Magnetoelectric Properties Of $(Pb_{0.60}Sr_{0.40})TiO_3$-CFO Composite Thin Film Synthesized By Metallo-Organic Decomposition

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Abstract. $(Pb_{0.60}Sr_{0.40})$ TiO_3-CFO composite thin films were grown on $Pt/TiO_2/Si$ substrate by novel metallo-Organic process using spin coating technique. The structural, surface morphology and micro structural properties were confirmed by X-Ray diffraction (XRD), Raman spectroscopy, atomic force microscope (AFM) and TEM respectively. The lattice constant of the composite thin film crystallized in the pervoskite and spinel phase was 3.9531 and 8.571 Å. Excellent ferroelectric behavior at 10V was observed, a room temperature magnetic hysteresis shows good results. The saturation magnetization value of the bilayer thin film is lower than that of the pure CFO film which is may be attributed to presence of non ferromagnetic PST layer A high initial behavior of dynamic ME response coefficient for the film was observed. The ME effect of the film strongly depends on the magnetic bias.

Keywords: Spin coating, XRD, AFM, Ferroelectric radiant, VSM.
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INTRODUCTION

The pursuit of multifunctionnality in a single phase or composite materials has lead to a considerable research in developing the multiferroic materials. These materials, mostly artificially synthesized, have coupled electric, magnetic, and/or structural order parameters that result in simultaneous ferromagnetic, ferroelectric, and/or ferroelastic behavior. Due to these novel properties, multiferroic materials offer potential applications in many fields ranging from data storage to spintronic devices to sensors and many others. The magnetoelectric materials posses simultaneous ferroelectric and ferromagnetic properties, which allow both electronic charge and spin to be manipulated by applied electric and magnetic fields [1]. Due to the incompatibility between the conventional cation-off center distortion mechanism, a very few natural multiferroic materials exist and also, it is very hard to find a single material having good ferroelectric and ferromagnetic properties at and above the room temperature. Recently, the composite materials for investigating the multiferroic properties have been extensively studied due to their much stronger magnetoelectric coupling with low leakage problem. These composite materials pave a way for tuning the multiferroic properties through controlling the thin film thickness of desired material [2]. Alternatively, multiferroic composites have been studied both theoretically and experimentally for their several orders of ME magnitude larger than that in the single phases resulting from the effective stress-mediated ME coupling between the piezoelectric and piezomagnetic phases at room temperature [3].

The nanocrystalline ferroelectric -ferrite thin films can be easily fabricated by metallo-organic decomposition (MOD) method which has distinct advantages, such as easy processing steps, stable solution, low cost, controllable morphologies and crystalline sizes.

EXPERIMENTAL DETAILS

PST (bottom layer) and CFO (upper layer) 2-2 type layered composite thin films have been prepared by using lead 2-ethylhexanoate $(C_7H_{15}COO)_2Pb$ with 20% Pb in excess, Strontium 2-ethylhexanoate $(C_7H_{15}COO)_2Sr$, tetra-*n*-butyl orthotitanate, cobalt-2ethylhexanoate $(C_7H_{15}COO)_2Co$ and iron-2ethylhexanoate $(C_7H_{15}COO)_2Fe$ as precursor solutions. The detail about synthesis is described

