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Invited Paper

Multiferroic Thin Film Composite of $Pb(Zr_{0.52}Ti_{0.48})O_3$ and Co-50%Fe Alloy

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Abstract. *A magnetoelectric composite composed of PZT as a piezoelectric material and Co-50%Fe as a magnetostrictive alloy was produced. The $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) layer was deposited on a magnetic alloy via sol gel spin coating and Pulsed Laser Deposition (PLD) processes. The results show that the sol gel prepared PZT film exhibits a single perovskite phase, but the sample prepared using, the PLD method, is susceptible to creating a pyrochlore phase. The prepared PZT films demonstrated good dielectric properties and have large potential applications in multifunctional devices. Based on acceptable electrical and magnetic properties; ε_r of 894 and magnetostriction coefficient of 70×10^{-6}, it seems that these samples will have also good magnetoelectric properties.*

Keywords: *Multiferroic; PZT; Composite; Magnetoelectric; Thin film.*

INTRODUCTION

Multiferroic material is an interesting category of materials with a coexistence of at least two ferroic orders (ferroelectric, ferromagnetic, or ferroelastic), which have great potential for applications as multifunctional devices. In multiferroic materials, the coupling interaction between the different order parameters could produce new effects, such as a magnetoelectric (ME) effect. The magnetoelectric response is the appearance of an electric polarization, P, upon applying a magnetic field, H (i.e., the direct ME effect, designated as ME_H effect: $P = \alpha H$), and/or the appearance of a magnetization, M, upon applying an electric field, E (i.e., the converse ME effect, or ME_E effect: $M = \alpha E$). A magnetoelectric composite consists of a piezoelectric phase and a magnetic phase. Neither the piezoelectric nor the magnetic phase has the ME effect, but composites of these two phases have a remarkable ME effect. For example, in a direct ME effect, the induced magnetic field results in a strain in the magnetic layer due to the magnetostriction effect, and this strain will transport to a piezoelectric layer via the interface, and so make an electric polarization or electric field due to the piezoelectric effect. ME composites can have technological applications including magnetic field sensors (thus complementing Hall sensors and current measurement probes), transducer, filters, oscillators, phase shifters, memory devices and so on [1-3].

Different kinds of magnetoelectric composites have been fabricated since the first magnetoelectric composite prepared in the Philips laboratory using the unidirectional solidification of a eutectic composite of $BaTiO_3$-$CoFe_2O_4$. Although bulk magnetoelectric composites theoretically have a higher magnetoelectric coefficient, layered composites actually have better magnetoelectric properties due to their resistance to current leakage from the magnetic phase [1].

Different processing techniques have been used to fabricate this class of composite, including unidirectional solidification, conventional ceramic processing, and bonding piezoelectric and magnetostrictive phases by epoxy [1-3]. Various kinds of piezoelectric phase such as $BaTiO_3$ [4], PZT [5] and PMN-PT [6], and magnetic phases like nickel zinc ferrite [7] cobalt ferrite [8] and Ni [9], and the giant magnetostrictive alloy of $Tb_{1-x}Dy_xFe_2$, known as Terefenol-D [10] were used in these composites.

Recently, multiferroic nanocomposite thin films of ferroelectric and magnetic oxides have been produced

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by physical deposition techniques, such as pulsed laser deposition PLD, and chemical solution processing like the sol-gel spin-coating method. However, the mechanical constraint arising from the film on the substrate, and the good bonding between the two phases in nanostructured composite films are the main problems affecting the magnetoelectric coupling interactions [11].

In this work, we produce a multiferroic thin film composite via a sol gel spin coating and the pulsed laser deposition of PZT on a magnetic alloy of Co-Fe. These processing techniques are fairly simple and it is easy to produce thin film composites from nanometric to micrometric thickness. Furthermore, in this case, there is no mechanical constraint from the substrate, because the substrate is a magnetostrictive material and thus we expect the composite to show good magnetoelectric properties without the clamping effect due to the substrate.

