

# Effect of poly(vinyl acetate) on structure and property of bismuth-doped strontium titanate thin films derived by sol–gel method

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## Abstract

Bismuth-doped strontium titanate thin films with pure perovskite phase have been successfully deposited on Pt (1 1 1)/Ti/SiO<sub>2</sub>/Si substrate by polymer-assisted sol–gel method. Poly(vinyl acetate) (PVAc) in precursor solution promoted the formation of perovskite phase during the heat treatment. SEM results revealed an increasing thickness from 40 to 80 nm every single layer and a porous structure with the addition of PVAc. The addition of polymer made the dielectric constant decrease from 140 to 40 and the tunability slightly increase compared with films without polymer in precursor.

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*Keywords:* C. Dielectric properties; Polymer-assisted sol–gel; Bismuth-doped strontium titanate

## 1. Introduction

Although alkoxide-based sol–gel method is a popular and wide spread technique for preparing ceramic coating films in laboratories, people in industry are not encouraged enough to employ this technique for mass production. One of the disadvantages is the low critical thickness, i.e., the maximum thickness achievable without crack formation. In laboratories, film coatings are realized by multiple cycles of gel deposition and firing, where coating solutions of low viscosities are used to make the single-layer thickness as small as 50 nm. Such repetitive deposition, however, is time consuming and impracticable in industries [1]. Meanwhile, films tend to be broken down at lower dc bias due to its extreme thin thickness. Meanwhile, films probably cover the substrate unevenly and some portion of the substrate may not be covered. The uneven substrate resulted from the sputtering process of the bottom electrode. The thinner areas of the films tend to be broken down more easily. Even the worse, the uncovered areas lead to direct contact between top and bottom electrodes.

Chelating agents and diols as solvents [2] are reported to be effective in increasing the critical thickness of coating films to about 700 nm for every single layer. Thicker films could not be made because of the low solution viscosity, and the viscosity could not be raised by reducing the solvent content because of low solubility of strontium acetate. Chelating agents can only make the system below concentration of about 0.3 mol/L, which is not enough to increase the film thickness. Kozuka [3] found that the critical thickness of gel-derived films can be increased by incorporating polymer in the precursor solutions.

The present paper reports the study on precursor solution with poly(vinyl acetate) (PVAc) to increase the thickness of thin films. Addition of the polymer brings along an increase of the thickness as well as porous structures and properties of the films, i.e., decreasing the dielectric constant and increasing the tunability of the films.

## 2. Experimental procedure

Two kinds of Bi<sub>0.1</sub>Sr<sub>0.85</sub>TiO<sub>3</sub> precursor solutions were synthesized by sol–gel method, one with PVAc added in the precursor solution and the other none. Bismuth nitrate [Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O] and strontium acetate (Sr(CH<sub>3</sub>COO)<sub>2</sub>·(1/2)H<sub>2</sub>O) and tetrabutyl titanium (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>) were used as starting materials. Ethylene glycol monomethyl ether [CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH], acetic acid [CH<sub>3</sub>COOH] and acetylac-

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tone [ $\text{CH}_3\text{COCH}_2\text{COCH}_3$ ] were used as solvent, catalyst and chelating agent, respectively. One gram of poly(vinyl acetate) per 100 mL precursor solution was added to enhance the thickness of the film.

Strontium acetate was dissolved at 40 °C in ethylene glycol monomethyl ether–acetic acid solution (ethylene glycol monomethyl ether:acetic acid = 2:3) stirred for 1 h. Tetrabutyl titanium was dissolved at room temperature in ethylene glycol monomethyl ether–acetylacetone solution (tetrabutyl titanium:acetylacetone = 1:2), and then the solution was stirred for 1 h. The titanium solution was added to the strontium solution with continuous stirring at room temperature for 0.5 h, called as solution A. Bismuth nitrate (15 mol.% excess) was dissolved at room temperature in ethylene glycol monomethyl ether. The bismuth solution was added to solution A after 0.5 h of stirring. The final mixture has been stirred for additional 2 h to make a homogeneous solution. The color turned to be transparent yellow. The concentration of solution was adjusted to approximately 0.3 mol/L.

