters containing cations) and oxygen molecules (ions or atoms). The cations (or clusters containing cations) in plasma generated by laser ablation had less chance to collide with oxygen molecules (ions or atoms) at a lower oxygen pressure. This resulted in a higher thermal energy of adatoms (or adclusters), and consequently, less defects or better crystal quality at a lower oxygen pressure. The higher saturation magnetization obtained at a lower oxygen pressure can be attributed to the better crystal quality at a lower oxygen pressure. At the same time, a higher thermal energy of adatoms and adcluster at a lower oxygen pressure resulted in a better relaxation process, which resulted in a degree of cation inversion close to the bulk value. At a high

oxygen pressure, collisions between oxygen molecules (ions or atoms) and Mn²⁺ cations (or clusters containing Mn²⁺ cations) may oxidize Mn²⁺ to Mn³⁺, which results in a high degree of cation inversion, since Mn³⁺ ions strongly prefer B sites. Since Mn³⁺ cations on the surface are unstable, it reduces to Mn²⁺ cations instantly by trapping one electron. Mn²⁺ cations may however stay at B sites, since the low thermal energy caused by the collisions is not enough to move atoms.

The oxygen pressure during deposition effected uniaxial magnetic anisotropy through two major mechanisms. First, the thermal expansion coefficient of MgO [$\alpha_{\text{MgO}}=10 \times 10^{-6} / \text{K}$ (Ref. 7)] is smaller than that of MnFe₂O₄ [$\alpha_{\text{MnFe}_2\text{O}_4}=12 \times 10^{-6} / \text{K}$ (Ref. 8)]. Observing the negative magnetostriction constant along $\langle 100 \rangle$ directions (λ_{100}) of manganese ferrite,⁹ magnetostriction may explain the negative uniaxial magnetic anisotropy field at high oxygen pressure.¹⁰ However, this mechanism is unable to explain the positive uniaxial magnetic anisotropy at low oxygen pressure. Since the uniaxial magnetic anisotropy field versus the MnO-to-Fe₂O₃ ratio curve kept almost flat when the chemical composition in the manganese-rich region, we deduced that Mn³⁺ might not contribute the uniaxial magnetic anisotropy at low oxygen pressure. In fact, the low oxygen pressure may introduce Fe²⁺ ions in the artificial films, which results in a positive λ_{100} and consequently a positive uniaxial magnetic anisotropy field. It should be noted that the Fe²⁺ ions concentration sensitively depends the oxygen pressure, which explains the sensitive dependence of uniaxial magnetic anisotropy on oxygen pressure at low oxygen pressures.

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