Fabrication and Properties of $SmFe_2$-PZT Magnetoelectric Thin Films

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ABSTRACT

Magnetoelectric (ME) thin film composites are attracting a continually increasing interest due to their unique features and potential applications in multifunctional microdevices and integrated units such as sensors, actuators and energy harvesting modules. By combining piezoelectric and highly magnetostrictive thin films, the potentialities of these materials increase. In this paper we report the fabrication of $SmFe_2$ and PZT thin films and the investigation of their properties. First of all, a ~ 400 nm thin SmFe film was deposited on top of Si/SiO_2 substrate by magnetron sputter deposition. Afterwards, a 140 nm Pt bottom electrode was sputtered on top of the SmFe film forming a bottom electrode. Spin coating was employed for the deposition of the 150 nm thin PZT layer. A PZT solution with 10 %Pb excess was utilized for this fabrication step. Finally, circular Pt top electrodes were sputtered as top electrodes. This paper focuses on the microstructure of the individual films characterized by X-Ray diffractometer (XRD) and scanning electron microscopy (SEM). A piezoelectric evaluation system, aixPES, with TF2000E analyzer component was used for the electric hysteresis measurements of PZT thin films and a vibrating sample magnetometer (VSM) was employed for the magnetic characterization of the SmFe. The developed thin films and the fabricated double layer SmFe-PZT exhibit both good ferromagnetic and piezoelectric responses which predict a promising ME composite structure. The quantitative chemical composition of the samples was confirmed by energy dispersive spectroscopy (EDX).

Keywords: magnetoelectric materials, multiferroics, magnetostriction

1. INTRODUCTION

The constant strive towards device miniaturization stimulates much scientific and technological interest in combining magnetic and electric properties into multifunctional materials. This way, single devices could potentially serve as multifunctional ones, reducing the volume of the system. The presented research mainly focuses on the development of such materials. Specifically, magnetoelectric (ME) materials are suitable for such applications and can offer revolutionary device designs. They are based on the ME effect which is primarily defined as the phenomenon of generating magnetization by applying an electric field or polarization by applying a magnetic field. This effect can occur in single phase materials but most of them generally do not exhibit strong coupling at room temperature. Single phase ME materials are the ones that possess at least two of the "ferroic" properties, such as ferroelectricity, ferromagnetism or ferroelasticity [1- 2.] Yet, the ME effect obtained in composites, multiphase materials composed of different phases such as composites consisting of piezoelectric and magnetostrictive materials, is larger than that of single-phase ME materials by up to several orders of magnitude[1-5].

ME composite thin films are attracting a continually increasing interest compared to bulk composites due to their unique features and potential applications in multifunctional microdevices and integrated units such as sensors, actuators, electric field-controlled magnetic data storage and energy harvesting modules. However, most of the attempts up to now to design such composites, which combine excellent ferromagnetic and ferroelectric properties with a high ME coefficient, have proven to be unexpectedly difficult. This is mostly due to technological challenges during fabrication e.g. controlling the chemical stoichiometry of the multiple phases, eliminating impurities, avoiding interdiffusion between the different phases. Thus, a key aim of the authors is to overcome these challenges and achieve the development of such thin film materials. Specifically, by combining piezoelectric and highly magnetostrictive materials, the potentialities of these composites can increase[3].

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Smart Sensors, Actuators, and MEMS VI, edited by Ulrich Schmid, José Luis Sánchez de Rojas Aldavero, Monika Leester-Schaedel, Proc. of SPIE Vol. 8763, 87630G · © 2013 SPIE
CCC code: 0277-786X/13/$18 · doi: 10.1117/12.2016769

In this paper, the combination of piezoelectric materials with rare earth-iron alloys in order to enhance the ME effect is reported. Such alloys e.g. $TbFe_2$ and $SmFe_2$ exhibit large magnetostriction at room temperature. However, due to the exceptionally high material cost of Tb, $SmFe_2$ is considered to be a good solution for a broader range of applications. In the case of thin films, rare earth-transition metal compounds are considered to be amorphous thus expected to exhibit soft magnetic properties since magnetocrystalline anisotropy is absent. We describe the results of the investigations of the properties of PZT and $SmFe_2$ thin films and their correlation with the deposition conditions.

