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Preparation and Characterization of $(1\text{-}x)BiScO_3\text{-}xPbTiO_3$ Thin Films through Metal-Organic Compounds

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Perovskite $(1\text{-}x)BiScO_3\text{-}xPbTiO_3$ binary system is known to have a morphotropic phase boundary (MPB) and higher Curie temperature than $Pb(Zr,Ti)O_3$, and to exhibit excellent dielectric and ferroelectric properties. In this study, ferroelectric $(1\text{-}x)BiScO_3\text{-}xPbTiO_3$ thin films were synthesized by chemical solution deposition method. Homogeneous and stable precursor solutions were prepared by selecting appropriate starting metal-organic compounds and 2-methoxyehanol as a solvent. Perovskite $BiScO_3\text{-}PbTiO_3$ single-phase thin films were synthesized at 750°C on $Pt/TiO_x/SiO_2/Si$ substrates. The dielectric permittivity of $0.35BiScO_3\text{-}0.65PbTiO_3$ thin film with the MPB composition was found to be ~1700 with dielectric loss tangent less than 5% at room temperature. The remnant polarization (P_r) and coercive field (E_c) of the film were approximately 31 $\mu C/cm^2$ and 70 kV/cm, respectively.

Keywords: $BiScO_3\text{-}PbTiO_3$, Chemical solution deposition, Thin film, Morphotropic phase boundary, Electrical properties

1. INTRODUCTION

$Pb(Zr_xTi_{1-x})O_3$ (PZT) system is extensively studied and widely used as ferroelectric and piezoelectric materials for a long time. The highest dielectric, ferroelectric and piezoelectric properties in the PZT system are observed near the morphotropic phase boundary (MPB) separating the rhombohedral and tetragonal phases.[1,2] Although the PZT has the excellent ferroelectric properties, PZT ferroelectrics exhibit relatively low Curie temperatures (T_C=386°C at MPB) which limit the temperature range for their application.[3]

Recently, high T_C ferroelectric perovskites in $(1\text{-}x)BiMO_3\text{-}xPbTiO_3$ (M=Sc, Fe, Ga, etc.) type MPB systems have been discovered and investigated.[4-7] Among them, the $(1\text{-}x)BiScO_3\text{-}xPbTiO_3$ (BS-PT) system was reported to exhibit a T_C=450°C and peak piezoelectric coefficient d_{33}=460pC/N near the MPB composition (x=0.64).[4] These properties suggest that the BS-PT system is an attractive candidate for applications requiring excellent temperature stable properties, such as ferroelectric and piezoelectric thin film devices.

In this work, ferroelectric BS-PT thin films are prepared by the chemical solution deposition (CSD) method, because the CSD process using metal-organic compounds is useful for the achievement of high homogeneity and the precise control of the chemical composition. The crystallization of perovskite BS-PT films on $Pt/TiO_x/SiO_2/Si$ substrates is investigated for several processing conditions, including PT content of BS-PT. Ferroelectric and dielectric properties of the synthesized BS-PT films are also evaluated.

2. EXPERIMENTAL PROCEDURE

$Bi(O^tC_5H_{11})_3$, $Sc(O^iC_3H_7)_3$, $Pb(CH_3COO)_2$ and $Ti(O^iC_3H_7)_4$ were selected as starting materials for preparing

(1-x)BiScO$_3$-xPbTiO$_3$ (x=0.50, 0.60, 0.65, 0.70) precursor solutions. 2-Methoxyethanol was dried over molecular sieve and distilled prior to use. The desired amounts of starting materials with 5 mol% excess Bi and Pb were dissolved in absolute 2-methoxymethanol. Acetylacetone was added to the solution as a stabilizing agent. Then, the mixed solution was refluxed for 20 h yielding a 0.1 M homogeneous precursor solution. The entire procedure was conducted in a dry N_2 atmosphere.

Films were fabricated using the precursor solution by spin-coating on Pt/TiO$_x$/SiO$_2$/Si substrates. As-deposited BS-PT precursor films were dried at 150°C for 5 min and calcined at 400°C at a rate of 10°C/min for 1 h in an O_2 flow. And then, the calcined films were crystallized at 750°C at a rate of 10°C/min for 1 h in an O_2 flow. The thickness of BS-PT films was adjusted to be approximately 250 nm by repeating the coating / calcining cycle.

