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# Influence of oxygen partial pressure on the epitaxial $MgFe_2O_4$ thin films deposited on $SrTiO_3$ (1 0 0) substrate

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ABSTRACT

Epitaxial $MgFe_2O_4$ (MFO) thin films have been deposited on $SrTiO_3$ (STO) (1 0 0) substrates via a pulsed laser deposition technique under different oxygen partial pressures at 650 °C. The various oxygen partial pressures showed significant influence on the sticking coefficient and the spatial distribution of target materials. The lattice constant of the MFO thin films was decreased with increasing an oxygen partial pressure. The thin films synthesized at high oxygen partial pressure showed rough surface morphology. Also, epitaxial MFO thin films showed anisotropic magnetic behavior and the film grown at the oxygen pressure of 40 mTorr exhibited the highest saturation magnetization of 194 emu/cc.



## 1. Introduction

Spinel ferrites of the type $MFe_2O_4$ (M = Mg, Cu, Ni, Zn, etc.) have been considered to be the important materials for developments in magnetic storage, electronics, ferrofluid technology, magnetocaloric refrigeration and bio-medical applications. Thin films of spinel ferrites show excellent chemical stability and high corrosion resistivity. Among the spinel ferrites, $MgFe_2O_4$ (MFO) has been considered as an important material because of its partially inverse spinel structure [1] and a soft magnetic n-type semiconducting properties [2]. MFO has been investigated for many applications, including microwave devices [3], catalysis [4], and fuel cells [5].

In case of high frequency applications, the grown epitaxial thin film materials facilitate to reduce the attenuation of light, microwave and electrical current. The growth of the epitaxial thin film is mainly dependent on the similarity of crystal structure and the small difference of lattice mismatch and thermal expansion coefficient between the deposited materials and substrates. The epitaxial growth of various spinel ferrites has been reported on $SrTiO_3$ [6], MgO [7], Si [8] substrate. The epitaxial thin film growth on single crystal substrates results in an epitaxial strain due to the lattice mismatch between film and substrate. The stress-induced magnetization of epitaxial ferrite thin films on various buffer layers and substrates were investigated [9,10]. These reports indicated that the magnetic property of the epitaxial films possessing a proper compressive stress was reached to the bulk value. Therefore, microstructure related properties of epitaxial films have become interesting issues for the investigations. Even though there are few reports on the epitaxial growth of $MgFe_2O_4$ (MFO) thin film on STO due to large lattice mismatch, but the influence of oxygen partial pressures on the epitaxial growth behavior of MFO thin films have to be investigated.

In this study, the epitaxial MFO films were deposited on STO substrates via a pulsed laser deposition (PLD) under different oxygen pressures. The structural and magnetic properties of MFO thin films were studied as a function of the oxygen pressures.

## 2. Experiment

The stoichiometric MFO target was prepared by a conventional solid-state reaction method. MFO target sintered at 1300 °C for 4 h and XRD analysis confirmed the lattice parameter was 8.37 Å, which was in agreement with the JCPDS # 17-0464 of $MgFe_2O_4$. The lattice mismatch between MFO and STO (3.905 Å) substrate is about 7.3% and tends to induce a compressive strain of the film. The MFO thin films were deposited on STO (1 0 0) substrate via a pulsed laser deposition (PLD) system with a KrF (248 nm) eximer laser. The MFO film was deposited at different temperatures and different oxygen partial pressures with the laser energy of 1.2 J/cm$^2$ and 10 Hz. The distance between the target and the substrate was 6 cm. The influences of the oxygen partial pressures were investigated in the range from 5 to 80 mTorr at 650 °C.

