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# Effect of A-Site Substitution on Electrical Properties of $Pb(Zr_X,Ti_{1-X})O_3$ Thin Films with Chemical Solution Deposition

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A-site of $Pb(Zr_X,Ti_{1-X})O_3$ (PZT) thin film was partially substituted for barium (PBZT) to deposit high κ thin films for high voltage DC bus filter application and to develop environmental compatible ferroelectric thin films with a Chemical Solution Deposition (CSD). The amount of A-site substitution was half of Pb and the electrical properties of the PBZT thin films deposited onto a $Pt/Ti/SiO_2/Si$ substrate were measured to determine the morphotoropic phase boundary (MPB). As a result, MPB for PBZT determined by the lattice parameters sifted toward the Ti rich composition compared with the PZT thin films. XRD result also showed that the deposited PBZT thin films had randam orientation. The remanent polarization ($P_r$) and dielectric constant ( ε ) for the PBZT film with X=0.3 exhibited highest values and was considered to be a MPB composition. This result was consistent with the result determined by the lattice parameter. The $P_r$ value and the dielectric constant for the PBZT thin film of MPB composition deposited from alkoxide precursor solution increased because of the improved microstructure. Further improvement of the electrical properties will be carried out by controlling the film orientation.

Key words: PBZT, thin film, CSD, MPB composition, electrical properties

## 1. INTRODUCTION

Lead zirconate titanate ($Pb(Zr,Ti)O_3$:PZT) thin films have been attracting worldwide interests in exploring their potential properties [1-3] or the origins [4-6] of their excellent dielectic, ferroelectric, piezoelectric and pyroelectric properties. In order to deposit PZT films, various techniques have been used, such as chemical solution deposition (CSD), sputtering, and metal organic chemical vapor deposition (MOCVD). Among these techniques, CSD technique is advantageous for producing PZT films due to its simplicity, easy control of homogeneous composition and film thickness for large substrates, and low processing temperature, as compared with other techniques.[7-9]

Electrical properties of PZT films are excellent, however, environmental compatibility is the current topics. Therefore, lead free or reduced ferroelectric thin films are required in recent years. In this paper, A-site of perovskite-type $Pb(Zr_X,Ti_{1-X})O_3$ (PZT) thin film was partially substituted for barium (PBZT) to deposit high κ thin films for high voltage DC bus filter application [10] and to develop environmental compatible ferroelectric thin films with a Chemical Solution Deposition (CSD).

## 2. EXPERIMENTAL

The precursor solutions of $(Pb_{0.5}, Ba_{0.5})(Zr_X,Ti_{1-X})O_3$ were prepared from lead iso-propoxide $[Pb((CH_3)_2CHO)_2]$, metal barium (Ba), zirconium n-propoxide $[Zr(OC_3H_7)_4]$ and titanium iso-propoxide $[Ti((CH_3)_2CHO)_4]$. Lead iso-propoxide was dissolved in absolute ethanol by refluxing for 1 h and then metal barium was added to the Pb-precursor solution, followed by the refluxing for 1 h. After that, titanium iso-propoxide and zirconium n-propoxide were mixed and refluxed for 4 h with a Pb-Ba-mixed precursor solution to form PBZT precursor solutions with various composition (X=0.1～0.53). Methoxyethanol was used to stabilize the precursor solution.

PBZT precursor film was deposited onto a $Pt/Ti/SiO_2/Si$ substrate by a spin-coating. The deposited film was dried at 115°C for 10 min. to remove water, pyrolyzed at 350°C for 10 min. to remove residual organics and then rapid thermally annealed at 600°C for 5 min. in air (RTA). This coating process was repeated several times to increase the film thickness of about 1 μm or more, and then finally annealed at 650 °C for 2 h to obtain a dense film.

Crystal symmetry and lattice parameters for the deposited PBZT films were analyzed by an X-ray diffraction (XRD) to determine a MPB composition. XRD patterns for the PBZT films were fitted by the Lorentz function to identify a crystal symmetry. The microstructure was observed by a scanning electron microscope (SEM). In order to evaluate electrical properties, gold top electrode with an area of 2 by 2 mm were deposited on the film. The dielectric property was

measured with an impedance analyzer (HP 4284A). The polarization (P-E) hysteresis loops were measured with a ferroelectric test system (Radiant; RT-6000S).