1.1 Magnetoelectric Effect

The magnetoelectric effect (ME) represents the generation of magnetization by an electric field or the generation of polarization by a magnetic field. The first observation of the ME effect, received great scientific and technological interest due to the exciting potentials of the coupling between the magnetic and electric properties of matter. Yet several obstacles, such as the restricted number of compounds displaying it and the difficulties in developing useful applications, hindered the evolution of this research field. Recently the interest in the ME effect intensely revived due to the impressive advances in micro and nanotechnology.

The ME effect can either be classified as "direct ME effect" or as "converse ME effect"[6-7]. Specifically, when electric polarization is caused by the application of a magnetic field the effect is called direct and when magnetization is caused by the application of an electric field then the effect is called converse[8]. The direct ME effect is generally characterized by the magnetoelectric voltage coefficient[9]:

$$\alpha_E = \frac{\partial E}{\partial H} \ (\mathrm{Vm^{-1}Oe^{-1}}) \tag{1}$$

Similarly, the converse ME effect is characterized by the converse coefficient:

$$\beta_M = \frac{dH}{dE} \ (\mathrm{OemV^{-1}}) \tag{2}$$

where E and H are the electric and magnetic field respectively.

2. EXPERIMENTAL

2.1 Design

When a magnetic field is applied on ME composites the magnetostrictive phase induces a strain in terms of a shape change or a change in the material's dimensions, which in turn exerts stress on the piezoelectric phase, resulting in an electric polarization and the generation of a voltage. Basically, the ME effect in composite materials is a result of the product of the magnetostrictive effect in the magnetic phase and a result of the piezoelectric effect in the piezoelectric phase. It is a coupled electrical and magnetic phenomenon through elastic interaction which means that the ME effect in composites is extrinsic. It depends on the microstructure of the composite and the coupling interaction across the magnetic and piezoelectric interfaces. Most of the recent research activities involving thin films are devoted to oxide compounds (e.g. consisting of Ni or Co ferrites)[5].

In this research we investigated new types of materials. Rare earth-iron alloys in the Laves phase as mentioned in the introduction (e.g. $TbFe_2$ or $SmFe_2$) are excellent candidates for the ME composite thin films[3]. Specifically, they are the most widely used giant magnetostrictive alloys and they exhibit a much higher magnetostriction (over 2000 ppm) than the magnetic oxides mentioned above. Therefore, the composites of these alloys with piezoelectric materials such as lead zirconate titanate (PZT) and aluminum nitride (AlN) are expected to have a large ME response. Fig. 1 shows the design of the developed ME composite consisting of a SmFe and PZT layer.

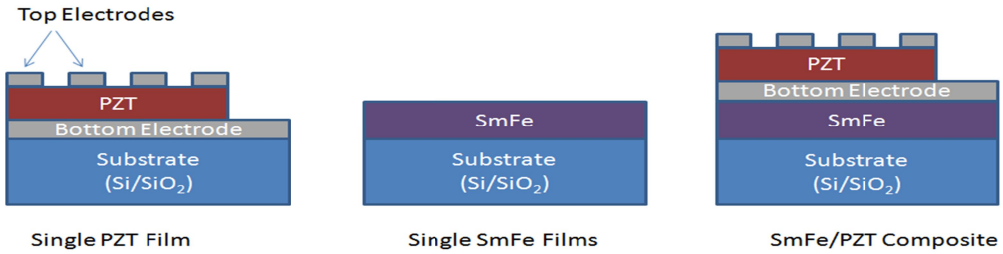

Figure 1. Designof the individual thin film layers and the ME composite in the form of a double layer thin film.

2.2 Thin Film Fabrication & Characterization

Compared to bulk ME composites, ME composite thin films have unique advantages. They provide more degrees of freedom regarding the modification of the ME behavior. They can be designed and fabricated by combining different phases at the atomic-level as well as by precisely controlling the lattice matching. This assists the deeper understanding of the ME coupling at the atomic scale[10]. In order to achieve these advantages, it is essential to prepare the ME composite thin films with high quality.

