Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) S283–S288

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

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

M. Saeed Khan, Wei Ren*, Zhao Wang, Peng Shi, 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

Received 26 October 2014; accepted 10 March 2015
Available online 2 April 2015

Abstract

Bismuth zinc niobate (BZN) thin films with excess Zn contents were deposited from the ceramic targets containing various excess amounts of ZnO (0–20 mol%) on $Pt/TiO_2/SiO_2/Si$ substrate by RF magnetron sputtering at room temperature. As-deposited thin films were post-annealed at a temperature $\leq 200\,^{\circ}C$, which is compatible with PCB substrates. The effect of Zn deficiency and Zn excess on the microstructure, dielectric, and electrical properties of BZN thin films was studied. As-deposited and post-annealed BZN thin films at a temperature $\leq 200\,^{\circ}C$ were amorphous in nature. An appropriate amount of excess zinc improves the dielectric and electrical properties of BZN thin films, while too much excess zinc leads to deteriorate the properties. BZN thin film with 5 mol% excess Zn content exhibits the maximum dielectric constant of 64 with a very low loss of 0.6%, measured at 10 kHz and the leakage current of less than 1 μA at an applied electric field of 200 kV/cm.

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

1. Introduction

As the electronics industry experiences a miniaturization of electronic packages, the demands of packing more and more circuitry into smaller spaces grow constantly, as do those for greater functionality, speed, and portability, higher reliability, and lower cost. The ratio of passive to active components in modern electronic products is likewise increasing rapidly. Therefore, the utilization of embedding passive (EP) components into the printed circuit boards (PCB's) is a powerful solution for miniaturization and overall performance [1,2].

The fabrication of EP components into the PCB requires a low temperature process of $\leq 200\,^{\circ}C$ [3]. Recently, embedding decoupling capacitors (EDC's) have attracted considerable interest because capacitors are the major components in terms of number, size, and weight among the various passive components [3–13]. EDC's into the PCB holds promise of achieving both high packaging density and reliability by removing solder joints from the surface mount capacitors and improved electrical performance by minimizing the signal and power path, thereby reducing parasitic noise. In addition, lower costs can be achieved by reducing discrete capacitors and the quantity of fluxes and solders, as well as by saving on assembly costs. However, materials which exhibit a high dielectric constant and better leakage current characteristics at low processing temperature ($\leq 200\,^{\circ}C$) are required in order to enable embedded capacitors to utilize their potential as cost-effective and higher-performance alternatives to discrete capacitors [1,4].

Recent studies have shown that bismuth zinc niobate with a composition of $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ fabricated at PCB-acceptable temperatures is a promising candidate for the PCB-embedded capacitors [3,12] over other high dielectric, ferroelectric (PZT, PLZT, BST) [14–16], and paraelectric oxide (SiO_2, Al_2O_3 and Ta_2O_5) materials. BZN thin films showed good dielectric and leakage current performance even when they were fabricated at

*Corresponding author.
E-mail address: wren@mail.xjtu.edu.cn (W. Ren).

http://dx.doi.org/10.1016/j.ceramint.2015.03.234
0272-8842/

low temperature. However, they have some practical limitations in terms of stoichiometry and large area deposition [3,12]. Because of the easy volatility of Bi and Zn in the process of deposition, Bi_2O_3 and ZnO content can strongly affect the structural and electrical properties of BZN thin films [3,17].

In this paper the effects of Zn deficiency and excess on the structure, dielectric and electrical properties of BZN thin films deposited at room temperature on $Pt/TiO_2/SiO_2/Si(100)$ substrates were studied. To vary the Zn content, BZN ceramic targets with varying amounts of excess Zn (0–20 mol%) were prepared. As the BZN thin films are sensitive to their composition, the RF magnetron sputtering technique was employed to deposit the thin films because it has the advantage of having a better control over stoichiometry, deposition of uniform films, and low temperature deposition, while enabling large area deposition.

2. Experimental procedure

$Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ ceramic targets with various Zn contents (BZN-*n*, where *n* is excess of Zn content=0, 5, 10, 15 and 20 mol%) were prepared by a solid state reaction method. The starting materials Bi_2O_3, ZnO and Nb_2O_5 with a purity of $>99\%$ were weighed according to the stoichiometric ratios and ball milled with ethyl alcohol and alumina balls for 4 h. The mixed slurries were dried in a conventional oven for 24 h and calcined at 800 °C for 2 h. The calcined powder was ball milled again for another 4 h and subsequently dried. 5 wt% poly vinyl acetate (PVA) was added in a dried powder as a binder and passed through an 80 mesh sieve and pressed into 4-inch diameter disks by applying 2000 MPa of pressure. Finally, the ceramic targets were sintered in a temperature range of between 900 °C and 1000 °C for 6 h in air through a 500 °C binder burnout for 2 h and then furnace-cooled. To minimize the loss of Bi and Zn in the targets, all sintering processes were performed in sealed crucibles.

