Strain gradient mediated magnetoelectricity in Fe-Ga/P(VDF-TrFE) multiferroic bilayers integrated on silicon

Aliona Nicolenco a,b,∗, Andrés Gómez c, Xiang-Zhong Chen d, Enric Menéndez e, Jordina Fornell a, Salvador Pané d, Eva Pellicer a, Jordi Sort a,e,∗

a Departament de Física, Universitat Autònoma de Barcelona, 08193, Cerdanyola del Vallès, Spain
b Institute of Applied Physics, Chișinău, 2028, Republic of Moldova
c Institut de Ciència de Materials de Barcelona, Campus UAB, 08193, Cerdanyola del Vallès, Spain
d Multi-Scale Robotics Lab, Institute of Robotics & Intelligent Systems, ETH Zurich, Zurich, 8092, Zurich, Switzerland
e Institució Catalana de Recerca i Estudis Avançats, Pg. Lluís Companys 23, 08010, Barcelona, Spain

A R T I C L E   I N F O

Article history:
Received 20 December 2019
Accepted 22 January 2020

Keywords:
Magnetoelectricity
Fe-Ga
P(VDF-TrFE)
Ferroelectric
Magnetoelectric
Strain gradient

A B S T R A C T

The primary advantage of magnetoelectric heterostructures exhibiting direct magnetoelectric effect is the possibility to induce and modulate the electrical response of the ferroelectric phase directly with an external magnetic field (i.e., wirelessly, without applying electric field). Nevertheless, the magnetoelectric coupling in such heterostructures is commonly limited by substrate clamping which hinders effective strain propagation. In this work, 1 μm thick ferromagnetic Fe-Ga layers were electrodeposited onto rigid Si/Cu substrates and subsequently coated with ferroelectric P(VDF-TrFE). Under magnetic field, the (110) textured Fe-Ga alloy is compressed along the z-direction by 0.033%, as demonstrated by X-ray diffraction. The experimental results suggest that while the bottom of the Fe-Ga layer is clamped, its air side exhibits a pronounced tetragonal deformation thanks to the residual nanoporosity existing between the columnar grains, that is, a strain gradient develops across the thickness of the Fe-Ga film. This strain gradient in Fe-Ga induces a change in the piezoresponse of the adjacent ferroelectric P(VDF-TrFE) layer. These results pave the way to the design of high-performance microelectromechanical systems (MEMS) with magnetoelectric response integrated on rigid substrates.

© 2020 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Magnetoelectric (ME) coupling in multiferroic heterostructures is the keystone in energy-efficient magneto-electronic technologies, which encompass the new generation of spintronic-based random access memories [1–3], magnetic field sensors, microelectromechanical systems (MEMS) transformers, energy harvesters [4,5], nanorobotic drug delivery and water remediation systems [6–8]. The coupled ferromagnetic (FM) and ferroelectric (FE) constituents allow for the modulation of the electric polarization in the FE by magnetic stimulation in the absence of an external electric field (known as direct ME effect), or the electric control of magnetism in the FM (converse ME effect) [9].

Both direct and converse ME coupling can be mediated by strain transfer across the FM/FE interface. Heterostructures operated via converse ME effect are commonly engineered to comprise a thick FE phase (which serves as a substrate) and a thin FM layer, e.g. (0.5 mm)-BaTiO3/(15 nm)-CoFe [10] or (25 μm)-polyvinylidene fluoride/(60 nm)-FeGa [11]. In such heterostructures, the voltages required to generate magnetic effects in the FM phase are extremely high due to the large thickness of the FE, that is, 0.5 kV (10 kV/cm) or 1 kV (400 kV/cm), for the two cases mentioned above, respectively. A means to reduce the required voltage values is to make the FE thinner [2], which, however, is not so straightforward neither for rigid nor for flexible substrates due to their dielectric breakdown, i.e. an increased leakage current and number of pin-holes of the FE layer. In addition, thin FE layers deposited onto non-FE rigid substrates, like silicon, suffer from the clamping that hinders in-plane strain and, therefore, essentially limits the ME coupling. The growth of nanoporous [12] or vertically aligned ME heterostructures (e.g., nanopillars) [13–15] has been proposed to overcome this problem. Such configurations minimize clamping effects with the substrate and promote larger deformation in both x and y directions.
when distancing from the film/substrate interface. Nevertheless, the magnetic moment arising from a nm-thick FM phase could be very small (due to the limited amount of material). Thus, most of film-based heterostructures exhibiting converse ME effect are targeted for recording media and flexible electronics, while those applied to MEMS are bulky specimens [16].