## 3. RESULTS AND DISCUSSION

### 3.1. XRD and SEM

Figure 1 shows X-ray diffraction patterns for the PBZT thin films grown on $Pt/Ti/SiO_2/Si$ substrate. All the films exhibited a single phase perovskite and random orientation. For the PZT film deposited from the alkoxide precursor solution, the XRD intensities of (001)&(100) and/or (111) planes are relatively high, while the $BaTiO_3$ film shows random orientation [11-13]. In this paper, the film orientation was similar to the $BaTiO_3$ film. This result suggested that the PBZT films crystallized homogeneously, not epitaxially. The reason for the difference will be ascribed to the homogeneity of the precursor solutions. In addition, there was no difference in XRD patterns for the PBZT films

Figure 2 exhibits the SEM image of the cross-section for PBZT film with X=0.3. PBZT thin film with X=0.3 consisted of the fine grains less than 100 nm and relatively large grains of several hundred nm. This SEM image also suggested that the nucleation occurred randomly in the fim on the course of annealing. In addition, SEM image also exhibited that the film density was not high enough, leading to the relatively high loss.

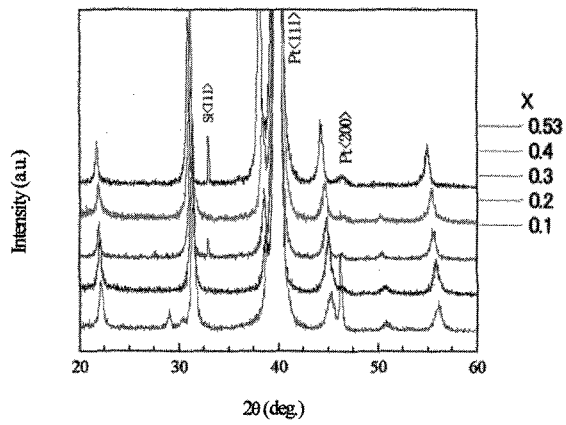


Fig.1. X-ray diffraction patterns for the PBZT thin films with different compositions (X=0.1~0.53).

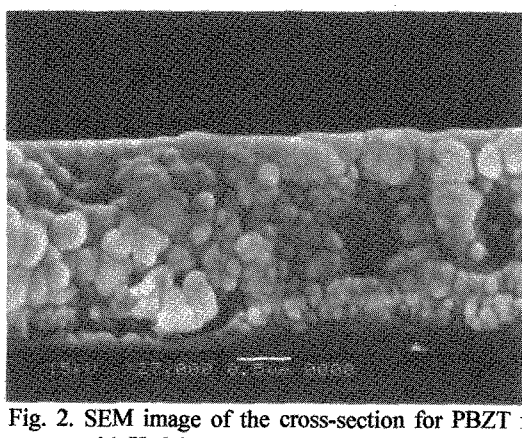

Fig. 2. SEM image of the cross-section for PBZT film with X=0.3.

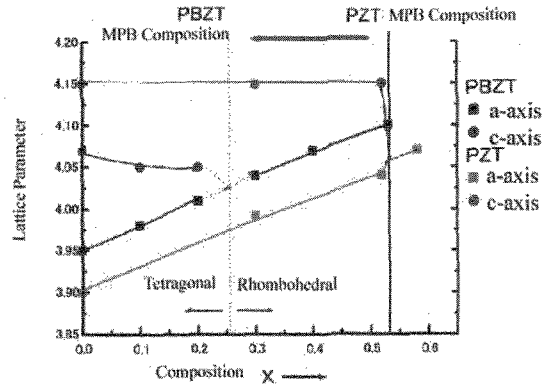


Fig .3. Change in the lattice parameters of PBZT thin films with composition X.

