

Effects of the sol concentration on the texture of $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ thin films derived by sol–gel method

Wanhai Chen · Boyu Ni · Wenbiao Wu ·
Jinrong Cheng · Dongwen Pen · Shenwen Yu ·
Zhongyan Meng

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Abstract $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ (PST) thin films were deposited on Pt coated Si (100) substrates by sol–gel techniques using a series of different sol concentrations (0.15, 0.20, 0.25, 0.30, and 0.40 M). Both structural and dielectric characteristics of PST films as a function of the sol concentration were investigated. PST thin films reveal typical crystalline structure with columnar texture when the sol concentration is lower than 0.30 M. With the concentration increasing up to 0.30 M, the columnar-grained structures can not be obtained. Among all the PST thin films, the thin film derived with 0.25 M sol has better dielectric characteristics. The dielectric constant, dielectric loss, tunability and FOM are 329, 0.011, 58.0% and 52.8, respectively.

Keywords PST thin films · Sol concentration · Columnar-grained structure · Tunability · Dielectric property

1 Introduction

Barium strontium titanate (BST) system is well known that its dielectric constant has strong response to an applied DC bias field. This property is very attractive to be used to develop tunable microwave devices.

Unfortunately, higher dissipation factor of BST films at high frequency range limits its practical application. An extensive research has been done to decrease the intrinsic

losses by fine tuning the composition of BST [1, 2] and adding different dopants, such as Al, Bi and Fe [3–5] into the system. However, usually it has been observed that the lowering of the losses also causes the lowering of tunability and vice versa in BST system. In practice there is a trade-off between dielectric tunability and material loss tangent. Hence, it is needed to engineer some reliable materials, which can reduce dissipation factor and get appropriate dielectric constant, by keeping the tunability in the necessary range to optimize figure of merit (FOM) i.e. tunability/dissipation factor.

Lead strontium titanate ($\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$, PST) thin films have attracted attention in the last few years. $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ compositions with $x \leq 0.4$ are paraelectric at room temperature and exhibit ferroelectric phase transition below room temperature. Also, only one phase transition [6] in the PST system was recorded. It is indicated that PST thin films in the paraelectric phase is a potential candidate for applications of tunable microwave devices. Recently, Kim and Chang-II [7, 8] reported that the LaNiO_3 (LNO (100)) coated Si and MgO (100) buffered Si substrates were adopted to offer the benefits of better lattice matching and thus to grow highly (100) oriented PST thin films with improved dielectric and tunable properties. In addition these properties significantly depend on the anisotropic in-plane strain in the thin films deposited on the orthorhombic NdGaO_3 substrates [9]. However, we found that the dielectric characteristics are strongly related to the texture of thin films, which can be controlled by the sol concentration. Decreasing the sol concentration the films deposited directly on the Pt/Ti/SiO₂/Si substrates grew up the columnar-grained texture, which was formed by island growth. Hence, the highly textured PST thin films have been obtained to optimize the dielectric characteristics.

W. Chen · B. Ni · W. Wu · J. Cheng · D. Pen · S. Yu ·
Z. Meng (✉)
School of Material Science and Engineering, Shanghai University,
Shanghai 200072, China
e-mail: zymeng@staff.shu.edu.cn

In this paper, the dielectric characteristics of the $Pb_{0.3}Sr_{0.7}TiO_3$ thin films related to the texture structure are presented. More attention will be paid on the phenomenon of the texture caused by different sol concentrations.

2 Experimental

$Pb_{0.3}Sr_{0.7}TiO_3$ films with excess plumbum acetate of 10 mol.% were prepared by using lead acetate tri-hydrate ($Pb(OAc)_2 \cdot 3H_2O$), strontium acetate ($Sr(OAc)_2$) and titanium-tetrabutoxide ($Ti(OC_4H_9)_4$) as starting materials. Glacial acetic and 2-methoxyethanol were used as solvents or complexing agents for sol–gel method. PST solutions were diluted to the desired concentrations with the addition of 2-methoxyethanol and spun on the Pt/Ti/SiO₂/Si substrates at 3000 rpm for 30 s. After spin coating, the films were heated at 500 °C for 4 min to remove the organic substance, then at 650 °C for 5 min to crystallize into perovskite phase. The films with desired thickness were obtained by repeating the spinning-heating cycles. Finally the deposited films were annealed by RTA at 750 °C for 10 min in air. For electrical measurements, a gold electrode array with dots of 400 μm in diameter was deposited on the annealed PST thin films by DC sputtering.

The phase formation was examined by X-ray diffraction with Rigaku-D/Max diffract meter. The microstructure and morphology were observed by field emission scanning electron microscope (FE-SEM, XL30 FEG). The dielectric properties, dielectric tunability and leakage current were carried out by using a Precision impedance analyzer (Agilent 4294A, Japan) and a HP 4140B PA Meter/DC Voltage Source, respectively.