The crystallographic phases of prepared BS-PT thin films were characterized by X-ray diffraction (XRD) analysis using CuKα radiation with a monochromator. The surface morphology of the crystallized thin films was observed using an atomic force microscope (AFM). The electrical properties of films were measured using a Pt top electrode deposited by DC sputtering onto the surface of BS-PT films followed by annealing at 400°C for 1 h. The Pt layer of the Pt/TiO$_x$/SiO$_2$/Si substrate was used as a bottom electrode. The electrical properties of the films were evaluated using an impedance/gain phase analyzer [SI-1260, Toyo Corp.] and a ferroelectric test system [FCE-1, Toyo Corp.] at room temperature.

3. RESULTS AND DISCUSSION

3.1 Crystallization of BS-PT thin films on substrates

Figure 1 illustrates XRD patterns of (1-x)BiScO$_3$-xPbTiO$_3$ (BS-PT, x=0.50, 0.60, 0.65, 0.70) thin films fabricated on Pt/TiO$_X$/SiO$_2$/Si substrates after heat treatment at 750°C. BS-PT thin films (x=0.60, 0.65, 0.70) were found to crystallize in the perovskite BS-PT single phase, without any second phase like pyrochlore. On the other hand, BS-PT thin film (x=0.50) crystallized in the perovskite BS-PT with a small amount of pyrochlore phase as shown in Fig. 1(a). The end member of perovskite BiScO$_3$ (BS) was known to have an unstable

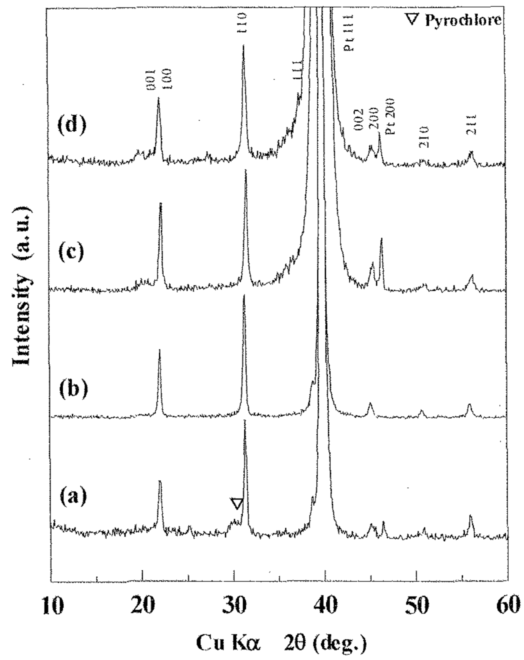

Fig. 1 XRD patterns of (1-x)BiScO$_3$-xPbTiO$_3$ thin films on Pt/TiO$_x$/SiO$_2$/Si substrates after heat-treated at 750°C, (a) x=0.50, (b) x=0.60, (c) x=0.65 and (d) x=0.70.

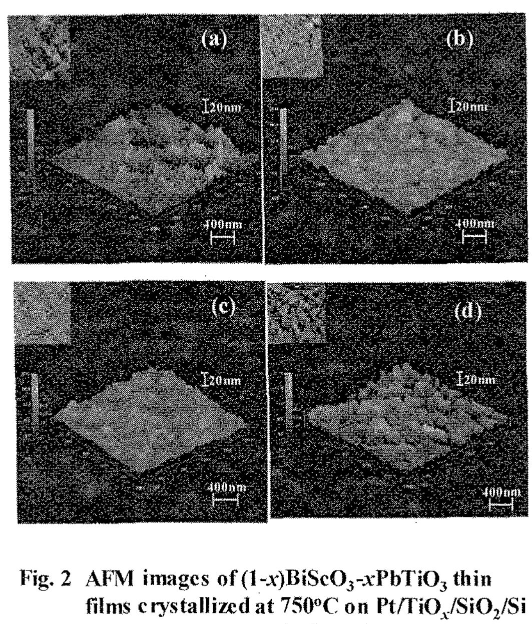

Fig. 2 AFM images of (1-x)BiScO$_3$-xPbTiO$_3$ thin films crystallized at 750°C on Pt/TiO$_x$/SiO$_2$/Si substrates, (a) x=0.50, (b) x=0.60, (c) x=0.65 and (d) x=0.70.

