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Magnetically tunable dielectric, impedance and magnetoelectric response in $MnFe_2O_4/(Pb_{1-x}Sr_x)TiO_3$ composites thin films

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ABSTRACT

We have synthesized piezomagnetic–piezoelectric composites thin films $MnFe_2O_4/(Pb_{1-x}Sr_x)TiO_3$, where x=0.1, 0.2, and 0.3, using the metalorganic deposition (MOD) reaction method. The structural and microstructural analysis using the X-ray diffraction (XRD), AFM, and SEM reveals the presence of homogenous growth of both pervoskite and spinel phases in the composite films. Our results show that all the composites films exhibit good multiferroic as well as considerable magnetoelectric coupling. The impedance (Z' and Z'') and electrical modulus (M' and M'') Nyquist plots show distinct electrical responses with the magnetic field. Our analyses suggest that this electrical response arises due to the coexistence of the high resistive phase and the comparatively conductive phase in the MFO/PST composite films. The maximum magnetoelectric coefficient (α) is found to be 4.29 V Oe^{-1} cm^{-1} and 2.82 V Oe^{-1} cm^{-1} for compositions x=0.1 and 0.2. These values are substantially larger than those reported for bilayer composites thin films in literature and make them interesting for room temperature device applications.

1. Introduction

Magnetoelectric (ME) composites with strong coupling between the ferroelectric and the ferromagnetic phases have attained worldwide attention because of their emergent technological applications [1,2]. The ME phenomena include the voltage-modulated magnetization or magnetic-field-induced polarization and exist in both single-phase and composite thin films [3]. The single phase multiferroics exhibit intrinsic ME coupling which require the co-existence of magnetic-order and electric dipoles with long-range arrangement. However most of the single phase materials have either low polarizations or low magnetizations at room temperature and thus exhibit weak ME coupling, which hinder their applications potential [4,5]. Therefore, the ME composite thin films which composed of layered ferroelectric and ferromagnetic materials are of special interest. In these thin films, the strong ME coupling arises due to its layered structure which result in low leakage current, ease of poling to align the electric dipoles at low electric filed. In addition, the nanostructure of these thin films enhances the bonding between ferromagnetic and ferroelectric phases. The response of magnetoelectric coupling depends on the interface quality (k), thickness of the bottom layer, and functional properties of ferroelectric and ferromagnetic layers [6–8].

Many experimental works have shown that the composite thin films composed of perovskite ferroelectrics such as $BaTiO_3$ and $Pb(Zr,Ti)O_3$ and spinel ferromagnetic materials such as $CoFe_2O_4$ and $NiFe_2O_4$ show good magnetoelectric coupling behavior [9,10]. It is further shown that the microstructure and interface between the magnetic and ferroelectric material have great influence on the multiferroic as well as on the magnetoelectric properties [11,12]. In addition, $MnFeO_4$ (MFO) and $(Pb,Sr)TiO_3$ (PST), which are of particular interest of this study, are good functional materials: PST is a piezoelectric material with piezoelectric coefficient (d) ~90 pm/V and MFO shows magnetostrictive behavior with magnetostriction coefficient (λ) ~-35×10^{-6} [13,14]. Therefore, in the present work, we have selected $MnFe_2O_4$ (MFO) and $(Pb_{1-x}Sr_x)$ TiO_3 (PST) as ferromagnetic and ferroelectric materials, respectively, for our composites thin films.

It has been found in our earlier studies that the composite thin films synthesized using the metal organic deposition (MOD) method show good structural, multiferroic and magnetoelectric properties [15]. The films also have well-developed, homogeneous microstructure and uniform deposition along with the excellent mechanical strength while avoiding the defects which arise due to the combination of two different functional phases. Additionally, the raw materials used for the synthesis are more economical when compared with the other chemical methods such as sol-gel or other chemical solution methods. We have therefore synthesized the $MnFe_2O_4/Pb_{1-x}Sr_xTiO_3$ (MFO/PST) (where,

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x=0.1, 0.2, and 0.3) composite thin films with various Sr concentrations using the MOD method. It is also known that the effect of magnetic field on the AC electrical properties is important for establishing the ME response in the multiferroic thin films [16–18]. In the present work, we have therefore studied the role of magnetic field on the electrical properties of grains, grain boundaries, and electrode interface of the MFO/PST thin films by varying the Sr concentration. The experimental data is analyzed using the Nyquist (Cole-Cole) plot. The capacitance of grain and grain boundaries in various thin films is strongly affected by applied magnetic field. Finally, we have confirmed the strong room temperature ME coupling using the dynamic mode measurement at low Sr concentrations which decreases with increasing Sr concentration.

2. Experimental details

MFO/PST composites thin films with various Sr concentrations were synthesized by the MOD method and deposited on $Pt/TiO_2/SiO_2/Si$ substrates using the spin coating technique. The detailed synthesis process was given elsewhere [15]. X-ray diffraction pattern using X′ Pert PRO with Cu Kα radiation (λ=1.54 Å) was recorded to probe the structural phase and crystallographic orientation of the thin films. Microstructure, surface morphology, and thickness of composite films were measured by using the atomic force microscopy (AFM) with AFM Ntegra, NT-MDT and cross-sectional scanning electron microscopy with Nova Nano. Room temperature in-plane magnetic measurements were done by using a vibrating sample magnetometer (Micro senses EV7-VSM) with magnetic fields up to 15 kOe. For electrical measurements, platinum top electrodes with a diameter of 0.5 mm were deposited on the surface of thin films with a shadow mask by RF sputtering. The room temperature current density and polarization were measured by Keithley source meter 2611 and ferroelectric tester with radiant precision multiferroic system at 13 V, respectively.