The spin-coated wet films were dried at 400 °C for 3 min and 700 °C for 5 min sequentially by a rapid thermal annealing method. The process of spin-coating/annealing was repeated several times to reach the required film thickness. For electric measurements, gold electrodes were deposited by a sputtering method on the surface of the thin films using a ceramic mask. Then the films with gold electrodes were heated at 150 °C for 30 min in an oven to improve adhesion between metal and film. For convenience, a film with PVAc in precursor solution is named as film P, and that without polymer in precursor solution as film N.

Thermal analysis of PVAc powders and powders dried from  $\text{Bi}_{0.1}\text{Sr}_{0.85}\text{TiO}_3$  precursor solution was investigated by a TA SDT Q600 thermo-analyzer system. Microstructure and crystallization of  $\text{Bi}_{0.1}\text{Sr}_{0.85}\text{TiO}_3$  films were investigated by a JEOL JSM-6700F field emission scanning electron microscope (FESEM) and a Rigaku D/MAX-2400 X-ray diffractometer (XRD).  $P$ – $E$  hysteresis loops were determined by an AIXACCT 2000 TF analyzer system with an FE module. Dielectric properties were measured by an Agilent 4192A precision impedance analyzer.

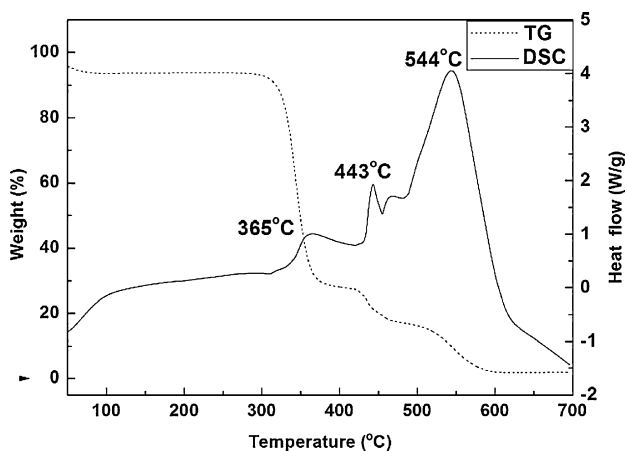


Fig. 1. DSC and TG curves of PVAc powders.

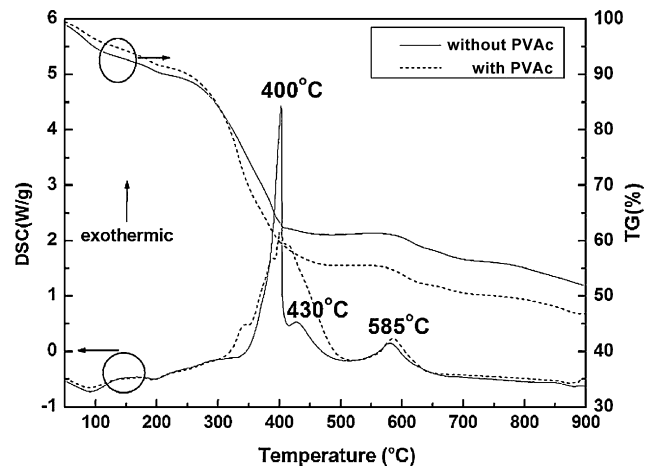


Fig. 2. DSC and TG results of the two precursor powders dried from precursor solution, solid line for sample without PVAc, dash line for sample with PVAc.

### 3. Results and discussion

Fig. 1 shows the DSC and TG curves of PVAc powders. It can be seen that the main exothermic peak is at 544 °C and no weight loss is observed as PVAc is heated over 600 °C.

