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Microwave dielectric properties of bismuth zinc niobate thin films deposited on alumina by pulsed laser deposition

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Abstract

$Bi_2Zn_{2/3}Nb_{4/3}O_7$ thin films were prepared on Al_2O_3 substrates by pulsed laser deposition. The phase compositions and microstructures were characterized by X-ray diffraction and atomic force microscopy. The as-deposited films were all amorphous in nature. All films were crystallized after the post annealing at the temperature range of 700–900 °C for 30 min in air. The texture characteristics change with annealing temperature. A split post dielectric resonator method was used to measure the microwave dielectric performance at the resonant frequencies of 10, 15 and 19 GHz. For the films annealed at 900 °C, the preferential orientation is similar to the monoclinic BZN bulk. The microwave dielectric constants at 10, 15 and 19 GHz are 69.4, 58.9 and 47.9, respectively, which are closer to these of the monoclinic BZN bulk.

Keywords: A. Films; C. Dielectric properties; E. Capacitors; $Bi_2Zn_{2/3}Nb_{4/3}O_7$

1. Introduction

In recent years, thin films of Bi_2O_3–ZnO–Nb_2O_5 (BZN) has drawn a lot of attention for their excellent dielectric properties such as moderate high dielectric constant, low dielectric loss, lower crystallization temperature and dielectric tunability [1–3]. There are two main phases in the BZN system: a cubic pyrochlore based on $Bi_{1.5}ZnNb_{1.5}O_7$ (c-BZN) composition and a monoclinic zirconolite based on $Bi_2Zn_{2/3}Nb_{4/3}O_7$ (m-BZN) composition [4]. In previous works, it was found that $Bi_2Zn_{2/3}Nb_{4/3}O_7$ (m-BZN) bulk material has low sintering temperature, relatively moderate dielectric constant (~80 at 10 kHz), low dielectric loss (5×10^{-4} at 10 kHz) and low temperature coefficient of dielectric permittivity (150 ppm/K) [4,5]. Several deposition methods have been used to prepare BZN thin films, such as metal organic decomposition, RF magnetron sputtering, metal organic chemical vapour deposition, and pulsed laser deposition (PLD) [6–8]. Compared to other deposition methods, PLD has merits in excellent control of stoichiometric composition of oxide films with complex components, especially for BZN thin films due to high volatility of Zn and Bi [9]. The dielectric properties of m-BZN thin films have been studied by several researchers [10,11]. In this paper, PLD deposition was used to prepare the m-BZN thin films. The post annealing crystallization and microwave properties of m-BZN thin films have been investigated.

2. Experimental details

$Bi_2Zn_{2/3}Nb_{4/3}O_7$ (m-BZN) ceramic targets were synthesized by a solid state reaction processing. Raw materials of Bi_2O_3, ZnO and Nb_2O_5 of high purity were weighed in stoichiometric proportions, ball milled for 24 h, then sintered for 3 h at 960 °C. The m-BZN films were prepared by PLD using a KrF excimer laser. The thin films were deposited directly on alumina substrates, without use of a metallic electrode. The PLD chamber was evacuated to a pressure of 4×10^{-4} Pa. The laser was operated at a laser repetition frequency of 3 Hz, with an energy density of 250 mJ/pulse. The substrate temperature was set at 600 °C and the chamber oxygen pressure during deposition was set at 10 Pa. The deposition was carried out for 60 min. After the deposition, the films were post-annealed in a rapid thermal annealing furnace at the

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temperature range of 700–900 °C for 30 min in air. The thicknesses of these films were measured by a stylus profiler (Dektak 6 M, Veeco) and are 540–580 nm.

The phase composition and crystallization of the BZN thin films were characterized by X-ray diffraction (XRD, D/Max-2400, Rigaku). Surface morphology was examined by an atomic force microscope (AFM, Nanoscope, Veeco). Electron probe micro-analysis (JXA-8100, JEOL) was used to determine the composition of the films. Microwave dielectric properties of these films were measured by a split-post dielectric resonator (SPDR) technique. The dielectric resonator was connected to a microwave network analyzer (HP8720ES, Agilent) and the resonant frequencies were 10, 15 and 19 GHz, respectively.

