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Orientation control of $(Bi,La)_4Ti_3O_{12}$ films by addition of various silicates and germanates

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1. Introduction

Ferroelectric Random Access Memory (FeRAM) is one of the most promising non-volatile memories. At present, both 1T1C-type and 1T-type are being studied and the requirement for ferroelectric materials is different between them. That is, a large remnant polarization (Pr) value is needed for 1T1C-type FeRAMs because of similarity of the cell structure to DRAM, while a relatively small value is needed for 1T-type FeRAMs. Thus, it is important in these applications to control the orientation of ferroelectric films, particularly in case of $Bi_4Ti_3O_{12}$(BIT) or $(Bi,La)_4Ti_3O_{12}$ (BLT) films whose Pr values are much different along a- and c-axis. We succeeded in forming very thin films by adding a sol-gel solution of Bi_2SiO_5(BSO) to that of BIT[1]. Based on this result, we attempted in this paper to add other silicates and germanates and found that addition of germanates as well as silicates was effective in control of the orientation of BLT films.

2. Experiment

The ferroelectric films were formed by spin-coating sol-gel solutions (Mitsubishi Materials Corp.) of BLT and silicates or germanates on a $Pt/Ti/SiO_2/Si$ structure. Thickness of the crystallized films is about 100nm. Crystallization annealing was conducted at 700°C for 30 min in O_2 atmosphere. The sol-gel solutions were prepared by admixing the solution of additives with that of BLT, after hydrolyzing both solutions. The mixed mole ratio R of additives to BLT was 0.1. Ferroelectric properties of the prepared films were measured by depositing Pt top electrodes.

3. Results and discussion

Figure 1 shows XRD (X-ray diffraction) patterns for various silicate-added BLT films. As can be seen from this figure, a Bi_2SiO_5(BSO)-added BLT film has a random orientation because the XRD pattern consists of both (00*l*) and (117) peaks. On the other hand, La_2SiO_5 (LSO)- and $ZnSiO_3$(ZnSO)-added BLT films show (00*l*)-predominant patterns and a $ZrSiO_4$(ZrSO)-added BLT film shows a (117)-predominant pattern. Figure 2 shows XRD patterns for various germinate-added BLT films. We can see from Figs. 1 and 2, that the preferred orientation of crystallites in the silicate- and germanate-added BLT films in mainly determined by metal atoms. .

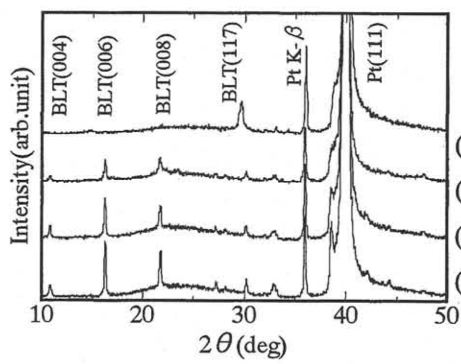

Fig. 1 XRD patterns for silicates-BLT films:
(a) Bi_2SiO_5-BLT, (b), La_2SiO_5-BLT
(c) $ZnSiO_5$-BLT, (d) $ZrSiO_4$-BLT.

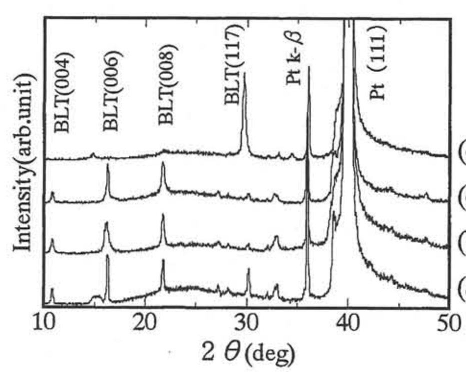

Fig. 2 XRD patterns for germanates-BLT films:
(a) Bi_2GeO_5-BLT, (b) La_2GeO_5-BLT,
(c) $ZnGeO_5$-BLT, (d) $ZrGeO_4$-BLT.

SEM images for various germanate-added BLT films are shown in Fig. 3. As can be seen from this figure, randomly oriented and (117)-oriented films in (a) and (d) have small grains, while the c-axis oriented films of (b) and (c) have large grains. Especially the surface morphology of the sample shown in (c) is like a plate.

