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Effect of excess Bi_2O_3 on structures and dielectric properties of $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ thin films deposited at room temperature by RF magnetron sputtering

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Abstract

To compensate for bismuth loss that occurred during the film deposition process, $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (BZN) thin films were deposited at room temperature from the ceramic targets containing various excess amounts of bismuth (0–20 mol%) on $Pt/TiO_2/SiO_2/Si$ substrates by using RF magnetron sputtering technique. The effect of bismuth excess content on the microstructure and electrical properties of BZN thin films was studied. The microstructure and chemical states of the thin films were studied by SEM and XPS. EPMA was employed to assess the film stoichiometry. The X-ray diffraction analysis reveals that the BZN thin films exhibit the amorphous structure in nature. An appropriate amount of excess bismuth improves the dielectric and electrical properties of BZN thin films, while too much excess bismuth leads to deterioration of the properties. BZN thin film with 5 mol% excess bismuth exhibits a dielectric constant of 61 with a loss of 0.4% at 10 kHz and leakage current of 7.26×10^{-7} A/cm^2 at an electric field of 200 kV/cm.

Keywords: A. Films; C. Dielectric properties; E. Capacitors; BZN

1. Introduction

Bi_2O_3–ZnO–Nb_2O_5 (BZN) thin films with a composition of $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ have recently attracted much attention due to their high-frequency dielectric applications and potential application of the embedded capacitors in the printed circuit boards (PCBs) [1–4]. BZN thin films exhibit high dielectric constant and low loss. At present, BZN thin films have been successfully fabricated by several processing routes, such as metal-organic decomposition [1], pulsed laser deposition [2,5] and sputtering techniques [3,4]. However, it is difficult to obtain cubic pyrochlore BZN thin films with ideal $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ stoichiometry due to easy volatility of Bi in the process of fabrication, which might be responsible for the poor reproducibility of BZN thin films. Recently, Zhang et al. studied the effect of bismuth excess on the crystallization of BZN thin films prepared by pulsed laser deposition [2]; Back et al. studied the excess Bi concentration on the tunability of BZN film by a reactive sputtering [3]. They suggested that the composition control of BZN thin films can strongly affect the structure and physical properties and might be a vital factor to achieve high dielectric constant.

Due to the volatility of Bi, the oxygen vacancies will be generated accompanying with Bi vacancies. These oxygen vacancies act as defects, deteriorating the dielectric and electrical properties of BZN thin films. Based on those considerations, to compensate the loss of Bi, BZN thin films were sputtered at room temperature from ceramic targets containing excess bismuth content (0–20 mol%) by RF magnetron sputtering. The effect of excess Bi_2O_3 content on the microstructure, stoichiometry, dielectric and electrical properties of the thin films has been investigated.

2. Experimental procedure

BZN thin films with thickness of 200 nm were deposited at a room temperature from 4-inch diameter ceramic

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targets containing an excess content of bismuth (0%, 5%, 10%, 15% and 20 mol%) on $Pt/TiO_2/SiO_2/Si$ substrates by using RF magnetron sputtering technique. Prior to deposition, the chamber was initially evacuated to a base pressure of 1.5×10^{-4} Pa. The deposition ambient was a mixture of Ar and O_2 with Ar/O_2 flow ratio of 85/15, and the deposition pressure was maintained at 2.8 Pa. The RF power was kept at 110 W. For convenience, the BZN thin films with various contents of excess Bi will be denoted as BZN-*n* (*n* is the mol ratio of excess bismuth).

The crystal structure of the films was characterized by an x-ray diffractometer equipped with Cu K_α radiation (XRD, D/Max-2400, Rigaku). Thickness and surface roughness were measured by a stylus profiler (Dektak 6 M, Veeco) and an atomic force microscope (AFM, Nanoscope, Veeco). Electron probe micro-analysis (EPMA) was employed to assess the film stoichiometry. The chemical binding state of the films was investigated by X-ray photoelectron spectroscopy (XPS) by using monochromatic Mg $K\alpha$ radiation. For dielectric and electrical measurements, Pt top dot electrodes of 0.5 mm in diameter were deposited on the films via a shadow mask by RF sputtering at room temperature. The dielectric properties were measured by using a precision impedance analyzer (4294 A, Agilent) with a DC bias fixture. The leakage current behavior of the film samples was obtained using a semiconductor characterization system (4200-SCS, Keithley).

