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Effect of crystalline phases on the ferroelectric properties of $HoMnO_3$ thin films

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Abstract Ferroelectric $HoMnO_3$ thin films were deposited on the Si (100) substrates at 700°C for 2 h by metal–organic chemical vapor deposition. When the films were post-annealed at 800°C for 1 h in air, the single phase of hexagonal $HoMnO_3$ was detected, and the remnant polarization (Pr) and coercive field (Ec) were decreased due to the decrease of c-axis orientation. With an increase of annealing time, the crystalline phase of $HoMnO_3$ was changed from the single hexagonal to the mixtures of the hexagonal and orthorhombic phases of $HoMnO_3$, and/or $HoMn_2O_5$. Leakage current density was related with charge valence of Mn ion and surface roughness of thin film. Pr of hexagonal $HoMnO_3$ thin films with high c-axis orientation was 136 nC/cm^2 and the leakage current density was 10^{-6} A/cm^2.

Keywords Ferroelectric properties · $HoMnO_3$ thin film · C-axis orientation · MOCVD

1 Introduction

According to Bertaut et al. [1], the hexagonal rare-earth manganite ($ReMnO_3$) phase showed both ferromagnetic and ferroelectric ordering, while the orthorhombic $ReMnO_3$ phase only showed the magnetic ordering. Hexagonal phase is the lowest energy structure and structural phase transition from hexagonal to metastable orthorhombic can also take place upon annealing under high pressure [2].

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Recently, much attention has been paid to the ferroelectric thin films available to nonvolatile memories [3, 4]. One of these materials is rare-earth manganite ($ReMnO_3$). Because $ReMnO_3$ does not contain volatile elements such as Bi and Pb, but have a heavy and hard deoxidizing element as well as only one polarization axis. This material has a great potential for the application of nonvolatile memory device.

For the practical applications, it is necessary to conduct the systematic studies of $ReMnO_3$ system and CVD due to the advantages such as easy composition control, uniform large area deposition and the coverage of non-planar shapes [5]. Among $ReMnO_3$ materials, however, ferroelectrics characteristics of $HoMnO_3$ thin films have not yet been studied in details.

In this work, $HoMnO_3$ thin films were prepared on the Si (100) substrate by a metal–organic chemical vapor deposition (MOCVD). Crystalline phases of $HoMnO_3$ thin films were investigated as a function of post-annealing temperature and time, and the dependence of the crystalline phase on ferroelectric properties was evaluated. The effects of charge valence of Mn ion and surface roughness on electric properties of the $HoMnO_3$ thin film were also discussed.

2 Experimental procedure

$HoMnO_3$ thin films were deposited on Si (100) substrates by MOCVD. Holmium tris [(2,2,6,6-tetramethyl-3,5-heptandionate)] : (98%, Sigma Aldrich, St. Louis, MO, USA) and methylcyclo-pentadientl manganese tricarbonyl $[(CH_3C_5H_4)Mn(CO)_3]$: (97%, Sigma Aldrich) were used as the precursor materials. P-type Si (100) wafers were used as a substrate. The substrate was boiled into tetrachoethylene and cleaned by acetone and ethanol. After degreasing, the substrate was dipped into the solution of $HF:H_2O$(=1:10) to

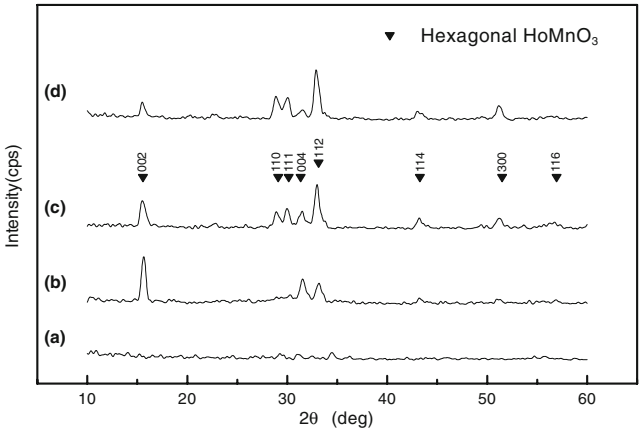

Fig. 1 XRD pattern of $HoMnO_3$ thin films deposited on Si (100) at 700°C for 2 h and post-annealed at various temperatures for 1 h in air; (**a**)750°C, (**b**) 800°C, (**c**) 850°C, (**d**) 900°C