Initially, single PZT thin films were fabricated and investigated. First of all, a 20 nm Ti layer was sputtered on a Si/SiO_2 substrate forming an adhesion layer for the 140 nm Pt bottom electrode which was consequently sputtered. The wafers were cut in pieces of dimensions 10×5 mm^2 by an automated dicing tool. Prior to thin film deposition they were cleaned using acetone and IPA each for 5 min in an ultrasonic bath.

Standard sol-gel deposition technique was employed for the deposition of the 150 nm thin PZT layer. A Pb $(Zr_{0.52}Ti_{0.48})O_3$ solution with 10 % Pb excess was utilized for this fabrication step. The solution was dispended through a 0.2 μm filter and spun at 3000 rpm. A prebake step at 300°C followed for 10 min for each layer; the process was repeated three times to achieve the desired thickness. The PZT film was then annealed for crystallization at 650 °C for 30 min under air using a tube furnace. For the electrical characterization, circular top Pt electrodes with diameters of 0.2 μm and 0.4 μm were sputtered through a shadow mask. Ferroelectric hysteresis was then measured using a piezoelectric evaluation system, aixPES, with TF2000E analyzer component.

For SmFe thin film investigations a Sm (99.95 % purity) target and a Fe (99.95 % purity) target both disks of 2″ in diameter, were placed at a distance of 14 cm away from the Si substrate. The film deposition was carried out in an aluminium vacuum chamber with $P = 9 \times 10^{-8}$ mTorr. The chamber was evacuated using a turbo-molecular pump supported by a mechanical rotary pump.

Different deposition conditions such as substrate temperature and deposition power were tested in order to obtain the optimum conditions for the deposition of uniform SmFe thin films with the desired atomic composition. Table 1 summarizes the main growth parameters of some of the developed samples which were chosen for further investigation. The deposition time was 30 min and the Ar pressure was kept at 5 mTorr. The thickness of the developed thin films was measured using a Profilometer and their surface was observed by Scanning Electron Microscopy (SEM). It was shown from these experiments that doubling the power during DC sputter deposition of Fe, at room temperature yielded uniform 400 nm thin layers. Additionally, the deposition temperature appeared to influence the surface of the thin films which was rougher when the substrate was heated. Thus, it was decided to continue with sample A for the investigation of the effect of Ar pressure during deposition in the microstructure and atomic composition of SmFe. Table 2 summarizes these experiments.

Table 1. Main growth parameters for SmFe samples selected for further investigation; T_d: deposition temperature, τ: thickness.

ID Sample	Sm & Fe Power (W)		DC/RF	T_d °C	τ (nm)
A	Sm	100	RF	27	400
	Fe	200	DC		
B	Sm	100	RF	200	425
	Fe	200	DC		

C	Sm	100	RF	27	170
	Fe	100	DC		
D	Sm	100	RF	300	330
	Fe	100	DC		

Table 2. Main growth parameters for Sample A selected for further investigation; T_d: deposition temperature, t_d: deposition time, P: Argon pressure, τ: thickness.

ID Sample	T_d (°C)	td (min)	P (mTorr)	τ (nm)
A1	27	30	1	300
A2	27	30	5	400
A3	27	30	10	450
A4	27	30	15	460
A5	27	30	20	260
A6	27	30	25	230

The structural characterization of the PZT and SmFe thin films was performed by XRD (X-Ray Diffraction) using Cu-Kα radiation and the quantitative chemical composition of all samples was measured by Energy Dispersive Spectroscopy (EDX). A Vibrating Sample Magnetometer (VSM) was used to measure the magnetic properties of the developed SmFe films before and after annealing. All the measurements were taken at room temperature with an externally applied magnetic field of up to 1 T.

3. RESULTS AND DISCUSSION

Fig. 2 shows the XRD pattern of the fabricated PZT thin films confirming the formation of a tetragonal along with a rhombohedral perovsite structure. Fig. 3 plots the ferroelectric hysteresis loop of the PZT thin films measured at room temperature at differenct applied voltages.

