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Effects of composition and stacking sequence on dielectric properties of the multilayered (Pb,Sr)TiO_3 thin films for tunable device application

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Abstract

Multilayered $(Pb_{1-x}Sr_x)TiO_3$ (PST(x)) thin films consisted of uniform, PST(x) and heterostructure, PST(x)–PST80 were synthesized by coating the solutions with different Sr contents ($50 \leq x$, Sr(mol%) ≤ 80), respectively. Their structural and dielectric properties were investigated in terms of composition and stacking sequence of each film. Among uniform PST(x) thin films, the PST60 films showed the highest dielectric constant and tunability, while so lower figure of merit which is an important parameter for microwave tunable device application was obtained due to relatively higher dielectric loss. In an effort to bring down the dielectric loss, the PST(x) thin films were alternately coated with PST80 thin layer. Dielectric properties of the heterostructured PST(x)–PST80 films were found to be dependent on the intrinsic dielectric values of each film composition and corresponding phase transition temperature shift effect. Furthermore, surface roughness became smoother by inserting PST80 thin layer, resulting in decrease in dielectric loss. In case of the PST60–PST80 heterostructured film, despite of slight decrease in tunability, the figure of merit on account of lowered dielectric loss was effectively improved (>40%), compared to that of the uniform PST60 film.

Keywords: Films; Sol–gel process; Dielectric properties; Perovskite; Tunable device

1. Introduction

Thin films based on $(Ba_{(1-x)}Sr_x)TiO_3$ (BST) have recently received considerable attention as promising candidates for applications in tunable microwave devices. These tunable devices are based on the large variation of permittivity with electric field, which results in a change in phase velocity in the microwave device, allowing it to be tuned in real time for a particular application.[1] In the case of the $(Pb_{(1-x)}Sr_x)TiO_3$ (PST), systems, Sr addition to $PbTiO_3$ offers good control over many of the desired room temperature dielectric and piezoelectric properties as reported in the studies based on bulk ceramics[2] and thin films.[3,4]Especially Somiya et al.[5] have suggested these PST ceramics for promising tunable device application. While in the case of PST based thin film, there are few studies regarding dielectric tunable characteristics. Considering that PST thin films with high dielectric constant also have high dielectric loss, there is a trade-off between dielectric tunability and material loss tangent, practically for microwave tunable device application. Tunability means dielectric constant of nonlinear response to an applied dc electric field at room temperature. Also this is defined by $\{\varepsilon r(\max) - \varepsilon r(\min)\}/\varepsilon(\max)$.[1] Hence, it is needed to engineer some reliable material, which can reduce the dielectric constant and loss tangent, by keeping the tunability in the necessary range to get optimum figure of merit (FOM, tunabilty/loss tangent). For BST thin film systems, various experimental methods, such as use of dopants,[6] control of annealing process[1] and formation of $(BT/ST)_n$[7] or $(Ba_xSr_{1-x})Ti_{1+y}O_{3+z}$ layer,[8] have been tried to improve its FOM.

In this study, the structural and dielectric properties of $(Pb_{1-x}Sr_x)TiO_3$ $(0.5(\mathrm{PST50}) \leq x(\mathrm{mol}) \leq 0.8(\mathrm{PST80}))$ films were investigated. And PST(x)–PST80 heterostructured thin films, by sequential deposition of PST(x) and PST80 layer, were synthesized with the aim to achieve composite PST films and with the desired dielectric properties, where the PST80 film composition, containing relatively higher Sr content, was chosen primarily because of its low dielectric constant and low loss tangent. And it also might influence the surface morphology

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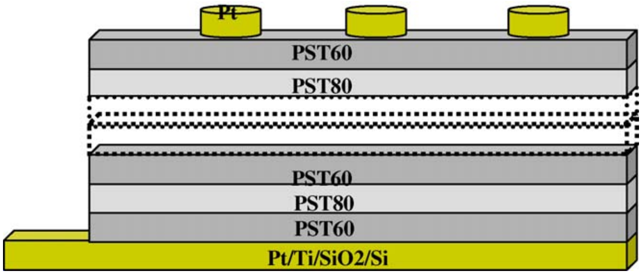

Fig. 1. Cutting plain of the heterostructure film.

of thin film. As a result, the dielectric properties and tunable device characteristics, especially FOM, of the heterostructured thin films were discussed in terms of film composition and surface roughness.