Figure 3 shows the change in the lattice parameters of the resultant PBZT thin films with different compositions, together with those of the PZT. For the PBZT films with Ti rich compositions, crystal symmetry was identified as tetragonal, while the PBZT films with Zr rich compositions exhibited rhombohedral symmetry. As a result, the morphotropic phase boundary was considered to exist between X=0.2 and X=0.3, judging from the Lorentz fitting of XRD patterns. In the case of the PZT, MPB composition exists at around X=0.53. On the other hand, MPB composition for the barium zirconate titanate (BZT) is considered to be X=0.8. Therefore in this study, MPB composition for the PBZT lied between those for PZT and BZT and this result is seems to be quite reasonable, although the MPB is affected by the residual stress in the thin film. If the MPB composition for the PBZT films exists at around X=0.3, the electrical properties such as ferroelectricity and piezoelectricity for the PBZT film with this composition should exhibit highest value. Therefore, the dielectric constant and P-E hysteresis loops for the resulting PBZT films were measured. PBZT films are also expected as a high κ thin films for high voltage DC bus filter.

### 3.2. Electrical properties

Figure 4 shows the P-E hysteresis loops for the PBZT films with different compositions. All PBZT films exhibited ferroelectricty, however, the vlues of the remanent polarization for the films were not so good and the saturation was not enough. This result should be ascribed to the film quality as mentioned in the figure 2. On the other hand, PBZT films with X=0.3 showed highest ferroelectricity, corresponding to the result of the lattice parameters.]

To confirm the change in the electrical properties, frequency dependence of the dielectric constant for PBZT thin films with different compositions was measured and shown in figure 5. The PBZT films with Zr rich composition more than X=0.3 exhibited relatively higher dielectric constant compared with those for the PBZT with X≤2. This result suggested that the PBZT films with rhombohedral symmetry had higher dielectric constant. In addition, PBZT thin film with X=0.3 showed highest dielectric constant. Therefore,

MPB composition for the PBZT was considered to exist at around X=0.3, judging from the above results.

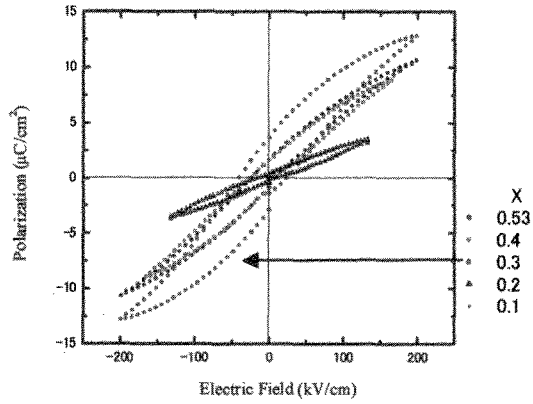


Fig 4. P-E hysteresis loops for the PBZT films with different compositions.

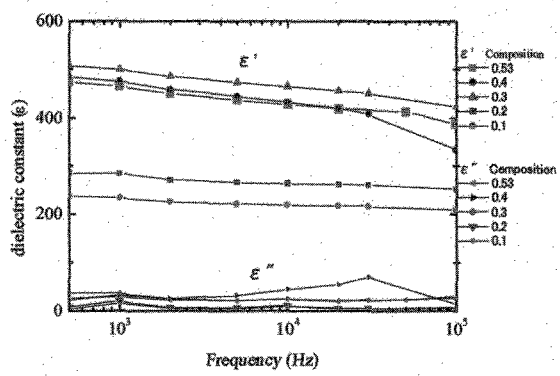


Fig.5. Frequency dependence for PBZT thin films with different composition.

The results for the dielectric and ferroelectric measurements are summarized in figure 6. This figure clearly shows the existence of the MPB composition at around X=0.3.

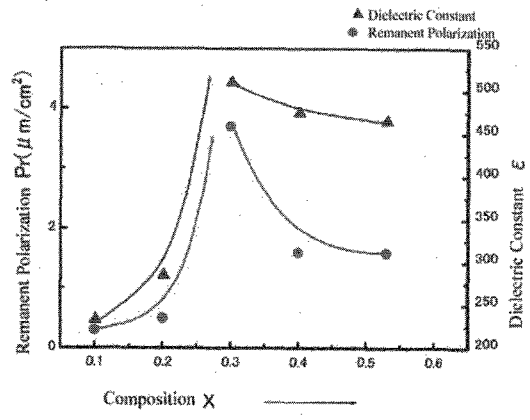


Fig.6. Relation between dielectric constant at 1 kHz, remanent polarization of the PBZT thin films and composition X.

