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Preparation and dielectric tunability of bismuth-based pyrochlore dielectric thick films on alumina substrates

Feng Xiang, Hong Wang *, Minghui Zhang, Xu Sun, Xi Yao

Electronic Materials Research Laboratory, Key Laboratory of Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

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Abstract

Metal–insulator–metal capacitors structures, employing the cubic pyrochlore $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (BZN) thick films, were fabricated by screen-printing techniques on alumina substrates. Chemical compatibility and microstructure between layers was studied by EDS/SEM analysis. The dielectric properties of BZN thick films have been investigated as a function of temperature and frequency. The films exhibited the dielectric constant up to 130, and the dielectric loss less than 0.005 at 1 MHz. The dielectric tunabilities of the films have been compared at different temperature. The BZN thick film showed low tunability of about 1.8% at 10 kHz under 100 kV/cm dc bias voltage in temperature from −150 to 180 °C. The temperature stability of dielectric properties for BZN thick film should be useful for designing temperature stable frequency agile.

Keywords: A. Films; C. Dielectric properties; E. Functional applications

1. Introduction

Recently, electrically tunable dielectrics have attracted much attention in frequency or phase agile microwave devices. They can be applied to tunable microwave components such as filters, varactors, oscillators, phase shifters, etc. [1–3]. Among numerous materials, $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (BZN) ceramic with the cubic pyrochlore structure has attracted particular attention [4–7]. The cubic pyrochlore $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ ceramics have relatively high permittivity (150), low dielectric loss (tan δ $\sim 5 \times 10^{-4}$ at 1 MHz) and modest temperature coefficient of dielectric ($\alpha_\varepsilon \sim -470$ ppm/°C at 100 kHz) [8,9]. Furthermore, BZN thin films exhibit a large tunability as high as 55% (tan δ $\sim 5 \times 10^{-4}$ at 1 MHz) under a maximum applied bias field of 2.4 MV/cm at room temperature [4]. The excellent tunability properties and low dielectric loss of BZN make it an attractive material for tunable microwave device applications.

At present, BZN thin films and barium strontium titanate (BST) thick films [1,10] with dielectric tunability have been extensively studied. But BZN thick films have been less reported. The preparation of thick film by screen-printing technique is a relatively simple and convenient method to produce thick layers with thickness up to 100 μm. With typical thickness in the range from 10 to 100 μm, screen-printed BZN thick films also effectively fill the technological gap between thin films and bulk ceramics [10]. In this paper, BZN thick films were studied for applications of electrically tunable devices. The dielectric properties of BZN thick films have been investigated as a function of temperature and frequency. The dielectric tunability of BZN thick films has been compared at different temperatures.

2. Experimental procedure

$Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ powder was synthesized by conventional mixed oxide method from niobium oxide (>99%, Zhu-Zhou Harden Alloys Co. Ltd., China), bismuth trioxide (>99%, Shu-Du Powders Co. Ltd., China) and zinc oxide (>99%, Zhu-Zhou Harden Alloys Co. Ltd., China), and is reported in detail in Refs. [8,9]. The sintered BZN ceramics was mechanically grinded and ball-milled for 4 h to obtain the BZN ceramic powders. The powders showed a mean grain size of $D_{50} = 0.67$ μm after milling.

BZN thick films have been fabricated on 96% alumina substrates using a conventional screen-printing method. The screen printable paste was prepared by combining BZN powder

* Corresponding author. Tel.: +86 29 82668679; fax: +86 29 82668674.
E-mail address: hwang@mail.xjtu.edu.cn (H. Wang).

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with organic vehicles (ethyl cellulose + α-terpineol) at a solids loading of 40 vol.%. The BZN films are drying at 100 °C for 30 min, fired at 500 °C for 1 h to remove the organic components and sintered at 800 °C for 2 h. The obtained films presented a thickness ranging from 10 to 80 μm, depending on the number of layers. To form metal–insulator–metal capacitors structures (MIM) for the electrical measurements, bottom electrode was screen printed using the Ag–Pt paste annealed at 850 °C for 10 min and 2 mm in diameter and silver, top electrode was also fabricated by screen printing the Ag paste annealed at 600 °C for 10 min.

The phase structures of BZN thick film were characterized by X-ray diffractometry (XRD). The XRD patterns were obtained using a Rigaku D/max-2400 X-ray diffractometer with Cu Kα radiation with $2\theta = 0.02^\circ$ step width. The microstructure and chemical composition were analyzed using a scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS) attachment (JSM-6460, JEOL Ltd., Japan).

The dielectric properties were measured using a high-precision HP4284A LCR meter in the range of 1 kHz to 1 MHz. For temperature measurement between −170 and 180 °C, a computer-controlled Delta 9023 temperature chamber (Delta Design, Inc., San Diego, CA) with a heating rate of 3 °C/min was used.