EXPERIMENTAL PROCEDURE

Common starting materials for the sol-gel preparation of PZT composition include: lead acetate trihydrate ($Pb(CH_3COO)_2.3H_2O$) (Merck), zirconium propoxide ($Zr(OC_3H_7)_4$) (Fluka), titanium isopropoxide ($Ti(OC_3H_7)_4$) (Merck), 2-metoxyethanol ($CH_3OCH_2CH_2OH$) (Merck), formamide (Merck), and acetylacetone (Merck), which are used in this research. For preparation of PZT sol, lead acetate trihydrate with an excess of 15% to the stoikiometri composition was dissolved in 50 ml of solvent, 2-methoxyethnaol. Then, distilling was done in a 0.2 bar vacuum to remove the solvent and chemical water from the lead acetate. The lead acetate was dissolved in 50 ml of solvent and stirred at 90°C for 1 hr; this solution was used as the lead precursor. Zirconium propoxide and titanium isopropoxide were dissolved in 2-methoxyethnaol. Acetylaceton was added to the solution as the chelating agent to stabilize the sol. Finally, the zirconium and titanium precursor was added to the lead precursor solution to achieve the desired molar ratio (Pb:Zr:Ti=1.15:0.52:0.48). In order to achieve better homogeneity, the solution was refluxed for 4 h at 120°C and formamide was added as a crack inhibitor agent. Finally, the distilling was done in a 0.3 bar vacuum to reduce the amount of solvent. The concentration of the final sol was 0.5 M.

The PZT suspension for the hybrid sol gel method was prepared by mixing 15 g PZT sol with 1.5 g submicron PZT powder (PZ27 from Ferroperm) and 0.11 g acetyl acetone by an attrition mill at 180 rpm speed for 1 hr. PZT sol and suspension layers were coated onto a 100 μm thickness Co-50%Fe magnetic alloy with the commercial name of VACODUR 50 by a spin coater in the speed range of 1000 to 3000 rpm. After coating, each layer was dried at two stages on a hotplate at 130°C and 350°C for 3 and 4 minutes, respectively. Finally, annealing was done at 650°C for 30 min. For the samples prepared by the Pulsed Laser Deposition (PLD) method, a KrF excimer laser (248 nm) was used. The details of the deposition condition for the PLD are listed in Table 1.

Table 1. Deposition conditions of the PZT thin film prepared by PLD.

Parameters	Values
Target diameter	1 in.
Substrate target distance	15 cm
Substrate (heater) temperature	650°C
Base vacuum	2×10^{-7} Torr
O_2 pressure	2×10^{-3} Torr
Laser source	KrF excimer
Laser energy used	250 mJ/pulse
Repetition rate	5 Hz
Deposition time	60 min

Au conductive contacts were deposited on the PZT surface of the samples by the sputtering method. The crystallinity and phase identification of the samples were performed on a Bruker Advance D8 X-ray diffractometer using Cu Kα as the radiation source and Ni as the filter. The surface quality and thickness of the PZT layers were determined by a field emission scanning electron microscope (FESEM), XL30-FEG. AFM analysis was performed by a Veeco multimode atomic force microscope. Electrical properties, such as permittivity and loss factor, were measured by an ARMA ALC-850 LCR meter, using the magnetic substrate as the bottom electrode and 200 μm Au dots as the top electrodes. Magnetic hysteresis loops of the sample were measured by the Lakeshore 7404 VSM system.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the PZT layers under three different conditions of processing. In Figure 1a, the XRD pattern of the sample prepared using the PLD method, shows a weak peak of the pyrochlore phase. The formation of pyrochlore in this case is due to the evaporation of lead oxide from the surface, due to low oxygen partial pressure in the PLD chamber. EXAD analysis shows that the lead evaporation causes a decreasing in lead content in the $Pb(Zr_{0.52}Ti_{0.48})O_3$ composition from the stoichiometric value of 63.6 wt% to 47.1 wt%. Figure 1b is the XRD pattern of the sample, prepared using 4 layers of spin coated sol on the substrate. The thickness of the PZT layer is about 200 nm, which contains a mixture

