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Lead free heterogeneous multilayers with giant magneto electric coupling for microelectronics/microelectromechanical systems applications

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Lead free magneto electrics with a strong sub resonant (broad frequency range) magneto electric coupling coefficient (MECC) is the goal of the day which can revolutionise the microelectronics and microelectromechanical systems (MEMS) industry. We report giant resonant MECC in lead free nanograined Barium Titanate–CoFe (Alloy)-Barium Titanate [BTO-CoFe-BTO] sandwiched thin films. The resonant MECC values obtained here are the highest values recorded in thin films/multilayers. Sub-resonant MECC values are quite comparable to the highest MECC reported in 2-2 layered structures. MECC got enhanced by two orders at a low frequency resonance. The results show the potential of these thin films for transducer, magnetic field assisted energy harvesters, switching devices, and storage applications. Some possible device integration techniques are also discussed. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4818411]

INTRODUCTION

Research on multiferroic as well as magneto-electric materials is being conducted worldwide owing to their vast application potential in novel functional devices.[1,2] Composites with magnetic and piezo/ferroelectric individual phases are thought to be superior to single phasic multiferroic materials because of their strong magnetoelectric (ME) response compared to the very weak ME response usually observed in single-phasic multiferroic counterparts at room temperature.[3] Currently, the optimization of the ME coupling by tailoring properties of the two individual components of ME composites, the piezoelectric (PE) and magnetostrictive, is underway in different international laboratories.[4–9] Most of the investigations reporting a giant ME coupling employed bulk composites and were fabricated by either gluing the individual components to each other or mixing the magnetic material to a piezoelectric matrix. The most extensively investigated material combinations are lead zirconate titanate (PZT) or lead magnesium niobate-lead titanate (PMN-PT) as the piezoelectric, and terfenol-D as the magnetostrictive phase, and the coupling is measured in different configurations like transverse, longitudinal, and in-plane longitudinal.[4] Hence, fabrication of a lead free multiferroic composite with a strong ME response is the need of the hour from an industrial application point of view. Also, the multilayer structure is expected to be far superior to bulk composites in terms of ME coupling since the PE layer can easily be poled electrically to enhance the piezoelectricity and the ME effect.[10]

The ME effect of composite materials is a product tensor property.[11] Giant ME voltage coefficients in the range of 5.9 to 30.8 V/(cm Oe) were reported in bulk or 3-1 composites.[5–9] The ME output is increased by one to two orders of magnitude if the structures are driven in mechanical resonance, and the resonance frequency was in the range from tens to hundreds of kilohertz.[9,12] Although giant coupling was reported in terfenol-D based ME composites, the dc biasing magnetic field was relatively high, of the order of 400–500 Oe. Hence, a material with saturation magnetostriction in low applied dc magnetic fields is sought after for applications, as such a composite can deliver high ME outputs at low dc applied magnetic fields, which makes them cost effective and light.

Magnetic alloys are soft magnetic materials, with majority of them having square loop characteristics ($M_r/M_s \sim 1$) with high permeability, whose saturation magnetization and coercivity can be tuned by alloy composition and annealing process and have huge application potential.[13,14] Dong *et al.*[15] reported an extremely high ME voltage coefficient of 22 V/(cm Oe) at 1 Hz and about 500 V/(cm Oe) at resonance frequency 22 kHz for a 2–1 Metglas/PZT-fiber composite. Zhai *et al.*[16] reported a giant ME coupling in a composite with highly permeable Metglas ribbon that was glued on a polyvinylidene fluoride foil with a high piezoelectric voltage coefficient. In this composite, a ME coefficient of 7.2 V/(cm Oe) at 1 kHz and of 310 V/(cm Oe) at resonance at around 50 kHz (Ref. 16) was recorded. The 2-2 type horizontal heterostructures are easier to be fabricated when compared to the 3-1 type composites. This configuration overcomes the leakage problem as the ferroelectric layers shut off the circuit which could lead to a visible ME effect. However, low-frequency resonant 2-2 thin films are highly recommended for applications in magnetoencephalography and magnetocardiography.[17] A remarkably strong ME coupling was reported by Greve *et al.*[17] in thin film ME 2-2 structures consisting of AlN and amorphous $(Fe_{90}Co_{10})_{78}Si_{12}B_{10}$ layers with a thickness higher than several micrometers. In these thin film heterostructures, a ME

[a)]Authors to whom correspondence should be addressed. Electronic addresses: swapna.s.nair@gmail.com and mraiyer@gmail.com coupling of 3.1 V/(cm Oe) was obtained at out of resonance frequency (100 Hz) and 700 V/cm at resonance (753 Hz). However, the coupling coefficient dropped substantially at biasing magnetic fields above 20 Oe.[17] Duong and Groessinger[18] in 2007 reported that microstructure of the ferroelectric and ferromagnetic layers of ME composites also plays an important role in deciding the ME effects.