DSC and TG results of the two kinds of precursor-dried powders are given in Fig. 2. In the DSC and TG curves, it is clearly shown that evaporation of the organic solvent completes before 200 °C for both of the samples. Great weight loss

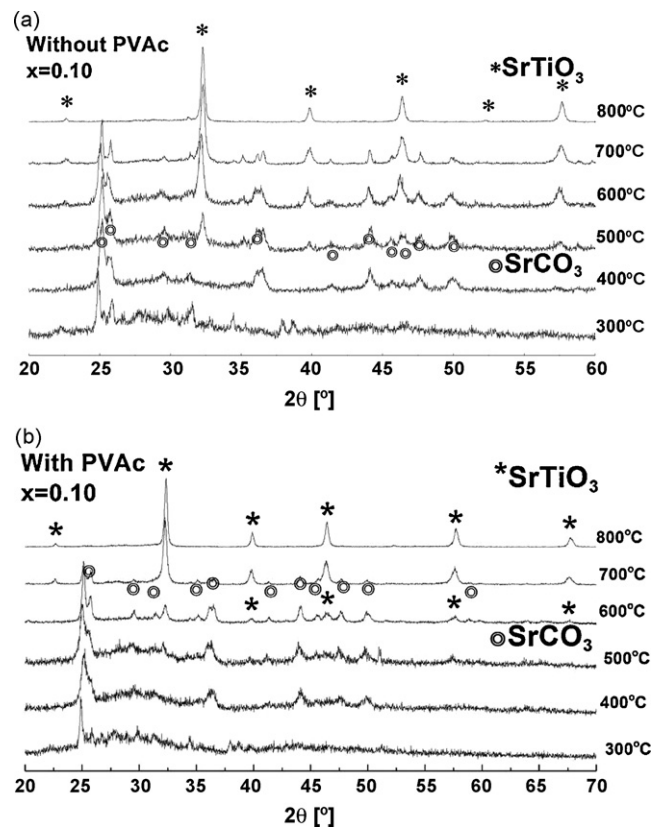


Fig. 3. X-ray diffraction pattern of powders sintered from precursor solution at different temperatures from 300 to 800 °C (a) for powder sample without PVAc in precursor solution and (b) for powder sample with PVAc in precursor solution.

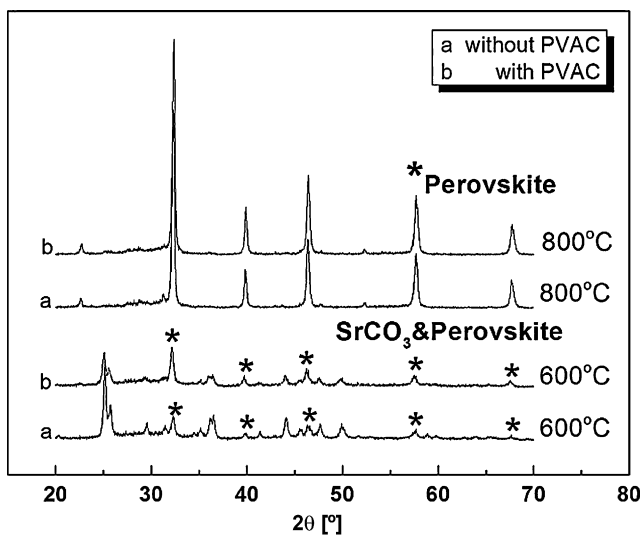


Fig. 4. X-ray diffraction pattern of film P and film N under heat treatment of 600 °C and 800 °C (a) for sample without PVAc and (b) for sample with PVAc.

happened between 260 and 404 °C, accompanied by an exothermic peak at 400 °C, due to decomposition and combustion of the organic and the formation of SrCO<sub>3</sub> phase proved by XRD patterns as shown in Fig. 3. Formation of SrCO<sub>3</sub> phase as well as decomposition and combustion of the polymer

happened concurrently. So exothermic peak between 300 and 500 °C was broader for a sample with PVAc in precursor solution. The exothermic peak at 430 °C which is absent in DSC curve of pure SrTiO<sub>3</sub> in the present author's related work without weight loss is probably related with bismuth ions into the perovskite lattice. The exothermic peak at 585 °C with weight loss corresponds to the formation of perovskite, which might not be effected by the main exothermal peak of PVAc at 544 °C.

