Available online at www.sciencedirect.com
SciVerse ScienceDirect
CERAMICS INTERNATIONAL
Ceramics International 39 (2013) S465–S469
www.elsevier.com/locate/ceramint

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

M. Saeed Khan, Wei Ren*, Peng Shi, Xiaofeng Chen, Xiaoqing Wu

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, China

Available online 23 October 2012

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

*Corresponding author. Tel.: +86 29 82666873; fax: +86 29 82668794.
E-mail address: wren@mail.xjtu.edu.cn (W. Ren).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2012.10.115

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 °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.

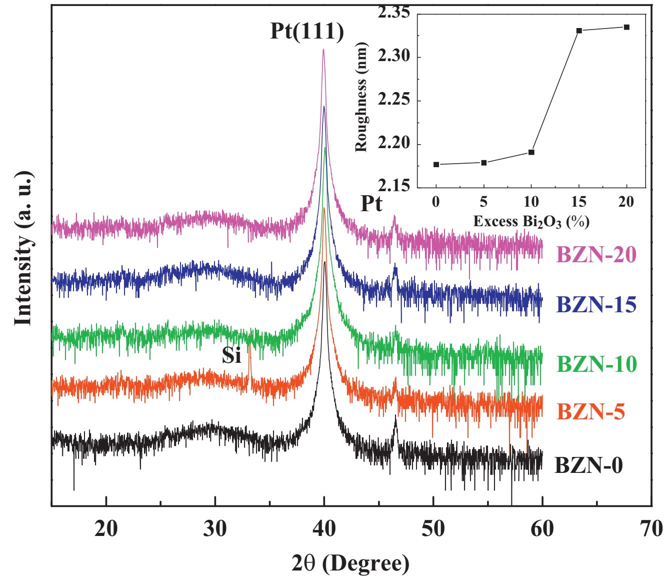

Fig. 1. X-ray diffraction patterns of BZN-n thin films (The inset shows roughness vs. bismuth excess content).

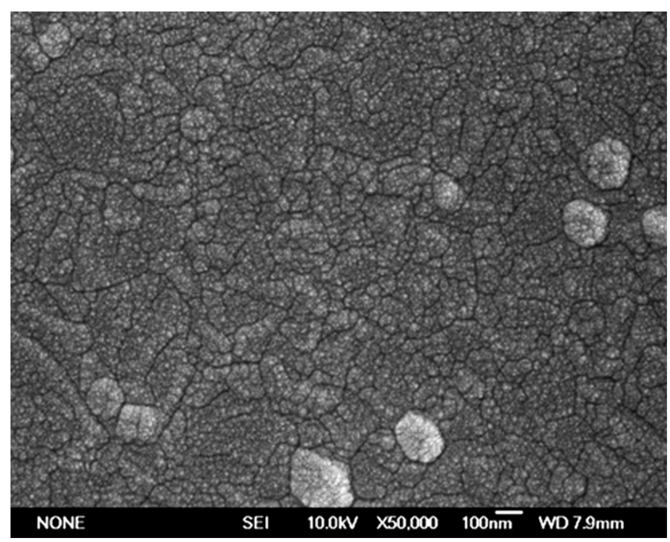

Fig. 2. SEM surface morpholgy of BZN-5 thin film.

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; 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.