Authors in this investigation synthesized magnetoelectric 2-2 layers based on BTO-CoFe-BTO sandwich structures. Barium titanate exhibits good ferroelectric and piezoelectric properties at and above room temperature along with excellent mechanical and chemical stabilities.[19] Cobalt rich magnetic alloys are an important class of materials as they are well known for their high initial permeability, and the magnetic field needed for the saturation of magnetostriction is much lower than that in ferrites and other ferromagnetic metals. However, a high magnetostriction is also a desired quality of a magnetic material to be chosen in magneto electric systems, for obtaining a higher magneto electric coupling coefficient (MECC). Hence, a soft magnetic alloy of the form Co-Fe is employed here. A sandwiched structure is opted so as to reduce the substrate clamping effect for the CoFe-BTO layer owing to another BTO layer deposited close to the substrate.

EXPERIMENTAL SECTION

Preparation of BTO-CoFe-BTO multilayer

BTO layers were synthesized by sol-gel spin coating technique by employing barium acetate, and titanium isopropoxide dissolved in 2-methoxy ethanol. The sol was homogenized after thorough stirring for 6 h and subjected to subsequent ultrasonification and ageing for 72 h. The sol was deposited on chemically and ultrasonically cleaned substrates at a speed of 6000 rpm in a programmable spin coater. The film was pyrolyzed at 250 °C for 30 min and finally annealed at 700 °C for 1 h under oxygen atmosphere. Commercially available CoFe alloy ribbon (cobalt rich) was deposited onto the formed BTO layer by physical vapour deposition technique (at room temperature) at a pressure of 10^{-6} Torr. Another BTO layer was deposited on top of the CoFe films by sol-gel spin coating following the procedure described above. The top BTO layer passivates the CoFe alloy layer from oxidation.

A $Si/SiO_2/Ti/Pt$ substrate was employed in the present work as such a substrate is a common selection, as far as integration with ferroelectrics is concerned.[20] Miniaturization and integration with silicon technology are essential for device applications. Hence, thin films on silicon based substrates are often preferred to their thick films/layered counterparts. Multilayers of BTO-CoFe-BTO were deposited on a $Si/SiO_2/Ti/Pt$ substrate. Thin films were etched at the corner with 5%HCl + HF solution so as to open the Pt electrode. Gold was sputtered on top of the surface BTO layer, and lead contacts were soldered for the ME coupling studies. Scheme 1 shows the concept of sandwich structure prepared for ME coupling measurement.

X-Ray diffraction (XRD) along with transmission electron microscopy (TEM), atomic force microscopy (AFM), scanning electron microscopy (SEM), and energy dispersive spectrometry (EDS) measurements were used for the structural, microstructural, surface, and elemental characterizations. Cross sectional SEM was used to determine the thickness of the multilayer. Magnetic and ferroelectric hysteresis loops were used for the magnetic and ferroelectric characterizations. Magneto electric coupling measurements were used to determine the MECC.

Magnetoelectric coupling measurements

The ME coupling was measured in a setup that consists of an electromagnet and a pair of Helmholtz coils that generate the dc bias field and the ac modulating field, respectively, extended with a lock-in amplifier (Model: DSP 7270). The frequency dependence was studied at 18 Oe dc magnetic field, ∼10 Oe ac modulating field. The data acquisition was automated by LabVIEW. The off-resonant MECC was determined at room temperature as a function of the biasing dc magnetic field by measuring the ME voltage developed when a low frequency (500 Hz) magnetic field with an amplitude of ∼10 Oe was applied to the thin film cantilevers. The low modulation frequency of 250 Hz was chosen as the starting frequency to avoid contributions from resonance effects. Frequencies less than 250 Hz was not applied in order to avoid the interfacial polarization effects and high losses usually present at very low frequencies. Frequency dependence was studied from 250 Hz to 10 kHz range. (As the measurement range is only 1 order, i.e., 0.25 kHz-10 kHz, the ac modulating field remains almost constant.) The MECC was measured at 100 kHz by readjusting the current so as to maintain the ac modulating field at 10 Oe.