2. Experimental

A precise procedure for preparing the PST precursor solution was presented in previous report.[3] Uniform PST(x) thin films were consisted of same composition layer containing x mol% Sr. While the heterostructured films, PST(x)–PST80 were synthesized by depositing the PST(x) and PST80 layer alternately. The coated films were dried at 100°C for 1 min and then layer-by-layer heat-treated at 700°C for 1 min, respectively, for each layer deposition. Such procedures were repeated (nine times) until a desired thickness was obtained. Finally, well-crystallized PST thin films were obtained at 700°C for 10 min by directly inserting the coated thin films into the preheated Rapid Thermal Annealer (Mila-3000-P-N, Sinku-Riko), resulting in film of about 300 nm in thickness and each layer thickness is about 320–340 nm. Fig. 1 shows the cutting plain of heterostructured film. X-ray Diffractometer (D/MAX 2C, Bruker) and Atomic Force Microscopy (SPM-9500J3, Shimadzu) were used to determine crystal structure, lattice parameter and surface morphology of the films. The dielectric properties were measured by employing an impedance analyzer (4294A, HP) at 100 kHz with an electric field of 200 kV/cm and Precision Pro (Radiant Tech), and then tunability and FOM values were calculated.

3. Results and discussion

Fig. 2 shows the XRD patterns of uniform (($Pb_{1-x}Sr_x$)TiO_3) and heterostructured (($Pb_{1-x}Sr_x$)TiO_3–($Pb_{0.2}Sr_{0.8}$)TiO_3) thin films. All the films exhibited a polycrystalline perovskite. With increasing Sr (x) content, the peaks slightly shifted towards higher angles, which implies the incorporation of Sr into the crystal structure by considering relatively smaller ionic size of Sr^{2+}(0.144 nm) compared to Pb^{2+}(0.149 nm).[9–11] It was confirmed by measuring the lattice parameters for both thin film series as plotted in Fig. 3. In the uniform PST films (Fig. 3A), c/a value decreases with adding $SrTiO_3$ with cubic structure and for $x \geq 70$, convergences about 1. These results further indicated that the composition range of tetragonal/cubic phase boundary at room temperature corresponds to $x = \sim 0.7$ (mol) for the PST thin film system, where this composition seems to be similar to the reported boundary composition in the Sr-modified PZT study and our previous report of PST thin film.[2,3,12] The effect of Sr content on tetragonality of PST thin film was well observed in the case of the heterostructured films which were coated alternately with PST80 thin film (Fig. 3B). For all PST(x)–PST80 heterostructured film, lower tetragonality value compared to that of uniform PST(x) film was obtained due to the low tetragonality of PST80 film, implying the shift of phase transition boundary of uniform PST(x) film to lower temperature by PST80 film.

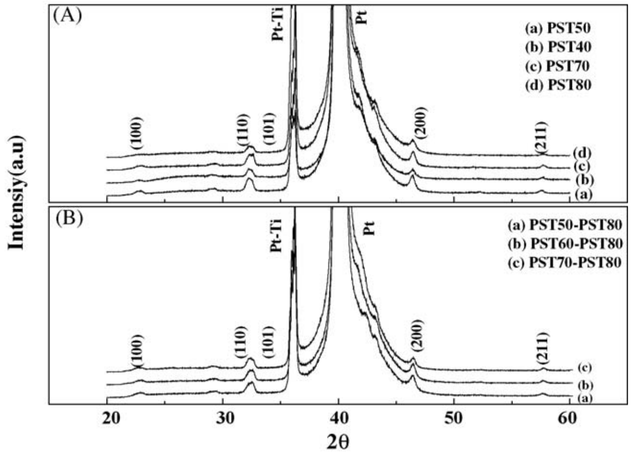

Fig. 2. XRD patterns of the uniform PST(x) thin films and heterostructure PST(x)–PST80 thin films.