The X-ray diffraction patterns of both film P and film N under heat treatment of 600 and 800 °C are shown in Fig. 4. Perovskite phase appeared under 600 °C heat treatment and peaks of perovskite were comparatively stronger for film P than that for film N. All the peaks for the powder heat-treated under 800 °C could be indexed as cubic perovskite with no evidence of SrCO<sub>3</sub> phase for both film P and film N.

SEM micrographs of the surface and cross section of Bi<sub>0.1</sub>Sr<sub>0.85</sub>TiO<sub>3</sub> film P and film N are shown in Fig. 5. Decomposition and combustion of PVAc left holes about 300 nm in diameter in the film P, while film N has pores less than 10 nm in diameter. Structure outside the holes of film P was denser than film N. From the cross section of the films, it is easy to conclude that thickness was increased from 40 nm for film N to 80 nm for film P in every single layer due to the addition of PVAc.

Electric field dependence of dielectric constant is shown in Fig. 6. The results indicated that the dielectric constant

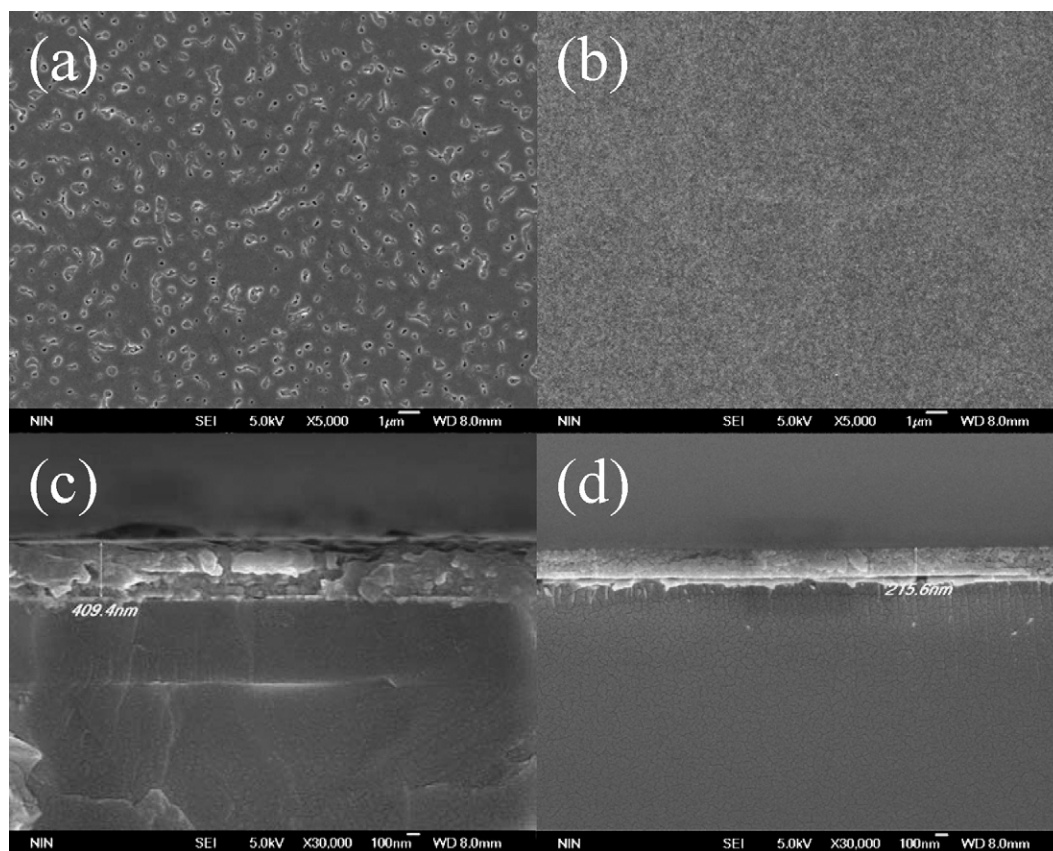


Fig. 5. SEM micrographs of the surface and cross section of Bi<sub>0.1</sub>Sr<sub>0.85</sub>TiO<sub>3</sub> films: (a) surface of Bi<sub>0.1</sub>Sr<sub>0.85</sub>TiO<sub>3</sub> film with PVAc in precursor solution, 5000 times magnified, (b) surface of Bi<sub>0.1</sub>Sr<sub>0.85</sub>TiO<sub>3</sub> film without PVAc in precursor solution, 5000 times magnified, (c) cross section of Bi<sub>0.1</sub>Sr<sub>0.85</sub>TiO<sub>3</sub> film with PVAc in precursor solution, 409.4 nm thick, 30,000 times magnified and (d) cross section of Bi<sub>0.1</sub>Sr<sub>0.85</sub>TiO<sub>3</sub> film without PVAc in precursor solution, 215.6 nm thick, 30,000 times magnified.