RESULTS AND DISCUSSION

Figure 1 shows representative XRD, TEM, AFM, and EDX results of individual BTO and CoFe layers. The XRD

SCHEME 1. Schematic of the prepared sandwiched multiferroic structure for magneto electric coupling studies.

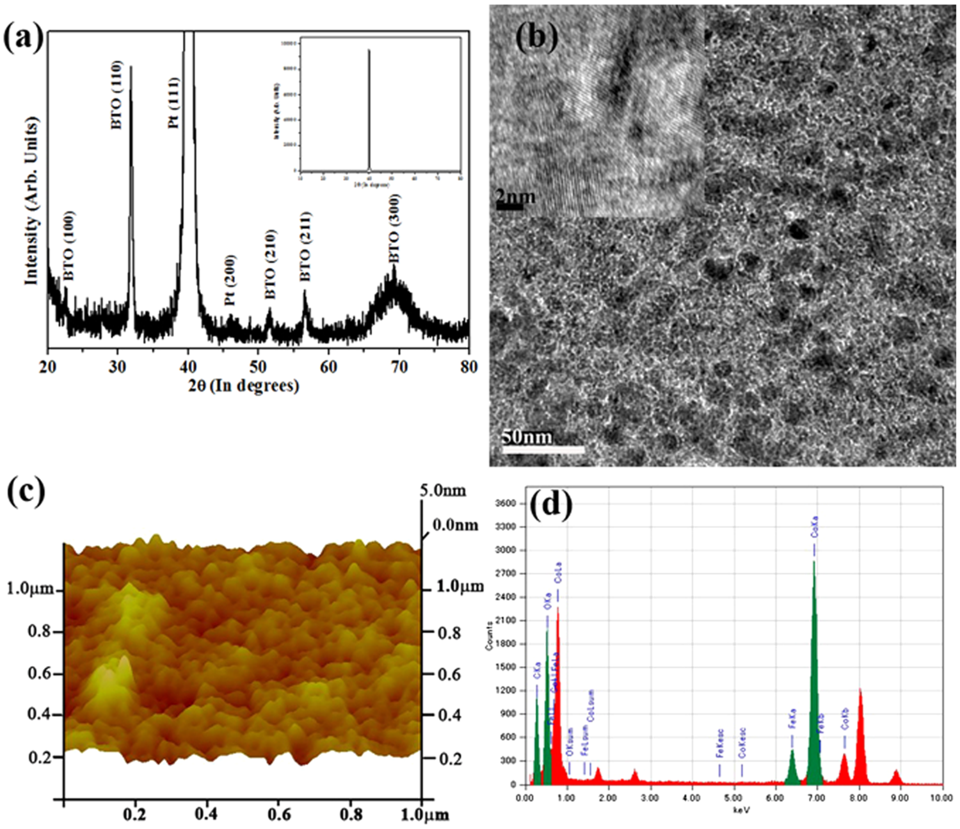


FIG. 1. (a) XRD 2θ scan for BTO thin film on platinum coated Si substrate. (b) TEM (HRTEM image of CoFe film is shown in the inset), (c) AFM image, and (d) EDS spectrum of the CoFe layer.

pattern is indicative of the perovskite structure of BTO thin films. The diffraction peaks are broad which point to the formation of small crystallites in the film upon annealing at 700 °C. The average crystallite size obtained as ~39 nm using Scherrer formula by taking account of the peak broadening at (110) diffraction line.[21]