3.3. Improvement of properties

From the XRD measurement and the electrical properties, a MPB composition for the PBZT thin film was successfully determined. However, SEM observation for the thin films revealed that the film quality was not enough to show the intrinsic electrical properties. Therefore in this study, improvement of the film quality was tried by changing the preparation method of the precursor solution. Namely, barium source was changed from metal barium to barium alkoxide.

As a result, a dense PBZT film of X=0.3 was successfully deposited as shown in figure 7. This figure showed the fine and homogeneous microstructure of the resultant PBZT film, together with the suppression of the exaggerated graingrowth.

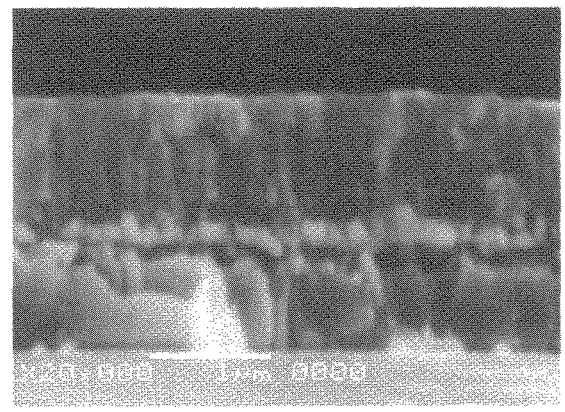

Fig.7. SEM image of the cross-section of PBZT thin film with X=0.3. The film was deposited from all-alkoxide precursor solution.

SEM observation suggested that the PBZT thin film with superior electrical properties was successfully deposited. Then the dielectric constant and the P-E hysteresis loop were measured and listed in the Table 1.

Table 1. Electrical properties of all alkoxide-derived PBZT thin film with X=0.3.

| Dielectric Constant at 1 kHz | RemanentPolarization |
|---|---|
| ≃ 680 | 7 μ C/cm2 |

As shown in Table 1, a dielectric constant and a remanent polarization of the resulting thin film were clearly increased compared with those for the PBZT film with a same composition by using the all-alkoxide derived precursor solution. The dielectric constant at 1 kHz increased by 200 and the remanent polarization became about double by improving the film microstructure. These values are appreciated but not enough because the film orientation could not be controlled. It is not clear from these results that the c-axis oriented PBZT film with a MPB composition has

the excellent electrical properties, if compared with those for the PZT thin films. Further investigation is indispensable. However, the PBZT thin film with X=0.3 exhibited enough properties because the film had random orientation.

Figure 8 shows the P-E hysteresis loop for the PBZT thin film derived from all-alkoxide precursor solution with X=0.3. P-E hysteresis loop for the PBZT thin film derived from all-alkoxide precursor solution with X=0.3 showed enough saturation and higher remanent polarization. This result suggests that the PBZT thin film is expected to show higher dielectric constant at high voltage and superior piezoelectricity.

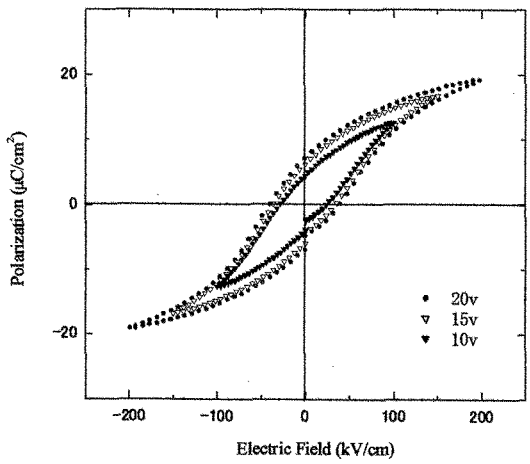


Fig.8. P-E hysteresis loops for the PBZT thin film with X=0.3 deposited from all-alkoxide precursor solution.

## 4.SUMMARRY

This paper focused on the MPB composition and the electrical properties of the ferroelectric PBZT thin films with a Chemical Solution Deposition. A MPB composition for the PBZT thin films shifted to Ti rich composition and existed between X= 0.2 and 0.3, compared with that for the PZT thin film. The remanent polarization ($P_r$) and the dielectric constant ($\varepsilon$) for the PBZT film with X=0.3 exhibited highest values and was considered to be a MPB composition. The $P_r$ value and the dielectric constant for the PBZT thin film of MPB composition deposited from all-alkoxide precursor solution increased because of the improved microstructure.

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