Effect of Annealing Process on the Dielectric and Tunable Properties of (Bi1.5Zn0.5)(Nb0.5Ti1.5)O7(BZNT) Thin Film

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Abstract. Bi1.5Zn0.5Nb0.5Ti1.5O7 (BZNT) thin films were deposited on Pt/Ti/SiO2/Si substrates by radio frequency (rf) magnetron sputtering. In this paper, by studying the phase structure, surface morphology, and dielectric properties of BZNT films, it is found that by increasing the initial temperature in the annealing process, the film formation quality, internal stress and dielectric properties of the film can be improved. and the best performance of the BZNT film is obtained under the annealing process at the initial temperature of 500°C. The tuning amount (Tu), Dielectric loss (Loss) and quality factor (FOM) are: 13.55 percent, 0.00298 and 45.46, respectively.

1. Introduction
In recent years, the production of microwave dielectric ceramic materials for multilayer chip capacitor (MLCC) is a new trend in the study of dielectric materials in the world, and it is also an urgent need for the development of microwave mobile communications [1, 2]. In the early 1990s, many scientists such as Yao Xi of Xi'an Jiaotong University and Ling of Bell Experiment focused on the electrical properties of BZN, the phase structure of ceramic polycrystalline, and the substitution and doping of various elements in the crystal, and achieved remarkable results. At the same time, many scientists from China, Germany, the United States, South Korea, France and Japan have also conducted in-depth research on the BZN material system [3-7].

As we know, the annealing process is indispensable after the film is prepared, and a suitable post-annealing process can improve the dielectric properties, crystallization degree, microscopic morphology and leakage current of the film material. Post-annealing can also eliminate the unfavorable stress inside the film due to the growth and crystallization process. In this article, the BZNT film is prepared by magnetron sputtering, and the influence of different heat treatment processes on the crystallization, micro-morphology, dielectric properties and leakage current parameters of the BZNT film is studied.
2. Experimental procedure

(Bi1.5Zn0.5)(Nb0.5Ti1.5)O7 (BZNT) ceramic target material adopts traditional ceramic preparation technology, weighing Bi2O3, ZnO, Nb2O5 and TiO2 powder according to a certain stoichiometric ratio, adding alcohol and mixing it thoroughly before putting it in Ball milling in a ball milling tank for 20 hours. In order to avoid the volatilization of Bi, pre-sintering is selected at 650°C. 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. Put the ceramic target into the magnetron sputtering chamber, after sputtering deposition with the parameters in Table 1, take it out into the heat treatment furnace for the heat treatment operation as shown in Table 2, and then label the film samples as: BZNT20, BZNT400 and BZNT500.

Table 1. BZNT thin film magnetron sputtering process

| Process parameters | Oxygen argon ratio | Sputtering pressure | Substrate temperature | Inherent vacuum | Sputtering bias | Sputtering time |
|--------------------|--------------------|---------------------|----------------------|-----------------|----------------|----------------|
|                    | 5:15               | 5Pa                 | 400°C                | 2.4×10⁻³ Pa      | 100V           | 3h             |

Table 2. Annealing process of BZNT film and sample number

| Sample No | Initial temperature | Heating rate | Target temperature | Holding time |
|-----------|---------------------|--------------|--------------------|--------------|
| BZNT20    | 20°C                | 10°C/min     | 700°C              | 10min        |
| BZNT400   | 400°C               | 10°C/min     | 700°C              | 10min        |
| BZNT500   | 500°C               | 10°C/min     | 700°C              | 10min        |

3. Results and discussion

In order to study the effect of the annealing process on the phase structure of the BZNT film, phase analysis was performed on three film samples, and the XRD patterns of the different samples obtained are shown in Fig.1. It shows that the three samples all have the standard peaks of the pyrochlore phase, and they are of a single pyrochlore phase structure. Since the final annealing temperature of the three BZNT films is 700°C, the phase of the film will not change significantly. With the increase of the initial temperature during annealing, the crystallization peak of the film decreases, and the degree of crystallization of the film becomes weaker, which may be due to the effect of the heating time of the film annealing. According to Scherrer formula [7] (1):