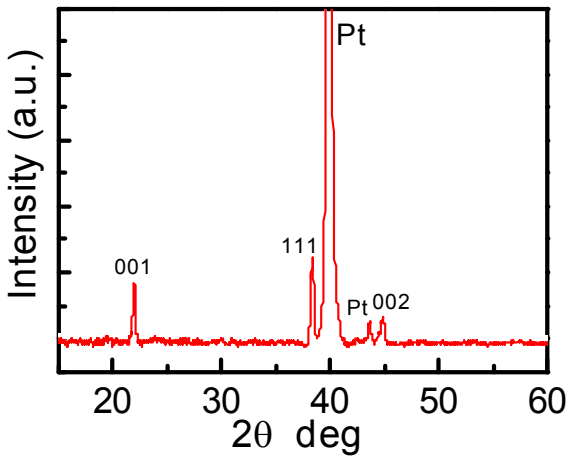

Figure 2. XRD Spectrum for PZT film showing perovskite peaks.

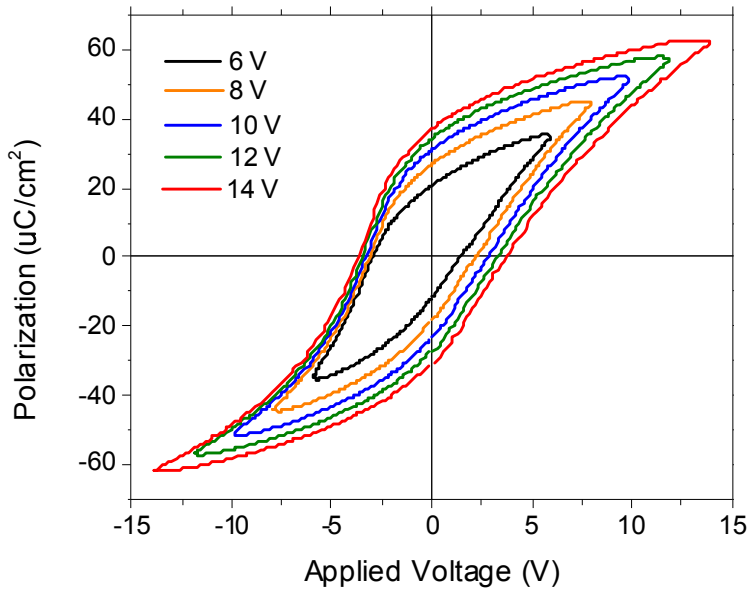

Figure 3. Measured ferroelectric polarization hysteresis loop.

Regarding the characterization of the SmFe thin films we began by indicating the composition dependence of the film on the Ar deposition pressure and on the magnetic properties. XRD results indicated that for Sm contents of 13 at% and above (as measured by the EDX) the thin films were amorphous and no clear peaks were observed. However for sample A5 with a Sm content of approximately 11 at%, where portions of Sm atoms have been oxidized to Sm_2O_3, a weak $SmFe_2$ (220) phase and an unidentified phase are detected. Fig. 4 shows the magnetic hysteresis loops for the samples of Table 2 measured with the applied field parallel to the planes of the SmFe films, which were deposited at room temperature with different Ar gas pressure.

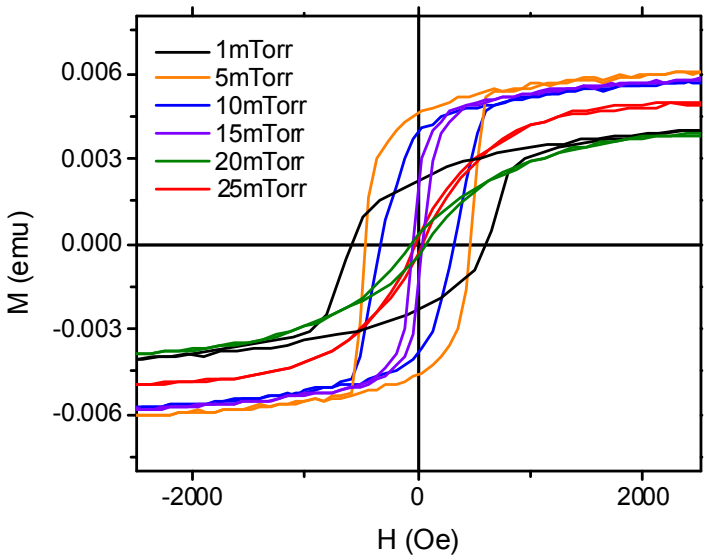

Figure 4. Magnetization curves of SmFe thin films show a clear dependence on the Ar deposition pressure.

