Microstructure of the Oriented Hexagonal HoMnO₃ Thin Films by PLD

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We have fabricated (0001) oriented hexagonal $HoMnO_3$ thin films with thickness of 300 nm using Pulsed Laser Deposition (PLD) technique on $Pt(111)/Ti/SiO_2/Si$ substrates. The XRD θ-2θ pattern shows only (0002), (0004), and (0008) reflection of a hexagonal phase, and the full width at half maximum (FWHM) of (0004) peak is under 1.6°. The chemical state of Mn from XPS spectra of the films reveals the presence of Mn^{3+} only. The temperature dependence of dielectric constant shows a weak anomaly at magnetic Néel temperature (T_N), which is about 70 K.

Keywords : multiferroic, $HoMnO_3$, thin film

1. Introduction

In the past few years, multiferroic materials have been attracted much attention because of coupling between magnetism and ferroelectricity [1, 2]. These materials have shown the magnetoelectric effect of tuning magnetic (electric) phase by electric (magnetic) field. They are expected to open new potential applications in magneto-electric and magneto-optical device. Various multiferroic materials have been recently investigated [3-7]. Among these, rare earth manganite ($RMnO_3$, R=rare earth metal) reveals that the structural phase transition arises from orthorhombic to hexagonal crystal structure between Dy and Ho ion. The rare earth hexagonal manganites ($RMnO_3$, R=Dy, Ho, Er, Tm, Yb, and Lu) are particularly intriguing materials, which give rise to a ferroelectric polarization along c-axis with electric Curie temperature (T_C) of 600-1000 K. Mn magnetic ordering lies in a-b plane, forming an antiferromagnetic coupling and geometrically frustration with magnetic Néel temperature (T_N) of 70-120 K [8-10]. The theoretical and experimental studies have been focused on single crystal and powder. However, in order to make a multifunctional device, it should be investigated with a form of thin film. Therefore, many researchers have attempted the deposition of the hexagonal $RMnO_3$ thin films [11-14]. In this work, we report the growth and multiferroic properties of oriented hexa-

gonal $HoMnO_3$ thin films. The films were deposited on $Pt(111)/Ti/SiO_2/Si$ substrate by pulsed laser deposition (PLD) technique. The microstructure and temperature dependence of dielectric constant anomaly at magnetic transition temperature were studied.

2. Experiments

The $HoMnO_3$ target was prepared by a standard solid-state reaction method. Starting materials of Ho_2O_3, and MnO_2 were mixed, ground, pressed into a cylindrical pellet, and sintered at 1200-1400°C for 12-30 h in air. The XRD pattern of target was indexed according to the single phase of hexagonal space group $P6_3cm$. The $HoMnO_3$ thin films were deposited on 12×12 mm⁻² Pt (111)/Ti/SiO₂/Si(100) substrate by using a pulsed laser deposition (PLD) technique. A base pressure in chamber was 1.0×10^{-6} Torr, and a substrate was located at a distance of 4.5 cm from the target. For deposition, we have used a KrF (248 nm) excimer laser operated at 3 Hz and pulse energy of about 2.0 mJ/cm² during rotation of target and substrate, which was fixed at 900°C without post-annealing process. The crystallization of the film depends on oxygen pressure. In case of low oxygen pressure, it has tendency of (110) axis orientation. On the other hand, under high oxygen pressure, it has tendency of random axis orientation. The best deposition condition was 50 mTorr oxygen pressures during 60 minutes. In these experiment conditions, thickness of the film was measured about 300 nm. Crystalline structure was measured

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with x-ray diffraction (XRD), and surface morphologies and thicknesses of HoMnO₃ thin film were characterized with atomic force microscope (AFM) and scanning electron microscope (SEM). To measure the temperature dependence of dielectric constant, we used the physical property measurement system (PPMS).