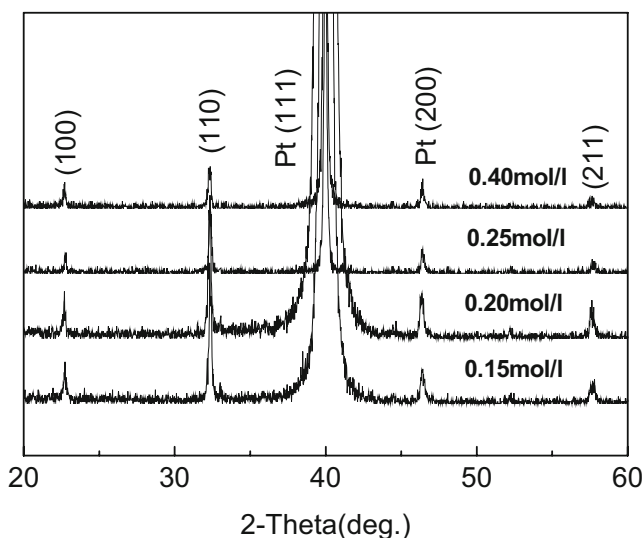


Fig. 1 XRD patterns of the PST (30/70) thin films prepared by the solutions with different concentrations

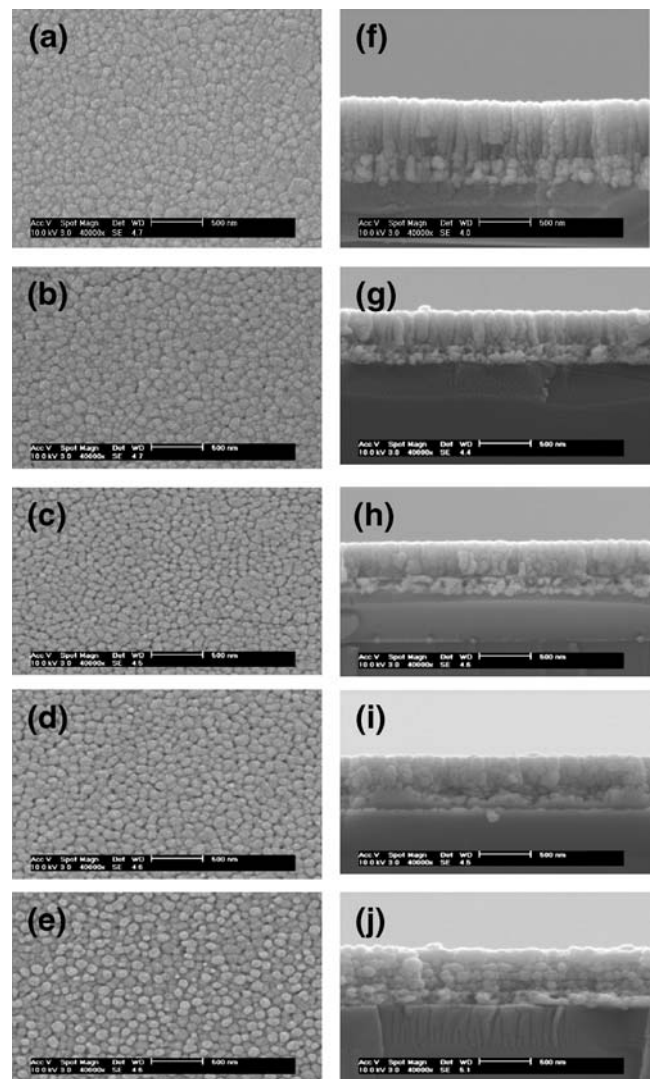


Fig. 2 FE-SEM surface and cross-section images of PST (30/70) thin films derived with different sol concentrations: (a, f) 0.15M; (b, g) 0.20M; (c, h) 0.25M; (d, i) 0.30M; (e, j) 0.40M

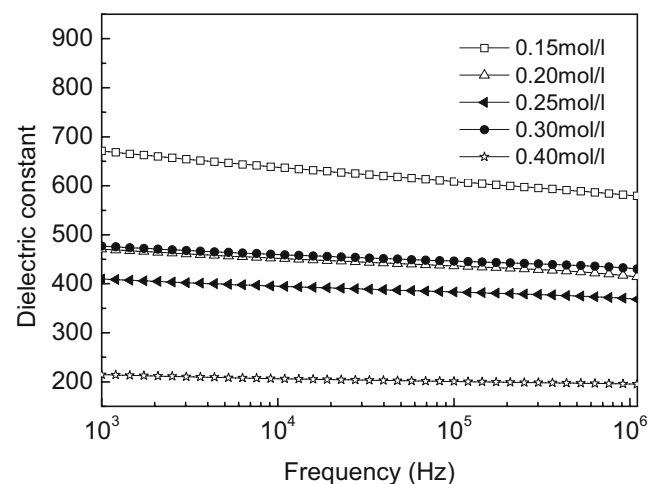


Fig. 3 The dielectric constant and dissipation factor of PST (30/70) thin films as a function of frequency

