Sputter-epitaxy and electric properties of multiferroic $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ thin films

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Growth conditions suitable for sputter-epitaxy of $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ (BFTO) thin films with layered structure have been investigated. The amount of oxygen during deposition was found to be specifically essential for obtaining a good-quality thin film of BFTO with a large *m*. The (001) epitaxial thin films of BFTO with *m* of nearly 10 which is expected to retain magnetic order up to room temperature have been successfully grown on (001) $SrTiO_3$ substrates under the determined optimum condition,. The film exhibited leakage current as low as order of $10^{-2} \sim 10^{-1}$ A/m^2 limited by Schottky emission at the interfaces between the electrodes and the film. In addition, the film showed a ferroelectric polarization curve with Pr= 6 μC/cm^2 for applied field of 35 MV/m at room temperature though the curve was unsaturated. These indicate that the BFTO (*m*=10) thin films are promising as multiferroics at room temperature.

Keywords: Multiferroics, Ferroelectric antiferromagnet, Aurivillius family, Bi oxides, Sputtered film, Epitaxy, Leakage current

1. Introduction

Multiferroics in which electric and magnetic orders coexist have attracted much attention in potential applications of spintronics. Some materials of them exhibited a magnetoelectric (ME) coupling that the magnetic and dielectric states have a cross interaction. Such a ME coupling allows the control of the magnetic order parameters or the magnetization reversal by an electric field. However, compounds exhibiting multiferroic properties above room temperature are very few except some perovskite oxides such as $BiFeO_3$ (BFO) [1].

$Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ (BFTO) is a ferroelectric antiferromagnet with a layered crystal structure which contains periodically a $(Bi_2O_2)^{2+}$ layer and m layers with a perovskite-like unit [2, 3]. An end member of this compound is the typical ferroelectrics with high Curie temperature, $Bi_4Ti_3O_{12}$ (m = 3). BFO can be regarded as a limiting case of layered perovskite-like structures with $m = \infty$ though the structure is not layered. Therefore, BFTO with a large number of m, i.e. with a large amount of Fe is expected to retain the magnetic order up to high temperature as well as BFO exhibiting high Neél temperature T_N = 643 K. However, no BFTO without impurity phases has been obtained for larger m than 5 due to volatility of Bi and/or structural instability increased with increasing m [3]. The BFTO having simultaneously magnetic and dielectric orders above room temperature has been not yet achieved in bulk and thin film forms.

In this study, we tried to epitaxially grow the thin films of BFTO with m=10 which is expected to retain magnetic order up to room temperature or more. This paper describes the growth conditions of epitaxial thin films of BFTO by sputtering and discuss the

structural and electric properties of the thin films prepared for m=10 in order to examine the response to applied electric field.

2. Experimental

The influence of growth parameters on the epitaxy were investigated on the thin films with m=4. This is because BFTO of m=4 is thermodynamically stable and the structural changes are easily compared with those prepared by bulk or other ways. In practice, the obtained thin films were compared with an epitaxial thin film with stoichiometric composition prepared by the chemical solution deposition (CSD) [4]. The thin films were grown on (001) $SrTiO_3$ (STO) and (001) Nb-doped STO (Nb: STO) at 400 °C and 450 °C by RF-magnetron sputtering using stoichiometric or 5 mol% Bi-overdosed oxide targets. Total gas pressure and the ratio of Ar to oxygen were changed in the range of 5 mTorr to 50 mTorr and 9/1 to 6/4, respectively, to examine the influence to the structural properties of the films.

Surface morphology and structural properties of the obtained thin films were characterized by atomic force microscopy (AFM), X-ray diffractmetry (XRD) and reflection high-energy-electron diffraction (RHEED). Ferroelectric and leakage measurements were carried out using ferroelectric test system for the BFTO / Nb: STO on which Au pads (200 μm in diameter) were fabricated as top electrode. The polarization hysteresis loop was measured at a frequency of 1 kHz.