The relative tunability of the films was measured at 10 kHz with a bias voltage source. The relative tunability of BZN thick film was calculated using the following equation:

$$n_r(V) = \frac{\varepsilon(0) - \varepsilon(V)}{\varepsilon(0)}$$

where ε(V) and ε(0) are the permittivity with bias voltage and without bias voltage, respectively. The $n_r(V)$ is the relative tunability under applied bias voltage.

3. Results and discussion

The XRD patterns of BZN ceramic powder and BZN thick film without top electrode are shown in Fig. 1. All samples showed the typical XRD patterns of a cubic pyrochlore structure.

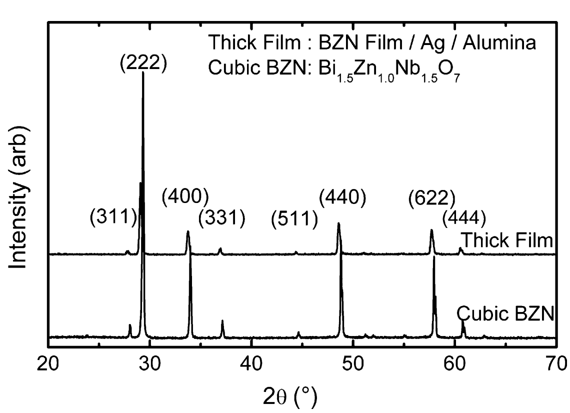

Fig. 1. XRD patterns of BZN thick film and BZN ceramic powder.

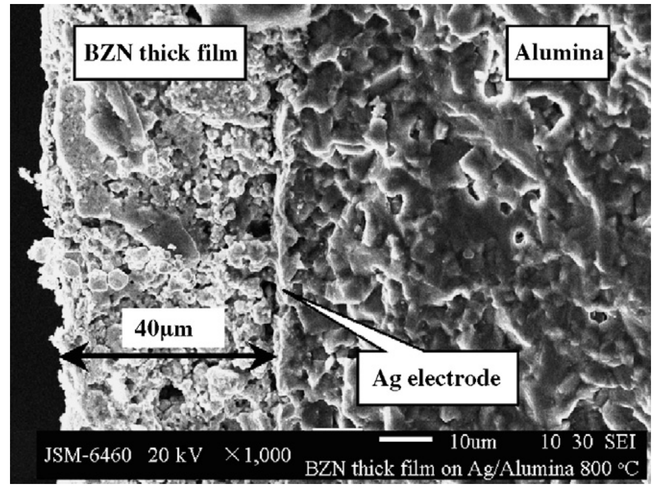

Fig. 2. SEM micrograph of the BZN thick film on an alumina substrate with Ag bottom electrode.

The SEM micrograph of a cross-section of BZN thick film is shown in Fig. 2. It can be seen that the thickness for BZN thick film was approximately 40 μm. The presence of certain amount of porosity was noticed but no visible cracks on the BZN thick film were observed. The interfaces between the BZN film, Ag–Pd electrode layer and alumina substrates are clear. The EDS analysis on the cross-section of the film showed that the highly active Ag^+ ions slightly diffuse into the BZN thick film. It is considered that part of the electrode material by screen-printing could diffuse inside BZN thick film through pores [10].

The frequency dependence of the permittivity and dielectric loss of BZN thick film are shown in Fig. 3. With increasing frequency, the permittivity and dielectric loss of film decreases significantly. The permittivity and dielectric loss show some dispersion at low frequencies, due to the space–charge polarizability in film. For the BZN thick film, the permittivity is 130 and the dielectric loss is approximately 0.008 at 1 MHz, which is close to the reported value of bulk BZN ceramic (ε_r ∼150 and tan δ ∼0.005) [8].

The permittivity and dielectric loss of BZN thick film as a function of temperature from −170 to 180 °C at frequency between 1 kHz and 100 kHz are shown in Fig. 4. The low-temperature dielectric relaxation, exhibiting a characteristic

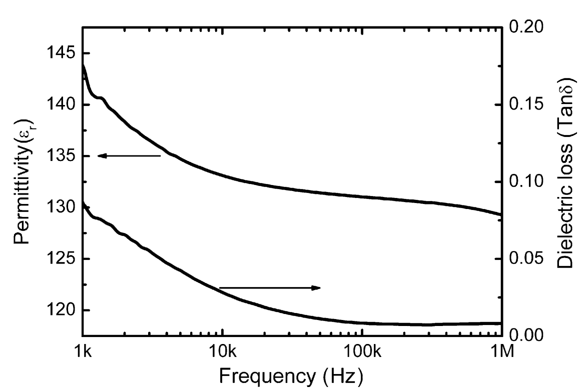

Fig. 3. Frequency dependence of permittivity and dielectric loss of BZN thick film.