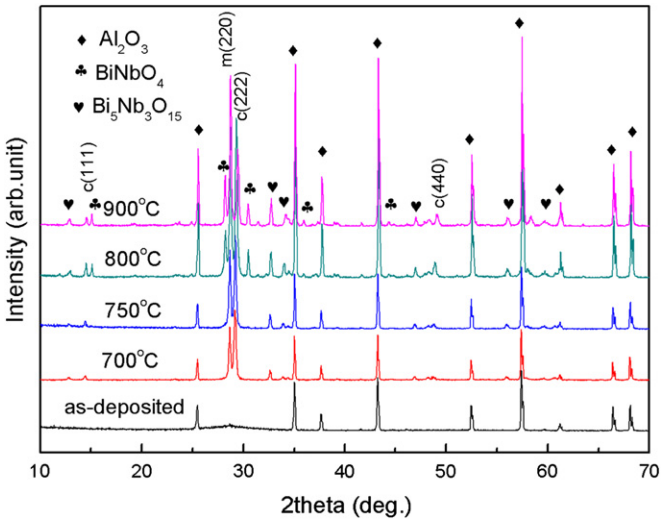

Fig. 1. X-ray diffraction patterns of $Bi_2Zn_{2/3}Nb_{4/3}O_7$ (m-BZN) thin films as a function of annealing temperature (c for cubic pyrochlore; m for monoclinic zirconolite-like pyrochlore).

3. Results and discussion

Fig. 1 shows the XRD patterns of both as-deposited and annealed m-BZN thin films. There are no other peaks detected in the as-deposited films except those from the substrates, which indicates that the as-deposited films are amorphous in nature. This is different from the as-deposited films deposited on $Pt/TiO_2/SiO_2/Si$ substrate with the same deposition conditions, which shows a crystalline structure. It suggests that the substrates have strong influence on the crystallization of m-BZN thin films. However, after post-annealing in air, the m-BZN thin films are crystallized. For the films annealed at 700 °C and 750 °C for 30 min, the mixing peaks of cubic pyrochlore BZN (2 2 2) and monoclinic zirconolite BZN (2 2 0) could be detected, which suggests that a cubic and a monoclinic zirconolite co-existed phase existed in BZN films. Meanwhile, the secondary phases of $BiNbO_4$ and $Bi_5Nb_3O_{15}$ appear when annealed over 800 °C, due to the significant loss of Zn volatility at high temperature (as discussed next). Meanwhile, the full width half maximum (FWHM) of m(2 2 0) peak gradually decreases and the FWHM of c(2 2 2) peak also decreases with annealing temperature, as shown in Fig. 2. It is well known that the FWHM values are related with the film crystallization. Hence, high annealing temperature can improve the film crystallization. However, high annealing temperature also introduces impurity secondary phases, like $BiNbO_4$ and $Bi_5Nb_3O_{15}$. It is noted that as the annealing temperature increases, the m(2 2 0) peak intensity increases and the c(2 2 2) peak intensity does not change much. Thin films annealed at 800 °C and 900 °C show stronger m(2 2 0) peak than the c(2 2 2) peak. This indicates that the monoclinic phase is dominant in the films when annealed at high annealing temperature. It indicates that the annealing temperature plays an important role in the crystallization of m-BZN thin films.