Fig. 5 shows the dependence of the SmFe thin film thickness for the samples of Table 2 on the Ar gas pressure. It is obvious that the thickness of the thin film increases with increasing Ar pressure up to 15 mTorr and then it suddenly decreases once the Ar pressure is further increased beyond 15mTorr (sample A5 and A6).

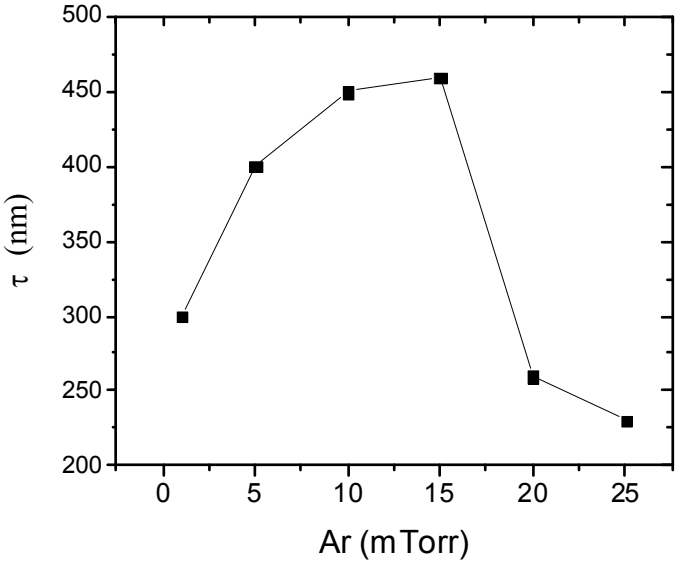

Figure 5. Dependence of the SmFe thin film thickness on the Ar gas pressure.

Additionally it was observed as shown in Fig. 6 that at an input power of 100 W for Sm RF deposition and 200 W for Fe DC deposition there is a clear decrease in coercivity as the Ar pressure increases up to 15 mTorr but at 20 mTorr there is again an increase in coercivity (sample A5). This could be due to the presence of new phases and the pinning effect precipitates to the domain walls and causes the coercivity to increase. In addition, the growth of nanograins of α-Fe could cause an increase in coercivity according to [11]. Due to this observations sample A5 was further investigated after annealing at 300°C for 60 minutes inside a furnace under Ar atmosphere and slowly cooled down to room temperature. The temperature was measured using a thermocouple connected to the substrate holder.

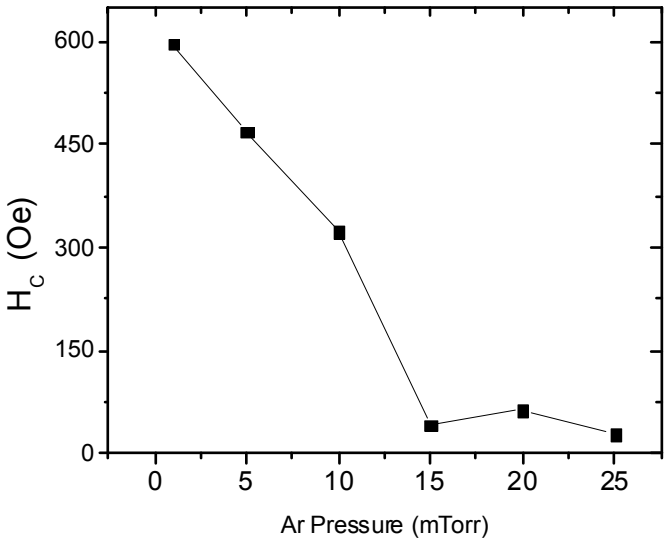

Figure 6. Dependence of the coercive field on the Ar gas pressure.

