Microstructures and electrical properties of BSTM multilayers with different periods

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ABSTRACT

5% Mn-doped BST (BSTM) multilayers with different periods have been prepared by a chemical solution deposition method. The X-ray diffraction results showed that all of the multilayers exhibited a single perovskite phase, randomly oriented polycrystalline structure. The crystalline qualities improved as the number of periods was increased. The building block consisting of dense and porous BSTM bilayer was characterized and confirmed by transmission electron microscopy (TEM) and spectrometer analysis. Strong frequency dispersion of the dielectric properties was found for all BSTM multilayers. The behaviors of the dielectric losses at high (>450 kHz) and low (<1 kHz) frequencies are related to the extrinsic resonance and the conduction mechanisms, respectively. The dielectric loss peak in the mid-frequency range monotonically decreased with an increase in the number of periods, which was assumed to be attributed to the interactions between the induced space charge polarization and dipolar complexes.

Keywords: BSTM; Multilayers; Reflectivity; Dielectric properties

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1. Introduction

Lead-free barium strontium titanate (BST) thin films have been studied for applications in dynamic random-access memories, microwave tunable devices, non-volatile memories and uncooled infrared detectors because of their favorable dielectric, ferroelectric, and pyroelectric properties [1-4]. In recent years, artificially fabricated superlattices and multilayers based on BST have emerged as a leading research topic and are becoming promising materials due to their dramatically improved or unique properties compared to their thin-film counterparts. A remarkable enhancement of dielectric constant was observed for epitaxial growth (111)-oriented $\text{BaTiO}_3/\text{SrTiO}_3$ superlattices, which is attributed to mechanical strain and the Maxwell-Wagner effect [5]. The voltage tunability was greatly increased due to the interfacial polarization in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{BaTiO}_3$ multilayers [6]. Dielectric properties of $\text{BaSrTi}_{1.1}\text{O}_3/\text{BaSrTi}_{1.05}\text{O}_3/\text{BaSrTiO}_3$ were also improved due to this interface [7]. Enhanced magnetization and saturation polarization were found for $\text{BiFeO}_3/\text{BaTiO}_3$ due to the coupling between ferroelectric and magnetic orders [8]. Enhanced electrocaloric and pyroelectric response from $\text{BaTiO}_3/\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ was also demonstrated [9]. These characteristics can thus create an opportunity to create new functional properties, as well as a new combination of desirable properties. Recently, we demonstrated the fabrication of distributed Bragg reflectors (DBRs) and F-P microcavities based on periodic BST multilayers consisting of dense and porous BST bilayers. Additionally, the performance of DBRs and microcavities are expected to be dynamically tunable with an externally applied electric field [10-11]. It has been

known for many years that the electrical properties of BST thin films are strongly dependent on the film thickness [12-13]. In this paper, the thickness dependence of the structural and electrical properties of the periodic BSTM multilayers was studied by changing the number of structure periods.

2. Experimental procedures

The $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Ti}_{0.95}\text{Mn}_{0.05}\text{O}_3$ solutions with a concentration of 0.3 M were prepared using $\text{Ba}(\text{CH}_3\text{COO})_2$, $\text{Sr}(\text{CH}_3\text{COO})_2 \cdot 1.5\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ and Polymer PVP (polyvinylpyrrolidone, K30) as starting materials. Detailed procedures can be found in Ref. [10]. An integrated metal-insulator-metal (MIM) structure was used to investigate the electrical properties of the device. Approximately 180 nm of conductive oxide LaNiO_3 (LNO) film to act as bottom electrodes for the samples was first deposited on SrTiO_3 (STO, 100) substrates by spin-coating. The growth of LNO films has been described elsewhere [14]. The BSTM multilayers were then directly deposited on the LNO buffered substrates by spin coating and annealing. The spinning rates were 3500 revolutions per minute (rpm). All the annealing procedures were carried out in a rapid thermal annealing furnace in atmospheric environment. The wet gel film was first dried at 180 °C for 180 s, and then pre-fired at 380 °C for 300 s to remove residual organics, and finally annealed at 750 °C for 360 s. To form the MIM configuration, circular top platinum electrodes with a diameter of 0.2 mm were finally added by using a dc sputtering instrument through a shadow mask. In this way, four samples with different periods denoted as 2Ps, 4Ps, 6Ps, and 8Ps, respectively, (Ps means periods) were fabricated

for comparison.

The microstructures of multilayers were characterized by X-ray diffraction (XRD) with a Cu $K\alpha$ radiation source and transmission electron microscopy (TEM, Tecnai G2 S-Twin F20, FEI). The reflectivity spectra were recorded by a Perkin Elmer Lambda 800/900 UV/vis spectrometer. Electrical properties were measured by using an Agilent E4980A precision LCR meter, and a Keithley 6430 sub-femto-amp remote source meter.

