Enhanced the dielectric and tunable properties of Pb$_{0.3}$Sr$_{0.7}$TiO$_3$ and (Bi$_{1.5}$Zn$_{0.5}$)(Nb$_{0.5}$Ti$_{1.5}$)O$_7$ trilayer film through adjusting heat treatment process

Shuang Hou$^{1,a}$, Xiuneng Li$^{2,b}$, Yijian Ma$^{3,4,c}$, Jianfu Tang$^{5,6,d}$, Xujing Wu$^{7,e}$

$^1$Zhejiang Academy of Special Equipment Science, Hangzhou, Zhejiang, China.
$^2$China Special Equipment Inspection and Research Institute, Beijing, China.
$^3$Zhejiang Academy of Special Equipment Science, Hangzhou, Zhejiang, China.
$^4$Key Laboratory of Special Equipment Safety Testing Technology of Zhejiang Province, Hangzhou, Zhejiang, China.
$^5$Zhejiang Academy of Special Equipment Science, Hangzhou, Zhejiang, China.
$^6$Key Laboratory of Special Equipment Safety Testing Technology of Zhejiang Province, Hangzhou, Zhejiang, China.
$^7$Zhejiang Academy of Special Equipment Science, Hangzhou, Zhejiang, China.

$^a$email: hou3343268@163.com, $^b$email:morerlee929@163.com, $^c$email:729752002@qq.com, $^d$email:770110436@qq.com, $^e$email: mayj@zjtj.org

Abstract. Pb$_{0.3}$Sr$_{0.7}$TiO$_3$ (PST) and Bi$_{1.5}$Zn$_{0.5}$Nb$_{0.5}$Ti$_{1.5}$O$_7$ (BZNT) thin films were deposited on Pt/Ti/SiO$_2$/Si substrates by Sol-gel and radio frequency (rf) magnetron sputtering, respectively. The dielectric and tunable properties of thin films were investigated as a function of heat treatment processes. It’s found that the heat treatment process at the appropriate temperature and time can be used to obtain a good thin film. The film has the best comprehensive dielectric properties by annealing at 650°C for 45min, the figure of merit (FOM) is 20.1.

1. Introduction

Dielectric materials have been widely used in microwave tunable devices due to their own dielectric properties, such as phase shifters, capacitors and tunable oscillators$^{[1-7]}$. As an ideal microwave material, it must have many characteristics such as high dielectric constant, high dielectric tuning, and low dielectric loss$^{[3,4,8-10]}$. Sheng-Xiang Wang et al. used magnetron sputtering to prepare a BZN/BST/BZN sandwich heterogeneous multilayer composite film, and found that the composite film has a lower dielectric loss, only 0.008 at 1MHz$^{[11]}$. Wangyang Fu et al. successfully prepared a BZN/Mn-doped BST heterogeneous double-layer film on a Pt/Ti/SiO$_2$/Si substrate using the pulsed laser deposition (PLD) method, and found that the tuning amount of the multilayer film was between 55% and 60%, and the dielectric loss of the multilayer film is below 0.5%, which effectively improves the performance of the film$^{[12]}$.

In general, PST thin film having a high dielectric constant and amount of tuning, and BZNT thin film having a moderate dielectric constant and low dielectric loss. Therefore, in order to obtain a thin
film sample with better comprehensive performance, it is necessary to composite two kinds of heterogeneous films, PST and BZNT, so as to obtain a higher tuning amount and lower loss. In this study, the BZNT and PST films are prepared by radio frequency (rf) magnetron sputtering and sol-gel methods respectively, and then the two films with better properties are heterogeneously composited. The effect of heat treatment on the dielectric properties of PST and BZNT trilayer films.

2. Experimental procedure

Preparation of PST film precursor: Lead acetate(Pb(CH$_3$COO)$_2$·3H$_2$O), strontium acetate(Sr(CH$_3$COO)$_2$·1/2H$_2$O), and tetrabutyl titanate(Ti(OC$_4$H$_9$)$_4$) were selected as raw materials, and glacial acetic acid(CH$_3$COOH), deionized water and glycol methyl ether(CH$_3$OCH$_2$CH$_2$OH) were used as solvents to prepare PST films. When using the Sol-gel method to prepare the PST precursor, dissolve lead acetate and strontium acetate in a hot glacial acetic acid aqueous solution according to a certain ratio, and stir at a constant temperature at 50°C to form a solution A. Take a certain amount of tetrabutyl titanate and ethylene glycol methyl ether and dissolve them in a beaker to form a B solution. Then slowly add B solution to the stirred A solution, and then slowly add a certain amount of acetylacetone as a stabilizer. The mixed solution is placed in a water bath at 90°C. and stirred at a constant temperature for 1 hour to form a stable solution, which is filtered to obtain a stable PST sol precursor. Store the obtained PST sol in a reagent bottle for 5~6 days for use[14,15].