Fig. 7 shows the magnetic hysteresis loop of sample A5 after annealing. It is observed that the easy magnetization direction rotates from in-plane to out of plance and the coercivity after annealing decreases from 63,8 Oe to 29,8 Oe. This could be because of the release of stress in the film. It is also noted that the hysteresis loop contains a so-called "knee". This shape is believed to be related with the presence of an α-Fe and could be caused by the combination of two magnetic phases in one sample.

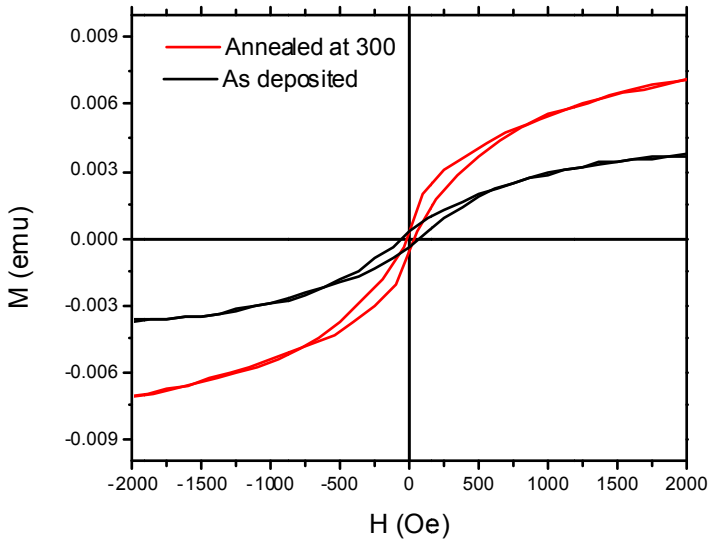

Figure 7. Magnetic hysteresis loop of sample A5 annealed at 300 °C.

Out of the other samples, sample A1 shows the closest SmFe film composition to the desired Laves phase $SmFe_2$. The film composition as analyzed by EDS shows a composition of $Sm_{32}Fe_{56}$ at%. Fig. 8 shows the EDS spectrum of sample A1 that was deposited at 1 mTorr of Ar along with a SEM surface image of the thin film. This sample also shows interesting magnetic hysteresis after annealing at 300°C. The coercivity is much reduced and the film magnetic easy access becomes in plane. Fig. 9 clearly shows this observation.

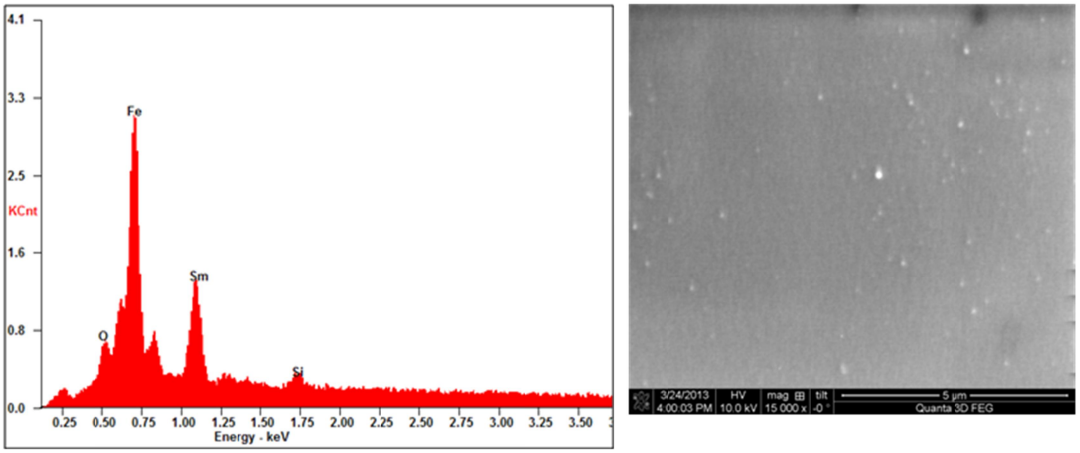

Figure 8. EDS spectrum analysis of sample A1 (left) and SEM image of the thin film surface (right).

