Transactions of the Materials Research Society of Japan 28 [1] 121-124 (2003)

Dielectric and Piezoelectric Properties of $Pb(Zr_{0.53}Ti_{0.47})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$ Thin Films with Preferred Orientation

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$Pb(Zr_{0.53}Ti_{0.47})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$ thin films were prepared by a chemical solution deposition (CSD). The influences of the composition and orientation on the crystallization, dielectric and piezoelectric properties of the resultant films have been investigated. The films with dielectric constant about 1600-1800 at room temperature have been obtained. It has been shown that there should be a composition which exhibited both high dielectric and piezoelectric properties. The effective longitudinal piezoelectric coefficients of the thin films have been evaluated using a charge integration technique based on direct piezoelectric effect, and a value of about 270-280 pC/N has been observed for the unpoled films.
Keywords: dielectric, piezoelectric, relaxor; PZT, PMN, thin film,

1. INTRUDUCTION

$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN)-based relaxor ferroelectric materials have attracted much attention recently because of the excellent dielectric and electromechanical properties.[1] The potential impact of these materials in integrated actuators and sensors applications has stimulated immense researches on the growth and characterization of these relaxor thin films.[2-7] However, it is difficult to synthesize pure perovskite phase PMN films at relatively low temperatures because of the stability of the pyrochlore phase relative to the perovskite phase. Despite this difficulty, a variety of thin film deposition techniques have been used to prepare PMN-based films. [2,3,5-7] The reported properties of the thin films are considerable lower than those of the bulk materials.[3] In the previous work, multi-layer structures of PZT and PMN were prepared to investigate the dielectric and piezoelectric properties of the resultant thin films. [8] This study focuses on the low-temperature deposition of the perovskite-type $Pb(Zr_{0.53}Ti_{0.47})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$ (hereafter abbreviated as PZTMN) single phase films and the properties of the PZTMN thin films deposited from a molecular designed precursor solution by a chemical solution deposition (CSD).

2. EXPERIMENTAL

PZTMN thin films were deposited from molecular-designed precursor solution by CSD on a $Pt/Ti/SiO_2$ /Si substrate using a spin-coating technique. Figure 1 shows the schematic illustration for the preparation of PZTMN precursor solutions. In this process, metal alkoxides of the perovskite B-site cations were polymerized to form columbite structure before reacting the Pb-precursor solution, leading to the low-temperature deposition of perovskite PZTMN thin films. $Pb(Zr_{0.3}Ti_{0.7})O_3$ layer was inserted as a seeding layer between electrode and PZTMN thin film to control the film orientation because the orientation of the $Pb(Zr_{0.3}Ti_{0.7})O_3$ film was easily controlled by changing the pre-annealing temperatures. PZT layer was rapid thermally annealed at 550℃ to deposite (100)&(001)- or (111)- oriented film before deposition of PZTMN layers. In order to investigate the effects of PMN content on the properties, two compositions of 10 mol.% PMN (9PZTMN) and 20 mol.% PMN (8PZTMN) precursor solutions were prepared. 20 mol% of excess lead was added to compensate the depletion of lead by the evaporation and diffusion into electrode during annealing. For each coated layer, the film was dried at 110 °C for 10 min to remove water, pyrolyzed at 350 °C for 10 min to remove any residual organic compound. A rapid thermal annlealing (RTA) at 750°C for 5 min was performed after deposition of PZTMN layer. The thickness of PZTMN and PZT seed layers in thin films were estimated to be about 60 nm and 150 nm, respectively, from the SEM images. Crystallization of the film was investigated by X-ray diffraction. The dielectric property was obtained through an impedance analyzer (HP-4192A). The piezoelectric property was measured through the direct piezoelectric effects, using a charge integration technique.[9]

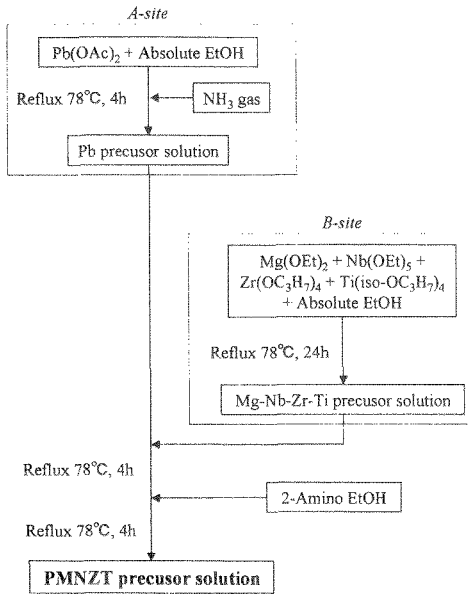


Fig.1 Schematic illustration for the preparation of molecular-designed PZTMN precursor solutions.