$$D_{hk} = \frac{k\lambda}{\beta \cos \theta}$$

Where $D_{hk}$ is the grain diameter along the hlk direction perpendicular to the crystal plane, k is Scherrer's constant (usually 0.89), $\lambda$ is the incident X-ray wavelength, $\theta$ is the Bragg diffraction angle, and $\beta$ is the half-width of the diffraction peak. The half-width of the (222) main peaks of BZNT20, BZNT400 and BZNT500 are 0.370°, 0.297° and 0.294°, respectively. According to the Scherrer formula, with the increase of the initial annealing temperature, the grain size of the film after crystallization shows an increasing trend.
In order to study the effect of annealing process on the surface quality of BZNT films, three BZNT samples were analyzed by atomic force microscope (AFM). Fig. 2 shows the surface morphology of the BZNT film with different initial annealing temperatures. It can be seen from the figure that the three groups of samples all have a good degree of crystallization, a dense surface structure, and a single defect-free surface morphology. The average grain size of the three film samples of BZNT20, BZNT400 and BZNT500 are 38, 45 and 56nm, respectively. That is, as the initial temperature during annealing increases, the average grain size of the film also increases, which further validates the XRD analysis. The half-width of the (222) peak is reduced. The reason for the increase in the grain size of the film may be that the film deposited at 400°C during magnetron sputtering has been basically crystallized, and the post-annealing is performed to further increase the degree of crystallization. When the film heats up from room temperature, the thermal activation energy obtained by the film is low, which is not enough to make some crystal grains with strong mobility expand to the nearby crystal grains. As the temperature further rises, each crystal grain is further crystallized. This process may also make the grain boundary pinned more than at room temperature, so it takes more energy to grow the crystal grains. When the film is directly placed in a furnace at 500°C, the thermal activation energy obtained by the film is larger, so that part of the grain boundaries with strong mobility can expand to the periphery and form large grains. This makes the grains of the samples with high initial annealing temperature larger. 

As the film undergoes different annealing processes, different types of stresses may exist inside the film during its crystallization process, and these stresses will change the properties of the film. Fig. 3
shows the XRD diffraction pattern of the (222) peak tested at different tilt angles ($\psi$) for the BZNT film samples. With the increase of the XRD test tilt angle ($\psi$), the peak positions of the two samples shifted to a low angle. Therefore, tensile stress exists in both films, and this phenomenon also appeared in the article reported by Jiwei Lu et al. [9]. Using Origin software to perform Gaussian simulation on the peak shape curve in the figure, the (222) peak position of the two samples can be obtained. Fig.4 shows the relationship between the peak position and $\sin^2\psi$ of (222), and then linearly simulate the obtained curve, and the linear simulation slopes of the BZNT20 and BZNT500 samples are: -3.1833 and -2.8526, respectively. BZNT20 and BZNT500 are the same material and should have the same K coefficient. According to the stress equation $\sigma=K\cdot M$ (K is the material's inherent parameter, M is the stress simulation slope), which shows that BZNT20 has a larger M value. That is, it has a greater tensile stress. The possible reason is that the heating time of the film can be reduced by increasing the initial annealing temperature, and the defects and stress inside the film can be reduced.

Fig.3. XRD diffraction patterns of BZNT film samples tested at different tilt angles: (a) BZNT20, (b) BZNT500

Fig.4. Relationship between (222) peak position and $\sin^2\psi$ change of BZNT film: (a) BZNT20, (b) BZNT500

Fig.5. The change spectrum of the dielectric constant and loss of the BZNT film with the applied electric field

Fig.6 The variation of the tuning value, dielectric loss and figure of merit of the BZNT film with the initial temperature
In order to study the dielectric properties of the film, three BZNT films were characterized by Agilent 4294A impedance analyzer. Fig.5 shows the variation spectrum of the dielectric constant and loss of the BZNT film with the applied electric field. It shows that, The dielectric constant of the film decreases with the increase of the external electric field. The dielectric loss of the film presents an asymmetric curve in the external electric field change, which may be caused by the asymmetry of the Pt/BZNT/Au electrode. Fig.6 shows the variation of the tuning value, dielectric loss and figure of merit of the film with the initial temperature. As the initial annealing temperature increases, the tuning value first decreases and then increases, and the maximum value is 13.55% at BZNT500; The loss of the film (LOSS) shows a decreasing trend, which may be due to the denser structure of the film with a high initial annealing temperature; the figure of merit (FOM=Tu/Loss) of the film shows an increasing trend, and BZNT500 shows the maximum 45.46. As we all know, the greater the dielectric tuning of the film and the smaller the dielectric loss, the better the dielectric properties of the film. Therefore, the dielectric properties of the film can be improved by increasing the initial annealing temperature.

4. Conclusions
In this experiment, the magnetron sputtering method was used to successfully prepare BZNT films with excellent performance on the Pt/Ti/SiO2/Si substrate, and the obtained film materials were modified by annealing to achieve the expected results. The best performance of the BZNT film is obtained under the annealing process at the initial temperature of 500°C. The tuning amount (Tu) , Dielectric loss (Loss) and quality factor (FOM) are: 13.55 percent, 0.00298 and 45.46, respectively.

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