3. Results and discussion

3.1 Optimization of growth condition

The structural properties of the obtained thin films strongly depended on the total gas and oxygen pressures during deposition. Figure 1 shows total gas pressure dependences of the XRD θ-2θ scans of BFTO films grown at 400 °C and Ar / O_2 = 9 / 1 using a stoichiometric target of m = 4. Excepting the {001} reflections and unassigned small peaks around 33° and 38° due to the STO substrate, the peaks observed for all films were assigned to (00$\underline{2l}$) reflections of the BFTO crystal. It was confirmed from the RHEED measurements that these films were epitaxially grown along the c-axis as shown in a latter example. This is consistent with that expected from the good in-plane lattice matching (0.5%) of BFTO <100> or <010> along STO <110>. However, with increasing the gas pressure, large shifts to higher angle were observed for the peaks except $l = m$+1, 2(m+1) as compared with that of the CSD thin film (m = 4). These shifts are due to changes of m. The number m of the perovskite-like layers per a half-unit cell of BFTO can be estimated from the observed ratio $d_{002\underline{m+2}}/d_{002\underline{m}}$ using the relationship of $c = 2md_{002\underline{m}} = 2(m+1)d_{002\underline{m+2}}$, where c denotes the lattice constant of c-axis, $d_{002\underline{m}}$ and $d_{002\underline{m+2}}$ the spacing of (00$\underline{2m}$) and (00$\underline{2m+2}$) planes, respectively. Table 1 summarizes the result. The number of m for thin film grown under higher gas pressure than 20 mTorr becomes larger, deviating from m=4 of the target, which means that Bi/(Fe+Ti) of the thin film was reduced and approached 1 with increasing the total pressure. This result is explained in terms of stronger affinity of Fe and Ti than Bi to oxygen and the increase of the absolute amount of oxygen itself. Figure 2 shows the θ-2θ scans of BFTO films grown under several Ar / O_2 at 5 mTorr. With increasing O_2, the remarkable enhancement of intensity and the reduction of the linewidth occured for the

satellite peaks (00$\underline{2l}$) of l=m-1, m, m+2, 2m, 2m+1 around the fundamental (00$\underline{2l}$) reflections of l= m+1 and 2(m+1) due to the unit cell of layered structure. These indicate that the increased oxygen prominently improved the local distortion and the stacking order of each perovskite-like layer due to oxygen deficiency.

On the basis of these results, the epitaxial thin films of BFTO (m=10) were grown under the following conditions; the total pressure of 10 mTorr, Ar/O_2=6/4, the substrate temperature of 450 ^{o}C. In addition, a 5 mol% Bi-overdosed target was used to compensate the loss of Bi due to volatilization.

3.2 Structural and electric properties of BFTO (m= 10) epitaxial thin films

Figure 3 shows the XRD θ-2θ scans of BFTO (m= 10) thin film, in comparison with that of BFTO (m= 4) thin film grown under the same condition. The scan exhibited only sharp and strong fundamental (00$\underline{2l}$) reflections along with weak satellite ones. This film showed streaky RHEED images dependent on the incident azimuth of electron beam as shown in Fig. 4. These directly indicate that the film was epitaxially grown with an in-plane axis relationship of film <100> or <010> // STO <110>. The lattice constant of c-axis obtained assuming in-plane stress-free was 8.95 nm for m=10 and 4.09 nm for m=4. These are consistent with the values expected or reported by earlier works [2, 3]. The layer number m of the BFTO thin film estimated by the same way as mentioned before is 9.4, slightly smaller than the nominal value (m=10). It is not clear at present whether such non-integer value is due to an experimental error or indicates the recurrent intergrowth formed by BFTO layers with m=9 and 10 [5]. The prepared

BFTO (m=10) thin film had smooth surface on nano-scale as seen in the AFM image of Fig. 5

Figure 6 (a) shows typical data of leakage current J as a function of applied electric field E for the BFTO (m=10) thin film (119-nm-thick) at room temperature. Data for both positive and negative biases have been graphed on the same axis, where we define the positive bias as the case when the top Au electrode is a higher potential than bottom Nb: STO electrode. The leakage current increased rapidly with an increase in the applied electric field, having the order of $10^{-2} \sim 10^{-1}$ A/m^2 at 8 MV/m though there is an asymmetry between J − E behavior for positive and negative biases. This order is much smaller than those ($10^{0} \sim 10^{3}$ A/m^2) reported for (100) BFO thin films [6-8], while is the same as that measured along the a-axis of $Bi_4Ti_3O_{12}$ (m=3) single crystal which is several orders-higher than along the c-axis [9].

