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Structural and dielectric properties of calcium doped bismuth zinc niobate thin films prepared by pulsed laser deposition at room temperature

Zhao Wang, Wei Ren*, Muhammad Saeed Khan, 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

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Abstract

$(Bi_{1.5}Zn_{0.1}Ca_{0.4})(Zn_{0.5}Nb_{1.5})O_7$ (BZNCa) thin films were prepared by pulsed laser deposition on $Pt/TiO_2/SiO_2/Si$ substrates at room temperature. The as-deposited films and films post-annealed from 100 °C to 175 °C for 10 min in air are all amorphous. The influence of the post-annealing process on structural and electrical properties was investigated. The surface morphology of BZNCa films remains almost same with the annealing temperature. While the dielectric and leakage-current properties of the films are strongly influenced by the annealing temperature. The film deposited at O_2 pressure of 4 Pa and then post-annealed at 150 °C shows the improved dielectric and leakage-current characteristics. The dielectric constant and loss tangent are 67.2 and 0.03 at 100 kHz, respectively. The leakage current density is less than 1 μA/cm^2 at an applied bias electric field of 400 kV/cm. The results indicate that calcium doped BZN thin films have potential applications for embedded capacitors.

Keywords: C. Dielectric properties; E. Capacitors; Amorphous film structure

1. Introduction

As micro-systems move towards increasing functionality, higher speed and portability in the consumer electronic products, there is a great deal of competitive pressure on manufacturers to pack more and more circuitry into smaller spaces with improving the overall performance. Embedding thin film capacitors with high permittivity dielectrics into printed circuit board (PCB) is one of the effective methods to approach these goals [1,2]. But in integrated circuit packages, the polymer substrates cannot sustain the temperature of more than 200 °C. However, ferroelectric thin films deposited at or near room temperature exhibit very low dielectric constants and high dielectric losses [3]. Moreover, the conventional paraelectric oxides such as SiO_2 (∼3.9), Ta_2O_5 (∼25) and Al_2O_3 (∼9) can be prepared at room temperature but they show low dielectric constants. Materials with high dielectric constant, low loss and compatible with the PCB substrates are of great technological and scientific importance. Bismuth-based pyrochlores have recently attracted much attention of researchers and are found to be promising candidate materials for low-fire temperature and high frequency dielectric applications [4–9]. Recently, $(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_7$ (BZN) thin film prepared by pulsed laser deposition (PLD) at low temperature (less than 200 °C) exhibits amorphous structure, excellent dielectric and leakage current characteristics, which may be attributed to the Bi metallic phase turning into oxides upon annealing at more than 120 °C or the nano-sized crystallites existing in the film. Typically, amorphous BZN thin film shows a superior dielectric property (ε_r=60–70 measured at 10 kHz) as well as low preparation temperature [10–12].

In this work, $(Bi_{1.5}Zn_{0.1}Ca_{0.4})(Zn_{0.5}Nb_{1.5})O_7$ (BZNCa) thin films were deposited by pulsed laser deposition at room temperature, and then post-annealed below 200 °C. The effects of post-annealing temperature on the phase structures, dielectric and electrical properties of calcium doped BZN thin films have been systematically investigated for embedded capacitor applications.

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

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2. Experimental details

Ceramic target with the formula of $(Bi_{1.5}Zn_{0.1}Ca_{0.4})(Zn_{0.5}Nb_{1.5})O_7$ (BZNCa) was prepared by a conventional solid-state reaction method and sintered at 1000 °C for 3 h. BZNCa thin films were deposited on $Pt/TiO_2/SiO_2/Si$ (100) substrates by PLD using a KrF excimer laser (COMPex Pro 205, Coherent Lambda Physik). The laser wavelength was 248 nm with a pulse width of 30 ns and a repetition rate of 3 Hz. The base pressure of the PLD chamber was evacuated to 4×10^{-4} Pa. Pure oxygen flowing into the chamber formed a pure oxygen atmosphere at a pressure of 4 Pa. The deposition was carried out for 60 min and the as-deposited thin films were then separately annealed at 100 °C, 125 °C, 150 °C and 175 °C in a rapid thermal annealing furnace in air for 10 min. The thicknesses of the films, measured by a stylus profiler (Dektak 6 M, Veeco) were 450–500 nm.