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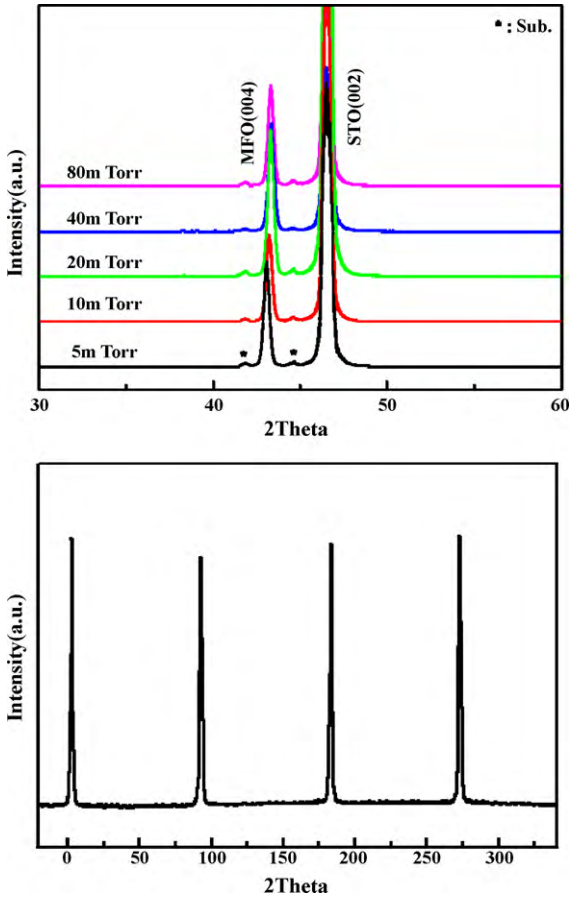


**Fig. 1.** The XRD patterns of the $MgFe_2O_4$ thin films prepared by 650 °C. (a) oxygen pressure dependence, (b) phi scan of sample deposited at 10 mTorr.

A base pressure under $2 \times 10^{-5}$ Torr was achieved with a turbo-molecular pump. The thickness of the MFO films was about 350 nm.

The crystal structure ($\theta$–$2\theta$) and rocking curve ($\omega$) of the films were investigated by a thin film X-ray diffractometer (Rigaku, D/MAX-RC, $\lambda = 1.5406$ Å) with Cu K$\alpha$ radiation. The phi scan ($\varphi$) of the film was investigated by a multi purpose X-ray attachment diffractometer (MPA-XRD: RIGAKU, D/MAX-2500). The lattice constants and FWHM of the films were calculated using a JADE 5 software. The thickness and surface structures were measured by scanning electron microscope (SEM: Philips XL30SFEG). The compositional analysis of the thin films was carried out using an energy dispersive X-ray spectroscopy (EDX). The magnetic properties were measured at room temperature by a vibrating sample magnetometer (VSM).

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the MFO thin films deposited under various oxygen partial pressures. In Fig. 1(a), only the peak corresponding to (0 0 4) plane of the MFO thin films was observed and convinces the epitaxial growth of the films along the [0 0 1] direction. Also, it is clearly observed that the peak of (0 0 4) plane of the each MFO films was shifted as a function of oxygen partial pressure. This phenomenon depending on oxygen pressure is a commonly observed in complex oxide systems [11,12]. One of the reasons for this phenomenon is the different spatial distribution of the each element in the plume. It is affected by collisions of gas molecules during a deposition process. In general, at higher pressures, a shock front acted like dynamic pressure was created between the plume and the surrounding gas during a plasma plume expansion [13]. The shock front disturbs the expansion of the plume and so that the sideward expansion of the plume increases, while the length of the plume decreases [14]. The other reason is the differences in sticking coefficient related to the volatility of the elements during film growth. These reasons indicated that the compositions of the films are strongly influenced by the change of the oxygen partial pressure. The phi scanning result of the MFO film prepared at the oxygen pressure of 10 mTorr is shown in Fig. 1(b). The (2 2 0) diffraction peak of the MFO thin film showed a four-fold symmetry indicating a cube-on-cube epitaxial growth behavior of the films on STO substrate.