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elsewhere [4]. The PVA was also added to act as surfactant or as a binder to reduce in volume the cationic spices in divided group during chemical reaction. The coating solutions were prepared by mixing the above precursors in required molar ratio in xylene. The 2-2 type layered films were deposited on $Pt/TiO_2/Si$ substrates by a spin-coating technique at 4300 rpm for 60 s. First of all PST layer was deposited and then dried for 5min at 350^0 C to remove the solvent and organic residue and then finally annealed at 650^0C for 2hr.The process was then repeated to deposit CFO as top layer and annealed at 650^0C for 2hr. The crystalline structure of thin films was examined by X-ray diffraction (X-Pert PRO). Film morphology and surface roughness were investigated by atomic force microscopy (NT-MDT) in the semi contact mode. The microstructures of the 2-2 type layered composite thin films were studied by transmission electron microscopy ((TECNAI-G^2 20 TEM)). Magnetic measurements of the films were performed at room temperature and at low temperature by a (VSM, Micro sense, USA) with at different magnetic field. The ferroelectric measurements were conducted on PST (40)-CFO 2-2 type layered film on substrate in a configuration with two Pt dots with a diameter of 0.5mm deposited on film surface through shadow mask by Pulse laser deposition. Ferroelectric measurements were carried out using Radiant Precision multiferroic tester technology at different voltages. The magnetoelectric signal was determined using a lock in amplifier while small AC magnetic field δH , was in parallel superimposed on a DC bias field H bias to activate the dynamic magnetostriction of the PST-CFO layer. The magneto electric voltage coefficient α_E was defined by $\alpha_E= (dV/t\delta H)$, where t is the thickness of the PST layer.

RESULTS AND DISCUSSIONS

Figure 1(a) shows X-Ray diffraction pattern of PST40 and PST40-CFO bilayer film. The pattern shows that the coexistence of the pervoskite (PST),spinel (CFO) phases with substrate peak. The PST and CFO layers are polycrystalline in nature and without any impurity phases. From XRD we reveled that there is no evidence of chemical reaction and phase diffusion between the PST and CFO layers thus confirm the successful formation of PST-CFO bilayer film. The decrease in lattice parameter for cubic phase in $Pb_{0.60}Sr_{0.40}TiO_3$ -$CoFe_2O_4$ and a low c/a ratio are which may be arise due to its influence of larger stress in the interface between the PST and CFO phases. [Fig 1(b)] From AFM topography, the image clearly indicates that the thin films has a granular morphology being formed densely packed with roughness are listed in table this indicates that film are smooth and polycrystalline in nature with uniform size. The random distributions of the particle with an average grain size 15nm are observed in the film from the AFM result. From the Raman spectra it clearly no extra phase without pervoskite and spinel phase were detect. Figure (b) also shows the HRTEM result conclude that bright and dark fringes for CFO and PST, because in PST heavy element of Pb than that of the CFO, and d- spacing from SAED (selected area electron diffraction pattern) result also coexist with XRD result.

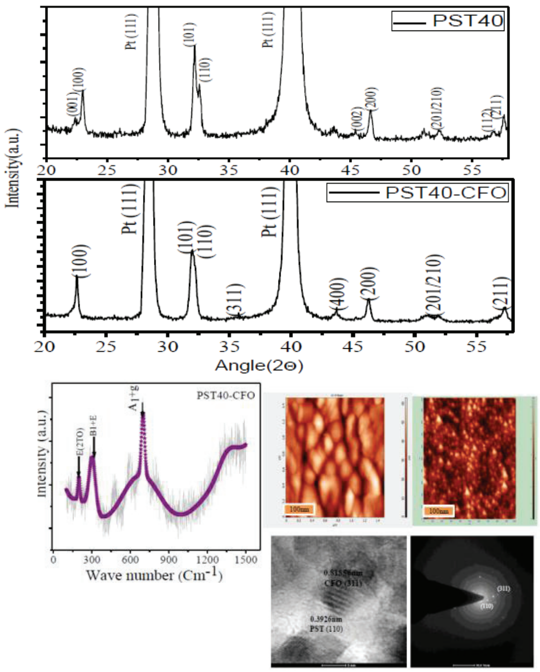

FIGURE 1. (a) XRD pattern of PST and PST40-CFO (b) Raman spectra, AFM and TEM images of CFO, PST40-CFO nanostructure.