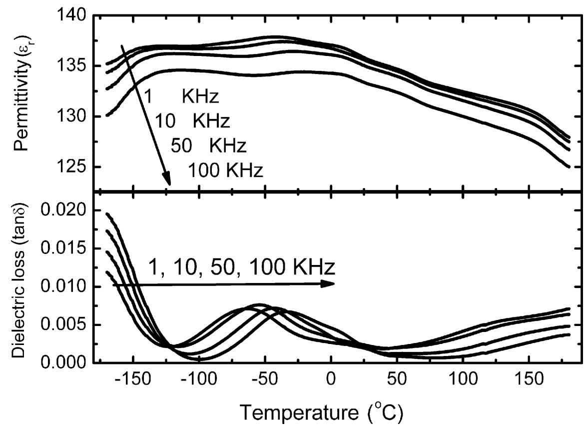

Fig. 4. Temperature dependence of permittivity and dielectric loss of BZN thick film.

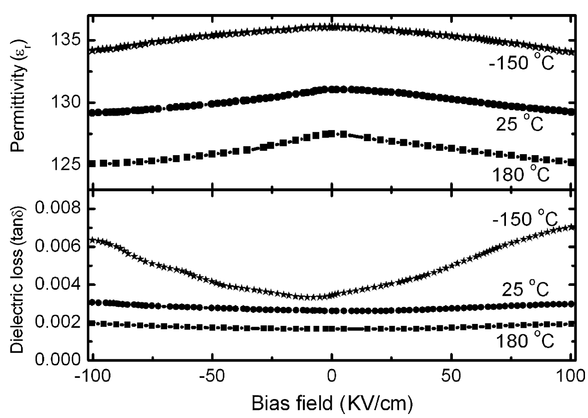

Fig. 5. The permittivity and dielectric loss of BZN thick film with bias field.

loss peak and drop in permittivity, could be observed in BZN thick film below −160 °C. This dielectric relaxation is a native characteristic of BZN ceramics [8,11], which has been inherited by the film.

Fig. 5 shows permittivity and dielectric loss of BZN thick film as a function of applied dc bias in a frequency of 10 kHz at different temperatures. The relative tunability of the BZN thick film was also shown in Fig. 6. The BZN thick films measured at −150 °C showed the maximum permittivity and dielectric loss.

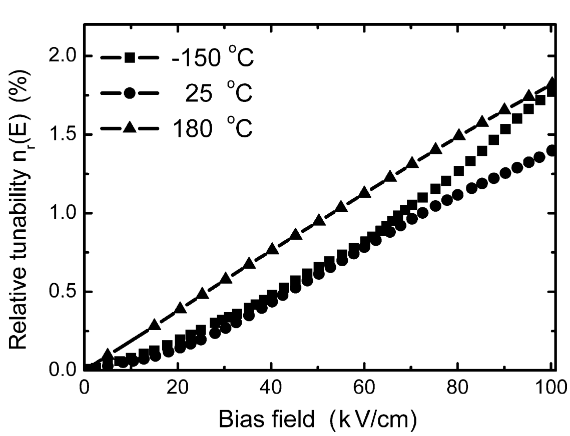

Fig. 6. The relative tunability of BZN thick film at different temperature.

The permittivity of film at −150 °C was 136 at 0 V bias, and decreased with increasing bias field. A tunability value of 1.5% was achieved at a dc bias field of 100 kV/cm. The loss tangent of film at −150 °C was below 0.4% at 0 V bias and remained below 0.8% up to a bias field of 100 kV/cm. Further increasing measured temperature to 180 °C, the permittivity and dielectric loss were significantly declined. The permittivity of film at 180 °C was 127 at 0 V bias. A tunability value of film was above 1.8%. The loss tangent of film at 180 °C was approximately 0.003 at 0 V bias and remained constant with increasing bias field. It can be seen that the dielectric tunability of BZN thick films showed weak temperature dependency. The temperature stability of dielectric properties for BZN thick film should be useful for temperature stable tunable microwave devices than other tunable ferroelectric materials.

The 1.8% tunability value under a bias field of 100 kV/cm for BZN thick film at room temperature was rather low due to lower bias voltages when compared with the BZN thin film reported as high as 55% under a bias field of 2.4 MV/cm [4]. Therefore, higher tunability of BZN thick film could be expected to be obtained by further increasing the bias voltage.

4. Conclusions

The cubic pyrochlore phase $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ thick films have been fabricated on 96% alumina substrates using a conventional screen-printing method. The thickness of BZN thick film was approximately 40 μm. It is found that the highly active Ag^+ ions slightly diffuse into the BZN thick film. For the BZN thick film, the permittivity was 130, the dielectric loss was 0.008 in 1 MHz, which is slightly smaller than the reported value of bulk BZN. The low-temperature dielectric relaxation inherited from the bulk ceramic could be observed in BZN thick film below −150 °C. The BZN thick film showed low frequency tunability of about 1.8% at 10 kHz under 100 kV/cm DC bias voltages in temperature from −150 to 180 °C. It can be seen that the dielectric tunability of BZN thick films is less temperature dependent which should be useful for temperature stable tunable frequency or phase agile microwave devices.

Acknowledgements

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