Research Article

Self-Assembled BaTiO₃-MnZnFe₂O₄ Nanocomposite Films

Guo Yu, Feiming Bai, and Huaiwu Zhang

State Key Laboratory of Electronic Thin Film and Integrated Devices, University of Electronic Science and Technology, Chengdu 610054, China

Correspondence should be addressed to Feiming Bai, fmbai@uestc.edu.cn

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Self-assembled nanocomposite BaTiO₃-Mn_{0.4}Zn_{0.87}Fe₂O₄ magnetodielectric films have been grown on (001)-oriented SrTiO₃ substrates by a pulsed laser deposition method. High resolution X-ray diffraction shows that both BaTiO₃ and MnZn-ferrite phases are epitaxial along the out-of-plane direction with a 0–3 composite structure in spite of very large lattice mismatch. The magnetic, ferroelectric, and dielectric properties of the nanocomposite films are reported. A saturated magnetization of 330 emu/cc and double remanent polarization of 40 $\mu\text{C}/\text{cm}^2$ were obtained. Structural and compositional factors limiting the effective permeability and the dielectric constant will be discussed.

1. Introduction

Ferromagnetic and ferroelectric materials individually provide magnetic and electrical tunability for adaptive RF and microwave devices, [1, 2]. Recently, a promising approach for tunable microwave devices, which combines the advantages of ferrite and ferroelectric devices, has been developed [3–5]. The technique involves the excitations of hybrid-spin-electromagnetic waves in ferrite-ferroelectric-layered structures. A number of bilayer-structured films, including Y₃Fe₅O₁₂/Ba_{0.5}Sr_{0.5}TiO₃ (YIG/BST), Ba_{0.5}Sr_{0.5}TiO₃/BaFe₁₂O₁₉ (BST/BaM), YIG/Pb(ZrTi)O₃ (PZT), NiFe₂O₄/BST, and PZT/NiFe₂O₄ have been fabricated and investigated based on this mechanism [6–12].

Another approach of utilizing epitaxial films with ferromagnetic nanostructure embedded in ferroelectric matrix may have even superior properties. First, the low thickness of nanocomposite films can push the dimensional resonance to much higher frequency, therefore greatly expanding the working frequency of ferrite. Secondly, the ferroelectric phase has an enhanced c/a ratio due to the constraint from substrate and therefore; enhanced dielectric constant can be achieved [13]. Finally, the effective resistance of nanocomposite films is several magnitudes higher than bulk ferrite, and therefore a low eddy-current loss and a simultaneously high initial permeability are expected. The growth of such

nanocomposite films has been demonstrated in BaTiO₃-CoFe₂O₄, [14] BiFeO₃-CoFe₂O₄ [15], BiFeO₃-NiFe₂O₄ [16]; and other systems grown on SrTiO₃ substrates.

In current work, our attention was given to BaTiO₃-(MnZn)Fe₂O₄ (BTO-MZF) system. MnZn-ferrite has simultaneous giant capacitance (dielectric constant $\sim 10^5$) and a rather large static permeability referred to as giant permeability [17]. However, due to its low electrical resistivity and the dimensional resonance effect, the working frequency of bulk MZF is lower than 2 MHz [18]. BaTiO₃ has high permittivity and high-quality factor thus low loss factor. The combined merits of nanocomposite films mentioned above may pave the way to applying MnZn ferrite in RF or even microwave frequency. In addition, to our best knowledge, such system has not been grown and investigated in the literature. It is thus the objective of current work to explore the flexibility to grow epitaxial BTO-MZF nanocomposite and perform initial studies of the magnetic and dielectric properties of the thin film.

2. Experiment

BTO-MZF nanocomposite films were grown onto (001)-oriented SrTiO₃ (STO) single-crystal substrates by pulsed laser deposition (PLD) from a two-phase target having

FIGURE 1: (00 l) line scans of BTO-MZF thin films by HRXRD, (a) as-deposited and (b) after annealed at 1020°C for one hour. The insert shows the (110) pole figure of the annealed sample.

FIGURE 2: AFM (left) and MFM (right) images of an annealed BTO-MZF thin film.

the composition $0.6\text{BaTiO}_3\text{-}0.4\text{Mn}_{0.4}\text{Zn}_{0.87}\text{Fe}_2\text{O}_4$. STO was selected because of its good lattice match with that of BTO phase. Excess amount of Zn was used to compensate its deficiency during deposition. SrRuO_3 was chosen as the lattice-matched bottom electrode to enable heteroepitaxy. The deposition temperature varied from 800 to 850°C and a film thickness of ~ 200 nm was obtained. The oxygen pressure was maintained at 100 mTorr during deposition. After the deposition, some samples were further annealed at 1020°C for one hour. High-resolution X-ray diffraction (HRXRD) was performed using a Phillips X'Pert MPD system. DC magnetization was characterized using a superconducting quantum interference device magnetometer (SQUID, Quantum Design, model XL7). Scanning probe microscopy (SPM)

studies were carried out using a Veeco DI 3100a system employing silicon cantilevers with standard MESP tips coated with a CoCr film. All domain studies were carried out at ambient temperature with the tip magnetized normally to the specimen surface. The dependence of dielectric constant on frequency measurements were taken on an Agilent-4294A impedance analyzer.