3. Results and discussion

3.1 Structural characterization

Fig. 1 shows XRD patterns of the BSTM samples. The results indicate the presence of (110), (111), (210) and (211) peaks of BSTM, suggesting the formation of a perovskite structure without a secondary phase. The (100) and (200) XRD peaks of the BSTM samples are covered in the figure by the peaks from the STO substrate. All of the samples are randomly oriented polycrystalline. The crystalline qualities were estimated from the intensities and the values of full-width-half maximum (FWHM) of the diffraction peaks. As the number of periods increased, the crystalline qualities of the BSTM multilayer gradually increased, which is attributed to the higher number of annealing cycles.

Fig. 2 presents a typical cross-sectional TEM morphology of the BSTM sample with 4Ps. The results exhibited a periodic structure consisting of dense and porous-BSTM bilayers, which is similar to our previous results and can be verified by the following reflectivity spectra. The thickness of the LNO layer was approximately

180 nm, and the thickness of 4 BSTM periods was estimated to be 600 nm as determined from the TEM results.

Fig. 3 shows the relative reflectivity spectra of the BSTM samples at room temperature. The incident light was perpendicular to the sample surface. As shown in Fig. 3, a stop band centered at 400-500 nm was found for each of the samples in the examined spectral range. The peak reflectivity increased as the number of periods increased. This is a typical feature of a one-dimensional photonic crystal, indicating the formation of a periodic sequence of alternating refractive indices. In our study, the alternating dense and porous BSTM layers result in this feature because the refractive index of the dense BSTM is higher than that of the porous BSTM. The slight red shift of the peak position is related to the increased optical thickness of one BSTM period.

3.2 Electrical properties

The frequency dependence of the dielectric constant and the loss tangent are shown in Fig. 4. It can be observed for all samples that the dielectric constants decreased rapidly with an increase in frequency. Such strong frequency dispersion implies that several mechanisms dominate the dielectric properties. At 1 kHz, the dielectric constants of 2Ps, 4Ps, 6Ps and 8Ps are 681, 727, 771 and 779, respectively. On one hand, the higher crystalline qualities of the BSTM samples with a high number of periods lead to the increase in the dielectric constant. On the other hand, the BSTM samples with a high number of periods will also exhibit characteristics similar to their bulk counterparts, resulting in an increase in the dielectric constant. The loss curves can be separated into three sections. An obvious increase in the $\tan\delta$

at low frequencies indicates that a conduction mechanism might play a dominant role [15]. The increased $\tan\delta$ with the increase in frequency beyond 450 kHz is due to extrinsic resonance behavior [16]. It should be noted that a dielectric loss peak can be found in the mid-frequency range for all samples, and the peak position monotonically decreased with the increase in the number of periods. The dielectric relaxation could be related to dipolar complexes, such as $Mn_{Ti}'' - V_o''$. The induced space charge polarization strengthened as the number of periods increased due to the presence of the increased number of nanopores and embedded interfaces. Additional contributions to dielectric loss could be due to the interactions between the space charge polarization and the dipolar complexes. Further study is needed to clarify this hypothesis.

Fig. 5 presents a plot of leakage current density versus applied electric field (J-E) of all samples at room temperature. The slight J-E asymmetry at positive and negative biases is thought to be related to the difference in electrodes. The leakage currents of samples with the higher number of periods are relatively lower than that of sample 2Ps. The lower leakage currents also lead to a lower resistive loss.

4. Conclusions

In summary, periodic BSTM multilayers with different periods were fabricated on LNO buffered STO substrates by chemical solution deposition. The thickness dependence of the structural and electrical properties of the BSTM multilayers was studied by changing the number of periods. The crystalline qualities and the insulating properties of the BSTM multilayers increased with increased device thickness. The

stop band in the reflectivity spectrum of the BSTM multilayer confirmed its periodic structure. The dielectric properties of all samples exhibited strong frequency dispersion. At low frequencies (<1 kHz), the dielectric loss is dominated by a conduction mechanism. The dielectric loss peak in the mid-frequency range is assumed to be attributed to interactions between the induced space charge polarization and dipolar complexes. At high frequencies (> 450 kHz), the $\tan\delta$ is due to extrinsic resonance behavior.

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Figure Captions:

Fig. 1. XRD patterns of the BSTM samples.

Fig. 2. Cross-sectional TEM morphology of the BSTM sample with 4Ps.

Fig. 3. Relative reflectivity spectra of the BSTM samples at room temperature.

Fig. 4. Frequency dependence of dielectric properties of the BSTM samples.

Fig. 5. Leakage current density versus applied electric field (J-E) of the BSTM samples at room temperature.

Figure 1 XRD

Figure 2 TEM

Figure 3 Reflectivity

Figure 4 CF

Figure 5 IV