3. Results and discussion

Fig. 1 depicts the XRD spectra of BZN-n thin films deposited with no intentional heating of substrate as a function of bismuth excess content. The major peak (222) plane of crystallized BZN is located near $2\theta \approx 29^\circ$, but that peak is not present here. Instead of a sharp peak, a broad peak is observed. The rest of the peaks come from Si and Pt. As no peaks are detected due to a crystalline phase in the as-deposited films, which indicate that the films are either amorphous or nano-crystalline in nature. In general, the paraelectric thin films exhibit amorphous phases with a very small dielectric constant ~25, when they are deposited at room temperature or annealed at a low temperature $< 200\ ^\circ C$ [5]. However, to obtain a high dielectric constant from pyrochlore films, including BZN, nano-sized crystallines are required to be formed in the films [5,6]. The rms roughness of BZN thin films with various Bi excess contents is very similar to that of the pure BZN and shows a little variation with the increase of Bi content, as shown in the inset of Fig. 1. Fig. 2 shows the SEM surface morphology of BZN-5 thin film. The surface is dense, crack free, homogeneous and exhibits small clusters of particles.

The compositional analysis was conducted to investigate the effect of Bi excess content on the dielectric and electrical properties of BZN-n thin films. Table 1 shows the compositions of films with respect to the cation ratios derived from the EPMA data. For the purposes of comparison, the nominal formulas of the films were normalized to seven oxygen atoms;

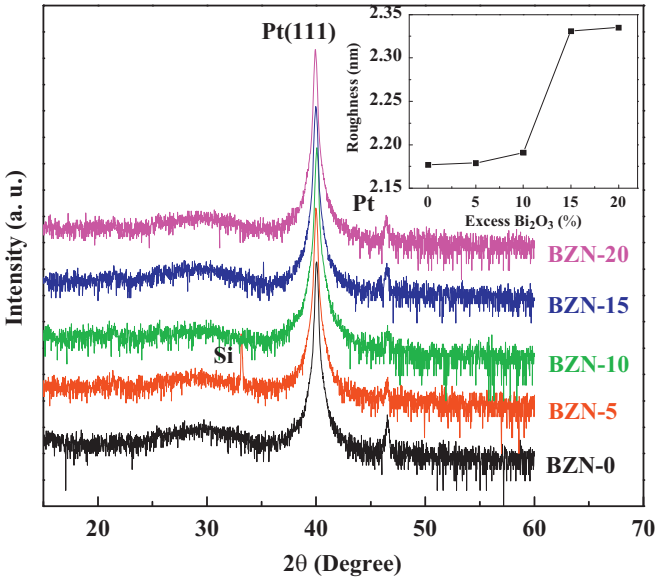

Fig. 1. X-ray diffraction patterns of BZN-n thin films (The inset shows roughness vs. bismuth excess content).

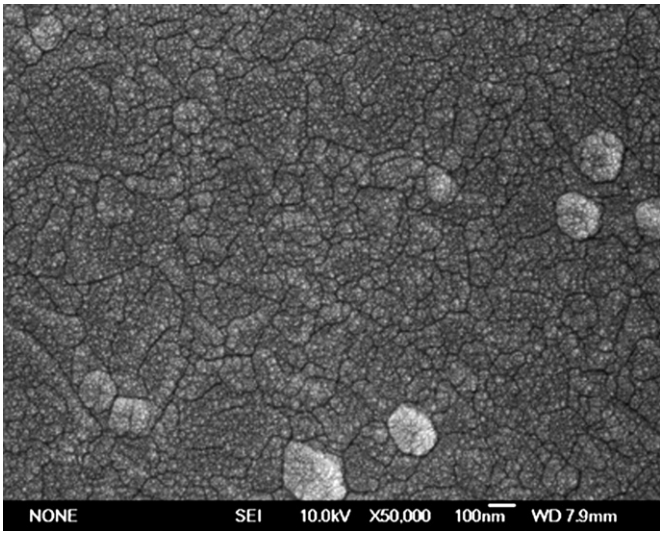

Fig. 2. SEM surface morpholgy of BZN-5 thin film.

to calculate the compositions, the ionic charge was balanced by considering the formal valence states of Bi, Zn and Nb as +3, +2 and +5, respectively. Bi element was revealed to be volatile and continuous increase of Bi in thin films was observed with increasing Bi excess content. Zn and Nb loss was also observed, but that loss is very slight and was not significantly affected by the increase of Bi excess content. The BZN-0 thin films are non-stoichiometric with insufficiency of Bi due to the Bi loss during calcination of ceramic target and deposition of the films. BZN-5 thin film composition is closest to stoichiometric composition $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$. 5 mol% Bi compensates the Bi constituent in the BZN thin film that is volatilized from the film surface during the deposition.