remove SiO_2 on the Si substrate. Ho and Mn source vapors were obtained by the passing of carrier gas (N_2) through bubblers kept at 160 and 20°C, respectively.

Top electrode of Au was deposited by sputtering to measure the electric properties of $HoMnO_3$ thin films. Crystalline phases were determined by an X-ray diffraction analysis (XRD, Philips X′pert MPD, New York, NY, USA). Microstructure and surface roughness of the films were observed by a field-emission-type scanning electron microscope (Hitachi S-4200, Tokyo, Japan), and scanning probe microscope (Topometrix accurex, Santa Clara, CA, USA), respectively. P–E hysteresis loops of the thin films were evaluated using a Sawyer–Tower circuit. Leakage current density (I-V) was measured using a Keithley 617 programmable electrometer. In order to identify Mn valence state of the film, X-ray photoelectron spectroscopy (XPS, ESCALAB 220i-XL, UK) was used.

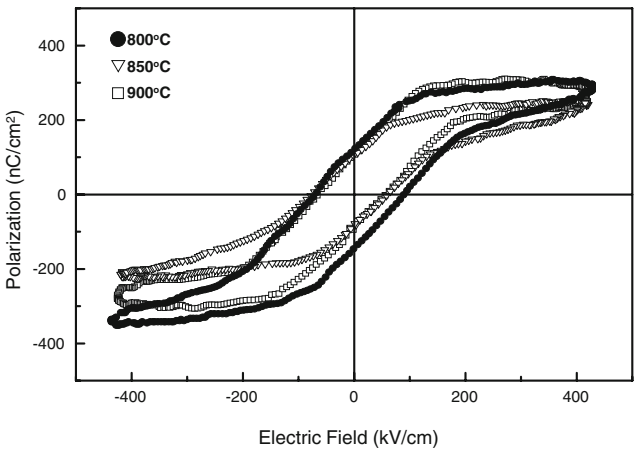

Fig. 2 Hysteresis loop of $HoMnO_3$ thin films on Si (100) deposited at 700°C for 2 h and post-annealing at various temperatures for 1 h

Table 1 The degree of c-axis orientation and ferroelectric characteristics of $HoMnO_3$ thin films.

Annealing temperature (°C)	$f=\frac{f^{film}_{(002)}-f^{powder}_{(002)}}{1-f^{powder}_{(002)}}$	$f=\frac{f^{film}_{(004)}-f^{powder}_{(004)}}{1-f^{powder}_{(004)}}$	Pr (nC/cm^2)	Ec (kV/cm)
800	0.220	0.152	136	88
850	0.118	0.079	101	65
900	0.109	0.076	92	63

3 Results and discussion

Figure 1 shows XRD patterns of $HoMnO_3$ thin films deposited on the Si (100) substrate at 700°C for 2 h and post annealed at various temperatures for 1 h in air. Crystallization began at the post-annealing temperature of 800°C and the hexagonal phase of $HoMnO_3$ was detected. With the increase of post-annealing temperature, c-axis orientation was decreased and the polycrystallinity of $HoMnO_3$ thin film was increased.

Figure 2 shows the ferroelectric hysteresis of $HoMnO_3$ thin films post-annealed at various temperatures. Yi et al. [6] reported that $ReMnO_3$ had a single polarization axis (00*l*), and the ferroelectric properties could be obtained for $ReMnO_3$ thin films with preferred orientation to polarization (00*l*).