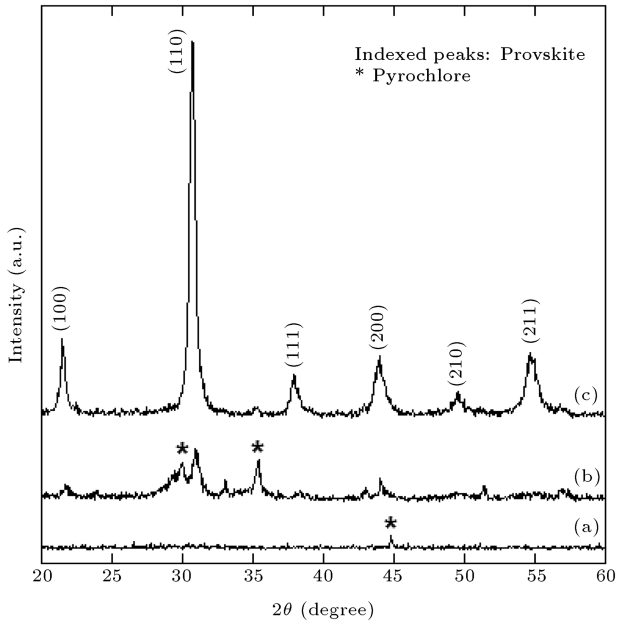

Figure 1. XRD patterns of PZT layers a) prepared by PLD method, b) prepared using PZT sol, and c) prepared using PZT suspension.

of perovskite and pyrochlore phases. Figure 1c shows the XRD pattern of the sample prepared by deposition of 2 PZT suspension layers and 5 sol layers with an approximate total thickness of 2.25 μm. This sample shows a fully perovskite structure. There is no evidence of undesirable pyrochlore phase peaks in this sample. Thus, by using the hybrid method, we can achieve a thicker PZT film with higher quality, compared to the normal sol gel method.

SEM micrographs of the samples are illustrated in Figures 2. Figure 2a shows a dense microstructure with no crack, prepared from PZT sol. There are some microcracks in the sample prepared by the hybrid method using PZT suspension, as illustrated in Figure 2b. In contrast with samples prepared via the sol gel route, the sample prepared by the PLD method is fully dense with a smooth and crack free surface (Figure 2c). Figure 3 shows a typical AFM image of the film surface prepared by the PLD method; the root-means-square of the surface roughness is about 2.7 nm, which is very smooth.

Although SEM micrographs reveal that the sample prepared using PZT sol has a better surface quality than the hybrid method, the sample prepared using PZT suspension shows better electrical properties, including ε_r and tanδ; 894 and 0.12, respectively. The sample constructed using PZT sol had poor electrical properties of ε_r and tanδ; 240 and 2.58, respectively. These results can be justified, based on the ferroelectric domain size effect on electrical properties [12]. Based on this theory, there is a critical grain size of 1 μm for optimum ferroelectric domain size; lower grain