Table 1
Cation ratios and nominal formulas of BZN thin films.

Excess Bismuth (mol%)	Film composition			
	Bi (%)	Zn (%)	Nb (%)	Nominal formula
0	36.6	23.2	40.2	$Bi_{1.43}Zn_{0.91}Nb_{1.58}O_7$
5	37.9	23.1	39.1	$Bi_{1.49}Zn_{0.91}Nb_{1.54}O_7$
10	39.0	22.5	38.6	$Bi_{1.54}Zn_{0.89}Nb_{1.52}O_7$
15	40.2	22.2	37.6	$Bi_{1.59}Zn_{0.88}Nb_{1.49}O_7$
20	41.3	21.8	36.9	$Bi_{1.64}Zn_{0.87}Nb_{1.47}O_7$

However, BZN thin films with 10–20 mol% excess bismuth show Bi over stoichiometric and Zn deficiency.

Fig. 3 shows the XPS spectra of Bi 4*f* and O 1*s* for as-deposited BZN-n thin films. The C 1*s* peak at 284.6 eV was used as a reference. The Bi $4f_{7/2}$ and $4f_{5/2}$ spin orbit doublet locate at 158.8 and 164.2 eV and the O 1*s* peak at 530.37 eV for a BZN-0 thin film. For BZN-5 thin film, Bi $4f_{7/2}$, Bi $4f_{5/2}$ and O 1*s* peak position shifts to higher binding energies at 159.2, 164.6 and 530.79 eV. This indicates that the oxygen vacancies may be present in the vicinity of Bi and Bi maybe in the $(+3-x)$ valence state (x is positive) in BZN-0 thin film. 5 mol% excess Bi added to the BZN causes the increase of binding energy of Bi 4*f* and O1*s* by 0.4 eV and 0.42 eV. This suggests that the chemical valence of Bi approaches to +3 valence state with 5 mol% bismuth in BZN thin films, which bring restraint of the oxygen vacancy concentration in the vicinity of Bi and suppress the oxygen vacancies. However, with further increase of bismuth content from 5 mol% to 20 mol%, the binding energy is decreased because the addition of more Bi increases the oxygen vacancy concentration, which may be due to the formation of extra bismuth oxide [7].

The relative permittivity is almost independent of frequency for all films, as shown in Fig. 4(a). BZN-5 thin film shows the maximum dielectric constant of 61 with a loss of 0.4% at 10 kHz, corresponding to the stoichiometric composition. Lower dielectric constant for BZN-0 may be caused by the non-stoichiometric composition. With further increase of Bi excess content, the dielectric constant decreases and dielectric loss slightly increases. Bi_2O_3 have the characteristics to reduce the crystallization temperature of ceramic as sintering aid in the ceramic sintering process and can promote the crystallization of the pyrochlore thin films [8]. As a result, BZN thin films deposited at low temperatures show a higher degree of order and exhibit higher dielectric constant than those of low-temperature deposited perovskite thin films [1]. High dielectric constant of BZN deposited at low temperature can also be due to the presence of nano-sized crystallites in the Bi-based pyrochlore thin films [3,8].

The capacitance density and dissipation factor versus electric field at 10 kHz show a flat shape exhibiting a non-hysteretic response, as shown in Fig. 4(b). BZN-0 exhibits