Figs. 4 and 5 display the microstructure and surface roughness imaging of PST thin films, which were measured with an AFM. For both uniform and heterostructured films, a crack free microstructure with similar grain size (0.08–0.1 μm) was exhibited. While the film surface seems to be smoother with higher Sr content. Also Fig. 5 shows that the surface roughness of PST(x) film was much decreased by forming the heterostructured films, PST(x)–PST80. These variations of surface state were confirmed by analyzing the root-mean-square (rms) roughness of uniform and heterostructured films as shown in Fig. 6. Such improvement in surface roughness of the heterostructure thin film indicates the effectiveness of PST80 layer with relatively smoother surface.

Fig. 7 shows that various electrical characteristics of uniform PST(x) thin films, where the PST60 films showed the

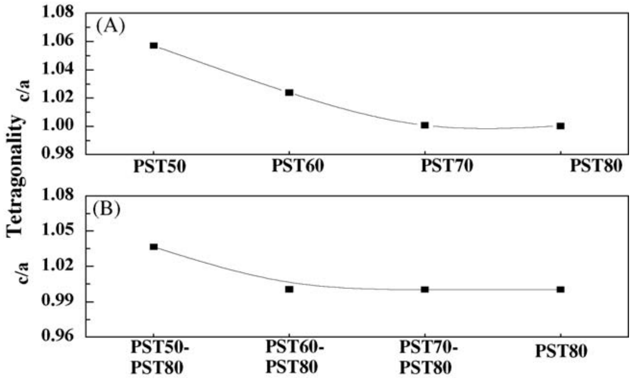

Fig. 3. Tetragonality (c/a) variation for the uniform PST(x) thin films and heterostructure PST(x)–PST80 thin films.