perovskite structure because of its low tolerance factor (t=0.907).[4] In the BS-PT system, the stability of perovskite phase decreases with increasing the BS content. Therefore, current BS-PT thin film with x=0.50 composition was considered to crystallize in a mixture of perovskite and pyrochlore phases.

3.2 Surface morphology of crystalline BS-PT thin films

Figure 2 shows the AFM images of synthesized BS-PT (x=0.50, 0.60, 0.65, 0.70) thin films on $Pt/TiO_x/SiO_2/Si$ substrates. It revealed from Fig. 2 that surface morphology of the BS-PT thin films was found to strongly depend upon the PT content. The average grain size of BS-PT thin films was varied within 10-30 nm, which affected by the amount of PT. In the $(1-x)BiMO_3-xPbTiO_3$ (M=Sc, Ga, Fe) solid solution ceramic systems, the crystal grains of polycrystalline samples are known to grow larger size with increasing the PT content.[8,9] For the BS-PT thin films prepared in this work, similar tendency was observed. Furthermore, BS-PT (x=0.65) thin film had relatively homogeneous surface and small roughness compared with the others as shown in Fig. 2(c).

3.3 Electrical properties of perovskite BS-PT thin films

Since perovskite BS-PT single-phase thin films were obtained for x=0.60, 0.65, 0.70 compositions as described in 3.1, dielectric properties of these films were investigated at room temperature. Figure 3 shows dielectric constant (ε_r) and dielectric loss (tanδ) of the BS-PT thin films crystallized at 750°C as a function of PT content. The measurement was performed at a frequency of 100 Hz and room temperature. The values of ε_r were approximately 1200, 1700 and 1000, corresponding to the x=0.60, 0.65 and 0.70 compositions, respectively. The maximum of ε_r was found to appear at x = 0.65, which composition was reported to be near the MPB on bulk BS-PT ceramics. For the current BS-PT thin films, the enhancement of dielectric constant was considered to be due to the presence of the MPB at around x=0.65 as in the case of bulk BS-PT samples. The values of tanδ were less than 5%, constant for various PT contents.

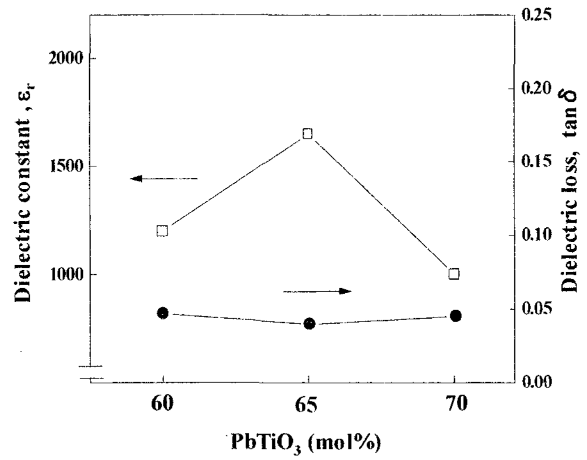

Fig. 3 **Dielectric properties of BS-PT thin films crystallized at 750°C on $Pt/TiO_x/SiO_2/Si$ substrates as a function of PT content. [measured at 100Hz and room temperature]**