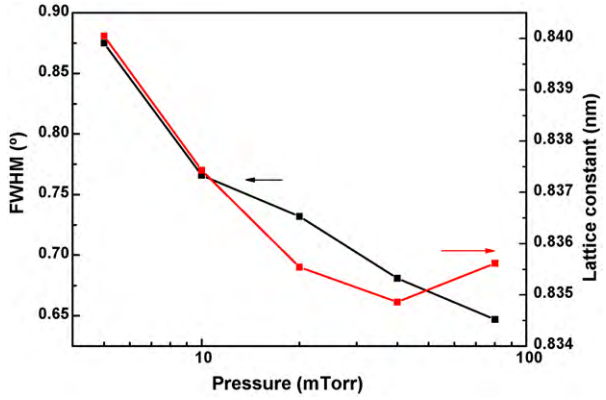


**Fig. 2.** The FWHM (°) and lattice parameters of the MFO films deposited at 650 °C and various oxygen pressure.

Fig. 2 shows the full width of the half maximum (FWHM) of the (0 0 4) peak and lattice constants of the MFO films deposited at 650 °C at different oxygen pressures. The FWHM of films deposited at different oxygen pressures exhibited a decreasing behavior with increasing oxygen partial pressure. In the literature, there are few reports on the films that reveal not always a decrease in FWHM values with increasing oxygen partial pressure [15]. In some cases [16], the crystal quality of thin films was degraded with in increase of the oxygen pressure. In the present study, the crystallinity of films was enhanced with the increase of the oxygen pressure that decreased the FWHM. The result may be attributable to the high reaction rate of the oxygen on the surface of thin films that facilitated at high oxygen pressures. Therefore, the oxygen vacancy concentration was decreased and the crystallinity of thin films was enhanced with an increase in the oxygen pressure. The MFO thin films were induced a compressive strain during the film depositions due to lattice mismatch (7.3%). The lattice constants of the MFO films fabricated as a function of different oxygen pressure exhibited a decrease to 8.348 Å up to 40 mTorr and then were tend to increase with the oxygen pressure. The result was attributed to the slight change in the composition of the MFO films influenced by the oxygen partial pressure. The compositional analysis of the MFO films by EDX is shown in Fig. 3. It is clearly observed that the sticking coefficient and the spatial distribution of the target materials depending on the oxygen pressures. These caused the small changes in the films' compositions. The ratio of heavy element (Fe: 55.847 amu) to light element (Mg: 24.305 amu) was increased below the oxygen pressure of 40 mTorr and then decreased at the higher pressure. Monte Carlo simulation [17] predicted that the ratio between the heavy species and light species was increased until the oxygen pressure reached to the specific gas pressure and then decreased. This is attributable to the differences in the gas pressures required for thermalization between heavy and light species. The deposition rate of light element decreases more quickly than that of heavy elements at low pressures (below the oxygen pressure of 20 mTorr). On the contrary, the deposition rate of heavy element decreases more rapidly at higher pressure.

Fig. 4 shows the SEM surface images of the MFO thin films prepared at 650 °C and different oxygen pressures. The films exhibited clean and smooth surfaces at lower oxygen pressures. The MFO thin film grown at the oxygen pressure of 80 mTorr showed a very poor surface morphology. It was indicated that an increase in the oxygen