The phase composition and crystallization of BZNCa films were analyzed by x-ray diffraction (XRD, D/Max-2400, Rigaku). Surface morphologies were characterized by atom force microscopy (AFM, Nanoscope, Veeco) and scanning electron microscopy (SEM, FEI Quanta FEG). In order to measure the dielectric and electrical properties of the films, Au top electrodes of 0.50 mm in diameter were deposited by DC sputtering onto the films through a shadow mask to form Au/BZNCa/Pt configuration. The dielectric properties were investigated by a precision impedance analyzer (4294 A, Agilent). The leakage-current (*I–V*) characteristics were examined with a semiconductor characterization system (4200-SCS, Keithley).

3. Results and discussion

A. Morphology and structure

Fig. 1 shows the XRD patterns of both as deposited and annealed BZNCa thin films. No peaks could be detected in all the films except the peaks from the substrates, which indicate that these films are amorphous. It is noted that all the films showed weaker and boarder peaks near 29° in the XRD patterns, which could be caused by small grains (typically in nanometer scale) in highly disordered amorphous matrix in the films.

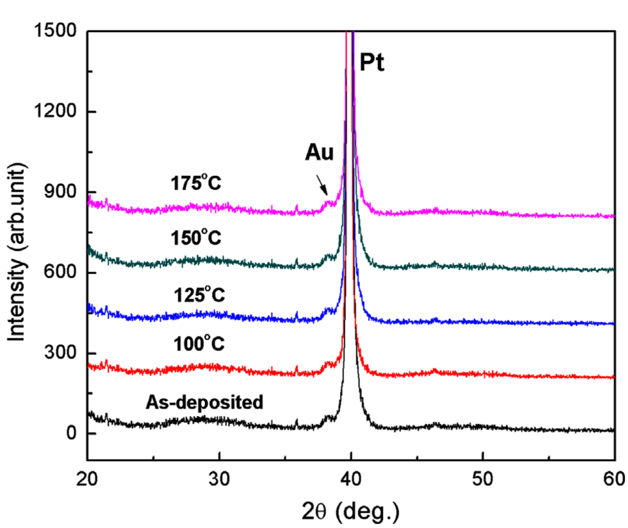

Fig. 1. XRD patterns of as-deposited and annealed BNZCa thin films.

Surface morphologies of BZNCa thin films were investigated by AFM and SEM. As seen in Figs. 2 and 3, the surface morphologies are almost the same, no grains or grain boundaries could be observed due to the amorphous structure. Both as-deposited and annealed thin films show a surface roughness of ~2.5 nm, which hardly changes with the annealing temperature. Fig. 4 shows SEM surface images of the as-deposited film and film annealed at 150 °C. No significant differences could be seen from these two images, which indicate that the surface morphologies do not change much during the post-annealing process.

B. Electrical characteristics

The dielectric behaviors of BZNCa thin films with different post-annealing temperatures were investigated. Dielectric properties of BNZCa thin films as a function of measuring frequency and annealing temperatures are shown in Fig. 5. The dielectric constants of all films decrease with increasing frequency, and while the dielectric losses have significant increase only in the higher frequency range. The dielectric constant shows a dramatic increase after the film was post-annealed. The dielectric constant gradually increases with post-annealing temperature and reaches a maximum at 150 °C, and then decreases when the annealing temperature exceeds 150 °C. The decrease in the dielectric constant for thin film annealed at 175 °C could be attributed to the high temperature migration of Bi [3]. The migration reduces the Bi–O contribution to the overall polarization in BZNCa thin film, which results in the drop of dielectric constant [3]. The as-deposited BZNCa film shows dielectric constant of 43.3 and loss tangent of 0.022 at 100 kHz. This result is superior than the pure BZN thin film prepared at room temperature [8], which may be attributed to the higher polarizability of Ca^{2+} than Zn^{2+}. Furthermore, the dielectric constant of the film annealed at 150 °C increases to 67.2, while the loss tangent is almost same (0.03). A small amount doping of Ca^{2+} may have changed the Bi–O contributions in the annealed film. Therefore, the loss tangent is larger than the pure BZN film [13].

Fig. 6 shows *I–V* characteristics of BZNCa thin films as a function of post-annealing temperature. It can be seen that the leakage current density shows a strong dependence on the annealing temperature. The as-deposited film and film annealed at 150 °C show excellent leakage current characteristics. The leakage current density of the as-deposited thin film is 9.64×10^{-7} A/cm^2 at a bias electric field of 400 kV/cm. For the film annealed at 150 °C, the leakage current density is also less than 1 μA/cm^2 at an applied bias electric field of 400 kV/cm. However, for the films annealed at other temperatures, the leakage current densities are larger than 1×10^{-5} A/cm^2 at a bias electric field of 400 kV/cm.

Leakage currents in the oxides can be attribute to four mechanisms, which are Schottky emission (Schottky), Poole–Frenkel emission, space-charge-limited current (SCLC) and