In order to investigate possible leakage-current limiting mechanisms for the BFTO thin film, we plotted our data as a function of electric field in the following three manners that are commonly observed in perovskite oxides [10]: The first is space-charge-limited conduction exhibiting J proportional to E^2. The second is bulk-limited Poole-Frenkel emission. If this is dominant, the semi log plots of the conductivity σ vs. $E^{1/2}$ will show straight line with a slope $(1/k_BT)(e^3/\pi\varepsilon_0K)^{1/2}$, where K is the high frequency dielectric constant (= n^2, n: refractive index) [11]. The third is interface-limited Schottky emission which arises from a difference in Fermi levels between the metal electrode and the film. If this controls the leakage current, the semi log plots of J/AT^2 vs. $E^{1/2}$ will show straight line with a slope $(1/k_BT)(e^3/4\pi\varepsilon_0K)^{1/2}$, where A is the Richardson constant. Our analysis showed that the former two can be ruled out as the leakage current limiting mechanism

for the measured range of electric field. This is because the experimental curve of J vs. E^2 is exponential and K (= n^2) extracted from the slope of the semi log plots of σ vs. $E^{1/2}$ is 163, much larger than that (K= 2.3 ~ 6.3) expected from the range of refractive index n= 1.5 ~2.5 for Bi oxides. On the other hand, the semi log plots of J/AT^2 vs. $E^{1/2}$ showed regions with straight fits to the data for positive and negative biases as shown in Fig. 6 (b). These plots yield K= 5.1 for a positive bias and 2.4 for a negative bias, which reflect the asymmetric structure of Au/BFTO/Nb:STO. These values are in the range expected from n= 1.5 ~ 2.5, indicative of the leakage current in the BFTO films being limited by Schottky emission at the interfaces. This result suggests that the sputtered BFTO thin films itself may have much large electrical leak due to oxygen deficiencies and stacking faults.

Figure 7 shows the polarization-electric field (P-E) curve for the BFTO (*m*=10) thin film (119-nm-thick) at room temperature. The curve exhibited a defined hysteresis loop though the loop was unsaturated. Polarization curves could not be exactly measured for higher E because of increased electrical leakage. The remanent polarization (P_r) for applied electric field of 35 MV/m was about 6 μC/cm^2, considerably small as compared with those reported for $Bi_4Ti_3O_{12}$ (*m*=3) (the remanent polarization of 37 μC/cm^2 along the *a*-axis [9]) and BFO thin film (60 μC/cm^2 [1]). This likely comes from that the curve was unsaturated. The coercive field of this curve was 23 MV/m, much higher than that (4 MV/m) of the $Bi_4Ti_3O_{12}$ (*m*=3) single crystal [9]. Since BFO and BFTO (*m*=4) thin films containing Fe ions have a high coercive field in the range of 10 MV/m to 25 MV/m [1, 12, 13], the observed high coercivity may be associated with the Fe occupation of octahedral sites in the perovskite-like layers. These indicate that the BFTO (*m*=10) thin film is ferroelectric at room temperature.

Magnetic properties of these films were particularly intriguing. However, magnetic measurements using vibrating sample magnetometer (VSM) at room temperature showed no sign indicating magnetic order within experimental error because of too small volume of the thin films. We have recently prepared a BFTO epitaxial thin film with m= 9 fully substituted by the isotope Fe^{57} using CSD and confirmed from conversion-electron Mössbauer spectroscopy that the film is antiferromagnetic with Neel temperature of about 310 K [14]. This suggests indirectly the prepared BFTO thin film with larger m (=10) retaining antiferromagnetic order above room temperature.