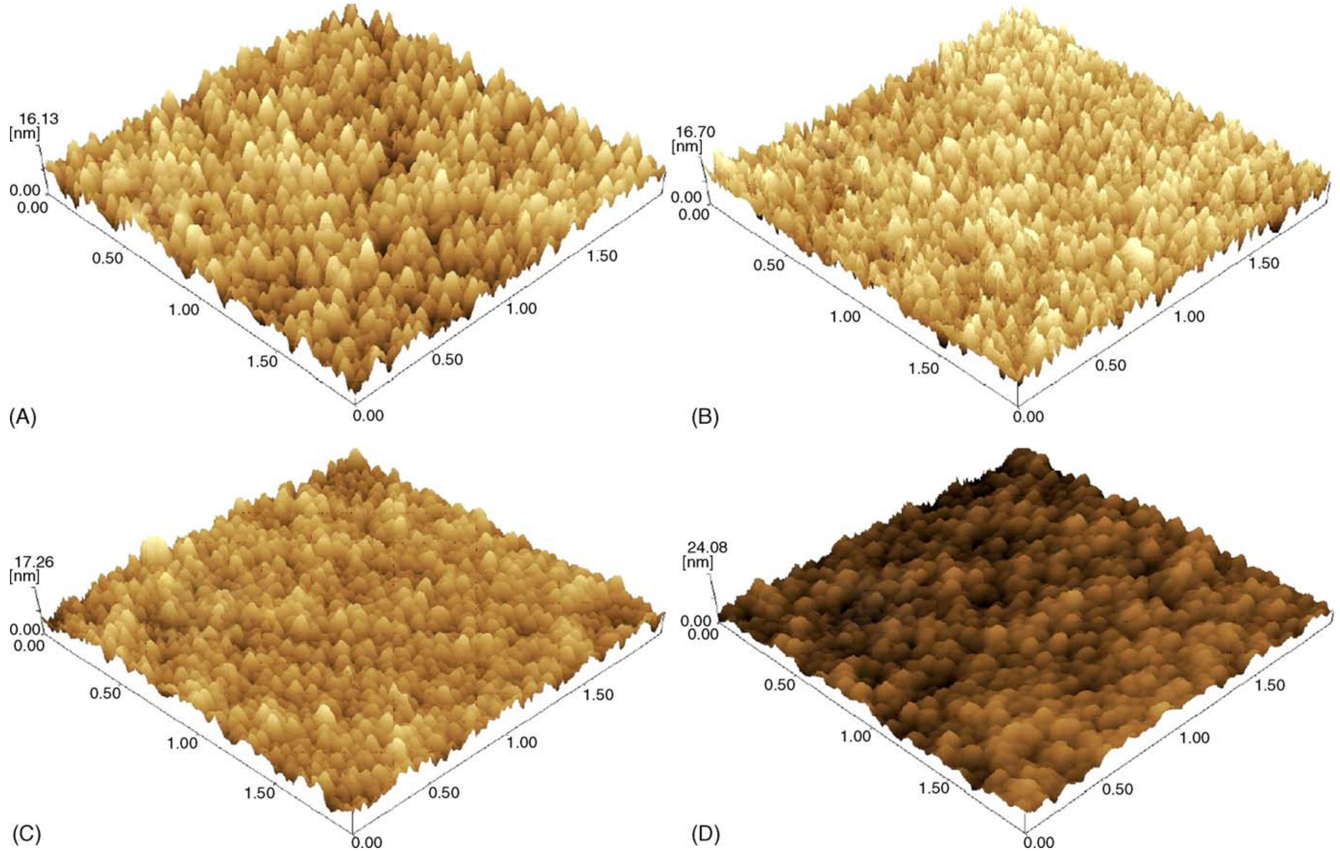

Fig. 4. AFM photographs of the uniform PST(x) thin films: (A) PST50, (B) PST60, (C) PST70, (D) PST80.

highest tunability(45.7%) as well as dielectric constant (875). It seems that at room temperature, this composition corresponds to the ferroelectric phase, existing near tetragonal (ferroelectric) to cubic (paraelectric) phase boundary (namely Curie temperature), as revealed from *c/a* analysis in Fig. 3. Similar results have been reported in PST ceramics and thin films.[2–4] However, the PST60 film showed relatively higher dielectric loss, resulting in poor FOM (∼8.3%). It has been desirable that the materials for tunable device application should always be used near the paraelectric phase close to the Tc, since additional losses due to spontaneous polarization and hysteresis are prevented there.[13] On the other hand, the PST80 film with higher FOM exhibited so lower tunability of about 30%. It means that the uniform PST(x) thin film should be modified in order to improve its tunable device characteristics.

Fig. 8 displays dielectric properties of the heterostructured thin films (PST(x)–PST80). Compared to the uniform PST(x) thin film, dielectric constants greatly decreased, while the tunabilities lowered so slightly. Especially increasing effect of FOM was found to be evident for the PST60/PST80 film. Considering the effective dielectric constant (k_{eff}) between PST(x) and PST80 films based on series capacitors structure,