3. RESULTS AND DISCUSSIONS

3.1 Phase development and film orientation

Figure 2 exhibits the X-ray diffraction patterns for PZTMN thin films with different compositions. As can been seen in Figure 2(a), PZTMN film with pure perovskite phase can be obtained at a low temperature of 750°C. PZTMN films without PZT seeding layer showed both (111)- and (100)&(001)-orientation. If the PZT seeding layer was pre-annealed at 350℃ and 420 ℃ , PZTMN films preferred (111)- and (100)&(001)- orientation, respectively, independent of the composition. However, it is difficult to prepare the films with epitaxial PZTMN films.

Figure 3 exhibited the typical microstructure of the films. It has been shown that the resultant PZTMN films were dense and well-crystallized.

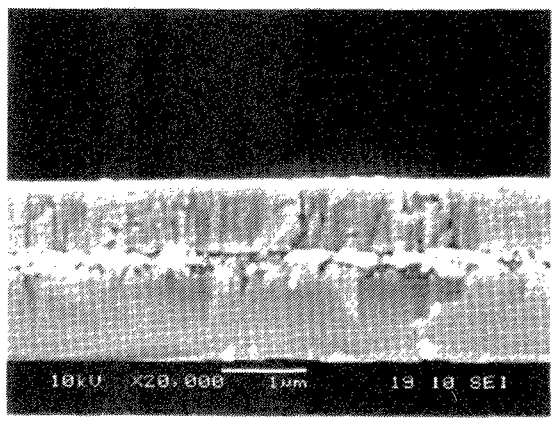


Fig.3 (a) SEM photograph of 9PZTMN film.

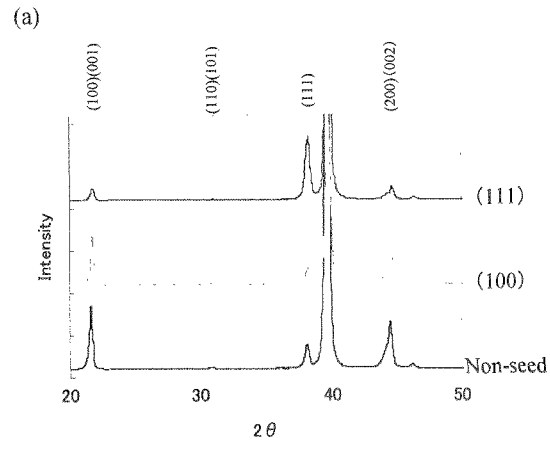


Fig.2 XRD patterns for the PZTMN films with (a) 9 PZTMN and (b) 8PZTMNannealed at 750 ℃.

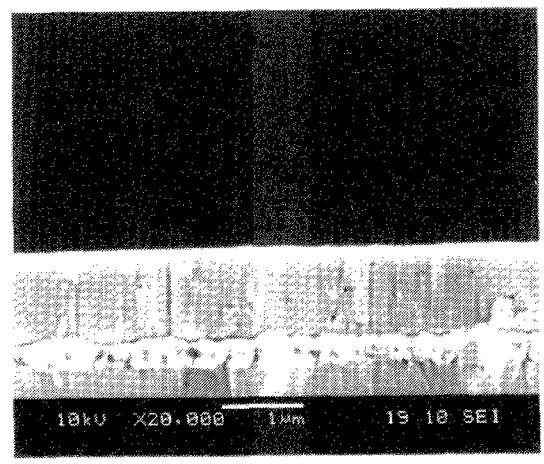


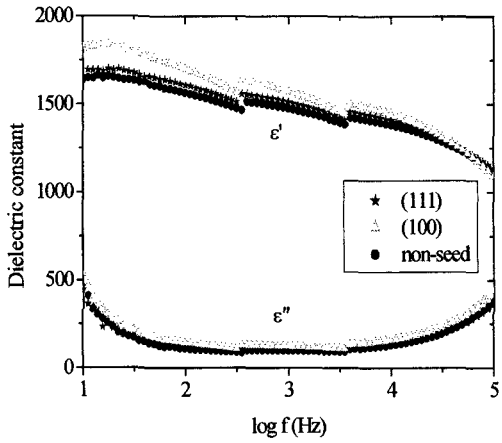
Fig.3 (b) SEM photograph of (100)&(001)-oriented 9PZTMN film.

