Dielectric properties of $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$/Mn-doped $Ba_{0.6}Sr_{0.4}TiO_3$ heterolayered films grown by pulsed laser deposition

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$Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$/Mn-doped $Ba_{0.6}Sr_{0.4}TiO_3$ heterolayered films have been deposited on (111) Nb:$SrTiO_3$ substrate by pulsed laser deposition. The heterolayered films were found to possess a medium permittivity around 200, a low loss tangent of 0.0025, and a relatively high tunability up to 25% measured with dc bias field of 850 kV/cm. The authors analyzed the bias field dependent permittivity of the heterolayered films using layer model. Based on the analysis, a structure with the tunability as high as 40% under a bias field of 420 kV/cm was suggested after optimizing the thickness of the component layers. © *2006 American Institute of Physics*.
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Tunable materials caused more and more interest due to the rapid developing demand of wireless microwave communications for applications, such as phase shifters and tunable antennas. For a microwave engineer, the ideal tunable materials should combine a high tunability with low dielectric loss. Recently, cubic pyrochlore phase $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (BZN) attracted much attention as a dielectric material for microwave tunable applications[1–3] mainly due to its very low dielectric loss (less than 5×10^{-4}).[4] However, its relatively low tunability is a limitation for potential practical applications.

Ferroelectric $(Ba,Sr)TiO_3$ (BST) is one of the most widely investigated tunable materials,[5,6] which possesses a particularly high tunability but high dielectric loss.[7] In order to reduce the dielectric loss of pure BST, methods such as doping has been used.[8,9] But in many cases, the reduction of the dielectric loss by doping is limited and its tunability falls down substantially at the same time. However, the assertion that the tunability decreases with reducing the dielectric loss does not always hold for ferroelectric materials containing dielectrics.[10] It seems that composite films have advantages in tunable materials design by using the compatibility and flexibility of the composites. The work on BST-BZN composite films fabricated by pulsed laser deposition (PLD) using BST-BZN composite targets was reported by Yan *et al.*, which showed low dielectric loss (10^{-3}) but low tunability (around 6%) as well.[11]

One interesting question is whether heterolayered mixture of a low loss dielectric BZN and a Mn-doped ferroelectric $Ba_{0.6}Sr_{0.4}TiO_3$ (Mn-BST) will further decrease the overall dielectric loss without strongly deteriorating the tunability of the composite. (The adoption of Mn-BST was benefited from the recent work of Yuan *et al.*[12]) In this letter, we report the fabrication of BZN/Mn-BST heterolayered films deposited on (111) Nb:$SrTiO_3$ (STO) substrate by PLD. A low loss tangent (tan δ) of 0.0025 and a tunability up to 25% were obtained under the bias field of 850 kV/cm, which gained a figure of merit (FOM) of 100.

The BZN/Mn-BST heterolayered films were grown by PLD technique using a 308 nm XeCl excimer laser operated at an energy density of about 2 J/cm^2. A stoichiometric $Bi_{1.5}ZnNb_{1.5}O_7$ target and a 2% Mn additional doped $Ba_{0.6}Sr_{0.4}TiO_3$ target were used. As for deposition, the target to substrate distance was maintained as 50 mm. An initial layer of 200 nm Mn-BST was grown on Nb:STO(111) substrate in 10 Pa of O_2 at 750 °C, followed by the additional growth of a 250 nm thick BZN film with $P_{O_2}=30$ Pa at the same deposition temperature. The durations of deposition were controled as 40 and 20 min, respectively. X-ray diffraction (XRD) measurements indicated that the deposited Mn-BST film was (111) oriented and the BZN film was polycrystalline, as shown in Fig. 1. Scanning electron microscopy (SEM) cross-section image inside Fig. 1 shows that the heterolayered films had distinct interfaces. For dielectric property measurements, a 100 nm thick Pt was deposited as top electrode to form a parallel-plate capacitor structure using PLD. Room-temperature dielectric measurements were taken using 50 mV oscillation voltage by an Agilent 4294A precision impedance analyzer.

