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Electrical Properties of $Bi_{4-x}Pr_xTi_3O_{12}$ (BPT) Thin Films Prepared by Sol-Gel Method

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$Bi_{4-x}Pr_xTi_3O_{12}$ (BPT) thin films were fabricated by the sol-gel technique on $Pt/Ti/SiO_2/Si$ substrates and their crystalline and electrical properties were characterized. It is shown that the partially replacing Bi with Pr in $Bi_4Ti_3O_{12}$ (BIT) film suppresses the formation of the pyrochlore phase. It is found that only poor ferroelectric properties can be obtained when the Pr composition is smaller than 0.3, probably because of the presence of the pyrochlore phase. On the other hand, a relatively large remanent polarization of 19 $\mu C/cm^2$ has been obtained for the BPT film with Pr composition of 0.5. In addition, a remanent polarization decreases with Pr composition when the Pr composition is larger than 0.5.

Key words: ferroelectric random access memory (FeRAM), sol-gel method, $Bi_{4-x}Pr_xTi_3O_{12}$ (BPT), $Bi_{4-x}La_xTi_3O_{12}$ (BLT)

1. INTRODUCTION

Recently, ferroelectric random access memory (FeRAM) has attracted much interest as a nonvolatile memory with low power consumption. There are mainly two types of FeRAM: one is a capacitor-type FeRAM [1, 2] and the other is a transistor-type FeRAM. A memory cell of the capacitor-type FeRAM consists of one transistor and one ferroelectric capacitor and it is also called 1T1C-type FeRAM. This type of FeRAM is now commercially available, although the density is not so large. On the other hand, a memory cell of the transistor-type FeRAM consists of only one ferroelectric-gate filed-effect-transistor (FET), where the ferroelectric thin film is used as a gate insulator. [3-7] This type is called 1T-type FeRAM and is considered promising for future high-density nonvolatile memory. However, the 1T-type FeRAM is still in the laboratory development stage, mainly because it is extremely difficult to deposit the ferroelectric thin film on semiconductors with good ferroelectric/semiconductor interface. Moreover, the ferroelectric-gate transistors usually suffer from short data retention time.

For high-density 1T1C-type FeRAMs, it is necessary to use a ferroelectric film with a large remanent polarization. International Technology Roadmap for Semiconductors (ITRS) suggests that a minimum switching charge required for 256Mb 1T1C-type FeRAMs in 2007 will be 40 $\mu C/cm^2$, which means that, roughly speaking, a remanent polarization of 20 $\mu C/cm^2$ will be required for the ferroelectric film.

Although $Bi_4Ti_3O_{12}$ (BIT) is a well-known ferroelectric material, it is rather difficult to fabricate BIT thin films with good electrical properties. Park et al. demonstrated that sol-gel-derived lanthanum-modified BIT, $(Bi,La)_4Ti_3O_{12}$ (BLT), has good electrical properties [8]. Since then, BLT has been considered as one of the candidates for future FeRAM applications, because BLT has a relatively large remanent polarization with a small coercive field and good fatigue endurance. However, the remanent polarizations, Pr, of the BLT films fabricated by various techniques are usually less than 20 $\mu C/cm^2$ with a few exceptions. [9] Substitution of Bi in BIT by other elements has already been studied. Matsuda et al. reported that relatively thick (1.2 μm) $Bi_{4-x}Pr_xTi_3O_{12}$ (BPT) films deposited by the chemical solution deposition (CSD) method on Ir/Si substrates have a large remanent polarization. In particular, when the Pr composition x is 0.3, a giant remanent polarization of more than 45 $\mu C/cm^2$ was demonstrated. However, a thickness of 1.2 μm as described in their report is too thick for practical applications.

In this work, we have fabricated thinner $(Ba,Pr)_4Ti_3O_{12}$ (BPT) films by the sol-gel technique on Pt bottom electrode. The thickness of the BPT films fabricated is 200 nm and we have used $Pt/Ti/SiO_2/Si$ substrates because Pt is more commonly used as a bottom electrode for ferroelectric film preparation.

2. EXPERIMENTAL PROCEDURE

$Bi_{4-x}Pr_xTi_3O_{12}$ source solution was spin-coated on a $Pt/Ti/SiO_2/Si$ substrate and dried at 240°C for 10 min. This process was repeated three times. Next, the film was crystallized at 750°C in oxygen ambient for 30 min. The Pt top electrodes were then vacuum evaporated using a

shadow mask. Finally, the sample was annealed again at 750°C for 10 min. The thickness of the BLT films fabricated in this work was 200 nm. The Pr composition, x, was varied from 0 to 1.0. The crystalline property and surface morphology of the samples were characterized by X-ray diffraction (XRD) and atomic force microscope (AFM), respectively. Polarization – electric field (P-E) and current – voltage (I-V) characteristics were measured to evaluate electrical properties.