Thermal annealing of the multilayer after deposition of BTO and CoFe layer initiates the formation of nanocrystallites in the CoFe layer with grain size of the order of 4–5 nm which is clearly visible in Figure 1(b). Inset of Figure 1(b) shows the HRTEM of CoFe alloy (recorded before the deposition of the surface BTO layer). (110) plane of CoFe is identified in the HRTEM. The grain size evaluation of CoFe alloy becomes relevant in understanding the magnetic and magnetostrictive properties of this alloy, as there are size induced properties and magnetostriction is often observed to be higher for nanoparticles than their bulk sized counterparts.[22] The statistical analysis of the topographical image recorded using AFM was carried out and the roughness of the film was found to be ~1.2 nm. Figure 1(d) gives the elemental analysis and semi quantification using EDX of the CoFe alloy layer coated over NaCl substrates. It shows that the alloy has the composition of Co 77% and Fe 23%. X-Ray photoelectron spectroscopic analysis again confirms the composition (XPS analysis can be found as supplementary data in Ref. 30). The elemental composition analysis is quite important as this determines the magnetic and magnetostrictive properties which are the major properties affecting the magneto electric coupling.

Figure 2(a) shows the surface SEM of the sandwiched structure, BTO-CoFe-BTO. The figure depicts the SEM of the annealed BTO film on the top. It shows uniform grain growth with low surface roughness. It is to be noted that although authors used an inexpensive technique of sol gel spin coating, that has not affected the surface quality of these thin films. From the surface morphology, the approximate grain size is around 35–40 nm, which is an order higher than the nanocrystallite size of the middle magnetic alloy layer.

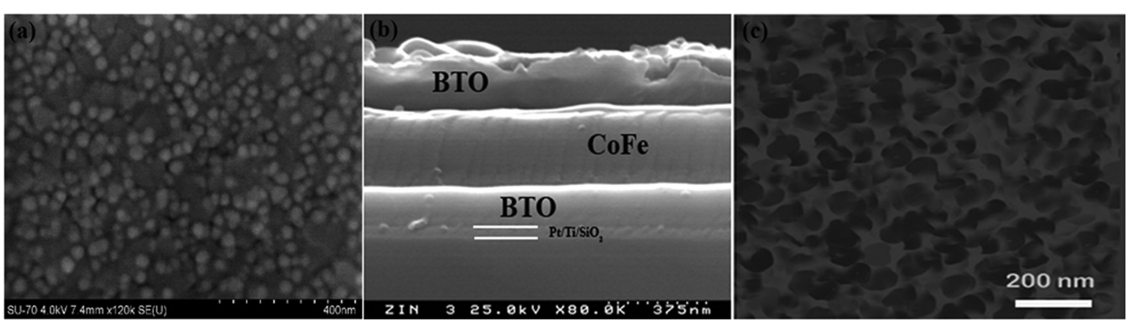


FIG. 2. (a) Top and (b) cross-section SEM images and (c) TEM image of BTO-CoFe-BTO multilayer films on Pt/Ti/SiO_2/Si substrate.

This is in agreement with the grain size obtained from XRD. The sandwiched structures were probed through SEM to observe the cross-sectional view in order to determine the thickness of the sandwiched structure as well as the individual layers. Cross sectional SEM images of the obtained BTO-CoFe-BTO 2-2 sandwiched layers are provided in Figure 2(b). From the micrograph, it can be concluded that the BTO-CoFe-BTO layers had a thickness of ~150, 260, 150 nm, respectively. The thickness of the BTO layer is kept high in order to avoid any possible electrical short circuit created on the evaporation of middle (CoFe layer) and top (Au top electrode) metal layers. Figure 2(c) shows the TEM image of the top BTO layer. This again confirms that the average grain size of barium titanate formed is around 40 nm.

Magnetic hysteresis loop in Figure 3(a) shows that the saturation magnetisation is very high (1175 emu/cc). A very high squareness ratio ($M_r/M_s = 0.9$) and low coercivity (~88 Oe) are retained in the CoFe alloy deposited by a cost effective method of physical vapour deposition. Normally, owing to different individual evaporation rate of the constituents, it is difficult to maintain the exact alloy composition that is there in the target material. Figure 3(b) represents a well defined ferroelectric hysteresis loop with a saturation polarization, $P_S \approx 6.7\ \mu C/cm^2$, and a remnant polarization $P_r \approx 3.3\ \mu C/cm^2$. The electric coercive field was 6.1 kV/cm. The reported P_S value for a good single crystal is 25 $\mu C/cm^2$ and for ceramics is around 19 $\mu C/cm^2$.[23,24] The nanosize of the crystallites in the film causes a decrease in values of P_s and P_r when compared to the bulk values.[25]

Magnetoelectric coupling measurement was performed in the passive mode (direct mode is the magneto capacitance measurements) in order to avoid the erroneous contributions from magneto resistance and interfacial polarizations. In order to avoid contributions from other static and stray signals, ME coupling studies were first performed over plane Si/SiO_2/Ti/Pt substrates followed by the BTO coated Si/SiO_2/Ti/Pt substrates. The obtained signal was provided as the reference signal for subtraction.