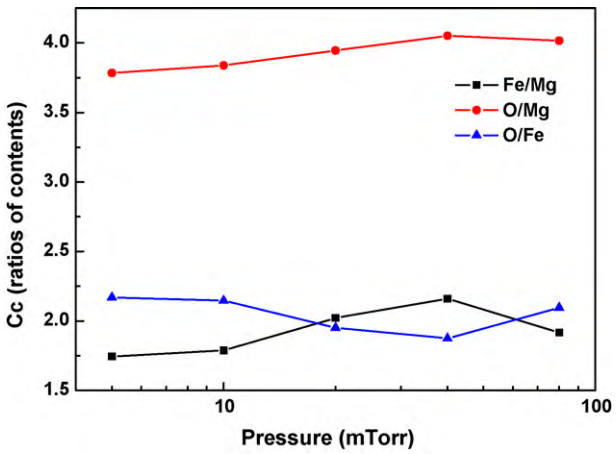


**Fig. 3.** The composition analysis (EDX) of the samples prepared at various oxygen pressure.

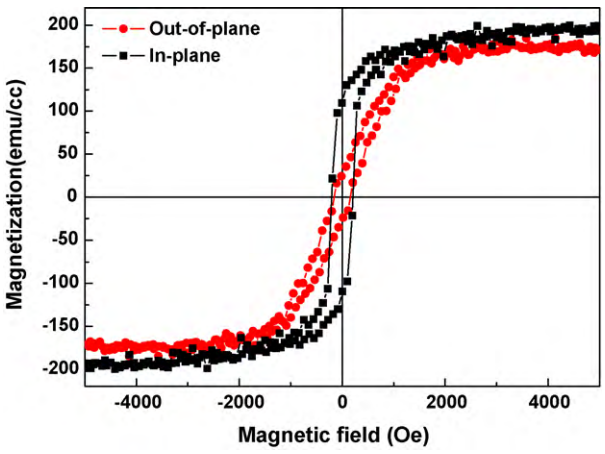


**Fig. 5.** The magnetization hysteresis of the MFO films prepared at 40 mTorr with the substrate temperature of 650 °C.

partial pressure led to a low quality surface morphology of the thin films. This is due to the grain growth of the MFO films as the oxygen pressure increased. The FWHM of MFO films was decreased as a function of the oxygen pressure as shown in Fig. 2. The increase in oxygen pressure led to the larger grain growth which was derived from FWHM in Fig. 2.

The magnetization in the MFO was derived from the site occupancy difference of $Fe^{3+}$ between tetrahedral and octahedral sites. And the magnetic properties of magnetic oxides were originated from the super-exchange interaction (M–O–M). Fig. 5 shows the magnetization hysteresis loops of the epitaxial MFO films deposited at the oxygen pressure of 40 mTorr with the substrate temperature of 650 °C. The epitaxially grown MFO film showed a soft magnetic behavior and a magnetic anisotropy. The in-plane direction is an easy magnetization direction. In the present study, the saturation magnetization for this deposition condition was ~194 emu/cc and the coercive field was ~206 Oe. The magnetization value is higher than the reported value 120 emu/cc [18].

Fig. 6 represents the saturation magnetization (in-plane) and the coercive field of MFO films as a function of the oxygen pressure at 650 °C. The $M_S$ of the MFO films were increased up to the oxygen pressure of 40 mTorr and further leads to a decrease, as shown in Fig. 6. The critical factors that influence on magnetism in spinel MFO were the concentration, distribution and valence states of magnetic ions (Fe) and oxygen defects. The dominant effect of the oxygen pressure is that oxygen vacancies in the films are decreased at high pressures and consequently lead to increase in the super-exchange interactions. Many researchers [19,20] reported that the saturation magnetization with the increase of the oxygen pressure was increased due to the reduction of oxygen vacancies that led a decrease in the super-exchange interactions. However, the oxygen concentration in the present study showed a different