3 Results and discussion

Figure 1 shows XRD patterns of the PST thin films deposited on the Pt (111)/Ti/SiO₂/Si with various sol concentrations. All the films show a well-developed perovskite structure with no evidences of secondary phase formation. Figure 2(a)–(j) are FE-SEM photographs for the surface and cross-section of the Pb_{0.3}Sr_{0.7}TiO₃ thin films, respectively. As shown in Fig. 2(a)–(e), it can be seen that all the PST films show crack free, dense microstructure and uniform grain structure, and that the average grain size is approximately 80 nm for the 0.15 to 0.25 M films and 100 nm for the 0.30 and 0.40 M films. Also, it was found that the film becomes more uniform and compact with increasing the sol concentration. These phenomena may be attributed to more uniform nucleation under higher sol concentration as the thin films were deposited at the same processing conditions. The ions of low sol concentration have higher free energy so as to difficulty assemble together compared with high sol concentration. Figure 2(f)–(j) show

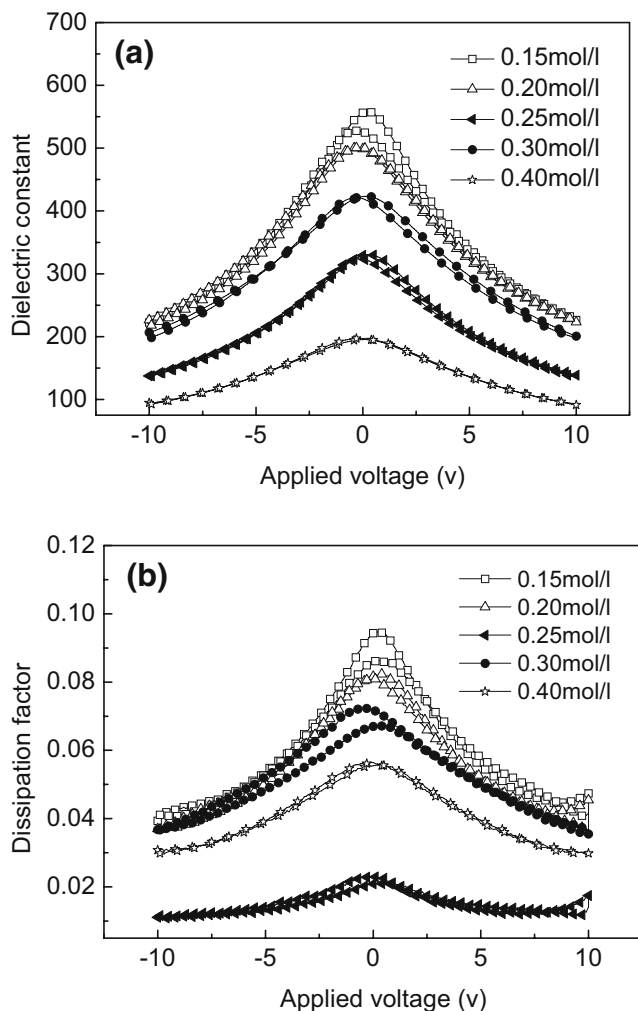


Fig. 4 The dielectric constant and dissipation factor of PST (30/70) thin films as a function of bias voltage at frequency of 1 MHz

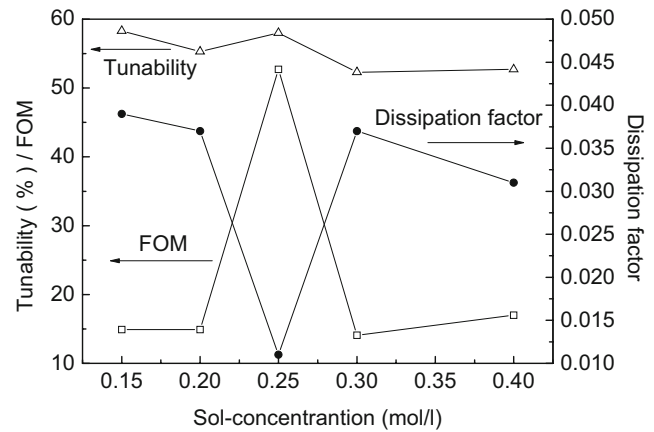


Fig. 5 Tunability and FOM of the PST (30/70) thin films as a function of sol concentration