3. Resusts and Discussion

Fig. 1 shows the XRD pattern of HoMnO₃ thin film on Pt(111)/Ti/SiO₂/Si substrate. We can see only (0002), (0004), and (0008) peaks of HoMnO₃ except for the Pt (111) substrate peak. The diffraction peaks correspond to the hexagonal phase at the base of powder diffraction pattern. The full width half maximum (FWHM) of (0004) peak is about 1.6°. This value indicates the preferred texture orientation of HoMnO₃ thin film along the c-axis. Our as-grown thin film reveals the single phase c-oriented crystallization. We also notice that FWHM of (0004) peak increases as deposition time decrease less than 60 minutes.

Fig. 2 shows SEM surface morphologies and cross sectional image of the film. It exhibits dense and crack free surface morphology, and RMS roughness measured with AFM is about 20 Å. Also, the microstructure of one grain shows well-align c-axis. However, grain size is randomly distributed. We believe that the random grain size distribution degrades the epitaxial growth of the HoMnO₃ thin film.

We have measured the XPS spectra of HoMnO₃ thin film surface to determine the ion state (in Fig. 3). The experiment data (dot) represented the fitted Mn($2p_{3/2}$) single peak (line) banding energy of 641.3 eV. Analysis

on Mn $2p$ level of the spectrum shows that Mn ion exists as Mn³⁺ ion state in the film surface. This indicates that Mn³⁺ ion state in the film surface is stabilized without the
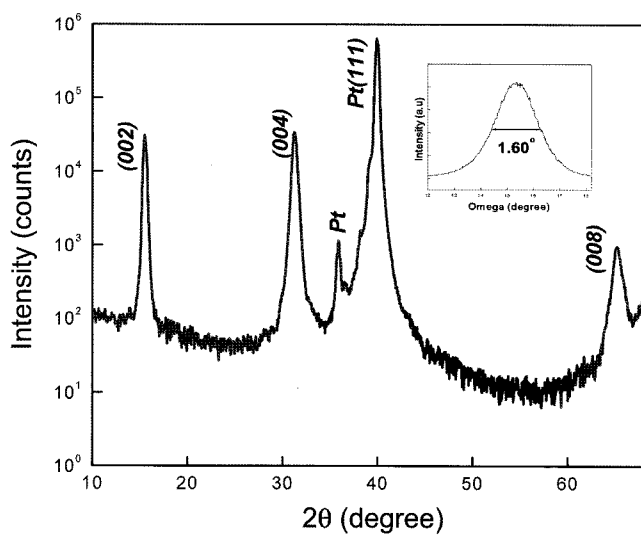

Fig. 2. SEM image of HoMnO₃ thin film a) surface and b) cross-section on the Pt(111)/Ti/SiO₂/Si substrate.

Fig. 1. X-ray diffraction patterns of HoMnO₃ thin film on the Pt(111)/Ti/SiO₂/Si substrate. The inset shows the rocking curve of the (0004) peak.
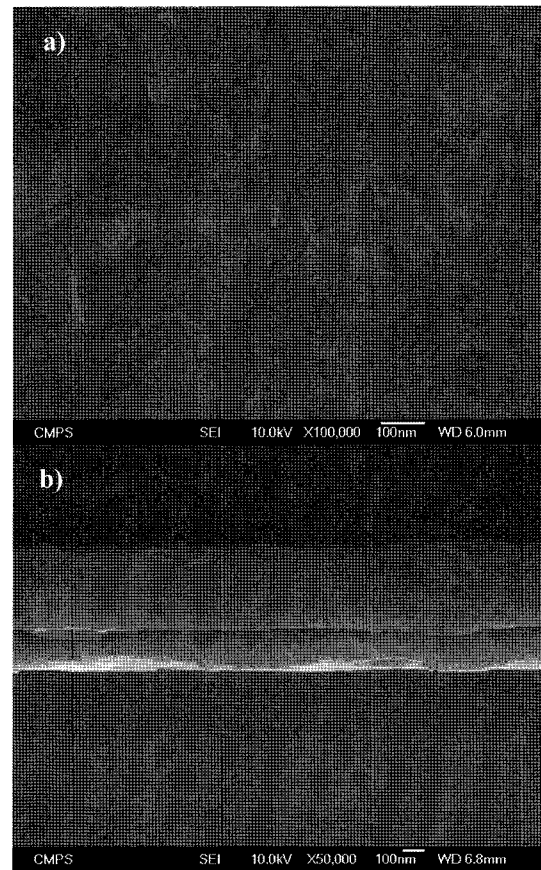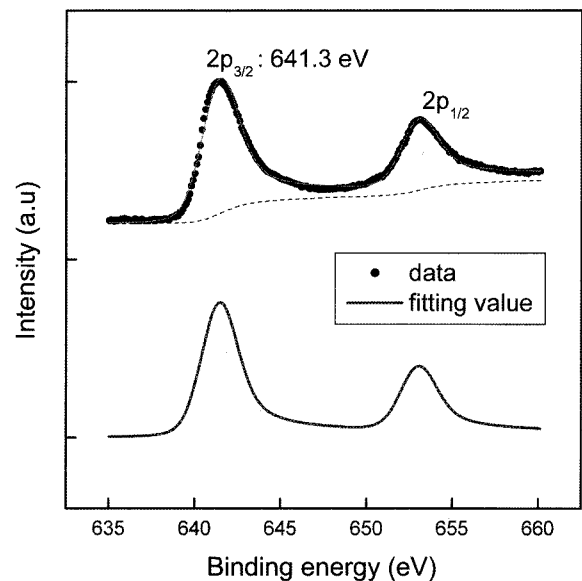