4. Conclusion

We have examined the growth condition suitable for sputter-epitaxy of BFTO thin films with layered structure. Among the growth parameters, the amount of oxygen was found to be specifically essential for obtaining a good-quality thin film of BFTO with a large m. We have successfully grown the (001) epitaxial thin films of BFTO with m close to 10 which is expected to retain magnetic order up to room temperature or more. The films exhibited leakage current as low as order of $10^{-2} \sim 10^{-1}$ A/m^2 limited by Schottky emission at the interfaces between the electrodes and the film. In addition, the film showed a ferroelectric polarization curve with Pr= 6 μC/cm^2 for applied field of 35 MV/m at room temperature though the curve was unsaturated. These indicate that the BFTO (m=10) thin films are promising as multiferroics at room temperature.

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Fig. 1. Total gas pressure dependences of the XRD θ-2θ scans of BFTO films grown at 400 °C and Ar / O_2 = 9 / 1 using a stoichiometric target of m = 4, where the scan of the thin film with m=4 prepared by the CSD is also shown for comparison.

Fig. 2. XRD θ-2θ scans of BFTO films grown under several ratios of Ar to O_2 at 5 mTorr using a stoichiometric target of m = 4.

Fig. 3. XRD θ-2θ scans of the BFTO (m=10) thin film, where that of the BFTO (m= 4) thin film grown under the same condition is shown for comparison.

Fig. 4. RHEED images of a BFTO (m=10) thin film taken along (a) <100> and (b) <110> azimuths of STO substrate. The wider spacing between the streak lines observed in (b) than (a) means that the film has in-plane epitaxial relationship of film <100> or <010> // STO <110>.

Fig. 5. AFM image of the (001) film surface of BFTO (m=10).

Fig. 6. (a) Typical J-E characteristics of the Au/BFTO/Nb:STO thin film structures and (b) plots of our data and fitting line in the Schottky emission mechanism, where K denotes high-frequency dielectric constant.

Fig. 7. Polarization curves for the BFTO (m=10) thin film at room temperature.

Table 1

m values of thin films grown at various pressures and Ar/O_2. The *m* values were determined from the observed ratio $d_{002\underline{m+2}}/d_{002\underline{m}}$ using the relationship of $c = 2m d_{002\underline{m}} = 2(m+1) d_{002\underline{m+2}}$, where *c* denotes the lattice constant of *c*-axis, $d_{002\underline{m}}$ and $d_{002\underline{(m+1)}}$ the spacing of (002*m*) and (002*m*+2) planes, respectively.

Total gas pressure (mTorr)	Ar/O_2	*m*
50	9/1	5.63
20	9/1	4.21
5	9/1	3.90
5	8/2	4.20
5	7/3	4.23
CSD	-	3.96

Fig. 1.