According to Hu et al. [7], the degree of c-axis orientation of the $HoMnO_3$ thin films on the Si (100) substrates could be evaluated by the fractional parameter in Eq. 1

$$f=\frac{I_r^{film}(00l)-I_r^{powder}(00l)}{1-I_r^{powder}(00l)} \quad (1)$$

where, I_r^{film} and I_r^{powder} are the relative intensities of $HoMnO_3$ thin film and powder. The relative intensity $I_r(00l)$ could be expressed $I_r(00l)=I(00l)/\sum I(hkl)$, and obtained from the intensity of the (00*l*) peak normalized by the summation of

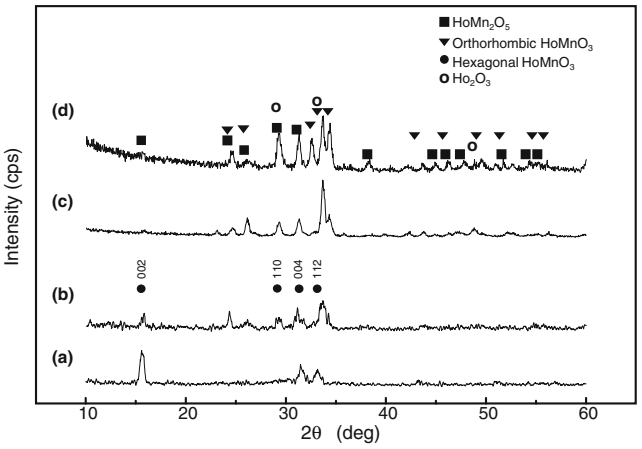

Fig. 3 XRD patterns of $HoMnO_3$ thin films on Si (100) deposited at 700°C for 2 h and post-annealed at 800°C for various times in air; (**a**) 1 h, (**b**) 2 h, (**c**) 5 h, (**d**) 10 h