(100)&(001)-oriented 9PZTMN film was slightly thicker because of the additional PZT seed layer of about 150 nm thick. This indicate that the composition of the (100)& (001)-oriented 9PZTMN film was different from non-seed 9PZTMN film.

3.2 Dielectric properties

The dielectric behavior of the PZTMN films was similar to that of the PZT films except for the slightly higher dielectric constant. For the 9PZTMN films, dielectric constant is almost same independent of the orientation. In addition, dielectric constant for the 9PZTMN films were higher than that for the 8PZTMN films. This suggested that the 9PZTMN composition is near the mophotoropic phase boundary because relaxor ferroelectrics usually have higher dielectric constant, whereas the 8PZTMN exhibited lower dielectric constant. This was confirmed by the change in dielectric constant of the films with applied field (Fig.5). Dielectric behavior is affected by the all domain motion. From the Fig.5 (a), 9PZTMN films were expected higher piezoelectricity. On the other hand, higher piezoelectricity was expected for the (111)-oriented 8PZTMN film. Therefore, the effective longitudinal piezoelectric coefficients d_{33} of the thin films

(a)



(b)

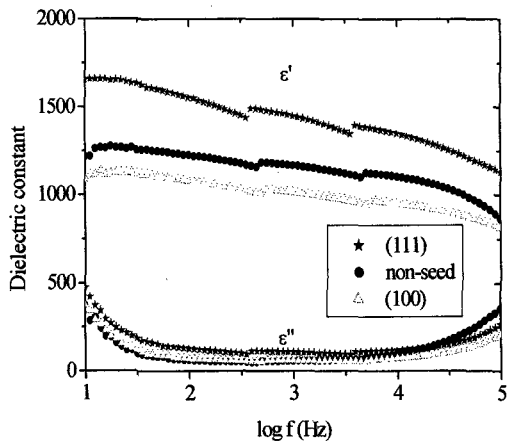
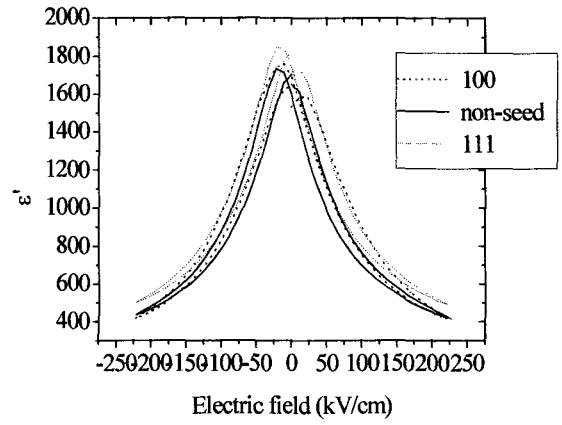


Fig.4 Dielectric constant for (a) 9PMNZT and (b) 8PZTMN thin films with different orientations and compositions as a function of frequency.

(a)



(b)

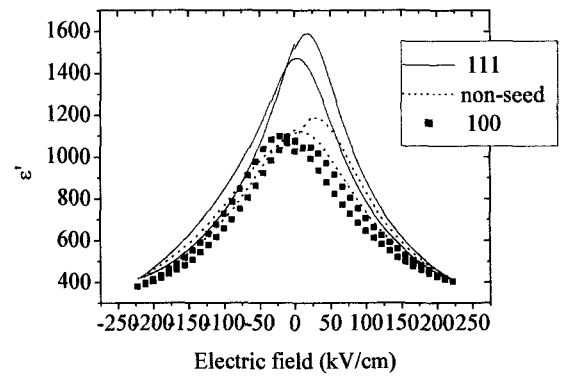


Fig. 5 Dielectric constant for the PZTMN films with different orientations and compositions as a function of applied field. (a) 9PZTMN, (b) 8PZTMN

were measured by a charge integration technique. The Measurements were performed by applying a static force (2.05 N) normal to the films and recording the stress-induced polarization with a charge integrator. Measurement Details have been described elsewhere. [9]

3.3 Ferroelectric and piezoelectric properties

Figure 6 shows the P-E hysteresis loops for the PZTMN films. In the PZT rich composition, the ferroelectric behavior is similar to that of PZT. On the other hand for 8PZTMN films, hysteresis loops were very slim and resembled to a relaxor ferroelectrics except for the (111)-oriented film. These results indicated that 9PZTMN films acted like displacement-type ferroelectrics and the 8PZTMN films acted as relaxor ferroelectrics.