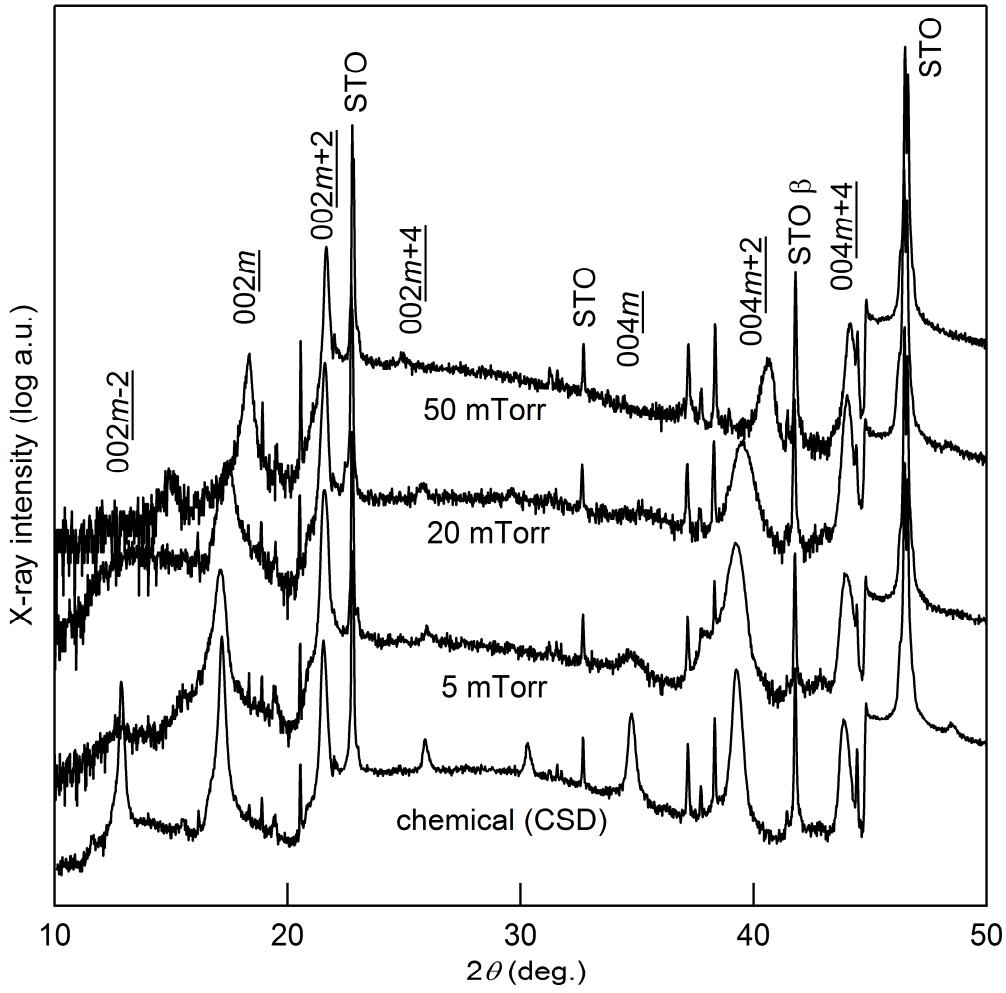
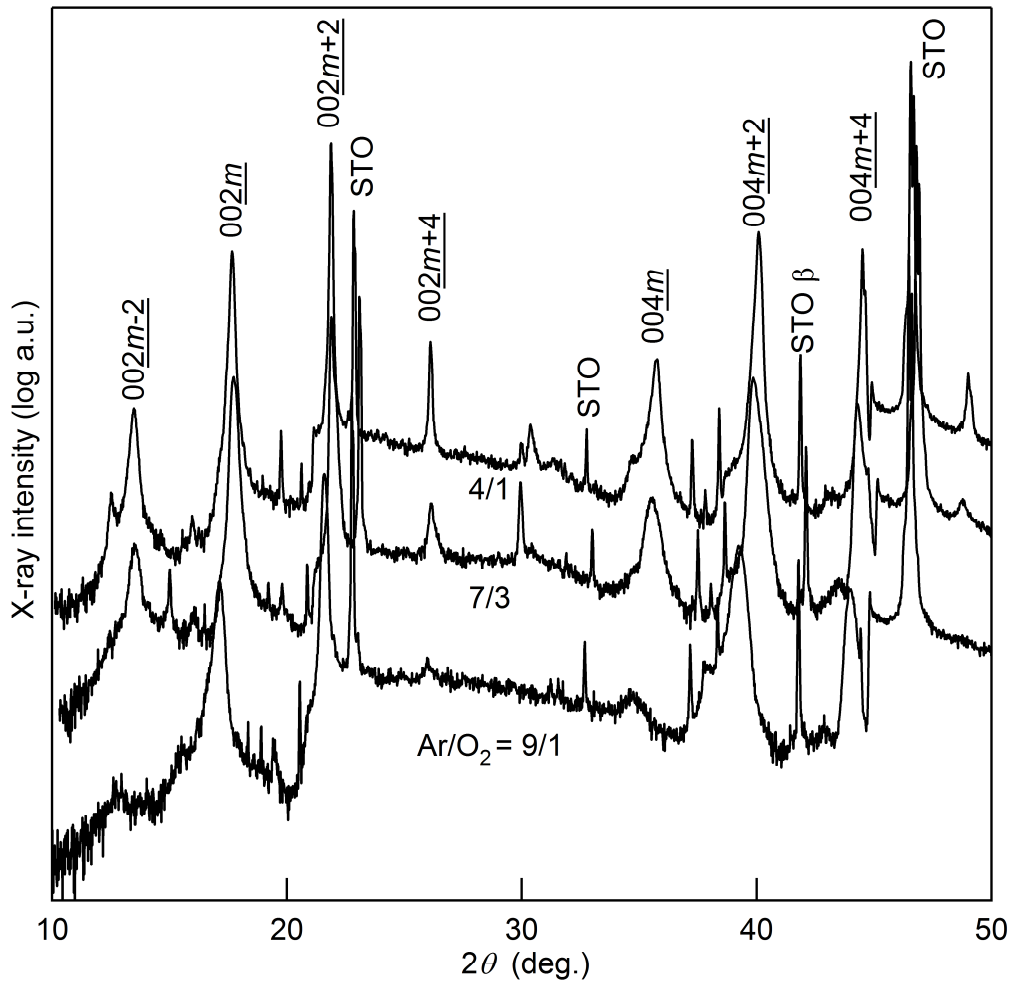