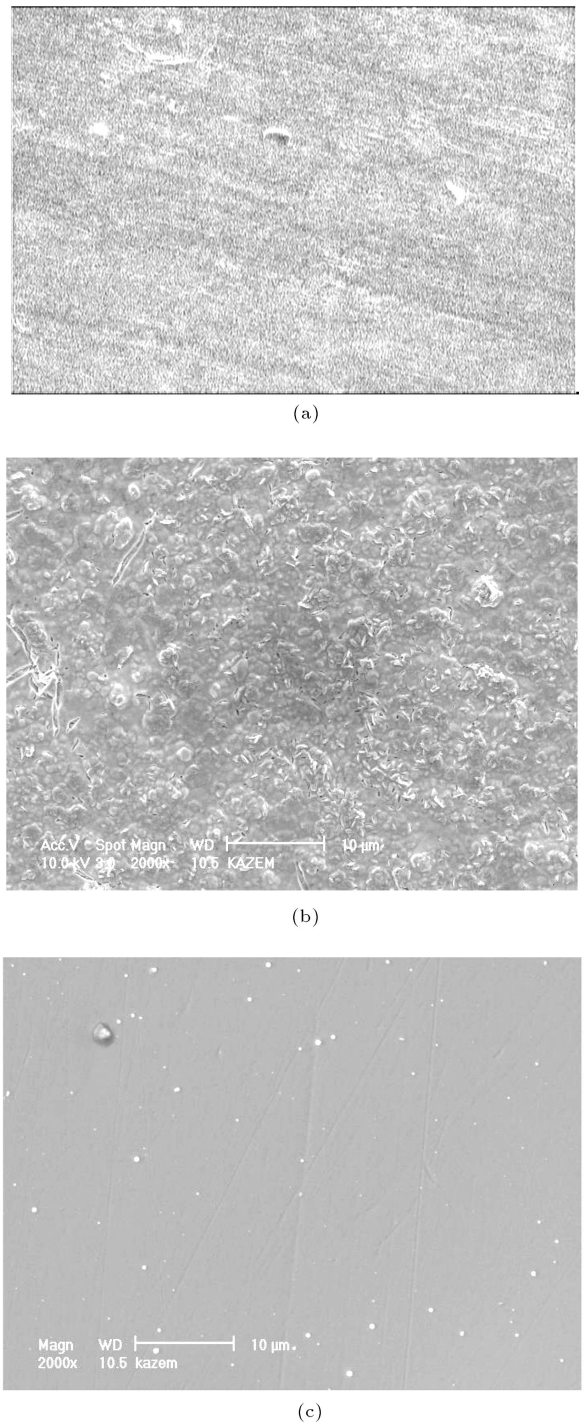

Figure 2. SEM micrographs of PZT film prepared via a) sol gel method using PZT sol, b) using PZT suspension and c) PLD method.

size leads to smaller domain size and this will cause a decline in electrical properties. Furthermore, the PZT powder used in the suspension was soft PZT powder that could relieve domain wall switching, and so enhance electrical properties. Figure 4 show the capacitance change via the frequency sweep for the sample prepared via the hybrid sol gel route. At high

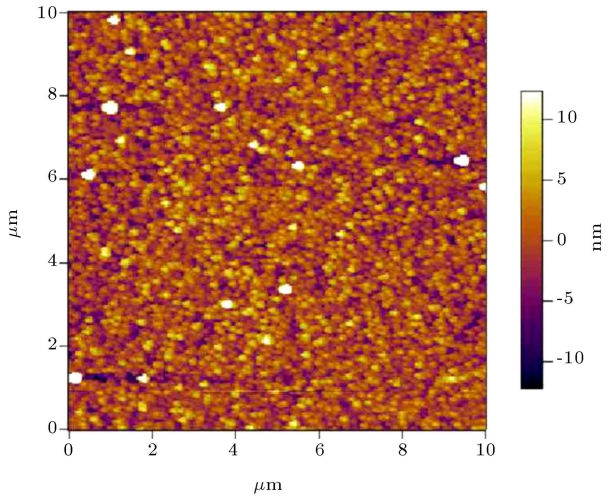

Figure 3. A typical AFM image of the PZT film prepared by PLD method.

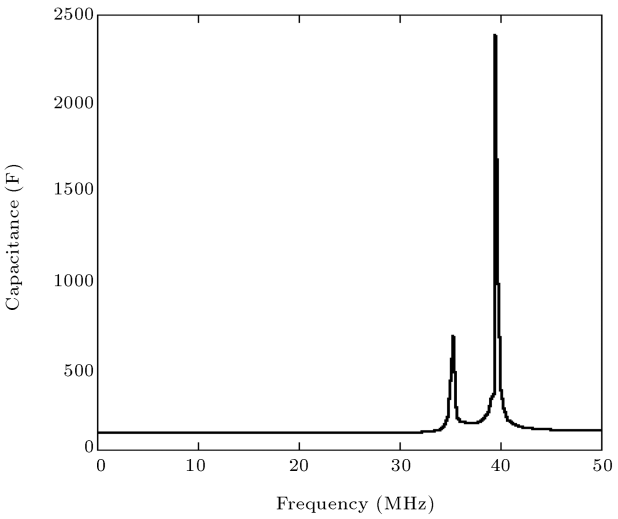

Figure 4. Capacitance of the PZT film at high frequencies.