Preparation of BST ceramic target: The BZNT ceramic target material adopts traditional ceramic preparation technology. Weigh the Bi$_2$O$_3$, ZnO, Nb$_2$O$_5$ and TiO$_2$ powders according to a certain stoichiometric ratio, add alcohol and mix them thoroughly, and put them in a ball milling tank for 20 hours. In order to avoid the volatilization of Bi, 650°C is used for pre-sintering. After the pre-fired sample is milled, it is placed in a corresponding mold and pressed at 120 Mpa. After the final sintering process at 1080°C for 2 hours, a target with a diameter of 60 mm and a thickness of 5 mm is made[13].

Preparation of PST and BZNT trilayer film: Prepare a layer of PST film on the substrate by sol-gel method. After the PST film is formed, place the film in the magnetron sputtering chamber to prepare the BZNT film with the magnetron sputtering preparation parameters are shown in Table 1, then use the sol-gel method to prepare a layer of PST film. Finally, the film structure of the PST and BZNT trilayer film is shown in Fig.1.

| Process parameters       | Values       |
|--------------------------|--------------|
| Oxygen argon ratio       | 6:14         |
| Sputtering pressure      | 4 Pa         |
| Substrate temperature    | 400°C        |
| Sputtering bias          | 100 V        |
| Sputtering time          | 15 min       |

The heat treatment process of PST and BZNT trilayer film is compared with the following parameters: 600°C annealing for 45min, 600°C annealing for 60min, 650°C annealing for 45min, 650°C annealing for 60min, 700°C annealing for 45min and 700°C annealing for 60min. These thin film samples were named 600-45, 600-60, 650-45, 650-60, 700-45, 700-60 respectively. For the
dielectric measurement, Au was deposited on the films as top electrodes using RF magnetron sputtering through a shadow mask with a diameter 0.3 mm. The dielectric properties of the films were characteristics at room temperature using a Agilent 4294A precision impedance analyzer.

3. Results and discussion

Put the prepared PST and BZNT trilayer film samples with different annealing methods into the corresponding test fixture, and use the Agilent 4294A impedance analyzer for test analysis. Figure 2 is a graph of the capacitance and dielectric loss of the composite film changing with the external frequency. As can be seen from the figure, in the low frequency stage, the capacitance and dielectric loss of the film decrease relatively quickly; in the high frequency stage, the decrease is relatively slow. Which may be due at low frequencies, the space charge can follow the external frequency response; at high frequencies, the space charge cannot follow the external frequency response. The highest capacitance is the film sample annealed at 700°C for 45 min, but its dielectric loss is also at a higher level. The lowest dielectric loss is the film sample annealed at 650°C for 45 minutes, and its capacitance is also at a higher level. In order to further discover the influence of the annealing method on the dielectric properties of the composite film, the dielectric tuning of the film needs to be tested.

Fig.2. Graphs of capacitance and dielectric loss of PST and BZNT trilayer film with different annealing methods as a function of external frequency

Figure 3 shows the variation of capacitance and dielectric loss of PST and BZNT trilayer film with different annealing methods with the applied bias voltage. As the applied bias voltage increases, the capacitance and dielectric loss of all samples show a decreasing trend, which is a tuning phenomenon of dielectric materials. The tuning amount of the dielectric film reflects the strength of the capacitance of the film with the applied bias voltage, the calculation formula is as follows:

\[ Tunability = \frac{\epsilon_r(T,0) - \epsilon_r(T,E_{\text{max}})}{\epsilon_r(T,0)} \]

As the annealing temperature and annealing time increase, the tuning amount of the film sample increases first and then decreases. Explain that proper heat treatment process can improve the dielectric properties of the film. Too low temperature affects crystallization, and too high temperature
will cause the loss of volatile elements (such as Pb and Bi) in the film, and the vacancy of the film crystal structure will increase the loss of the film. For 650-45 sample, the capacitance drops from 278pf at 0V bias to 141pf at 17.5V, the tuning amount is 49.9%, and the loss is 2.3%, which has the largest figure of merit (FOM).

![Graph of capacitance and dielectric loss](image)

Fig.3. Graphs of capacitance and dielectric loss of PST and BZNT trilayer film with different annealing methods as a function of applied bias voltage

4. Conclusions
The analysis of the above experimental results shows that due to the complex structure of the composite film, the annealing temperature should not be too high and the annealing time should be moderate. The film has the best comprehensive dielectric properties by annealing at 650°C for 45min, the dielectric loss is 2.52%, dielectric tunability is 45.3%, and figure of merit (FOM) is 20.1.

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