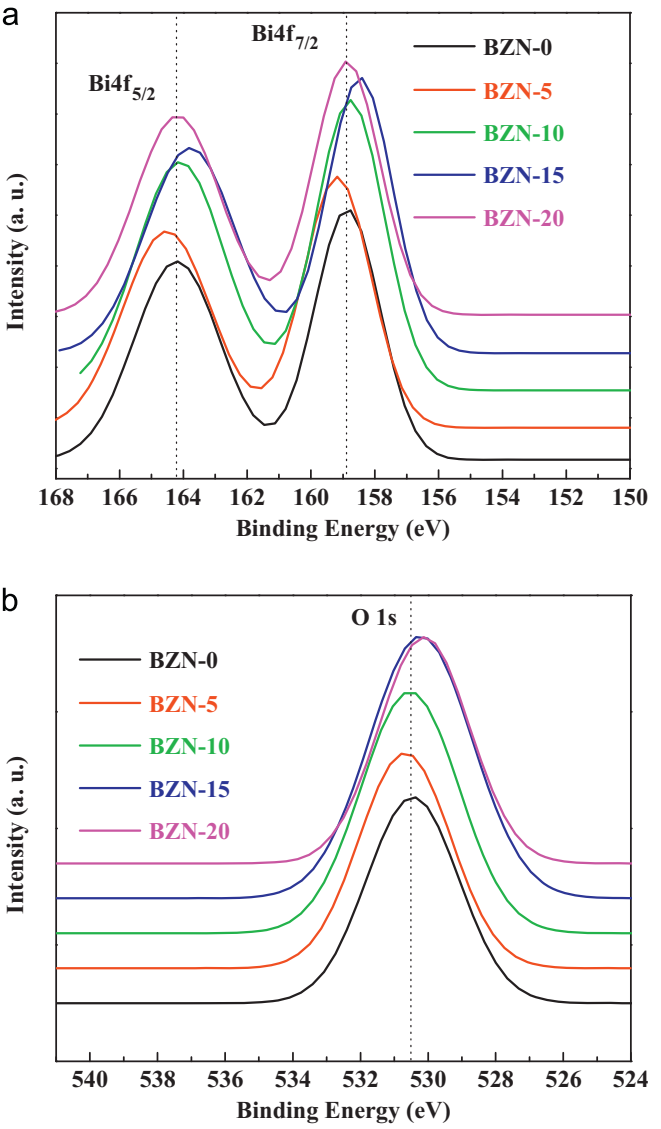

Fig. 3. XPS (a) Bi 4*f* and (b) O 1*s* spectra of BZN-n thin films derived from various contents of bismuth.

capacitance density of 181 nF/cm^2 with a dissipation factor of 0.7% in the voltage range of ±10 V. 5 mol% bismuth excess content greatly enhances the capacitance density of the film to 216 nF/cm^2 and reduces the dissipation factor to 0.4% in the same voltage range, while too much excessive Bi deteriorates the dielectric properties. The *C–V* curves for BZN-n thin films prepared at room temperature exhibit typical amorphous phase and may indicate the paraelectric behavior.

The relationship between leakage current density and applied electric field of BZN-n thin films as a function of excess Bi content is shown in Fig. 5. The leakage current densities show a slightly asymmetric behavior for negative and positive electric fields. Comparing the leakage current density at 5 V, the leakage current density of BZN thin

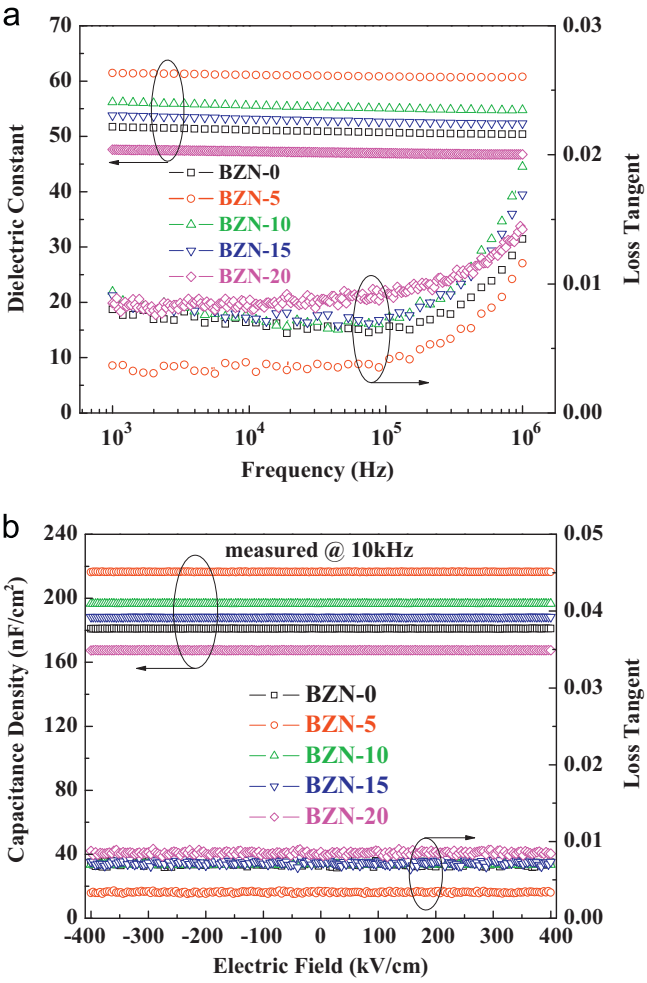

Fig. 4. (a) Frequency and (b) electric field dependence of the permittivity and dielectric loss of BZN-n thin films.