BZN-*n* thin films with various excess Zn contents (0–20 mol%) were fabricated on $Pt/TiO_2/SiO_2/Si(100)$ substrates by RF magnetron sputtering at room temperature, without any intentional heating of the substrate. $Pt/TiO_2/SiO_2/Si(100)$ substrates were cleaned with acetone, 2-propanol and de-ionized water and dried by pure N_2 gas. Prior to each deposition, a vacuum chamber was evacuated down to a base pressure of 1.5×10^{-4} Pa. The deposition ambient was a mixture of Ar and O_2 gas with an Ar/O_2 gas ratio of 85/15, and the working pressure was maintained at 3.0 Pa. The RF power was kept at 110 W and the thickness of dielectric thin films was 200 nm. All films were rapid thermal annealed in a rapid thermal furnace at 150 °C for 10 min to compensate for oxygen vacancies. Pt top electrodes were deposited by RF magnetron sputtering through a shadow mask with a dot of 0.5 mm diameter to form a metal-insulator-metal (MIM) structure. For better top electrode contact, the capacitors were again rapid-thermal-annealed (RTA) at 150 °C in air for 10 min.

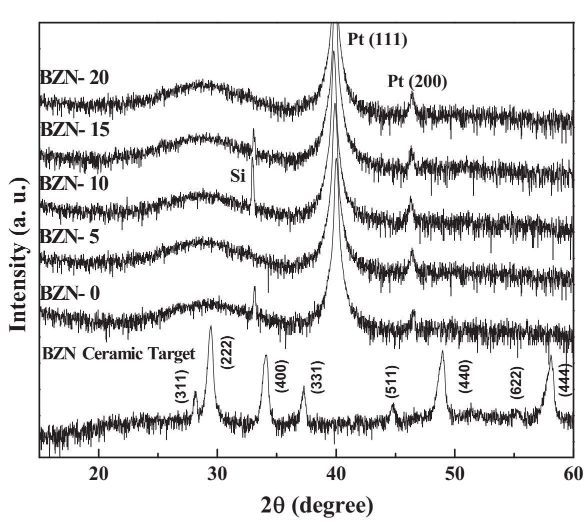

Fig. 1. XRD patterns of BZN ceramic target and BZN-*n* thin films with excess Zn content (0–20 mol%).

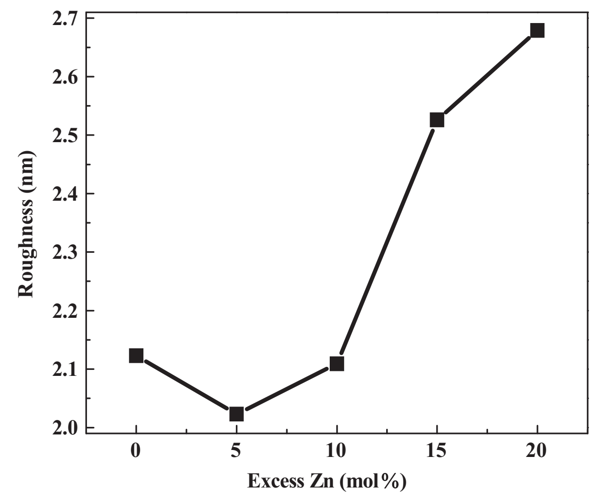

Fig. 2. Roughness of BZN-*n* thin films fabricated as a function of excess Zn content.

The structures of BZN-*n* thin films with various ZnO contents were analyzed via an X-ray diffractometer equipped with Cu Kα radiation (XRD, D/Max-2400, Rigaku). The thickness was measured by using a stylus profiler (Dektak 6M, Veeco) and further confirmed by studying the cross-sectional images of the films by using a scanning electron microscope (SEM, JEOL 7600). X-ray photoelectron spectroscopy (XPS) measurements were performed to study the chemical states of the thin films. The roughness of the thin films was measured by an atomic force microscope (AFM, Nanoscope, Veeco) and the composition was examined by electron probe micro-analysis (EMPA). The dielectric and electrical properties were then characterized by a precision impedance analyzer (4294A, Agilent) with an oscillation voltage of 500 mV and a semiconductor characterization system (4200-SCS, Keithley) at room temperature.

3. Results and discussion

Fig. 1 shows θ–2θ XRD patterns of BZN thin films with excess Zn content (0–20 mol%) deposited on $Pt/TiO_2/SiO_2/Si(100)$ substrates at room temperature under the same sputtering conditions (i.e., by RF magnetron sputtering without any intentional heating of the substrate and post-annealed at