3. RESULTS AND DISCUSSION

We first characterized the crystalline properties of BPT films. Fig. 1 shows XRD patterns of the BPT films which were crystallized at 750°C. The Pr compositions of the films are 0.1, 0.3, 0.5, 0.7, and 1.0.

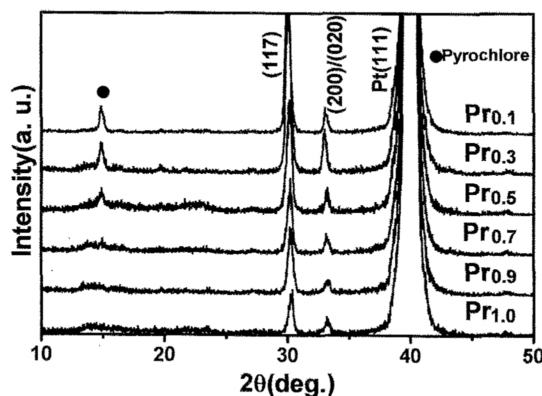

Fig. 1. XRD patterns of sol-gel derived BPT films, crystallized at 750°C.

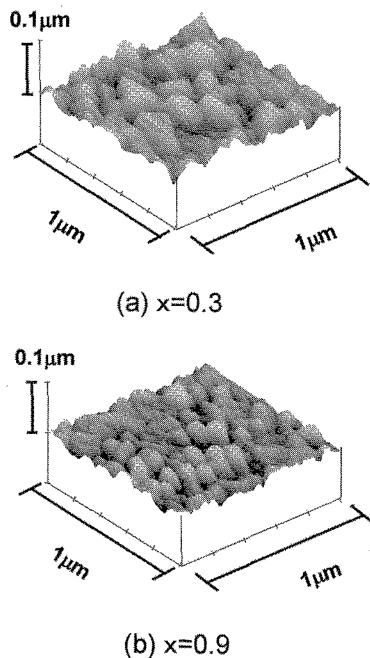

Fig. 2. Surface morphologies of sol-gel derived (a) $Bi_{3.7}Pr_{0.3}Ti_3O_{12}$ and (b) $Bi_{3.1}Pr_{0.9}Ti_3O_{12}$ films crystallized at 750°C.

BPT (117) diffraction peak is observed for XRD patterns of all samples. This is in contrast with the report by Matsuda et al., where BPT (00ℓ) diffraction peaks become dominant for the film with a Pr composition of 0.7. The discrepancy is probably because of the difference in bottom electrode material. It is interesting to note that the peak intensity decreases with Pr composition in our experiments, which suggests that the Pr substitution suppress the crystallization when the BPT films are crystallized at 750°C. At the same time, diffraction peak intensity from the pyrochlore phase, labeled by a closed circle in Fig. 1, also significantly decreases with Pr composition.

Figs. 2(a) and 2(b) show surface morphologies of the $Bi_{4-x}Pr_xTi_3O_{12}$ films observed by AFM. Pr compositions, x, of the films shown in the figures are (a) 0.3 and (b) 0.9. It is found that the crystalline grains in the $Bi_{3.7}Pr_{0.3}Ti_3O_{12}$ film are larger than those in the $Bi_{3.1}Pr_{0.9}Ti_3O_{12}$ film. We observed surface morphologies of the BPT films with other Pr compositions and found similar dependence of the grain size on Pr composition of the film. The grain size in the fabricated BPT films becomes smaller as Pr composition of the film increases. This is not contradictory to the XRD patterns shown in Fig. 1. Although it is observed that the Pr substitution suppresses the crystallization of the BPT film to some extent, an interesting aspect is that Pr substitution to BIT also suppresses the formation of the pyrochlore phase. Hence, improvement in electrical properties is expected by the Pr substitution.

We next examined the electrical properties of the BPT films. Fig. 3 shows P-E hysteresis loops of the BPT films fabricated by the sol-gel technique at 750°C. Large remanent polarization can be obtained when the Pr compositions are 0.5 and 0.7. The remanent polarizations, P_r, and coercive fields, E_C, for the $Bi_{3.5}Pr_{0.5}Ti_3O_{12}$ film are 19 $\mu C/cm^2$ and 79 kV/cm, and

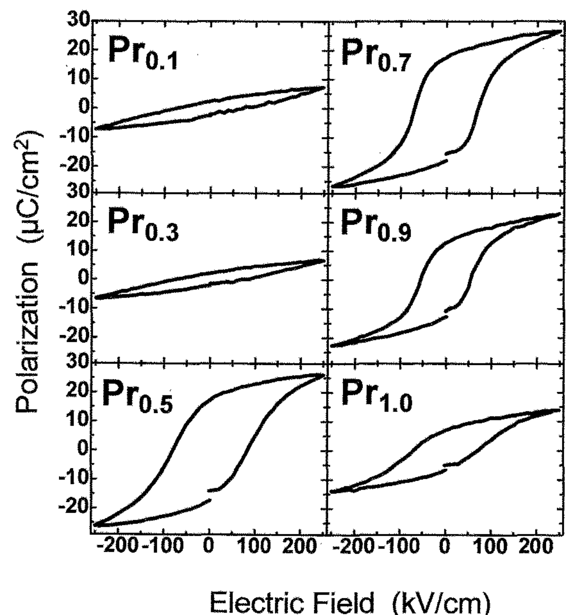

Fig. 3 P-E hysteresis loops of the BPT films. Crystallization annealing was carried out at 750°C.

