Multiferroic Properties of $Pb_{0.90}Sr_{0.10}TiO_3$-$CoFe_2O_4$ Nanostructured Bilayered Thin Film

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Abstract. $Pb_{0.90}Sr_{0.10}TiO_3$-$CoFe_2O_4$(PST10-CFO) nanostructured bilayered thin film were grown on Si (100) substrate by using metallo-organic decomposition chemical route and spin coating technique. Results show that PST (pervoskite structure) and CFO (spinel) phase coexist in the bilayered thin films, annealed at 650^0C for 2hr and no obvious impurity phase can be detected. The structural, surface morphology and micro structural properties were confirmed by X-Ray diffraction (XRD), atomic force microscope (AFM) respectively. Excellent ferroelectric behavior at different voltage was observed, with two platinum electrodes only at surface of the bilayer thin film. A room temperature ferromagnetic behavior was observed in the bilayered $Pb_{0.90}Sr_{0.10}TiO_3$-$CoFe_2O_4$ nanostructured thin film. The saturation magnetization and variation in coercivity value of the bilayer thin film is lower than that of the pure CFO film in the presence of non ferromagnetic PST layer which is the attributed that the significant coupling between the two phases.

INTRODUCTION

In the past few years, multiferroic materials have been considerable investigated due to their potential multifunctional application on transducers, highly sensitive sensors and actuators. These materials simultaneously exhibit ferroelectric and ferromagnetic properties which can be exploited for several device applications. One of the possible geometries in which these phases can be assembled is a horizontal multilayered structure consisting of alternate layers of a pervoksite and spinel material. There are various material ,$CoFe_2O_4$, $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) were studied by Nan and depositing sequence of PZT and CFO films was believed to have noticeable effect on ferroelectric and ferromagnetic properties[1]. Ferroelectric (Pb,Sr)TiO_3 (PST) thin films have been widely studied in past due to their potential applications in various tunable microwave devices. As for then $Pb_{.90}Sr_{10}TiO_3$-CFO bilayer thin films, ionic radius of strontium atom ($112A^0$) which is smaller than that of the ionic radius of lead ($120A^0$), so strontium is easily occupy the interstitial sites of lead atom. On the hand, $CoFe_2O_4$ thin films have attractive applications such as in magnetic recording media and magnetic sensors due to their high permeability, high resistivity and high Curie temperature. Therefore, due to these advantages the bilayer nanostructured of $Pb_{0.90}Sr_{0.10}TiO_3$-$CoFe_2O_4$ is an attractive material to be investigated for its technological application in devices.

In this paper 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. To our knowledge, this is the first example of a system where we get good multiferroic behavior of bilayered thin films by chemical solution using spin coating technique on silicon substrate.

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EXPERIMENTAL DETAILS

PST (bottom layer) and CFO (upper layer) bilayer 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 elsewhere [2]. The coating solutions were prepared by mixing the above precursors in required molar ratio in xylene. The bilayer films were deposited on Si (100) 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 (VECCO DI CP-II) in the semi contact mode. Magnetic measurements of the films were performed at room temperature by a vibrating sample magnetometer (VSM, Microsense, USA) with a magnetic field up to 15 kOe. The ferroelectric measurements were conducted on PST-CFO bilayer film on silicon substrate in a configuration with two Pt electrodes 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 two voltages 5V and 7.

RESULTS AND DISCUSSIONS

Figure 1(a) shows X-Ray diffraction pattern of PST10-CFO bilayer film. The pattern shows that the coexistence of the pervoskite (PST), spinel (CFO) phases with Si 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 PST10-CFO bilayer film on Si substrate. The decrease in lattice parameter for cubic phase in $Pb_{0.90}Sr_{0.10}TiO_3$ -$CoFe_2O_4$ 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. It may due to the thermal expansion mismatch between the PST ($12.0\times10^{-6}K^{-1}$) and silicon substrate ($2.62\times10^{-6}K^{-1}$).There are also various intrinsic and extrinsic reasons behind the strain and stress in the bilayer thin films. [Fig 1(b)] shows AFM image of PST-CFO bilayer films. Surface morphology shows that grain growth or grain size of pure CFO film is larger than that of the $Pb_{0.90}Sr_{0.10}TiO_3$-$CoFe_2O_4$ bilayer thin film. The microstructure is smooth and uniform with average grain size range 27nm. Grain size from AFM is calculated by plotting the histogram between the number of grain and scan scale which is 2micro meter in our case.

[Figure2 (a)] shows P-E hysteresis curves of PST10-CFO bilayer film on Si substrate at polarization voltages 5and 7 volt. Saturation polarization value ($P_{max.}$) is 39.78μC/cm^2 and remnant polarizations (P_r) is 9.4 μC/cm^2 at 5V which significantly increased to and ($P_{max.}$) 59.12 μC/cm^2 and (P_r) 27μC/cm^2 respectively at 7volt [3]. The observed change in polarization hysteresis loop and value in PST/CFO on the Si substrate means effective, strong coupling generate between the ferroelectric insulating PST layer and low resistance of the ferromagnetic CFO layer. Shown in [figure 2(b)] the observed value of Saturation magnetization (Ms) for CFO films is 339emu/cc and for $Pb_{0.90}Sr_{0.10}TiO_3$-$CoFe_2O_4$ bilayer thin film is 249emu/cc.The lower value of M_s for bilayer thin film is presences of nonferromagnetic PST layer. The slight increase in coercivety for $Pb_{0.90}Sr_{0.10}TiO_3$-$CoFe_2O_4$ bilayer is also noticed. This may be attributed to the greater stress in the interface between PST and CFO phases in the bilayer 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 bilayer thin film [4].