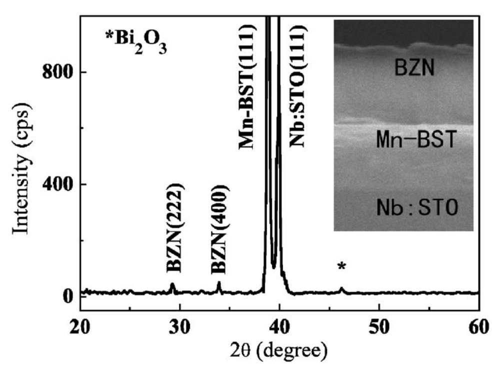

FIG. 1. XRD pattern of BZN/Mn-BST heterolayered films on Nb:STO(111) substrate. Inside is the SEM cross-section image of the heterolayered films.

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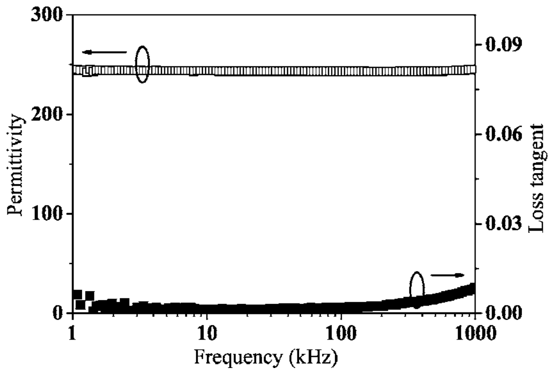

FIG. 2. Permittivity and loss tangent as a function of frequency for BZN/Mn-BST heterolayered films, measured without dc bias field.

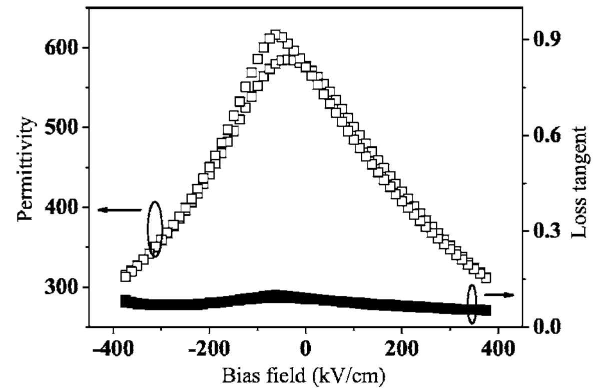

FIG. 4. Bias field dependent permittivity and loss tangent of the Mn-BST(111)/Nb:STO(111) single layer film deposited in a different run.

Figure 2 shows the frequency dependent permittivity and loss tangent of the heterolayered films measured without dc bias field. The permittivity exhibits a frequency independent characteristic, while the loss tangent increases with increasing frequency after 100 kHz. Lu and Stemmer[4] debated that such an increase in loss tangent that companied by a frequency independent permittivity might be attributed to the conductor loss contribution of the electrode.

The bias field dependent permittivity and loss tangent of the heterolayered films at frequencies of 10 and 100 kHz were measured. These two measurements were overlapped and the result at 100 kHz is given in Fig. 3. The square dots present our simulation based on the bias field dependent permittivity of a 200 nm thick Mn-BST(111) film deposited on Nb:STO(111) substrate in a different run, as shown in Fig. 4, using the same deposition parameters as that in BZN/Mn-BST heterolayered films. It should be mentioned that the permittivity of BZN here is taken as constant as 150,[1,3] whose tunability is neglected considering its small contribution to the whole. As for simulation, a layer model was introduced according to our experiment procedure. In this case, the layer model can be described as the in-series connection of two capacitors corresponding to the two components of the films, i.e., BZN and Mn-BST here.

The tunability of the heterolayered films is calculated from the average measured permittivity, as shown in Fig. 3, which is defined as the average of the twice measured permittivity under forward and backward dc bias fields at the same bias value. While the quality of the films is characterized by

$$\mathrm{FOM} = \left(\frac{\text{tunability}}{\tan\delta}\right) = \left\{\frac{[\varepsilon_{\mathrm{av}}(0) - \varepsilon_{\mathrm{av}}(E_{\max})]/\varepsilon_{\mathrm{av}}(0)}{\tan\delta}\right\}, \tag{1}$$

where $\varepsilon_{\mathrm{av}}(0)$ and $\varepsilon_{\mathrm{av}}(E_{\max})$ are the average permittivity of the heterolayered films at zero and maximum bias field, respectively.