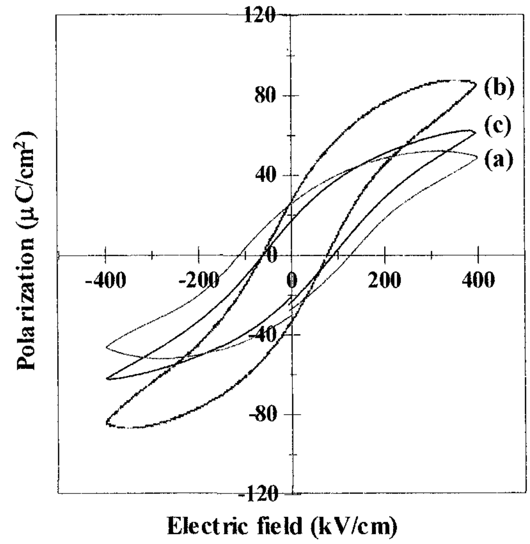

Fig. 4 P-E hysteresis loop of $(1-x)BiScO_3-xPbTiO_3$ thin films crystallized at 750°C on $Pt/TiO_x/SiO_2/Si$ substrates, (a) x=0.60, (b) x=0.65 and (c) x=0.70. [measured at room temperature]

P-E hysteresis measurement was also performed to characterize the ferroelectricity for the perovskite BS-PT thin films crystallized at 750°C. Figure 4 shows the P-E hysteresis loops of 250-nm-thick BS-PT (x=0.60, 0.65, 0.70) thin films measured at a frequency of 100Hz and room temperature. These thin films showed typical ferroelectric hysteresis loops at an applied voltage of 10V. The remnant polarization (P_r) and coercive field (E_c) of thin films were 26, 31, 21 μC/cm^2 and 119, 70, 76 kV/cm^2 corresponding to the x=0.60, 0.65 and 0.70 compositions, respectively. The enhancement of Pr at x=0.65 composition was attributed to the similar reason to that of the dielectric constant described above. These results indicated that the MPB of the current BS-PT thin film was considered to exist at around x=0.65. The Pr values of synthesized BS-PT (x=0.60, 0.65, 0.70) thin films were consistent with those reported bulk ceramics.[4] However, the squareness of P-E hysteresis loops and the E_c values were inferior to those of BS-PT bulk ceramics. The improvement of ferroelectric properties and the low-temperature fabrication of perovskite BS-PT thin films are now under investigation.

4. CONCLUSIONS

Ferroelectric (1-x)$BiScO_3$-$x$$PbTiO_3$ (BS-PT) thin films were successfully synthesized by chemical solution deposition process. Homogeneous and stable BS-PT precursor solutions were prepared by controlling the reaction of starting metal-organic compounds in 2-methoxyethanol. Perovskite BS-PT (x=0.60, 0.65, and 0.70) thin films were crystallized on Pt/TiO_x/SiO_2/Si substrates at 750°C. Among them, the BS-PT (x=0.65) thin film had the highest dielectric permittivity of approximately 1700 at room temperature. The BS-PT (x=0.65) thin film also showed the highest properties of ferroelectrics with the P_r value of 31 μC/cm^2 and E_c of 70 kV/cm at 10V. These results were derived from the existence of MPB composition at around x=0.65.

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REFERENCES

[1] B. Jaffe, R. S. Roth and S. Marzullo, *J. Appl. Phys.*, **25**, 809-810 (1954).

[2] H. Jaffe, *J. Am. Ceram. Soc.*, **41**, 494-498 (1958).

[3] S. E. Park and T. R. Shrout, *IEEE Trans. Ultrason. Ferroelectr. & Freq. Control*, **44**, 1140-1147 (1997).

[4] R. E. Eitel, C. A. Randall, T. R. Shrout, P. W. Reihrig, W. Hackenberger and S. E. Park, *Jpn. J. Appl. Phys.*, **40**, 5999-6002 (2001).

[5] D. I. Woodward, I. M. Reaney, R. E. Eitel and C. A. Randall, *J. Appl. Phys.*, **94**, 3313-3318 (2003).

[6] J. Cheng, W. Zhu, N. Li and L. E. Cross, *Mater. Lett.*, **57**, 2090-2093 (2003).

[7] R. E. Eitel, S. J. Zhang, T.R. Shrout, C. A. Randall and I. Levin, *J. Appl. Phys.*, **96**, 2828-2831 (2004).

[8] J. Cheng, R. E. Eitel and L. E. Cross, *J. Am. Ceram. Soc.*, **86**, 2111-2115 (2003).

[9] J. Cheng, R. E Eitel, N. Li and L. E. Cross, *J. Appl. Phys.* **94**, 605-609 (2003).

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