X-ray intensity (log a.u.)
002m-2
002m
002m+2
STO
002m+4
STO
004m
004m+2
STO β
004m+4
STO
50 mTorr
20 mTorr
5 mTorr
chemical (CSD)
10
20
30
40
50
2θ (deg.)

Fig. 2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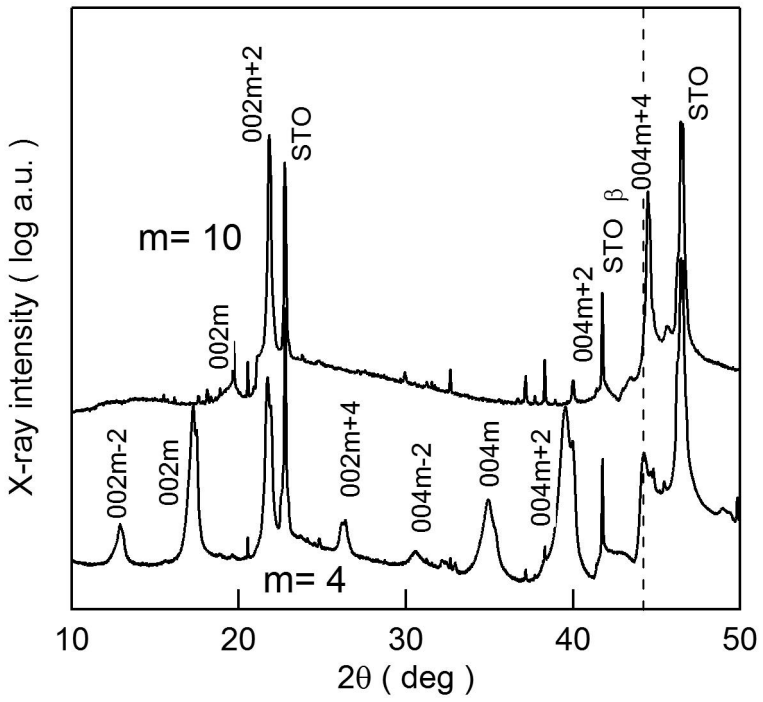
002m
002m+2
STO
002m+4
STO
004m
004m+2
STO β
004m+4
STO
4/1
7/3
Ar/O2 = 9/1
X-ray intensity (log a.u.)
10
20
30
40
50
2θ (deg.)

Fig. 3


X-ray intensity (log a.u.)
2θ (deg)
10
20
30
40
50
m= 10
m= 4
002m
002m+2
STO
004m+2
STO β
004m+4
STO
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002m
002m+4
004m-2
004m
004m+2