Based on these interesting results, sample A1 and A5 were chosen to make the double layer with the PZT. The double layer stack became as $Si/SiO_2/SmFe/Pt/PZT/Pt$ (as shown in Fig.1). These two double layer samples were examined for structural characterization with XRD. In addition, they were tested for both ferroelectricity and magnetic hysteresis. Fig. 10 shows an XRD spectrum of sample A1/PZT double layer. Clearly, peaks for PZT, Sm_2O_3 and Pt were detected. The double layer still exhibits a well-defined polarization curve as shown in Fig. 11. VSM also shows the existence of a magnetic order through the magnetization curve which is not far from the original SmFe sample A1 single film.

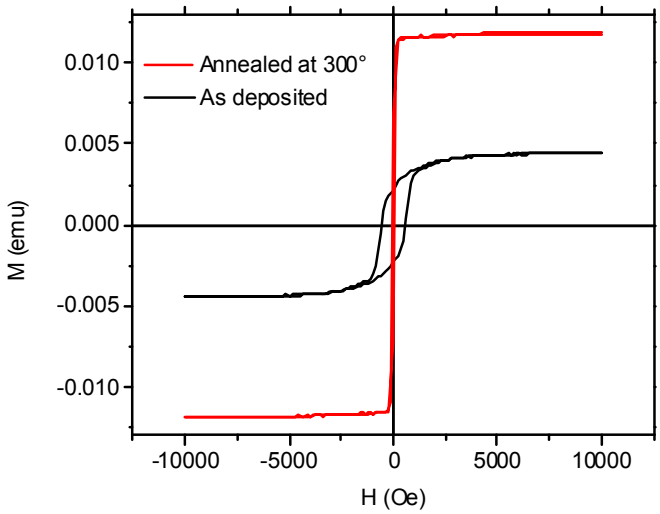

Figure 9. Magnetic hysteresis loop of sample A1 annealed at 300 °C.

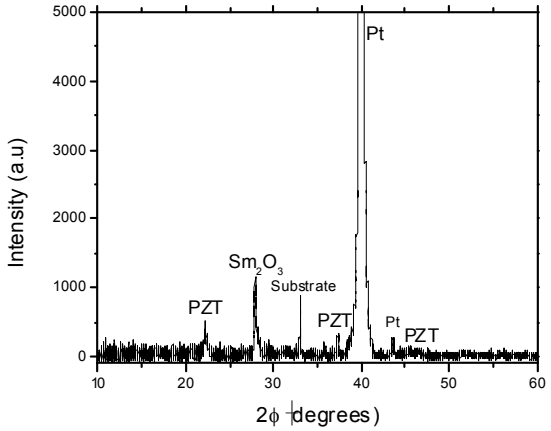

Figure 10. XRD spectrum of double layer SmFe/PZT.

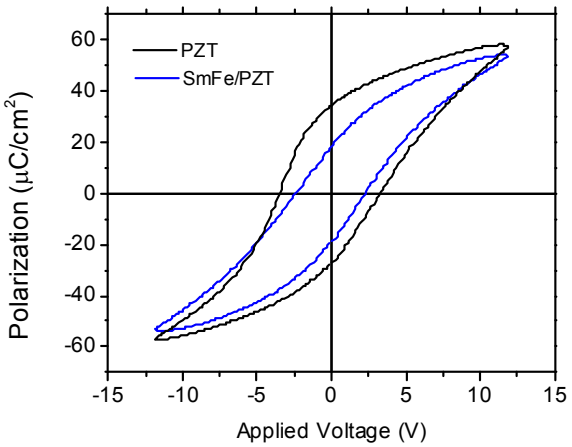

Figure 11. Polarization hysteresis of SmFe(A1)/PZT double layer compared to single PZT layer.

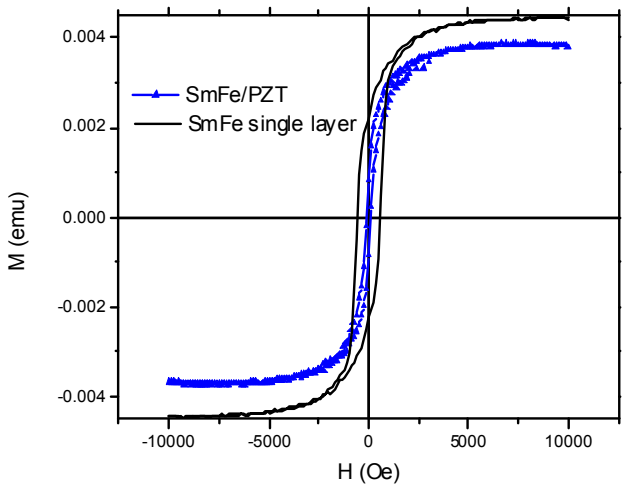

Figure 12. Magnetic hysteresis of SmFe(A1)/PZT double layer compared to the same SmFe samaple A1 single SmFe layer