18 $\mu C/cm^2$ and 70 kV/cm for the $Bi_{3.3}Pr_{0.7}Ti_3O_{12}$ film, respectively. Note that the P-E loop of the $Bi_{3.5}Pr_{0.5}Ti_3O_{12}$ film is more tilted than that of the $Bi_{3.3}Pr_{0.7}Ti_3O_{12}$ film. This is consistent with the XRD patterns as shown in Fig. 1, showing that there still exist the pyrochlore phase in the BPT film when the Pr composition is 0.5 and that almost no diffraction peak from the pyrochlore phase is observed for the film with a Pr composition of 0.7.

The observed remanent polarizations are plotted in Fig. 4 as a function of Pr composition, x. It is found that the remanent polarization increases with decreasing Pr composition of the film when the Pr composition is larger than 0.5. This is presumably because the crystalline quality is improved by reducing the Pr composition, as suggested by the XRD patterns shown in Fig. 1. However, a further decrease of the Pr composition results in the rapid decrease of the remanent polarization. Almost no ferroelectric properties are observed for the BPT film when the Pr composition is less than 0.3 as shown in Fig. 3. The formation of the pyrochlore phase cannot be suppressed when the Pr composition is less than 0.3, as shown in Fig. 1, which is probably a reason for the poor ferroelectric properties of the BPT films with low Pr compositions.

Finally, we examined fatigue endurance of the BPT films. Fig. 5 shows the remanent polarizations, $+P_r$ and $-P_r$, of the $Bi_{3.5}Pr_{0.5}Ti_3O_{12}$ film, continuously measured with applying ±5V (250kV/cm) switching voltage. Almost no degradation is observed up to 10^8 switching cycles. However, degradation of the remanent polarization is found after 10^9 switching cycles. Hence, improvement in fatigue endurance is necessary for practical use. The degradation of the remanent polarizations may be related to the presence of the pyrochlore phase in the $Bi_{3.5}Pr_{0.5}Ti_3O_{12}$ film, but the details are still under study.

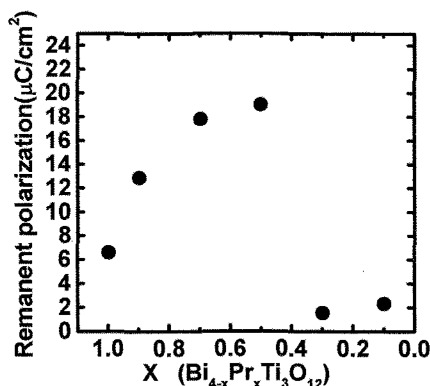

Fig.4 Remanent polarizations of the sol-gel derived $Bi_{4-x}Pr_xTi_3O_{12}$ films as a function of Pr composition, x.

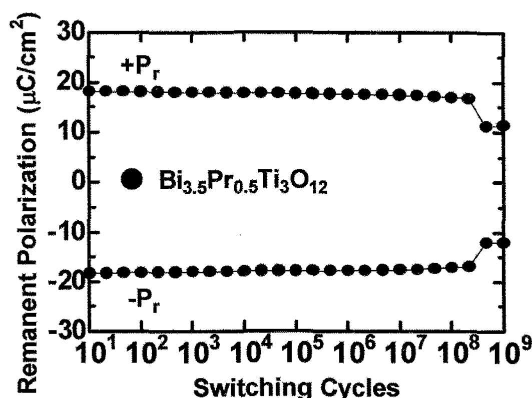

Fig.5 Fatigue characteristics of $Bi_{3.5}Pr_{0.5}Ti_3O_{12}$ film.

4. SUMMARY

We characterized the Pr substitution effect in sol-derived ferroelectric BIT films. The 200-nm-thick $Bi_{4-x}Pr_xTi_3O_{12}$ films were fabricated on $Pt/Ti/SiO_2/Si$ substrates by the sol-gel method with crystallization annealing at 750°C. It was demonstrated that the Pr substitution suppresses the formation of the pyrochlore phase, which results in large remanent polarization of the $Bi_{3.5}Pr_{0.5}Ti_3O_{12}$ and $Bi_{3.3}Pr_{0.7}Ti_3O_{12}$ films. However, it was also found that a further increase of the Pr composition results in the decrease of the remanent polarization, probably due to the degradation of crystalline quality.

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