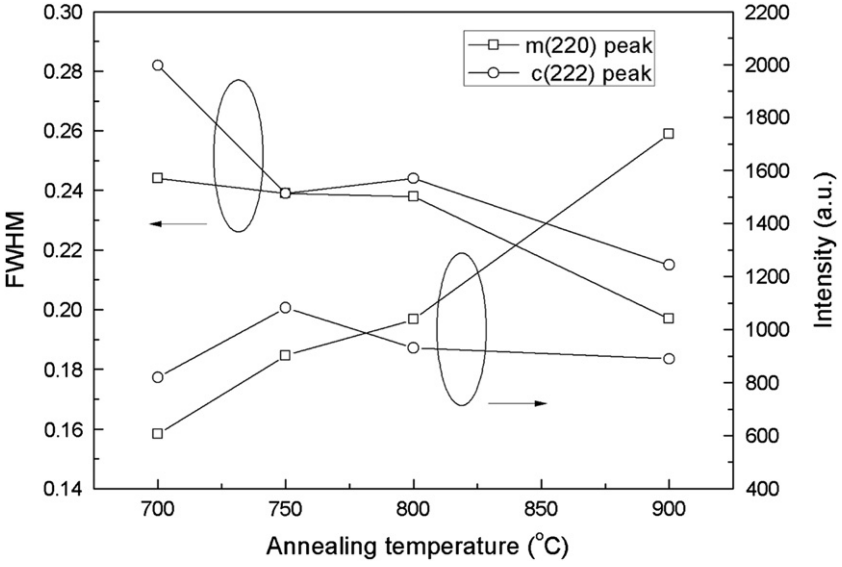

Fig. 2. FWHM and intensity values of c(2 2 2) and m(2 2 0) diffraction peaks of m-BZN thin films at various annealing temperatures.

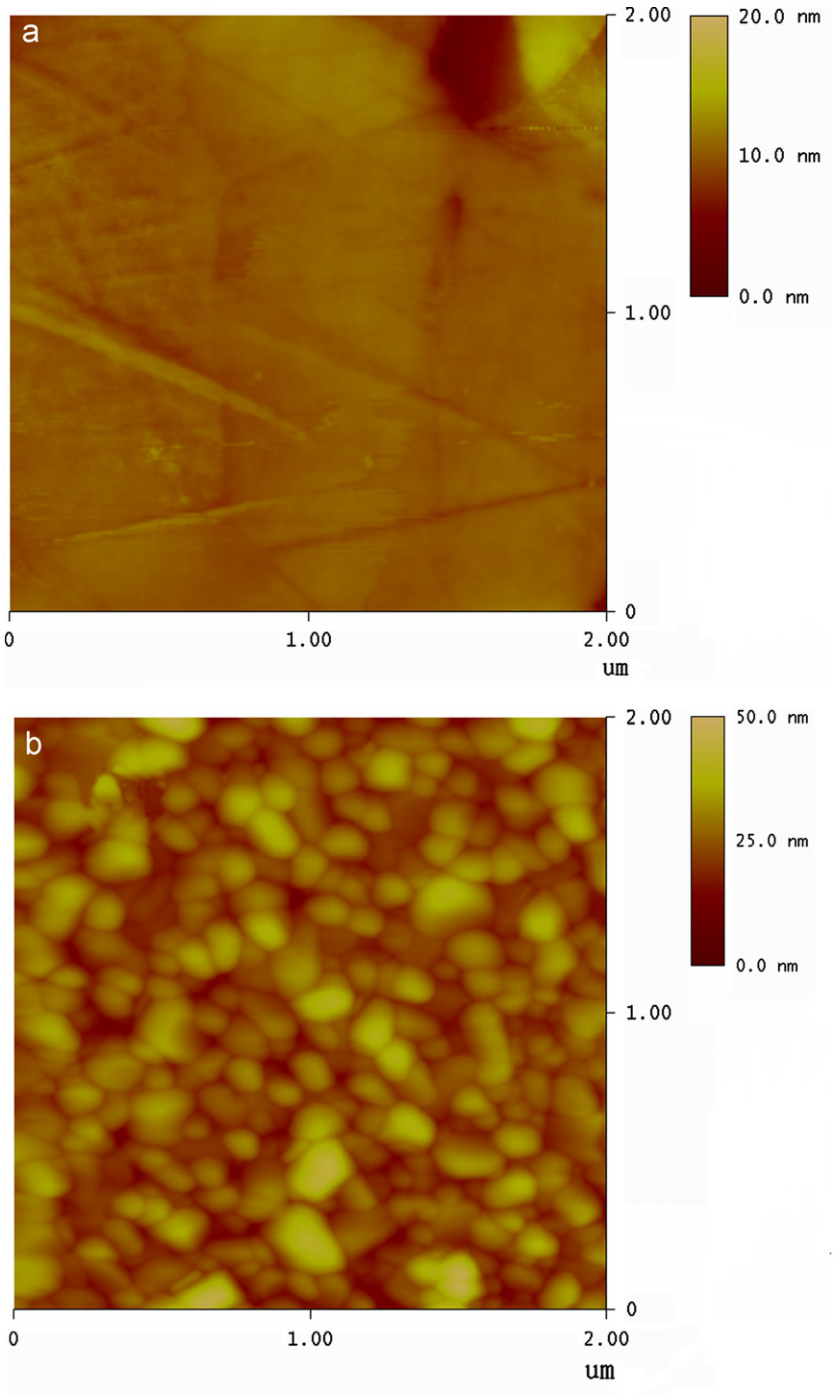

Fig. 3. AFM micrographs: (a) alumina substrate, (b) m-BZN thin film annealed at 750 °C.