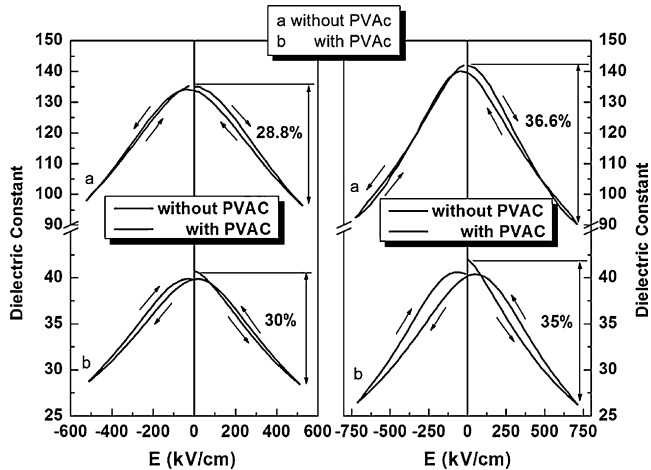


Fig. 6. Electric field dependence of the dielectric constant (a) for sample without PVAc and (b) for sample with PVAc.

decreased from 140 for film N to 40 for film P. The tunability is increasing from 28.8% for film N to 30% for film P under 500 kV/cm whereas decreasing from 36.6% for film N to 35% for film P under 700 kV/cm, where the tunability was defined as  $(\epsilon_{\max} - \epsilon_{\min})/\epsilon_{\max}$ . In the plots of Fig. 5, abnormal  $\epsilon$ - $E$  plots were observed in film P, which means the dielectric constant maxima precedes to the sweeping bias voltage. Electric field dependence of the tunability is shown in Fig. 7. The tunability for film P, compared with film N, is larger below electric field of 600 kV/cm whereas smaller above 600 kV/cm.

The  $P$ - $E$  hysteresis loops are shown in Fig. 8. The results indicated that the maximal polarization decreased from 6 to  $2 \mu\text{C}/\text{cm}^2$  due to the addition of PVAc.

Addition of PVAc does not present any significant effect on thermal behavior of the gel. The XRD patterns indicated that the addition of PVAc in the precursor promotes the formation of the perovskite phase.

The addition of PVAc increased the critical thickness of the film. Effect of PVAc to the stress in the film is uncertain. In Kazuka's study [1,4], polymer is thought to promote the

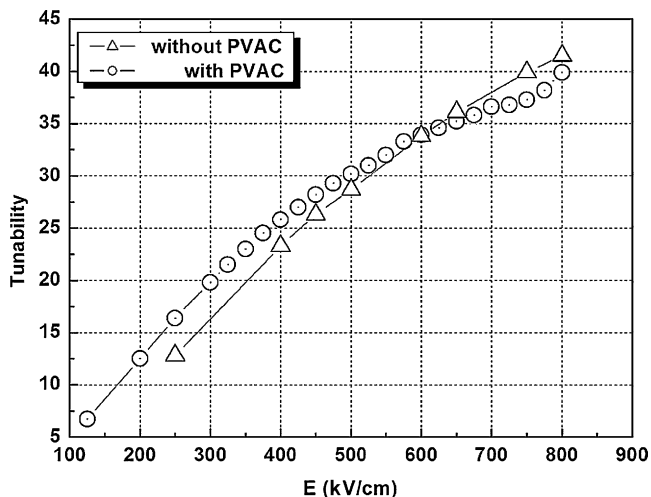


Fig. 7. Electric field dependence of tunability of the films ( $\Delta$ ) for sample without PVAc and ( $\circ$ ) for sample with PVAc.