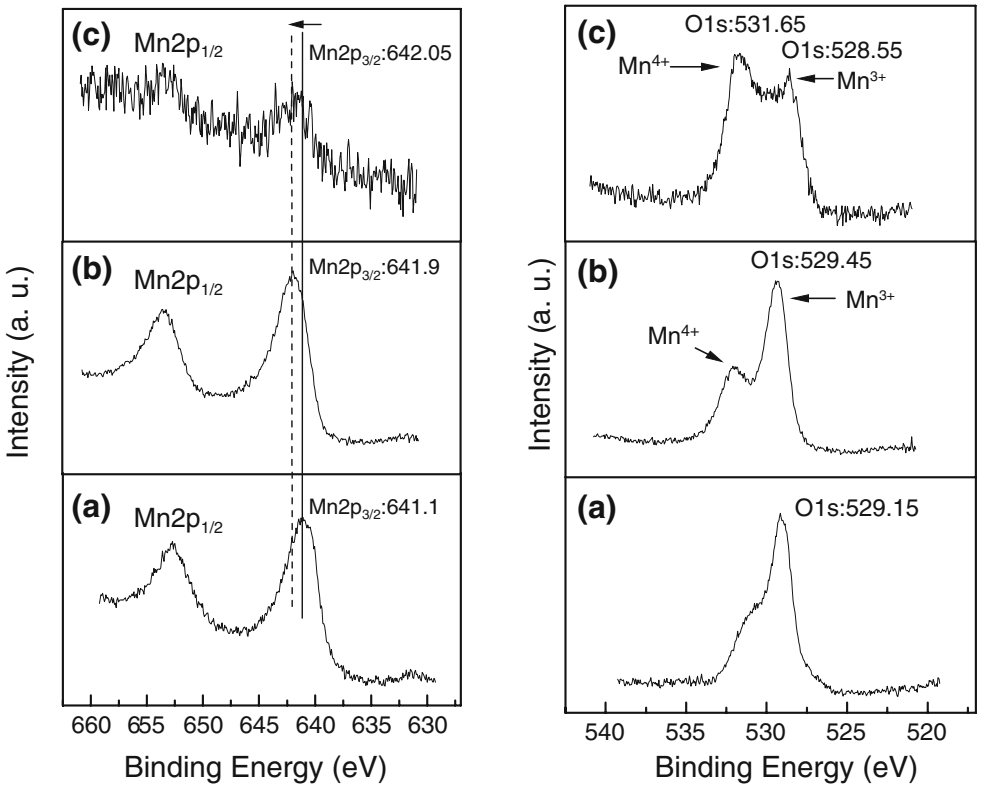

Fig. 4 XPS pattern of $HoMnO_3$ thin films on Si (100) deposited at 700°C for 2 h and post-annealed at 800°C for various times; (**a**) 1 h, (**b**) 2 h, (**c**) 10 h

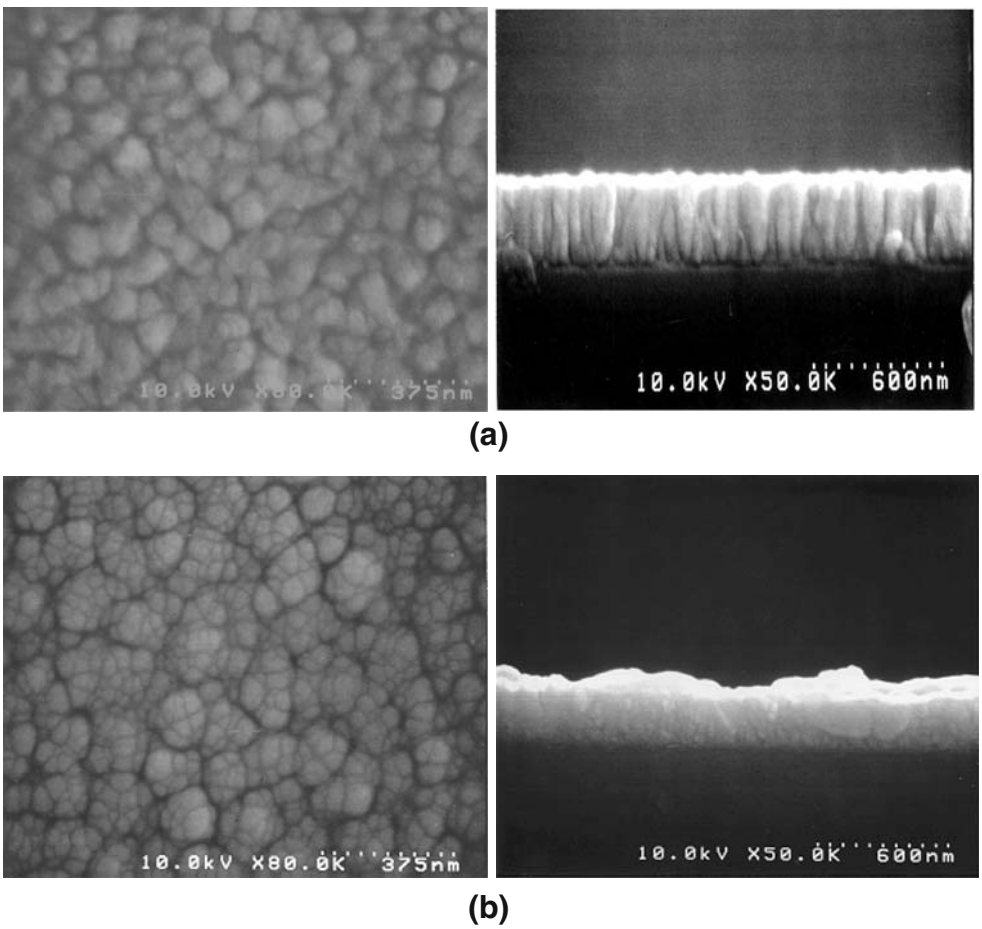

Fig. 5 Field-emission-type scanning electron microscope micrographs of $HoMnO_3$ thin films on Si (100) deposited at 700°C for 2 h and post-annealed at 800°C for various times; (**a**) 1 h, (hexagonal phase), (**b**) 2 h, (mixture of phase of hexagonal and orthorhombic phase)