The magnetoelectric coupling of MFO/PST films was computed using both the passive (direct) and the active (indirect) characteristic method at the room temperature. We used an in-house built measurement setup where the magnetic field was generated by using two 10 in. pole electromagnets which were capable of producing the constant as well as the AC magnetic fields. A gaussmeter was used to measure the exact value of the bias field produced by the external electromagnet. The AC voltage generated on the sample through the ME effect was measured using a lock-in amplifier (Sigma). In the passive mode measurements, the sample was kept between the poles of an electromagnet with the plane-of-the sample parallel to the magnetic field direction. The superimposed AC magnetic field H_{ac} with amplitude 1 Oe was applied using the Helmholtz coils, collinearly with a sweeping DC magnetic field from 0 to 8000 Oe. The ME coupling parameter α_E was then calculated using the relation $\alpha_E=(\delta E/\delta H)_{dc}=\delta V/(t\times\delta H)$, where '$V_0$' is the ME voltage across the sample and 't' is the thickness of the ferroelectric layer of composite films, as a function of magnetic bias field δH with a constant AC modulation field or as a function of the frequency f of the AC field with an applied constant bias field. The schematic representation of the transverse mode geometry set up was shown in Fig. 1. In the active mode method, we passed a test current through the sample and measured the dielectric and impedance response induced by the magnetic field. The magneto-dielectric and the magnetically tuned complex impedance were measured by using Wayne-Kerr impedance analyzer 6500B (UK) interfaced with a magnetic field in the frequency range 100 Hz–1 MHz at room temperature. We have used only zero and 3 kOe magnetic field for dielectric and impedance measurements instead of more values. In future we will try further, to study the dielectric constant and impedance at different values of dc magnetic field. Moreover, in this, paper we are interested only at with (3 kOe) and without (0 Oe) magnetic field for the study magnetodielectric and magneto-impedance measurements. However, the reason for selection of 3 kOe magnetic field is discussed in below response.

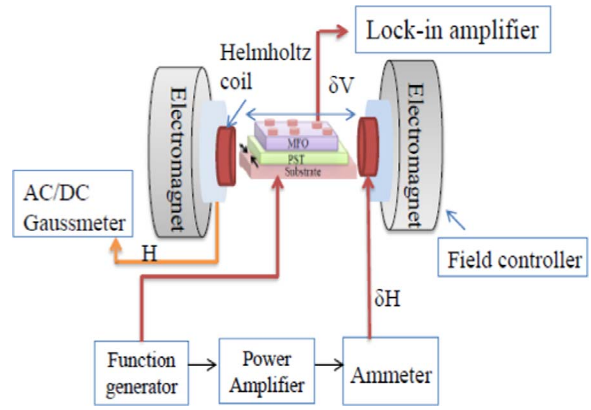

Fig. 1. Schematic diagram of the in-house built magnetoelectric measurement set up.

3. Results and discussion

3.1. Structural and microstructural properties

X-Ray diffraction (XRD) pattern of MFO/PST composites films with various Sr concentrations, shown in Fig. 2(a), clearly shows that thin films consist of both MFO and PST phase without any intermediate and impurity phase. This confirms that all thin films retain original ferroelectric (PST) and ferrite (MFO) phases without any chemical reaction or inter-diffusion among them. The 10% Sr addition in MFO/PST composite films shows (100)/(001) and (110)/(101) doublets that are the characteristics of the tetragonal structure. But 20% and 30% of Sr addition composite films show absence of (001) and (101) diffraction peaks, which is interpreted as formation of a cubic phase. The diffraction patterns of MFO/PST composite films show a peak at 2θ=33°, this is due to Si substrate indexed using the cubic structure (JCPDS No. 79-0613). However, a left shift in the PST (110) and (101) peaks is also observed. The splitting between these peaks decreases with increasing Sr concentration which shows the structural transformation of PST layer from a tetragonal phase to a pseudo-cubic phase. Furthermore, the Sr doping has negligible influence on the MFO layer. The MFO phase starts forming in the as deposited composite films, but the crystallinity and intensity are much lower than those for PST. The XRD patterns detect that there are only two main peaks i.e. (311) and (400) for MFO phase. This may be due to the fact that the average atomic number of MFO is smaller than that of PST and crystallization annealing temperature of PST film is not high enough for MFO to form perfect crystals in composite films [15]. However, higher crystallizations annealing temperature and longer annealing time would accelerate the volatilization of lead in PST phase, potentially deteriorating the ME coupling of the MFO/PST composites film. Hence, in MFO/PST composite films the structure formation for MFO phase confirms by only from these two (311) and (400) peaks.

The calculated lattice parameters and crystallite sizes of various MFO/PST thin films are listed in Table 1 along with the bulk parameters of MFO and PST taken from Refs. [19,20]. It is found that the lattice parameters for PST as well as MFO in the composites films are lower than the bulk value, which shows a compressive strain in MFO/PST films. A quantitative analysis shows that strain varies from −3.44% to −3.71% in MFO layer, whereas it is between −0.12% to −0.79% in PST layer in MFO/PST composites films with different Sr concentrations. The crystallite sizes of phases involved have been calculated from the most intense (101) and (311) diffraction peaks using Debye Scherer formula. The crystallite size values for the PST layer are 15 nm, 13 nm, and 11 nm, while that for MFO layer are 13 nm, 26 nm, and 12 nm, in MFO/PST10, MFO/PST20, and MFO/PST30 composite films, respectively. Furthermore, smaller crystallite/