Fig. 3. XPS Mn($2p_{3/2}$ nd $2p_{1/2}$) spectrum and fitting curve of HoMnO₃ thin film surface on the Pt(111)/Ti/SiO₂/Si substrate.
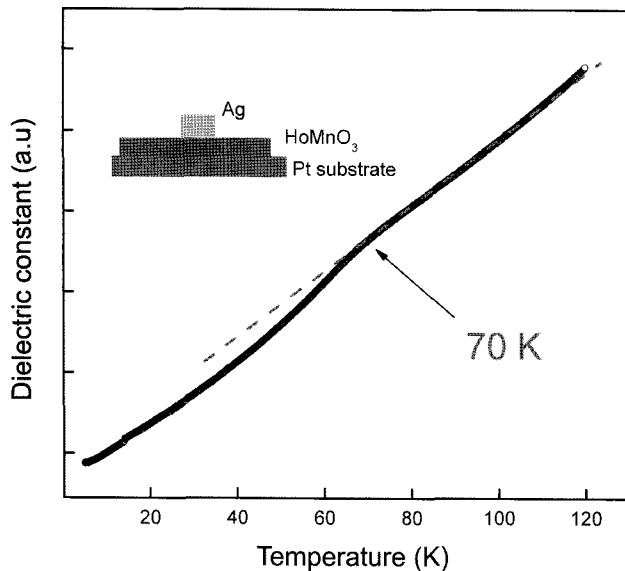
Fig. 4. The temperature dependence of dielectric constant of HoMnO$_3$ thin film on the Pt(111)/Ti/SiO$_2$/Si substrate.

influences from other Mn ion state and oxidation effect.

Fig. 4 shows the temperature dependence of dielectric constant of the film. Ag electrode was prepared on top of the film and Pt substrate was used at the bottom electrode. A weak dielectric constant anomaly was observed at 70 K. We have already reported the Mössbauer study of Fe doped HoMnO$_3$ powder in ref. 9. The Mössbauer spectra showed that the magnetic Néel temperature (T_N) of 1% Fe doped HoMnO$_3$ powders was determined to be 72 K. We believe that the weak anomaly is due to the magnetic phase transition. Therefore, the weak anomaly demonstrates the evidence of magnetoelectric coupling in oriented hexagonal HoMnO$_3$ thin film.

4. Conclusion

In summary, we fabricated (0001) oriented HoMnO$_3$ thin film on Pt(111)/Ti/SiO$_2$/Si substrate by PLD deposition method. We have investigated microstructure of the deposited film and observed the direct evidence of a coupling between the electric and magnetic order para-

meter in the HoMnO$_3$ thin film at magnetic Néel temperature.

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