frequency, the capacitance of the sample shows two resonances due to the change of polarization mechanisms in the sample, which is followed by a peak in loss factor almost at the same frequency illustrated in Figure 5, in which the change of loss factor with frequency is illustrated. The resonance frequencies of these samples are higher than the resonance frequency of bulk PZT. This is due to the thin thickness of the PZT layer and substrate effects, such as the magnetoelectric effect induced by the magnetostrictive substrate.

Figure 6 shows the magnetic hysteresis of Co-50%Fe alloy that is measured by VSM. The magnetic properties are $H_c \leq 2.0$ (A/cm), $\mu_{\max}$ and λ_s, 7000 and 70×10^{-6}, respectively. We expect better magnetic properties in comparison with cases where a ferrite is used as a magnetic material [8] in this category of composites. Furthermore the Curie temperature

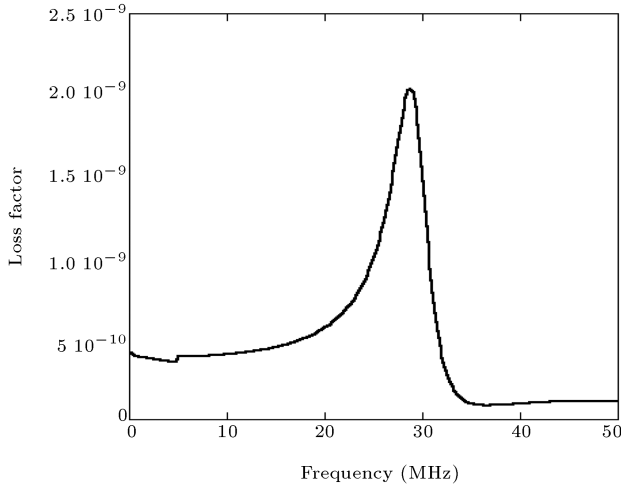

Figure 5. Loss factor of the PZT film at high frequencies.

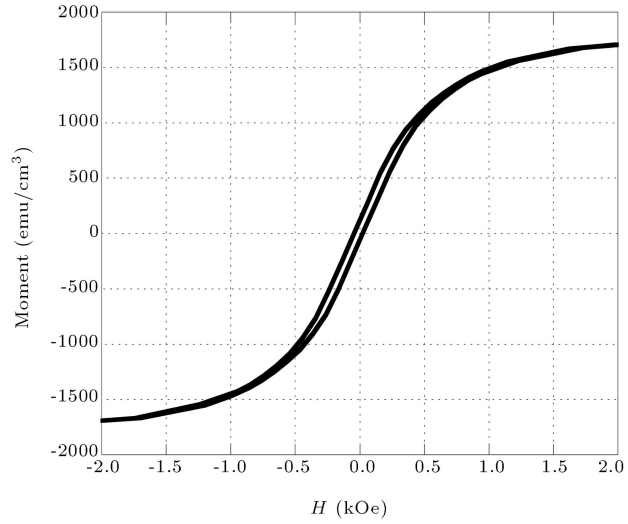

Figure 6. Magnetic hysteresis loop of Co-50%Fe alloy.

for Co-50%Fe alloy is 950°C; therefore, the alloy kept its ferromagnetic property during the firing process, as our maximum firing temperature was 650°C. Due to the good electrical and magnetic properties of the composite, it can be predicted to have acceptable magnetoelectric properties in this composite.