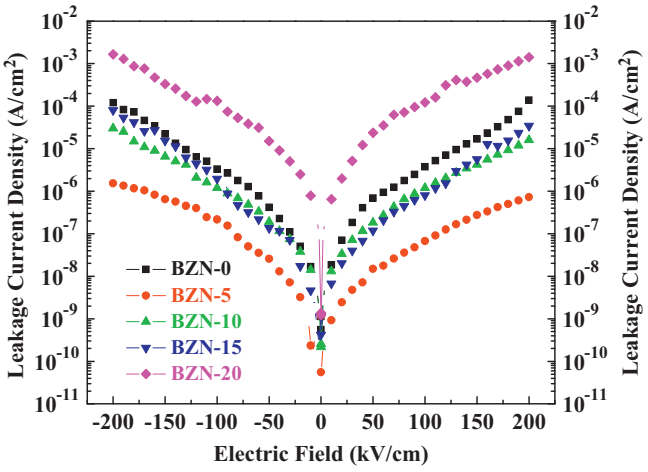

Fig. 5. Leakage current density for BZN-n thin films.

films slightly decreased with increasing excess Bi content up to 5 mol% and then considerably increased at 20 mol%. BZN-5 gives the lowest leakage current density of 7.26×10^{-7} A/cm^2 at an applied electric field of 200 kV/cm, which is approximately two order magnitude lower than that of BZN-0. Experimental results show that excess Bi added to the BZN thin film sample can decrease the leakage current density due to the compensation of bismuth volatility during fabrication; however, excess bismuth increases the leakage current density for the over stoichiometric compositions.

4. Conclusions

BZN-n thin films containing bismuth excess content (0–20 mol%) were prepared by RF magnetron sputtering at room temperature. It was revealed that addition of 5 mol% excess Bi makes the composition closer to the composition of $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ due to the compensation for Bi loss during the film deposition, yielding an improvement in the dielectric and electrical properties of BZN films. The deficiency and too much excess of Bi content in BZN films reduce the dielectric constant. XPS results suggest that the oxygen vacancies were suppressed by the addition of 5 mol% excess bismuth. BZN-5 exhibits the maximum dielectric constant of 61 with a very low loss of 0.4% at 10 kHz and lower leakage current 7.26×10^{-7} A/cm^2 at an applied electric field of 200 kV/cm.

Acknowledgments

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References

[1] W. Ren, S. Trolier-McKinstry, C.A. Randall, T.S. Shrout, Bismuth zinc niobate pyrochlore dielectric thin films for capacitive application, Journal of Applied Physics 89 (2001) 767–774.
[2] X.H. Zhang, W. Ren, P. Shi, Structures and properties of doped bismuth zinc niobate cubic pyrochlore thin films prepared by PLD, Ferroelectrics 381 (2009) 87–91.
[3] D.H. Back, Y.S. Lee, Y.P. Hong, J.H. Moon, Tunability of Bi-rich BZN cubic pyrochlore thin films by reactive sputtering, Materials Research Society Symposium Proceedings 783 (2004) 5.3.1- B5.3.6.
[4] I.I.-D. Kim, M.H. Lim, K.T. Kang, H.G. Kim, Room temperature fabricated ZnO thin film transistor using high-k $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ gate insulator prepared by sputtering, Journal of Applied Physics 89 (1–3) (2006) 022905/1-3.
[5] J.H. Park, W.S. Lee, N.J. Seong, S.G. Yoon, S.H. Son, H.M. Chung, Bismuth–zinc–niobate embedded capacitor grown at room temperature for printed circuit board applications, Applied Physics Letters 88 (2006) 192902/1-3.
[6] J.H. Park, C.J. Xian, N.J. Seong, S.G. Yoon, Development of embedded capacitor with bismuth-based pyrochlore thin films at

low-temperatures for PCB applications, Microelectronics Reliability 47 (2007) 755–758.
[7] X.J. Wang, X.B. Chen, Y.F. Qian, Jun, J.C. Shen, Structure, ferroelectric and dielectric properties of Bi_2WO_6 with different bismuth content, Integrated Ferroelectrics 85 (2006) 49–57.
[8] J.H. Park, C.J. Xian, N.J. Seong, S.G. Yoon, Realization of a high capacitance density in $Bi_2Mg_{2/3}Nb_{4/3}O_7$ pyrochlore thin films deposited directly on polymer substrates for embedded capacitor applications, Applied Physics Letters 89 (2006) 232910/1-3.