The AFM surface morphologies are shown in Fig. 3. Al_2O_3 substrate shows a smooth surface and the roughness is 1.123 nm. For the as-deposited m-BZN thin film, a flatten surface could be observed which does not show any crystalline grains (the AFM micrograph is not given here). For the films annealed at 750 °C, the agglomerate clusters with an average cluster size of 72.5 nm are observed in the AFM morphology as shown in Fig. 3(b). The surface roughness of the as-deposited and annealed films are 2.94 nm and 5.36 nm, respectively. After the annealing, the surface of BZN thin films turns rougher due to crystallization.

In the PLD deposition of the multi-component thin films, it is hard to ensure the stoichiometric composition transfer from target to substrate because of different element sticking coefficients. On the other side, element volatilization during the deposition may lead to the element deficiency in the thin films. In our previous study, Zn loss has been found in BZN films prepared by PLD [12].

Table 1
EPMA compositional analyses of m-BZN thin films annealed at different temperatures (in mole ratio).

Element	700 °C	750 °C	800 °C	900 °C	Theoretical composition
Bi	53.2	54	55.43	55.77	50
Zn	10.13	9.17	8.03	7.23	16.67
Nb	36.13	36.8	36.5	37	33.33

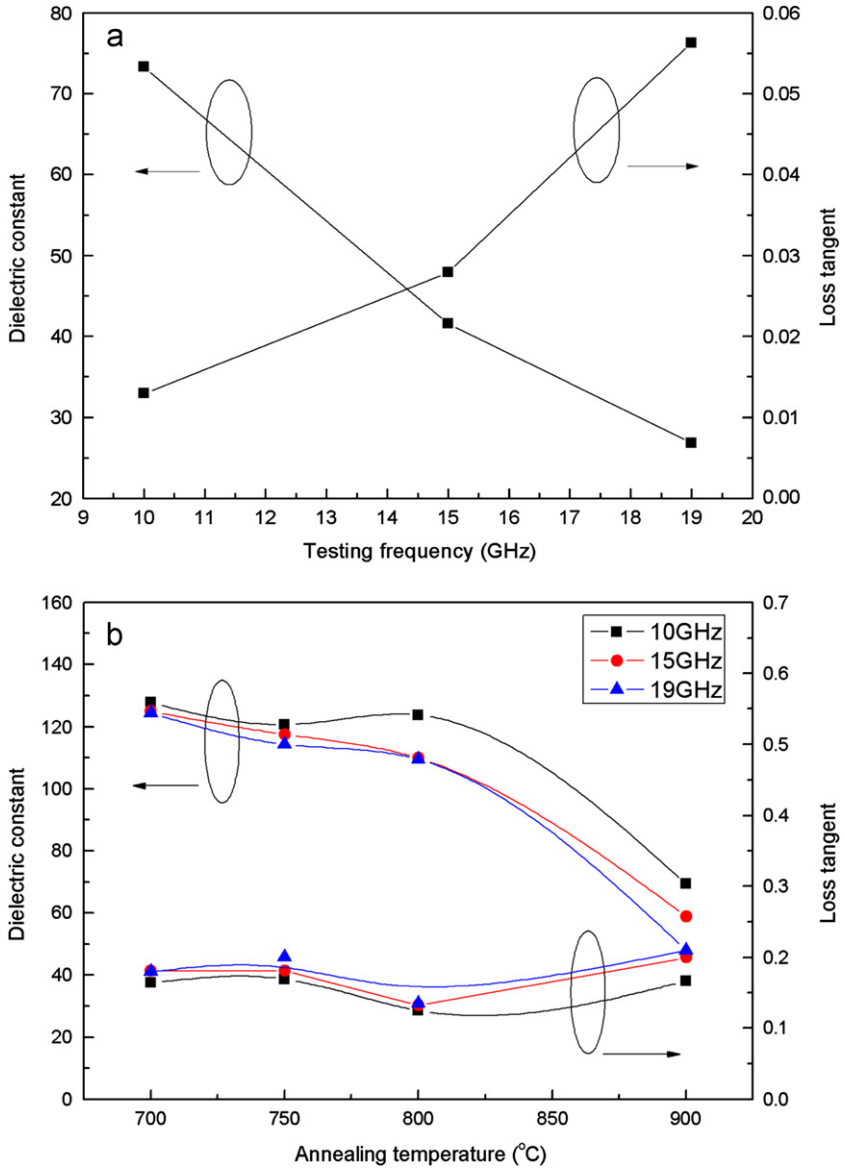

Fig. 4. Microwave dielectric properties of m-BZN thin films: (a) as-deposited, (b) annealed at different temperatures.

Here, BZN films deposited on alumina were examined by the electron probe microanalysis (EPMA) and the result is shown in Table 1. It can be seen that a significant Zn loss can be clearly seen from the EPMA result. As the annealing temperature increases from 700 °C to 900 °C, Zn composition gradually decreases from 10.63 to 7.23, which is much less than Zn stoichiometric composition. While, Bi and Nb composition do not change much. They are a slightly higher than the Bi and Nb stoichiometric compositions. It suggests that Zn composition in the m-BZN thin films strongly depends on the annealing temperature.

A split post dielectric resonator (SPDR) method was used to measure the microwave dielectric properties at the resonant frequencies of 10, 15 and 19 GHz. The microwave dielectric constant and loss tangent are calculated from the resonant frequency and unloaded quality factor [13]. The procedure

(software) was provided by the split post resonators supplier (QWED) and the details of microwave dielectric calculations were given by Krupka et al. [14,15].