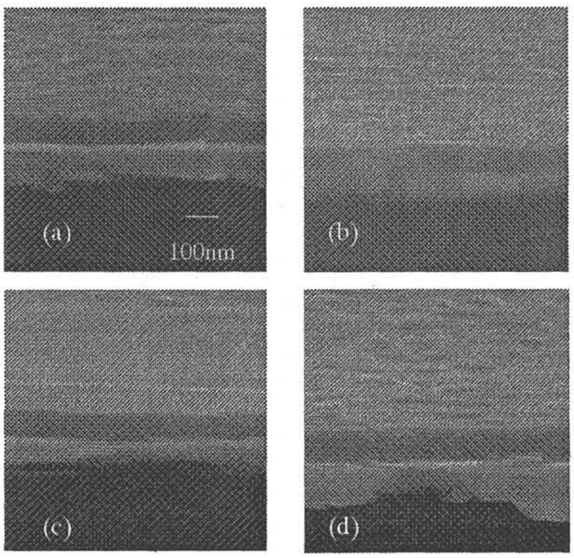

Fig. 3 SEM images of various germanates-BLT films: (a) Bi_2GeO_5-BLT, (b) La_2GeO_5-BLT, (c) $ZnGeO_5$-BLT, (d) $ZrGeO_4$-BLT.

Figure 4 shows P-V (polarization vs. voltage) hysteresis characteristics of typical silicate- and germanate-added BLT films. As can be seen from this figure, the hysteresis loops of these samples are well saturated. The BGO-added film with random orientation shows the Pr value of 10.2μC/cm^2, the LGO- and ZnGO-added films with c-axis-orientation show the Pr values of 9.3 or 5.0 μC/cm^2, and the ZrSO-added film with (117)-orientation shows the largest Pr value of 15.0μC/cm^2. The relation between orientations of these BLT films and Pr values are shown in Fig. 5. As can be seen from this figure, the stronger the c-axis peak intensity of $I_{(006)}$ relative to $I_{(117)}$ is, the smaller the Pr value is. We conclude from these results that the preferred orientation of BLT films can be controlled by addition of various silicates and germanates.

4. Conclusion

We prepared various silicate- and germanate-added BLT films and characterized their crystallographic and electrical properties. It was found that addition of both silicates and germanates was effective in controlling the orientation of BLT films. This technique is considered to be useful in fabrication of various types of FeRAMs.

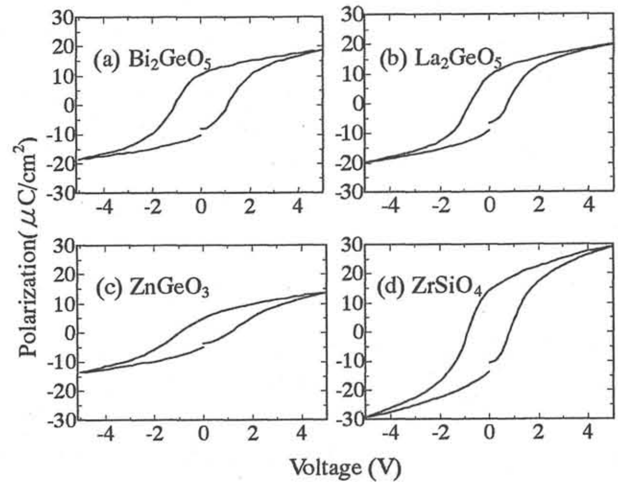

Fig. 4 Variation of the P-V hysteresis curves.

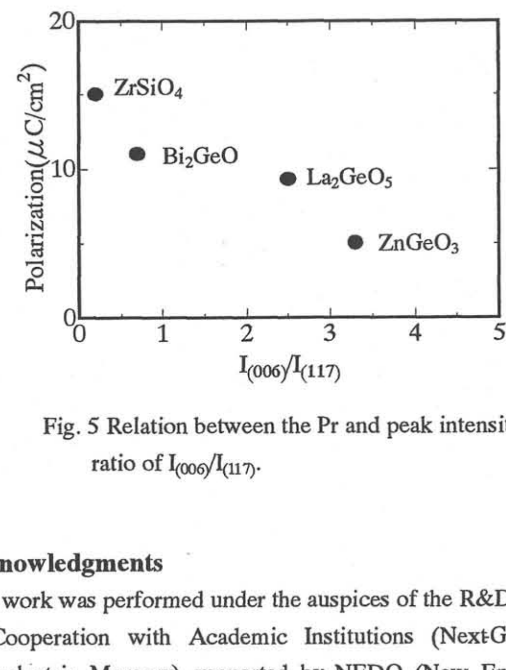

Fig. 5 Relation between the Pr and peak intensity ratio of $I_{(006)}/I_{(117)}$.

Acknowledgments

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References

[1] T.Kijima and H.Ishiwara, Abstract of 1st International Meeting on Ferroelectric Random Access Memory, Gotemba, Japan, p67, NOV.2001