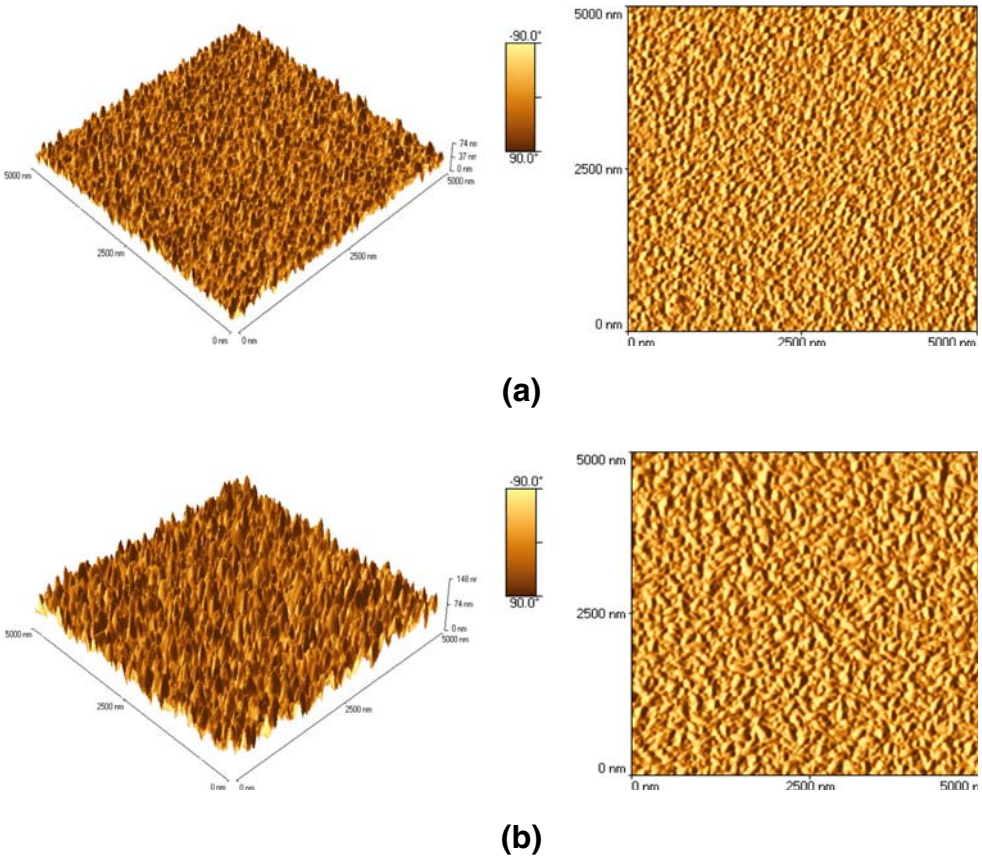

Fig. 6 Scanning probe microscope of $HoMnO_3$ thin films on Si (100) deposited at 700°C for 2 h and post-annealed at 800°C for various times; (**a**) 1 h, (hexagonal phase), (**b**) 2 h, (mixture of phase of hexagonal and orthorhombic phase)

the intensities of all the peaks of $HoMnO_3$ between $2\theta=10$ and 60°. For randomly oriented polycrystalline films, the degree of c-axis orientation (*f*) is equal to 0; for completely oriented film, $f=1$; and for partially c-axis oriented films, f falls between 0 and 1.

Table 1 summarized the degree of c-axis orientation from Eq. 1 and the ferroelectric properties (Pr, Ec) of $HoMnO_3$ thin film were obtained from Fig. 2. With the increase of post-annealing temperature, c-axis orientation and Pr, Ec were decreased. These were agreed with the results that the remnant polarization increased with the c-axis orientation of $YMnO_3$ thin films [7]. Therefore, c-axis orientation was an affecting factor on the ferroelectric properties (Pr, Ec) of $HoMnO_3$ thin film.