Fig. 4

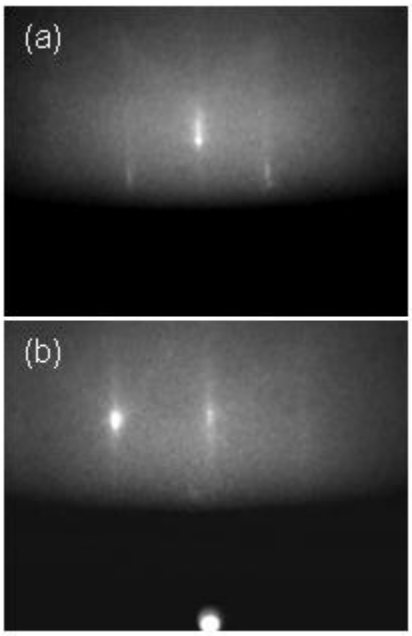


Fig. 5

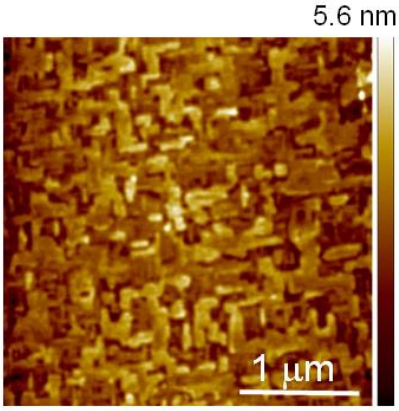


Fig. 6

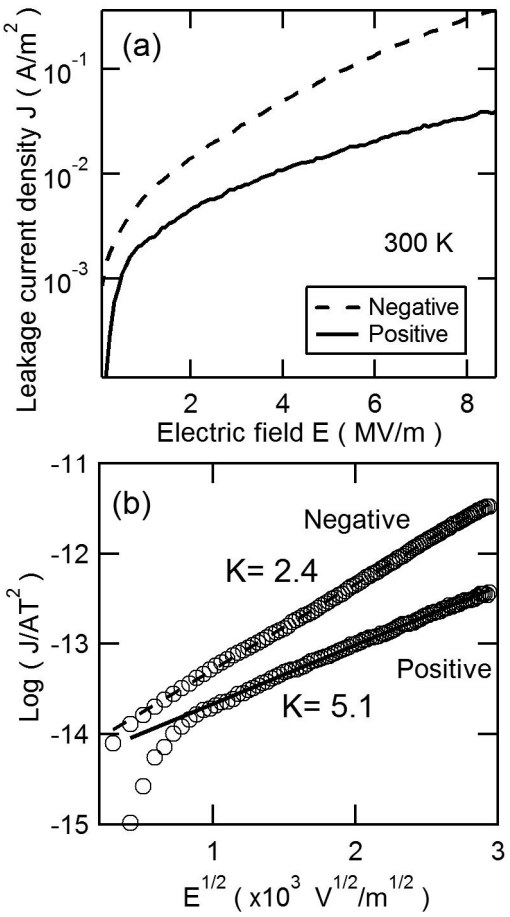
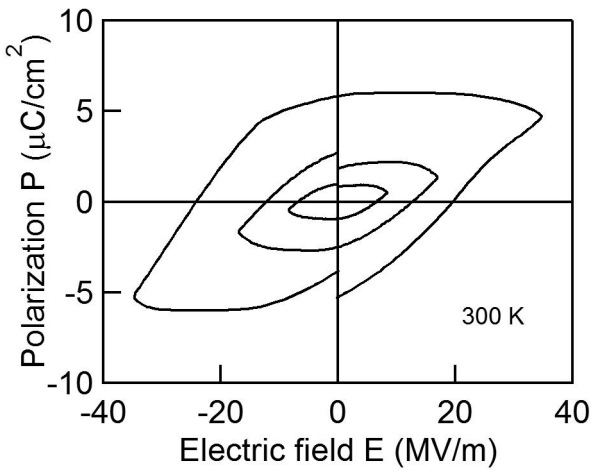

(a)
Leakage current density J (A/m^2)
10^{-1}
10^{-2}
10^{-3}
300 K
Negative
Positive
2
4
6
8
Electric field E (MV/m)
(b)
Negative
K= 2.4
Positive
K= 5.1
Log (J/AT^2)
-11
-12
-13
-14
-15
1
2
3
E$^{1/2}$ (x10^3 V$^{1/2}$/m$^{1/2}$)

Fig. 7


Polarization P (μC/cm²)
10
5
0
-5
-10
-40
-20
0
20
40
Electric field E (MV/m)
300 K