CONCLUSION

A multiferroic composite of PZT and Co-50%Fe magnetic alloy was prepared successfully by sol-gel spin coating and the PLD process with a layer thickness ranging from a hundred nanometres to several micrometers. Although the microstructure of the PLD prepared sample is crack free and smoother, it is more difficult to get a single perovskite phase. The electrical properties of the PZT thin film prepared by the sol gel method, ε_r and $\tan\delta$, were 890 and 0.12, respectively. The magnetostriction coefficient of the sublayer is

70×10^{-6}. Furthermore, in this case, the substrate is also a magnetic phase and bottom electrode, thus there is no constrain from the substrate, and the strain will directly transfer from the magnetostrictive layer to the piezoelectric layer, which leads to enhanced magnetoelectric phenomena.

REFERENCES

1. Nana, C.W., Bichurin, M.I., Dongb, S., Viehland, D. and Srinivasan, G. "Multiferroic magnetoelectric composites: Historical perspective, status, and future directions", *J. of App. Phys.*, **103**, 031101 (2008).
2. Priya, S., Islam, R., Dong, S. and Viehland, D. "Recent advancements in magnetoelectric particulate and laminate composites", *J. Electroceram*, **19**, pp. 147-164 (2007).
3. Bichurin, M.I., Viehland, D. and Srinivasan, G. "Magnetoelectric interactions in ferromagnetic-piezoelectric layered structures: Phenomena and devices", *J. Electroceram*, **19**, pp. 243-250 (2007).
4. Cao, H., Zhang, N. and Wei, J. "Doping effect on crystal structure of $BaTiO_3$ and magnetoelectric coupling of layered composites $Tb_{1-x}Dy_xFe_{2-y}$-$BaTi_{0.99}M_{0.01}O_{3+\delta}$", *Journal of Alloys and Compounds*, **472**, pp. 257-261 (2009).
5. Shi, Z., Ma, J. and Nana, C.W. "A new magnetoelectric resonance mode in bilayer structure composite of PZT layer and Terfenol-D/epoxy layer", *J. Electroceram*, **21**, pp. 390-393 (2007).
6. Dorr, K., Thiele, C., Bilani, O., Herklotz, A. and Schultz, L. "Dynamic strain in magnetic films on piezoelectric crystals", *Journal of Magnetism and Magnetic Materials*, **310**, pp. 1182-1184 (2007).
7. Srinivasana, G., Laletsinb, V.M., Hayesa, R. and Puddubnaya, N. "Giant magnetoelectric effects in layered composites of nickel zinc ferrite and lead zirconate titanate", *Solid State Communications*, **124**, pp. 373-378 (2002).
8. Weng, L., Fu, Y., Song, S., Tangb, J. and Li, J. "Synthesis of lead zirconate titanate-cobalt ferrite magnetoelectric particulate composites via an ethylenediaminetetraacetic acid-citrate gel process", *Scripta Materialia*, **56**, pp. 465-468 (2007).
9. Chashin, D.V., Fetisov, Y.K., Tafintseva, E.V. and Srinivasan, G. "Magnetoelectric effects in layered samples of lead zirconium titanate and nickel films", *Solid State Communications*, **148**, pp. 55-58 (2008).
10. Zhou, J.P., Zhao, W., Guo, Y.Y., Liu, P. and Zhang, H.W. "Magnetoelectric coupling in small $Pb(Zr,Ti)O_3$/terfenol-D laminate composites", *J. of App. Phys.*, **105**, 063913 (2009).
11. Palkar, V.R., Ganesh Kumara, K. and Malik, S.K. "Observation of room-temperature magnetoelectric coupling in pulsed-laser-deposited $Bi_{0.6}Tb_{0.3}La_{0.1}FeO_3$ thin films", *App. Phys. Let.*, **84**, pp. 2856-2858 (2004).
12. Damjanovic, D. "Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics", *Rep. Prog. Phys.*, **61**, pp. 1267-1324 (1998).

BIOGRAPHIES

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