Figure 3 shows XRD patterns of $HoMnO_3$ thin films deposited on Si (100) at 700°C for 2 h and post-annealed at 800°C for various times. With the increase of post-annealing time, the crystalline phase was changed from the hexagonal single phase for 1 h annealing to the mixture of hexagonal and orthorhombic phases for 2 h annealing, and that of orthorhombic $HoMnO_3$ and $HoMn_2O_5$ for more than 5 h. Even though 2% of Mn^{4+} was detected in

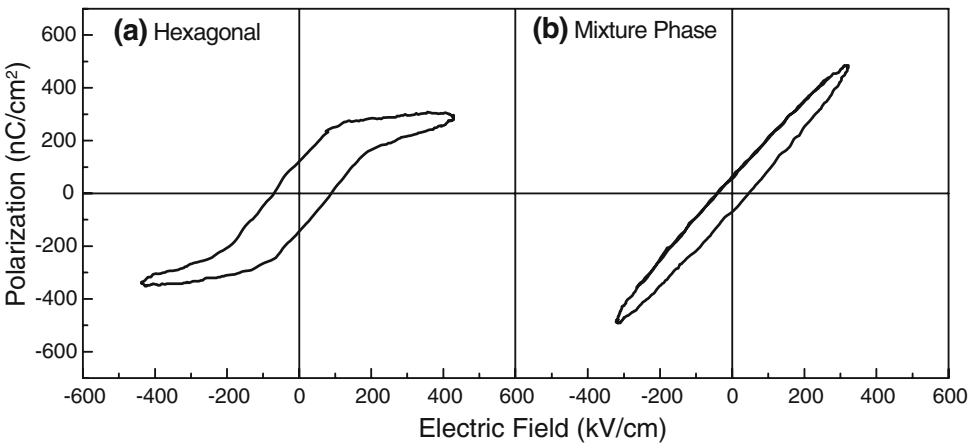

Fig. 7 Hysteresis loop of $HoMnO_3$ thin films with (**a**) hexagonal phase and (**b**) mixture phase of hexagonal and orthorhombic phase

$HoMnO_3$ bulk specimens annealed at 900°C for 12 h [8], the specimens showed metallic and/or the ferromagnetic behavior due to the transition of Mn^{3+} to Mn^{4+}. From XPS analysis of post-annealed films shown in Fig. 4, the valence state of Mn was Mn^{3+} for hexagonal single phase of $HoMnO_3$, however there were coexistence of Mn^{3+} and Mn^{4+} for the mixture of hexagonal and orthorhombic phases of $HoMnO_3$ [9]. With the increase of annealing time to 10 h, $HoMn_2O_5$ was formed due to the partial valence state transition of Mn resulted from the increase of reaction time between $HoMnO_3$ thin film and oxygen. Therefore, the proper heat treatment condition preventing the valence state transitions of Mn^{3+} to Mn^{4+} was essential to obtain the hexagonal single phase of $HoMnO_3$ with the good ferroelectric properties.

As shown in Figs. 5 and 6, the single hexagonal phase of $HoMnO_3$ thin films showed the fine homogeneous grain size (90–110 nm), the uniform thickness (260 nm) and the smooth surface (RMS: 9.2690 nm), while those of the mixture of the hexagonal and orthorhombic phases were 220–300 nm of grain size, 290–350 nm of thickness and 19.2268 nm of surface roughness, respectively.

Figure 7 shows the P–E hysteresis loop of $HoMnO_3$ thin films. Typical ferroelectric hysteresis loop was observed for the hexagonal single phase of $HoMnO_3$ thin film. However the ferroelectric hysteresis loop was not observed for the mixture of the hexagonal and orthorhombic phases of $HoMnO_3$ thin films. It is reported [10] that the MnO_5 bipyramids may play an important role in the ferroelectricity of hexagonal phase $YMnO_3$. MnO_5 bipyramids with weak Mn–O bonds may be deformed more readily to induce the displacement of ions in the ferroelectric phase, however the Mn–O bonds of MnO_6 in the orthorhombic phase are relatively short and strong. Therefore, the ferroelectric properties could not observe in the mixture phase of hexagonal and orthorhombic phases.