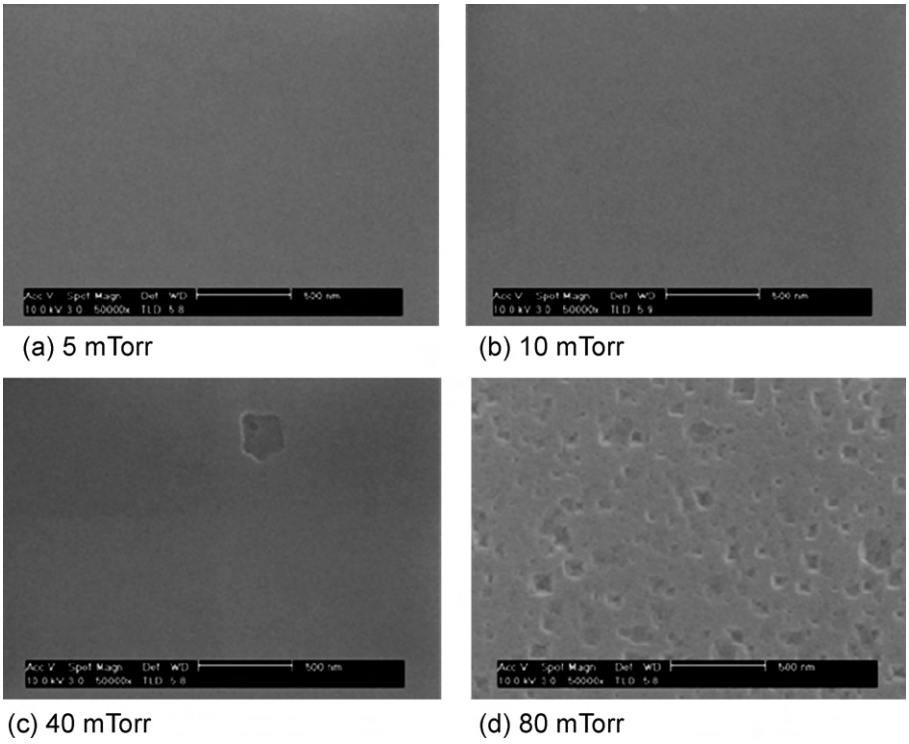


**Fig. 4.** The surface images of samples prepared at 650 °C with various deposition conditions (a) 5 mTorr, (b) 10 mTorr, (c) 40 mTorr, (d) 80 mTorr.

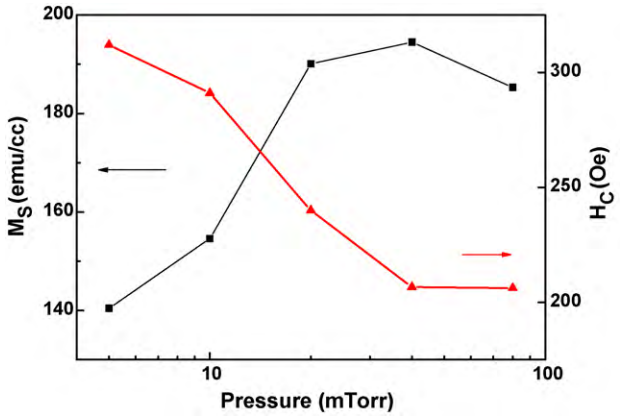


**Fig. 6.** The saturation magnetization and the coercivity of the MFO films with a function of oxygen pressure.

trend. The O/Fe ratio (Fig. 3) was decreased with increasing oxygen pressure up to 40 mTorr and then increased. Guo et al. [20] have reported that the oxygen concentration change between 200 and 800 mTorr was only 0.01 at.%, but that of metal cations showed about 0.1–0.5 at.%. The saturation magnetization was enhanced from 0.38 to 4.63$\mu_B$/f.u. in these pressure ranges. This result indicates that the increased quantity of magnetic cations resulted in the enhanced ferromagnetic ordering. The concentration of Fe ions in the present study was also increased up to the oxygen pressure of 40 mTorr and further leads to a decrease. The Fe/Mg ratio of the samples in Fig. 3 showed similar trends with $M_s$ and the lattice constant also had influence on the saturation magnetization. The atomic distance between $Fe^{3+}$ ions in the lattice was relatively short at the films having small lattice constant. This led to the enhancement of ferromagnetic ordering for the MFO films. Therefore, the saturation magnetization as a function of the oxygen pressure may be explained by the composition and the lattice constant of the film. The coercive field of the MFO film was monotonically decreased with increasing the oxygen pressure.

## 4. Conclusions

The epitaxial $MgFe_2O_4$ (MFO) thin films have been successfully deposited on the (0 0 1) STO substrate. The sticking coefficient and spatial distribution of species as a function of the oxygen pressure was changed slightly. Also, the oxygen partial pressure significantly influenced on the composition of the MFO films, which resulted in the modification of the structural and magnetic properties of the films. The lattice constant exhibited the minimum value at the oxygen pressure of 40 mTorr and corresponding maximum value of saturation magnetization of 194 emu/cc was appeared at 40 mTorr. However, the FWHM and surface morphology were not influenced by the compositional change of the deposited films.

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