Dc magnetic field dependence was studied both in longitudinal and transverse modes. Maximum ME coupling of 5.503 V/(cm Oe) (transverse) and 3.115 V/(cm Oe) longitudinal) was recorded at a dc biasing field of 18 Oe at 500 Hz as depicted in Figure 3(c). The frequency dependence of the ME coupling at a dc magnetic field of 18 Oe shows that there is a sharp resonance at 975 Hz with a giant MECC

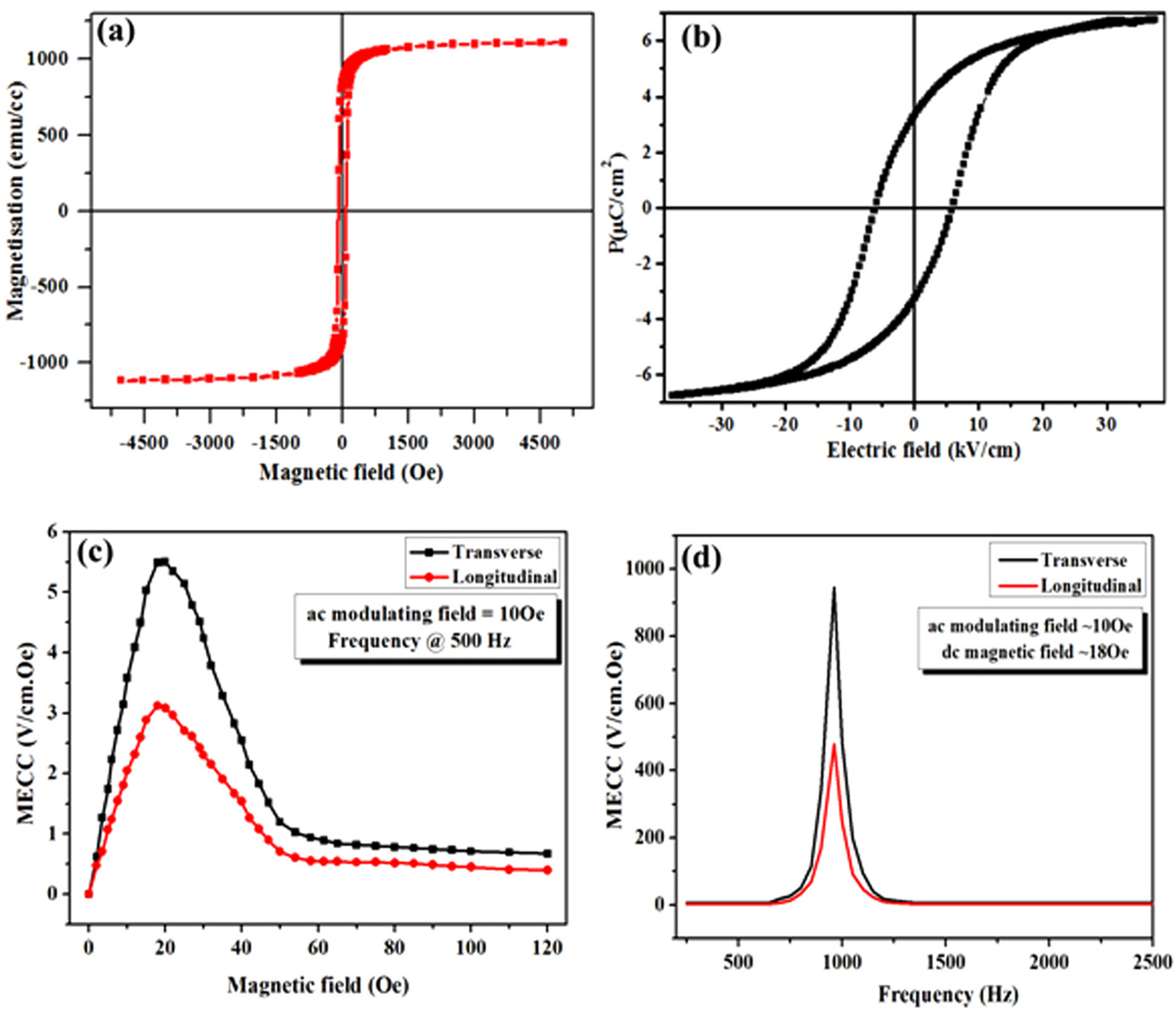


FIG. 3. (a) Magnetic hysteresis loop and (b) P-E hysteresis loop of BTO-CoFe-BTO multilayer. (c) DC biasing field dependence of the MECC measured at 500 Hz (peak coupling at $H_{dc} = 18$ Oe) and (d) low-frequency resonance in the transverse and longitudinal ME coupling.

of 944 V/(cm Oe) (transverse) and 478 V/(cm Oe) (longitudinal) (Figure 3(d)).

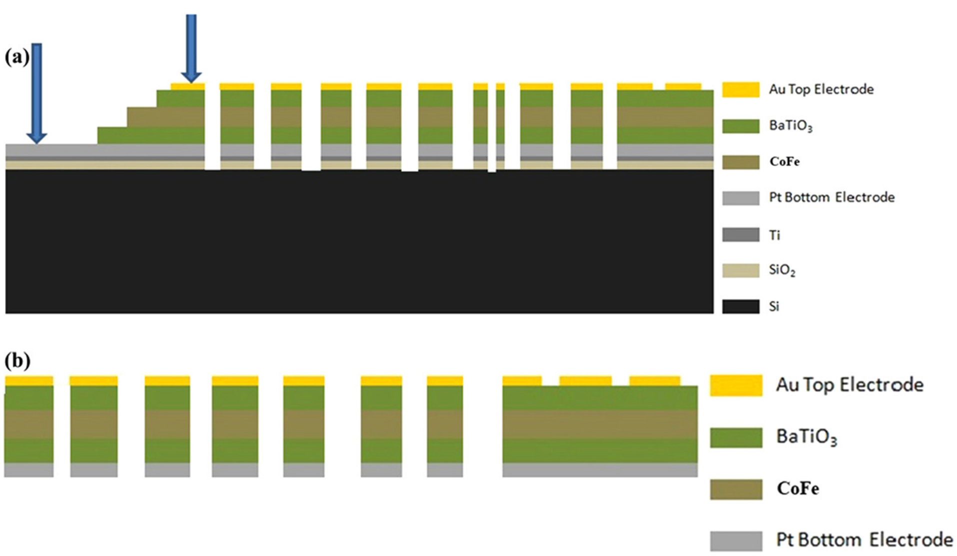
The obtained value is higher than 746 V/(cm Oe) reported in Metglas-AlN multilayers.[17] Following the equation given by Greve *et al.*[17] for the determination of resonant frequency of a multilayered structure deposited on a substrate, a frequency of 1045 Hz is obtained as the calculated value for the first order resonance which is close to the experimental value of resonance frequency (975 Hz). Frequency dependent studies show that the transverse MECC is 5.503, 5.681, 7.664, 9.932, and 53.354 V/(cm Oe) for 500 Hz, 2.5 kHz, 5 kHz, 10 kHz, and 100 kHz, respectively, at a relatively low dc applied field of 18 Oe, with an ac modulating field of ∼10 Oe. The off resonance values are very close to the highest reported values of MECC in 2-2, 2-1, and 3-0 ME heterostructures. The generated voltages are in millivolts range in this multilayer, while it is less than 1 μV in all other samples employed for the comparison.