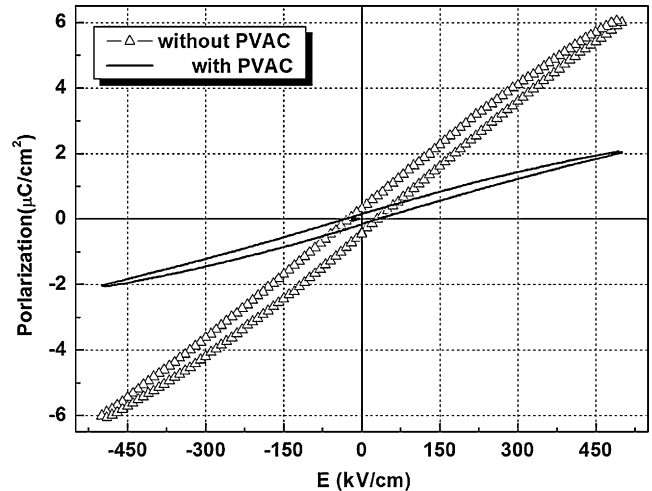


Fig. 8.  $P$ - $E$  hysteresis loop of the films ( $\Delta$ ) for sample without PVAc and solid line for sample with PVAc.

structural relaxation in the films and hence increase the critical thickness. However, in Hyun [5] and Shaw [7] study, the existence of stress decreased the dielectric constant. Shaw [7] proved that dielectric constant could be reduced due to the residual stress in the film according to the following relation:  $1/\epsilon_f = (1/\epsilon_u) - 4Q_{12}\sigma$ , where  $\epsilon_f$  is the permittivity of the stressed film,  $\epsilon_u$  the permittivity of the unstressed film and  $Q_{12}$  is the electrostrictive coefficient. Film P with much smaller dielectric constant than film N may result from the existence of stress in film P. Meanwhile, associated with the results above, the present author believed the porous structure as one of the reason for the reduction of dielectric constant.

The addition of PVAc increased the tunability under a comparative weak field whereas that decreased it when the field became stronger. The reason for this might be the multi-effect of porous structure, stress in the film and the interfacial dead layer.

Meanwhile, film P suggested an abnormal  $\epsilon$ - $E$  plots and this effect became obvious with the increasing electric field. Wei [6] believed that this abnormal  $\epsilon$ - $E$  plots in BST ceramics was related with the strong interaction between point defects and domain walls.

From the relation of  $\epsilon(E) \propto \partial P/\partial E$ , it is easy to conclude that reduction of dielectric constant is consistent with the decreasing of maximal polarization in  $P$ - $E$  plots.

In summary, polymer-assisted sol-gel process successfully resolved the problems of thin thickness. High tunability of the  $\text{Bi}_{0.1}\text{Sr}_{0.85}\text{TiO}_3$  film did not been affected by the addition of PVAc. The PVAc-induced decreasing effect of dielectric constant could be improved through modification of the addition of PVAc, deposition and firing process, which need more experiments.

#### 4. Conclusions

$\text{Bi}_{0.1}\text{Sr}_{0.85}\text{TiO}_3$  thin films of pure perovskite phase were obtained by adding PVAc in precursor solution. PVAc in precursor solution not only increased the thickness from 40 to 80 nm every single layer, but also promoted the formation of perovskite phase during the firing processes. Porous structure

caused by the addition of PVAc leads to a reduction of dielectric constant and slight increase of the tunability.

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