Figure 2(a) shows the magnetic hysteresis loop of the PST40-CFO and in the inset for CFO nanocomposite thin film, measured by applying magnetic fields either in plane or out plane to the thin film planes. From this reveled that out –of –plane loop that is much lower saturation magnetization Ms and evidently higher coercivity H_c than in the in-plane hysteresis loop. This may be attributed to the greater stress in the interface between PST and CFO phases in the composite thin films due to the negative magnetostriction value of CFO, so the compressive stress in the CFO phase (with large lattice mismatch between the CFO and PST phases) easy magnetization characteristics because of piezomagnetic effect in composite thin film.

Polarization (P-E) hysteresis loop, for the nanocomposite thin films are shown in figure 2(c) at 10V. Polarization-electric field hysteresis loop in the case of the PST40-CFO on Pt/TiO_2/Si even in the presence of cobalt ferrite upper layer means effective and strong coupling between the PST layer and CFO layer, due to low resistivity of CFO layer this will lead to high magnetoelectric voltage coefficient. The polarization loss can be occurred in a multiferroic material due to leakage current through the capacitor. As the resistance of the capacitor decreases charge loss and hence the gap width increases. But in this case PST40, thin film depict very low leakage current density and loops were almost square (high leakage current results in rounded loop), thus the resistive current may not be the play the role reason for this observation. So the origin of the discontinuity in the hysteresis loop observed here may be due to the polarization relaxation.

Figure 2 (d) also show the behavior magnetoelectric constant with dc magnetic field, the output reaches maximum value 0.0946$VCm^{-1}Oe^{-1}$ at 3000dc magnetic field and then decreases. When we compare the value of magnetoelectric coefficient with Rao Wei and Hong–Cai et al. [5]. We get the dynamic coupling behavior for PST40-CFO Layer (Pervoskite and Spinel Phase) composite thin film. As for the H_{bias} dependence of α_E, it essentially tracks the H_{bias} dependence of the piezomagnetic coupling coefficient $q=\delta\lambda/\delta H_{bias}$ .For most ferrites including $CoFe_2O_4$ once the magnetostriction attains the saturation value, the q decreases and the piezomagnetic coupling gradually becomes weak, resulting in a decrease of the ME effect.

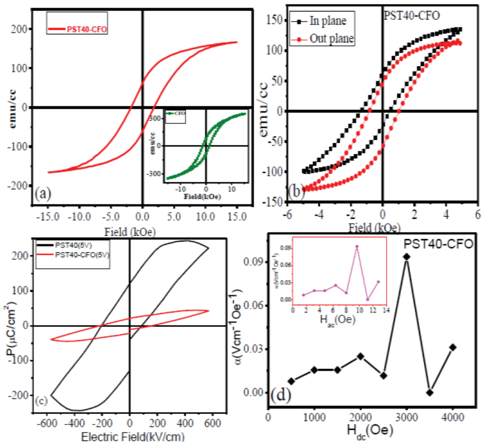

FIGURE 2. (a) MH (b) in-plane and out plane hysteresis curves (c) PE and (d) ME of $Pb_{0.60}Sr_{0.40}TiO_3$-$CoFe_2O_4$ nanostructured bilayer thin

TABLE 1. Characterizations value of PST-CFO bilayer film deposited by using MOD technique.

S. No	Crystallite size	Grain size(AFM)	c/a	Lattice constant	Hc(kOe)	emu/cc	Pmax.(5V)
CFO	26nm	31nm	-	8.2583	1.30	371	-
PST40-CFO	15nm,13nm	24nm	1.0461	8.0056	1.79	187	44.12

CONCULSION

PST-CFO bilayer thin films were grown on Pt coated silicon substrate using MOD method. It was shown in this study that PST-CFO bilayer thin films are crystalline in nature. The resulting bilayered structures possess a granular morphology, are chemically pure and are strong interface between the PST and CFO layers. The magnetic parameter such as M_s and H_c were also measured. The presences of the ferroelectric phase affect the value of M_s and M_r. In Ferroelectric hysteresis curves revels that saturation polarization and remnant polarization were changes at voltage. The films exhibit both good magnetic and electric properties, as well as magnetoelectric effect.

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