According to the magnetoelectric equivalent circuit[16] method, it is evident that a middle magnetic layer with a higher magnetostriction can result in a high strain in the nearby piezoelectric layers which will result in an enhanced magneto electric coupling. Hence, the fundamental prerequisite for the selection of the magnetic material for magneto electric applications is that they should possess a very high magnetostriction. However, recently, Hunter *et al.*[26] reported that a giant magnetostriction was recorded when the percentage of cobalt in CoFe alloy was maintained in between 60% and 75% only upon annealing the alloy at a temperature higher than 500 °C. The alloy composition employed in the present investigation closely matches with that discussed in Ref. 26. It is to be noted that the magnetoelectric multilayers were annealed in air at 700 °C. Normally annealing in open air can cause surface oxidation which is prevented here due to the presence of a surface BTO protection layer. The mechanism of enhanced ME response can be explained on the basis of the high value of magnetostriction of the middle layer of CoFe in BTO-CoFe-BTO. The high initial permeability and the high magnetostriction developed in the CoFe layer are believed to contribute to the giant MECC observed in our system consisting of BTO-CoFe-BTO sandwiched layers. A high magnetostriction is developed in the CoFe layer by the application of an external magnetic field which in turn causes a large value of strain in the upper and lower piezoelectric BTO layers. This strain mediates electrical polarisation in the upper and lower BTO layers resulting in a giant MECC.