3. Results and Discussion

Figures 1(a) and 1(b) show the (00 l) line scans of as-deposited and after-annealed BTO-MZF films obtained by HRXRD. In the as-deposited state, the very diffuse MZF peak indicates that the phase looks more like amorphous. We have

FIGURE 3: Magnetization versus applied magnetic field of an annealed BTO-MZF nanocomposite film along the in-plane (filled circle) and the out-of-plane (square) directions.

varied the deposition temperature from 800 to 850°C, and similar amorphous phase peaks have been found. Further increase of the deposition temperature was limited by our equipment. The peak center of BTO (002) is about 45.3°, very close to that of bulk phase [19]. After the sample was annealed at 1020°C for one hour, a distinct peak appeared at ~42.94°, corresponding to (004) peak of MZF. In addition, the peak intensity of BTO (002) also increased. Pole figure analysis further revealed that both the BTO and MZF phases in the annealed sample were epitaxial (see the inset of Figure 1(b)). However, the large full width at half maximum of peak (FWHM) may indicate either small grain size of MZF or the phase is not completely crystallized. According to [20], generally, very high deposition temperature is needed to grow well-crystalline MZF phase due to a large lattice mismatch between the MZF phase and the STO substrate.

Figure 2 shows the atomic force microscopy (AFM) and magnetic force microscopy (MFM) images of an annealed film at 1020°C for 1 h. The grain size is about 50 nm and the surface is very smooth according to AFM analysis. Figure 2(b) shows clear upward and downward magnetic phase contrasts. Diffuse magnetic domains across tens of grain size can be seen on the MFM image. However, if the sample is magnetized along the out-of-plane direction, isolated magnetic domain structure can be identified by MFM (not shown here). So it is difficult to determine whether the film is 1–3- or 0–3-type nanocomposite from AFM and MFM observation.

We thus performed the magnetization versus applied magnetic field (M-H) measurement of the annealed BTO-MZF film by SQUID along both the in-plane and out-of-plane directions, as shown in Figure 3. Note that the contribution from STO substrate has been deducted and the volume ration of MnZn ferrite phase has been accounted.

FIGURE 4: Polarization versus applied electrical field of an annealed BTO-MZF nanocomposite film, different voltages of 2 V, 4 V, and 6 V were applied.

The measured remanent magnetization along out-of-plane direction is slightly higher than that along in-plane direction. However, the very similar M-H curves indicate that the nanocomposite film has a 0–3 composite structure instead of a 1–3 one. Such 0–3 nanocomposite films have also been reported in BaTiO₃-CoFe₂O₄ film deposited by PLD at a temperature less than 850°C [14, 21]. Bulk MZF generally has a low saturation field, however, the measured saturation field of BTO-MZF is ~2000 Oe, which limits the maximum permeability. This can be partially explained by the large lattice mismatch between MZF and BTO phases. Another reason is that the MZF may not be fully decomposed from BTO matrix even after annealing at 1020°C for one hour. The latter can be confirmed by the measured saturated magnetization, 330 emu/cc, lower than the bulk value of 380 emu/cc [22].

Figure 4 shows the change of polarization as a function of the applied electrical field of the annealed BTO-MZF at a constant frequency of 1 kHz. The apparent asymmetric hysteresis loops along y-axis come from the very different work functions of the top (gold) and the bottom electrode (SrRuO₃) relative to the BTO-MZF film. With increasing the applied field from 10 MV/m (2 V) to 30 MV/cm (6 V), the remanent polarization $2P_r$ increases to 40 $\mu\text{C}/\text{cm}^2$. In order to eliminate the contribution from leakage current, we have further performed the positive-up negative-down (PUND) pulse polarization test, which shows $2P_r$ of 9.68 $\mu\text{C}/\text{cm}^2$.

Finally, we have compared the dielectric constant of the as-deposited and the annealed BTO-MZF in a frequency range from 1 kHz to 1 MHz with an applied ac field of 1 V. The results are shown in Figure 5. High dielectric constant about 300 can be measured in the as-deposited sample at low frequency, but it decreases to only 120 at 1 MHz, apparently because of the leakage current of the sample. After the sample was annealed at 1020°C for one hour, the dielectric constant increases significantly to >150 at 1 MHz. In addition, the

FIGURE 5: The dependence of dielectric constant (filled square) and loss factor (open square) on the frequency of applied ac field, from (a) the as-deposited and (b) the after-annealed BTO-MZF nanocomposite films.

loss factor also reduces for the annealed film in the whole measured frequency range. For a frequency of 1 MHz, the dielectric loss factor is less than 0.05. It is worth noting that BTO-MZF has a 0–3-dimensional embedding structure, so the low resistivity may come from the relatively high volume ratio of the MZF phase. So it is necessary to lower the molar ratio of MZF phase in order to improve the ferroelectric and dielectric properties of the nanocomposite film.

4. Conclusion

In summary, the growth of epitaxial $\text{BaTiO}_3\text{-Mn}_{0.4}\text{Zn}_{0.87}\text{Fe}_2\text{O}_4$ nanocomposite films has been demonstrated by a PLD method at $<850^\circ\text{C}$ in spite of very large lattice mismatch between the two phases. It is shown that postannealing is necessary to promote the decomposition and crystallization of the MnZn ferrite phase from the BTO phase. Structure and magnetic property analysis indicate that BTO-MZF have a 0–3 embedding structure instead of a 1–3 one. Magnetic measurements show that the nanocomposite film has a relatively low permeability due to large strain from both substrate and the BaTiO_3 matrix. It is suggested that reduction of the volume ration of MnZn-ferrite phase is necessary to reduce the leakage current and improve the dependence of dielectric constant on frequency.

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