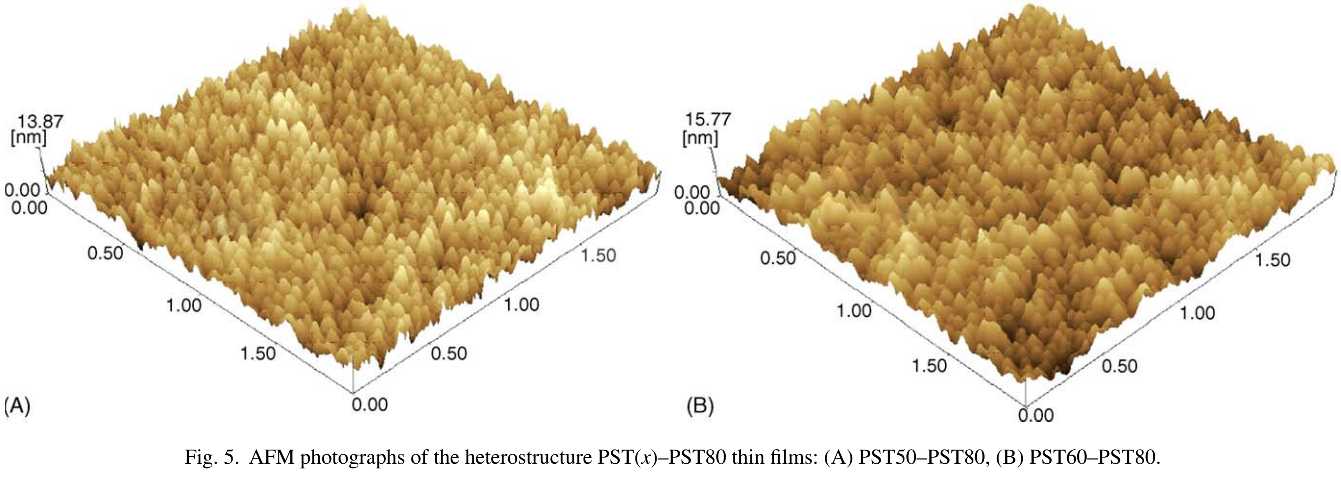

Fig. 5. AFM photographs of the heterostructure PST(x)–PST80 thin films: (A) PST50–PST80, (B) PST60–PST80.

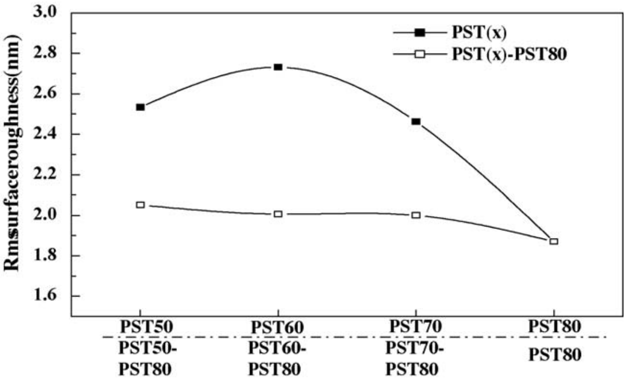

Fig. 6. Rms surface roughness for the uniform PST(*x*) thin films and heterostructure PST(*x*)–PST80 thin films.

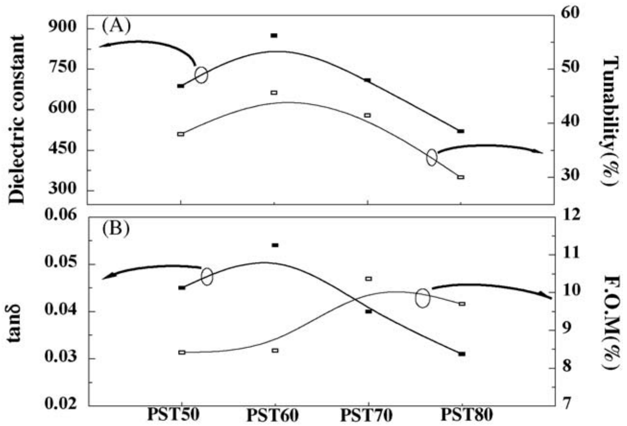

Fig. 7. Dielectric properties of the PST(*x*) thin films.