The piezoelectric property of the film was then examined. Figure 7 shows the piezoelectric behavior of PZTMN films.

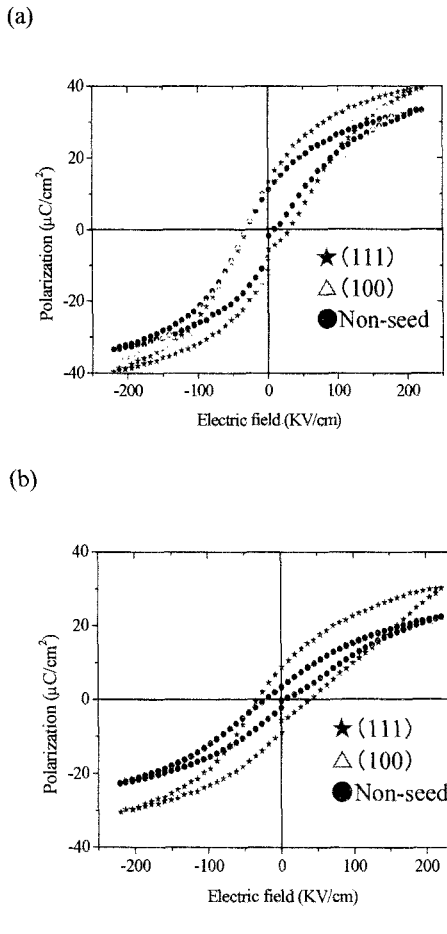


Fig. 6 P-E hysteresis loops for PZTMN films.
(a) 9PZTMN, (b) 8PZTMN

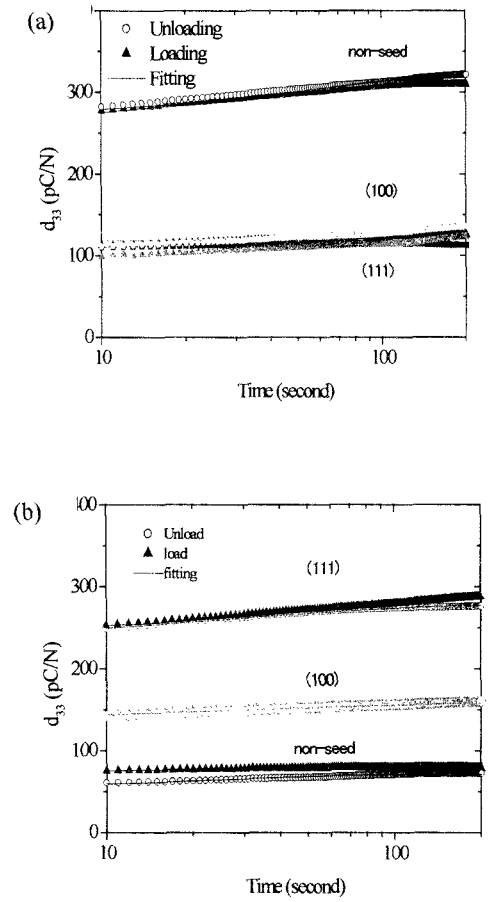


Fig. 7 Piezoelectric properties for PZTMN films with different orientations and compositions.
(a) 9PZTMN, (b) 8PZTMN

Typically, the reported d_{33} values of PMN-based thin films range from 50-100 pC/N.[3] These values are considerably lower than those of the bulk materials (2500 pC/N).[1] However, PZTMN thin films prepared in this study showed relatively higher values. Especially, 9PZTMN film without seed layer and 8PZTMN film exhibited considerably high d_{33} and relaxation (Fig.7). This indicated that the MPB composition in this system showed rhombohedral symmetry. In the case of the 9PZTMN film with PZT seed layer, the composition of the resultant films should be slightly PZT rich, leading to the lower d_{33} values. Therefore, we propose that the MPB composition in this system is located between 9PZTMN and 8PZTMN. We have tried further examination to confirm the detailed piezoelectric properties of the PZTMN films.

SUMMARRY

In summary, we have deposited PZTMN solid solution thin films at 750℃ by CSD. It was possible to control the film orientation by the PZT seed layer. The resultant films showed different piezoelectric behavior depend on the film orientation and composition. Relatively high effective longitudinal d_{33} of about 280 (pC/N) was obtained near the MPB composition.

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(Received December 21, 2002; Accepted January 31, 2003)