Kitahata et al. [11] reported that the transform from Mn^{+3} to Mn^{+4} ion of $YMnO_3$ in the excess oxygen atmosphere, resulted in the increase of leakage current density. The leakage current density of the mixture phase was higher than that of the hexagonal single phase of $HoMnO_3$ thin films, as shown in Fig. 8.

These were agreed with the results of XPS analysis in Fig. 4 and the microstructures in Figs. 5 and 6. Leakage current density was also affected by the surface roughness of thin film.

4 Conclusions

Hexagonal $HoMnO_3$ thin film with high c-axis orientation was deposited on the Si (100) substrate by MOCVD. Although a single phase of hexagonal $HoMnO_3$ thin films post-annealed at 800°C to 900°C was detected, the remnant polarization (Pr) and the coercive field (Ec) were decreased due to the degree of c-axis orientation. With an increase of post-annealing time at 800°C, the crystalline phase of $HoMnO_3$ thin film was changed from the hexagonal single phase to the mixture of hexagonal, orthorhombic and/or $HoMn_2O_5$ phases. For $HoMnO_3$ thin films with the single hexagonal phase, fine homogeneous grain size, the uniform thickness and smooth surface were observed, compared to those of the mixture of hexagonal and orthorhombic phases.

$HoMnO_3$ thin film with the single hexagonal phase showed the remnant polarization of 136 nC/cm^2 and the leakage current density of 10^{-6} A/cm^2 at an applied voltage of 1 V. Ferroelectric hysteresis characteristics were observed

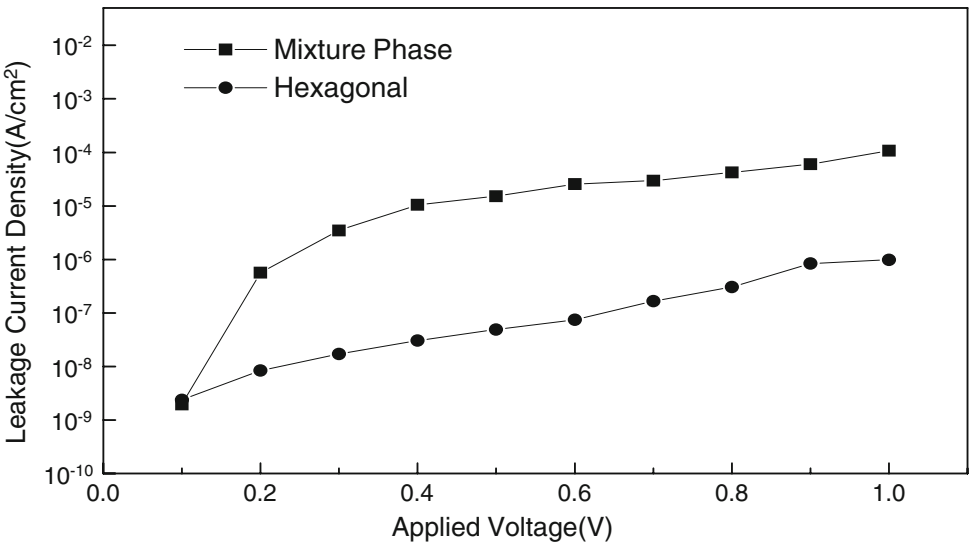

Fig. 8 Leakage current density of $HoMnO_3$ thin films with hexagonal phase and/or mixture phase of hexagonal and orthorhombic phase

only for the thin films with the single hexagonal phase, and leakage current density was depended on the valence state transitions of Mn^{3+} to Mn^{4+} and surface roughness.

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