relatively higher dielectric constant ($k = 602$) was obtained for the PST50–PST80 compared to its calculated effective dielectric constant ($k_{\text{eff}} = 571$) despite of the presence of PST80 layer with low dielectric constant. By inserting PST80 layer, Tc of the PST50 film, higher rather than room temperature, may shift towards room temperature, which probably acted to improve the room temperature dielectric constant of the PST50–PST80 film. While lower dielectric constants of 592 and 524 compared to $k_{\text{eff}} = 615$ and 591 were observed for PST60–PST80 and PST70–PST80 films, respectively. The Tc of the PST60 and PST70 films close to room temperature seems to be less effective to induce Tc shift in corresponding heterostructured films. This result also can be understood by comparing the tetragonality versus composition data shown in Fig. 3. As shown in Fig. 8B, dielectric loss was effectively suppressed for the heterostructured film because of lower and stable dielectric loss of PST80 layer. However, calculations of the response of series-connected capacitors including dielectric loss indicate that the lower loss of the PST80 film itself is likely insufficient to account for the observed reduction in the loss of the heterostructured PST(*x*)–PST80 films. So the effectively decreased dielectric loss is further interpreted by the reduced surface roughness of the uniform PST(*x*) films due to the insertion of PST80 layer with so smoother surface (rms = 1.9 nm). It is well-known that a rough film surface will cause the conductor loss of the device because smooth film surfaces can provide excellent adhesion with the Pt top electrode in the metal-insulator-metal (MIM) type capacitor.[6] Some researchers have been reported about the origin of the improved dielectric loss of the modified BST based thin film in terms of changes in the microstructure and reduced roughness of the primary film.[1]

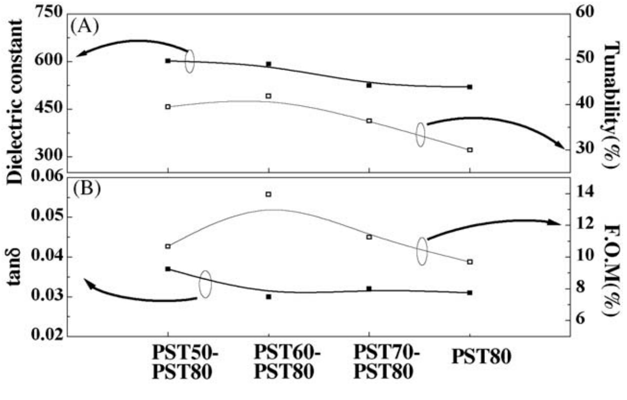

Fig. 8. Dielectric properties of the PST(*x*)–PST80 thin films.

Actually, the dielectric properties of PST60–PST80 film differ from the middle composition between PST60 and PST80, namely uniform PST70 film, which implies that the different nature of the interface layer may cause the different characteristics of the dielectric properties.[7,8] As a result, such lowered dielectric loss leads to increased FOM of the heterostructured films, ranging from 10% to 40% compared to corresponding FOM values of uniform PST(*x*) film as shown in Fig. 8.

4. Conclusions

Among uniform $(Pb_{1-x}Sr_x)TiO_3$ (PST(*x*)) film series, the PST60 film showed maximum tunability and dielectric constant, while its high dielectric loss caused lower FOM. Dielectric properties and surface roughness of all uniform PST(*x*) thin films were changed when PST80 thin film with relatively lower dielectric constant, loss and smoother surface was inserted alternately into each PST(*x*) film. Room temperature dielectric constants of the heterostructured $(Pb_{1-x}Sr_x)TiO_3$–$(Pb_{0.2}Sr_{0.8})TiO_3$ (PST(*x*)–PST80) films were mainly dependent on their intrinsic dielectric properties such as dielectric constant, loss and Curie temperature. Especially, suppressing effect of dielectric loss by inserting PST80 layer into each PST(*x*) film was relatively manifested, which can be interpreted due to the apparent decrease of surface roughness of uniform PST(*x*) films. Decrease in dielectric loss led to enhancement of the FOM of the heterostructured films, resulting in higher values of FOM of 12–14% for PST60–PST80 and PST70–PST80 films.

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