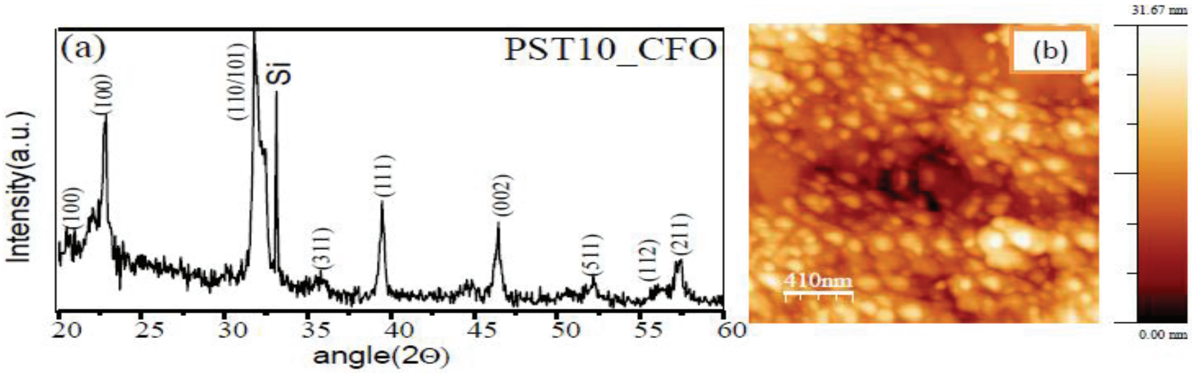

FIGURE 1. (a) XRD pattern of $Pb_{0.90}Sr_{0.10}TiO_3$-$CoFe_2O_4$ and (b) AFM images of $Pb_{0.90}Sr_{0.10}TiO_3$-$CoFe_2O_4$ nanostructured bilayer thin film deposited on silicon substrate, annealed at 650^0 C.

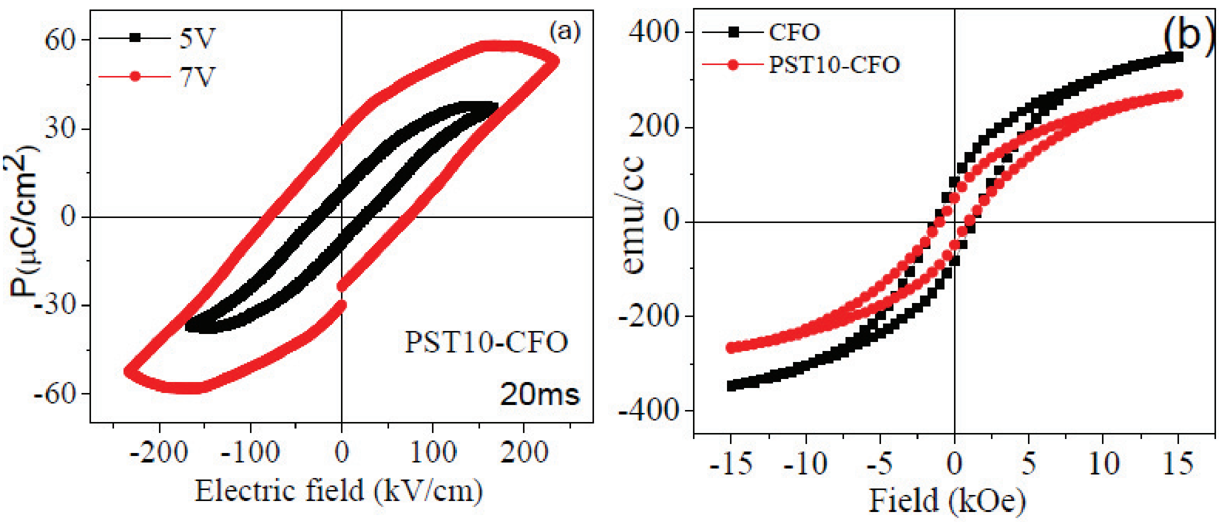

FIGURE 2. (a) PE and (b) MH hysteresis curves of $Pb_{0.90}Sr_{0.10}TiO_3$-$CoFe_2O_4$ nanostructured bilayer thin deposited on Si substrate annealed at 650^0C.

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.(μC/cm^2)
CFO	26nm	-		8.2583	13.75	339	39.78(5V)
PST10-CFO	15nm,13nm	24nm	1.0461	8.0056	15.71	249	59.12(7V)

CONCULSION

PST-CFO bilayer thin films were grown on Si/100 substrate using MOD method. It was shown in this study that PST-CFO bilayer thin films are crystalline in nature. Local aggregation or phase separations of the PST and CFO phase have been observed in the films .The resulting bilayer 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 with voltages.

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