Additionally, nanodimensions of magnetic alloys also contribute to the giant magneto electric coupling observed in these sandwiched structures owing to the large surface to volume ratio. The particle size ratio of ferroelectric to magnetic component is about 10 (from TEM, HRTEM, and SEM). Here, each ferroelectric grain corresponds to almost 10 magnetic grains. Hence, at the layer boundaries, there is big magnetic dipole dominance owing to the large surface to volume ratio of the magnetic grains. This surface effect contributes largely to the magneto electric coupling.[18] Also, charge redistribution induced by the interfacial boundaries of the ferroelectric layer may also induce changes in ferromagnetic ordering as per the polarization direction and thereby contributing to the giant magnetoelectric response.[27]

The investigation directly points towards the possible applications in the microelectronics and MEMS industry. Magneto-electric cantilevers can be fabricated by partial dissolving of the silicon substrates (Scheme 2). The size of the cantilever thus fabricated cannot be below micrometer scale (around 1 μm) due to the limitation of mask channel size.

As the total thickness of the multilayer system under investigation here can be tuned to any required value, they can form nanoelectromechanical systems like magnetic field sensors, transducers, etc. Another immediate application is in switching devices which can be controlled by electric and magnetic fields. MEMS/NEMS devices can also be grown by a bottom up process over silicon chip with properly designed masks (template assisted deposition[28,29]), or can be directly fabricated starting from a nanowire synthesised by self assembly/induced assembly (non template process) and hence the synthesis can be integrated to the silicon integrated device technology. Here, a 5 step deposition is needed (lower contact electrode, BTO, CoFe, BTO, upper contact electrode) which is to be deposited over a pre fabricated mask



SCHEME 2. Fabrication of magneto-electric cantilevers and microwire sensors through micromachining. (a) Dissolving the thin film and substrates to obtain desired size and shapes (assisted by pre designed masks). (b) Complete dissolution of the substrate to release the micro/nano magneto electric arrays (heterogeneous).

with ordered channels or pores. As the voltage is developed across the sample (of the order of few hundreds of nanometers), the top surface area can be limited to the point contact electrode size. For any high frequency applications, the voltage developed will be appreciably high so that no external amplifier is required and hence the system can be miniaturized. The initial voltage generation measurements on the 500 μm wide microcantilevers are conducted at an ac modulating field of 10 Oe, with a modulation frequency of 1 kHz and dc biasing magnetic field of 18 Oe for a total thickness of 225 nm. Here, the total magnetic to piezoelectric volume was kept as 1:2 (BTO-CoFe-BTO) and the voltage generated in such a system was 2.6 mV. Systematic study on different configurations with varying magnetic to piezoelectric volume ratio is in advanced stage.

CONCLUSION

In conclusion, this study investigated the magnetoelectric properties of the BTO-CoFe-BTO multilayer thin film. The giant MECC values obtained were explained on the basis of high magnetostriction of the middle CoFe layer which in turn increases the strain developed over upper and lower BTO layers. Also, the large surface to volume ratio of ferromagnetic and ferroelectric layers contributes to the giant ME coupling. The motto raised by the European commission and many other international agencies "NO LEAD in microelectronics/MEMS" can be achieved soon by suitably employing other materials for applications. Employment of other piezoelectric systems (in place of BTO) with a higher longitudinal and transverse piezoelectric d_{31} and d_{33} coefficients (like BZT, BZT-BCT, KNN) will hopefully enhance this effect to another order thereby opening up a possibility of obtaining appreciable ME signal without any external amplifier which can in turn reduce the volume of the integrated devices like sensors and transducers, involving ME materials as the major active element.

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