the cross-section FE-SEM image of all the films. It is found that columnar texture reveals when the concentration is lower than 0.3 M. As we all know, nucleation at the substrate/film interface can be used to control the preparation of epitaxial and highly textured films, the growth of highly textured thin films on substrates with different structures is due to morphological instability phenomena and abnormal grain growth. For the lower sol concentration, ions of each layer deposited on the substrate are comparatively less than those of the higher sol concentration, so the ions are more free in active space and turn into isolated grains (seeds) that possess a lower interfacial energy, subsequently, when the film is deposited onto this surface layer-by-layer, the isolated islands act as nucleation sites (seeds) for the growth of a highly textured film, for the higher sol concentration the thin film has a homogeneous distribution of the carbonate and oxide phases, the activation energy is nearly the same for all parts of the amorphous film. Once critical activation energy has been reached, a large number of very small crystallized grains

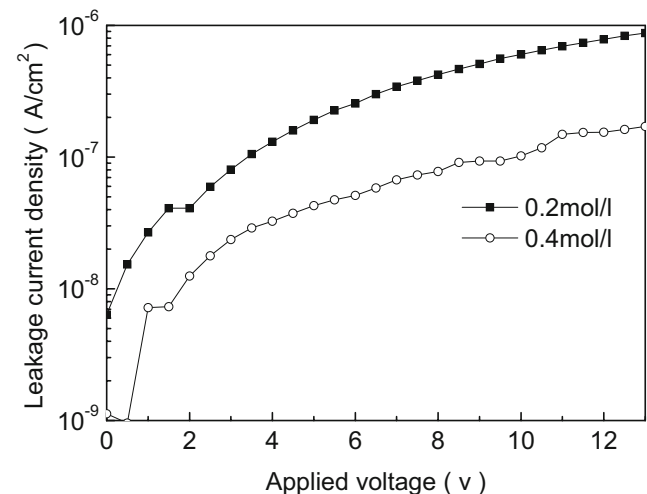


Fig. 6 Current density-applied voltage curves of the PST (30/70) thin films as a function of sol concentration

grow up throughout the film, so multiple layers are presented and the grains are spherical as shown in Fig. 2(j).

The dielectric constant of PST thin films as a function of frequency is shown in Fig. 3. It can be seen that the dielectric constants of the films from 0.15 to 0.40 M at frequency of 1 MHz are about 608.7, 436.7, 383.4, 446.5 and 200.7, respectively. It is clear that the thin films of low sol concentration have higher dielectric constant due to the columnar texture, which made the films easy to be polarized when an external electric field was applied on the films.

Figure 4 shows the dielectric constant and dissipation factor of PST thin films as a function of bias voltage. The curves were measured at 1 MHz with a cycling of DC bias voltage. As shown in Fig. 4(a), the tunability of all the films is above 50%, besides it is reasonable that the films of small concentrations, 0.15–0.25 M, obviously obtain higher tunability as these films reveal columnar texture. From Fig. 4(b), it can be noted that the loss tangents of the films become lower under the DC bias voltage. The minimum loss tangents of the films of 0.15 to 0.40 M are approximately 0.039, 0.037, 0.011, 0.037 and 0.031, respectively.

Figure 5 shows the tunability, dissipation factor and figure of merit (FOM) of the PST thin films as a function of the sol concentration. The tunability is defined as $(\epsilon_{\max} - \epsilon_{\min})/\epsilon_{\max}$, and FOM is defined as tunability (%) / $\tan\delta$ (%). As shown in Fig. 5, compared with the high sol concentration solution the low concentration solution makes the film comparatively more defects such as pin holes and non-compact which achieved during the annealing process, in addition compared with the layer structure the columnar structure makes the leakage current of the film higher due to the “fast tunnel” provided by the columnar structure for ion transport, as shown in Fig. 6. Therefore, the dissipation factor reaches at the same level of high concentration. When the solution reaches appropriate

concentration (0.25 M), the defects of the thin film reduce, so the dissipation factor decreases sharply. It can be easily seen that dissipation factor, tunability and FOM values of 0.25 M thin film are more optimized, which are obtained on the level of 0.011, 58.0% and 52.7, respectively.

4 Conclusion

The $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ thin films were derived with different sol concentrations on Pt/Ti/SiO₂/Si substrates by sol–gel technique. We found that the film demonstrates columnar grain structure when the concentration sol derived with enough low and leads to a higher tunability and dielectric constant, however, the dissipation factor slightly increases compared with the multilayer grain structure obtained with high sol concentration due to the contribution of higher leakage dissipation factor caused by columnar structure.

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