The microwave dielectric behaviours were investigated for m-BZN thin films annealed at the different temperatures. The frequency dependency of the microwave dielectric constant and dielectric loss of m-BZN thin films is shown in Fig. 4. According to the XRD analysis, as-deposited m-BZN thin films are amorphous. Thus, the as-deposited m-BZN thin films exhibit low dielectric constant and loss tangent. The dielectric constant and loss tangent of the as-deposited m-BZN thin film at 19 GHz are 26.77 and 0.056, respectively. The dielectric constant decreases and the loss tangent increases with increasing resonant frequency. Compared to the as-deposited m-BZN thin films, the annealed films obviously exhibit improved dielectric constant. As shown in Fig. 4(b), the dielectric constant and loss tangent of m-BZN film annealed at 750 °C are 114 and 0.20 at 19 GHz, respectively. The microwave dielectric constant is much larger than that of m-BZN bulk (~80 at 10 kHz). With the increase of frequency to 19 GHz, the dielectric constant shows a slight decrease, and the loss tangent increases a little. Meanwhile, the dielectric constant slowly decreases from 130 to 110 as the annealing temperature increases from 700 °C to 800 °C. However, the loss tangent remains between 0.1 and 0.15. Meanwhile, as the films were annealed at higher temperature, the microwave dielectric properties are deteriorated significantly. For films annealed at 900 °C, the microwave dielectric constants at 10, 15 and 19 GHz are 69.4, 58.9 and 47.9, respectively. The loss tangent at 10, 15 and 19 GHz are 0.21, 0.20 and 0.167, respectively. The dielectric constant is close to that of the m-BZN bulks. According to the XRD analysis, the monoclinic phase is dominant in the films at a higher annealing temperature. It reveals that the decreasing microwave dielectric constant of the films annealed at 900 °C is closely related with the monoclinic phase, which has a smaller dielectric constant than that of the cubic phase.

4. Conclusions

$Bi_2Zn_{2/3}Nb_{4/3}O_7$ thin films were deposited on Al_2O_3 substrate using PLD. The as-deposited films are amorphous and began to crystallize after post-annealing at the temperature range of 700–900 °C for 30 min in air. The films annealed in a range of 700–800 °C exhibit larger microwave dielectric constant than that of m-BZN bulk. However, for the films annealed at 900 °C, the monoclinic phase is dominant in the films. The dielectric constant and loss tangent of m-BZN film annealed at 750 °C are 114 and 0.20 at 19 GHz, respectively.

Acknowledgements

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