4. CONCLUSIONS

In summary, we have prepared by spin coating and co-sputtering ME thin films, consisting of PZT and SmFe, with a thickness of several nanometers deposited onto a Si/SiO_2substrate. It was revealed that the deposition conditions affect the microstructure of the SmFe samples and hence influence the coupling between the magnetostrictive and piezoelectric phases in the ME composites. The SEM observation confirmed that the layers are crack-free. The PZT layer possesses promising ferroelectric properties and the SmFe layer promising magnetic properties. The coexistence of both ferroelectric and magnetic hysteresis in the fabricated double layers of SmFe/PZT makes it a promising ME thin film composite worth investigating.

The magnetoelectric effect is currently under investigation. The variation of the ME coefficient is being determined by the electric field generated in the film under an AC driving magnetic field of 15Oe (generated by a solenoid) superimposed onto a DC magnetic bias field of up to 1.5 kOe (generated by an electromagnet).

REFERENCES

[1] K. F. Wang, J.-M. Liu, Z. F. Ren, Multiferroicity: the coupling between magnetic and polarization orders, Adv. in Phys. 58, 321-448 (2009).

[2] Davis, A. R., Bush, C., Harvey, J. C. and Foley, M. F., "Fresnel lenses in rear projection displays," SID Int. Symp. Digest Tech. Papers 32(1), 934-937 (2001).

[3] C. W. Nan, M. I. Bichurin, S. X. Dong, D. Viehland, G. Srinivasan, Multiferroic magnetoelectric composites: Historical perspective, status, and future directions, J. Appl. Phys.103, 031101 (2008)

[4] H. Greve, E. Woltermann, H. J. Quenzer, B. Wagner,E. Quandt, Giant magnetoelectric coefficients in (Fe90Co10)78Si12B10-AlN thin film composites, Appl. Phys. Lett. 96, 182501 (2010)

[5] M. Fiebig, N.A. Spaldin, Current trends of the magnetoelectric effect, Eur. Phys. J. B 71, 293–297 (2009)

[6] W. Eerenstein, M. Wioral, J. L. Prieto, J. F. Scott, N. D. Mathur, Giant sharp and persistent converse magnetoelectric effects in multiferroic epitaxial heterostructures, Nature Materials 6, 348 – 351; doi:10.1038/nmat1886 (2007)

[7] 11. S. Y. Chen, Q. Y. Ye, W. Miao, D. H. Wang, J. G. Wan, J.-M. Liu, Y. W. Du,Z. G. Huang, S. Q. Zhou, Direct and converse magnetoelectric effects in Ni43Mn41Co5Sn11/Pb(Zr,Ti)O3 laminate, Journal of Applied Physics, vol. 107, 09D901 (2010)

[8] Yao Wang, Jiamian Hu, Yuanhua Lin and Ce-Wen Nan, Multiferroic magnetoelectric composite nanostructures, NPG Asia Mater. 2(2) 61–68; doi: 10.1038/asiamat.2010.32 (2010)

[9] P. Record, C. Popov, J. Fletcher, E. Abraham, Z. Huang, H. Chang, R. W. Whatmore, Direct and converse magnetoelectric effect in laminate bonded Terfenol-D-PZT composites, Sensors and Actuators B, 126, 344-349 (2007)
[10] Jing Ma, Jiamian Hu, Zheng Li, Ce-Wen Nan, Recent Progress in multiferroic magnetoelectric composites: from bulk to thin films, Adv. Mater. 23, 1062-1087; doi: 10.1002/adma.201003636 (2011)
[11] G. Herzer, Scipta metal, Materi. 33, 1741 (1995)