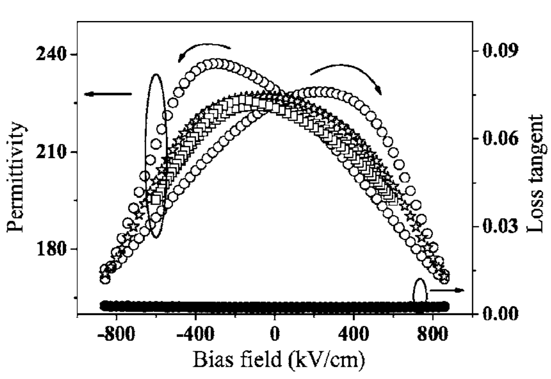

FIG. 3. Bias field dependent permittivity (empty circle dot) and loss tangent (solid circle dot) of the heterolayered films measured at 100 kHz. Also shown are the calculated average permittivity (asterisk dot) and the simulation (square dot). The average tunability was figured out as 25% at 850 kV/cm and the loss tangent was 0.0025 under the bias field, which gained a FOM of 100.

Comparing with the tunability of BZN films reported in previous studies,[1,4,13,14] which was about 10% at the bias field of 850 kV/cm, the tunability of the heterolayered films has a large improvement up to 25% while the loss tangent of the heterolayered films remains as low as 0.0025 under the bias field. As a result, a FOM of 100 is achieved, which is much better than that of the Mn-BST(111)/Nb:STO(111) single layer film whose FOM=7, as shown in Fig. 4. Although being difficult to accurately compare due to differences in measuring frequency and device layouts, the FOM of the BZN/Mn-BST heterolayered films is among the best results of tunable materials achieved up to now.[15,16] The simulation is also in good agreement with the average measured permittivity, indicating that the trend of the tunability of the heterolayered films can be predicted to some extent. The loss tangent of the heterolayered films is between that of the pure BST film (0.07) as shown in Fig. 4 and the pure BZN film[4] (5×10^{-4}), which indicates that the low loss tangent of the composite films comes from the BZN layer. Further work is needed to clarify such mechanism.

After careful calculation, we suggest that when the thickness of the BZN layer is 50 nm, the BZN/Mn-BST heterolayered films with a total thickness of 450 nm should exhibit a high tunability which we estimate to be about 40% under a bias field of 420 kV/cm. Higher tunability is expected at larger bias field. The corresponding simulations are presented in Fig. 5. Another heterolayered films composed of 100 nm BZN and 200 nm Mn-BST with the same structure and deposition parameters, which were comparable to the heterolayered films with 150 nm BZN layer simulated in Fig. 5, were also prepared and measured. The films showed a tunability of 21% under the bias field of 500 kV/cm, which agrees well with the trend we predicted above.

The butterflylike asymmetry of the bias field dependent permittivity of the heterolayered films was ascribed to the high concentration of movable ions or charges accumulated near the interfaces and oxygen vacancies formed during

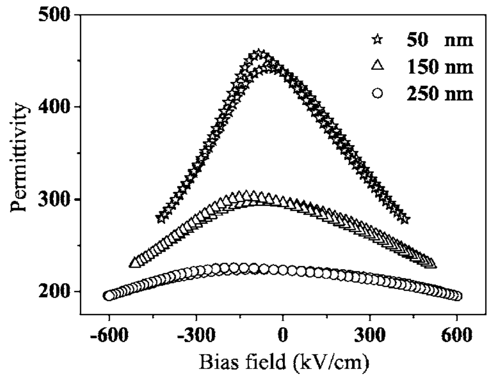

FIG. 5. Simulations of the bias field dependent permittivity of the BZN/Mn-BST heterolayered films with a total thickness of 450 nm. The thickness of the BZN layer varies from 50 to, 150, to 250 nm, whose tunabilities are calculated to be about 40%, 22%, and 13% under bias fields of 420, 510, and 600 kV/cm, respectively.

deposition, which are very common in depositing metal oxide by PLD.[17] This postulation was supported by annealing the heterolayered films in atmosphere at 750 °C for 2 min to improve the interfaces and complement the oxygen vacancies, which led to a low asymmetry.

In summary, the BZN/Mn-BST heterolayered films were fabricated by PLD. The heterolayered films exhibited a loss tangent of 0.0025 and a tunability up to 25% under a bias electric field of 850 kV/cm, which gave a FOM of 100. Furthermore, the tunability of the heterolayered films was analyzed with the layer model and a favorable simulation was obtained, which indicates an attractive prospect of the BZN/Mn-BST heterolayered films for potential tunable microwave device applications.

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