In MEMS based on the direct ME effect, heterostructures that comprise a thin FE phase (nm-thick) grown onto a thick FM layer (several μm) are of particular interest because such configuration will allow to balance the signal-to-noise ratio [16,17]. However, the design of such structures is rather challenging for several reasons: (i) most of the magnetostrictive FM materials are typically alloys with a complex composition (e.g., Morglas, Terfenol-D) or very thin oxides (up to a few hundred nanometers) (e.g., CoFe2O4, La1-xSr1-xMnO3, Fe2O4) because their synthesis relies mainly on physical deposition methods [5]; (ii) the substrate clamping effect cannot be reduced by inducing a high degree of porosity (opposite to the converse ME) because this generally worsens the mechanical properties of the materials and would ultimately cause brittleness of the device. To overcome these issues (and provide an alternative to bulky ME), high-power layered multiferroic hybrids have been proposed. For example, a heterostructure of this type was fabricated by magnetron sputtering onto a silicon cantilever. The FM (CoFe or FeCoSiB alloy) and the FE (AlN) layers were alternated in such a way that the total thickness of the magnetostrictive layer was around 1 μm [18]. Alternatively, direct ME coupling was also achieved in free-standing Fe-Ga/Poly(vinyldene fluoride-trifluoroethylene) (P(VDF-TrFE)) nanowires for magnetically-controlled targeted drug delivery purposes [6].

Among various materials with magnetostrictive coefficient larger than 300 ppm [4], Fe-Ga is probably the only one that can be grown by electrodeposition, alternatively to conventional physical deposition methods [2,19]. This provides the possibility to grow μm-thick layers with tunable composition and microstructure in a relatively easy manner on both flat [20] and curved substrates [21], or to even obtain complex shapes [6,22] while reaching high deposition rates [23] at ambient temperature and pressure.

This work reports on the direct ME effect in Fe-Ga/P(VDF-TrFE) heterostructured multiferroic continuous films grown onto a rigid Si/Cu substrate, where the occurrence of strain in the FM/FE interface is linked to a strain gradient which is induced across Fe-Ga due to the applied magnetic field. The Fe-Ga layers were prepared by electrodeposition, and the composition and thickness were adjusted by selection of appropriate electrochemical parameters. The magnetostrictive response of the 1 μm-thick Fe-Ga layer was investigated by X-ray diffraction (XRD) under the application of external magnetic fields. A thin P(VDF-TrFE) layer (≤100 nm) was grown on top of the Fe-Ga via chemical solution deposition method. Its FE properties were characterized by piezoresistance force microscopy (PFM) and direct piezoelectric force microscopy (DPFM). The ME coupling in the resulting Fe-Ga/P(VDF-TrFE) heterostructure was demonstrated by PFM under an external in-plane magnetic field and the local ME coupling coefficient was estimated from the obtained piezoresistance loops, i.e., from the variation of the electric coercive field due to the applied magnetic field.

2. Experimental details

Fe-Ga alloy films were electrodeposited onto [100]-oriented Si chips with working areas of 0.25 ± 0.01 cm² coated by a 100 nm-thick sputtered Cu seed layer. An aqueous electrolyte with the following composition: 0.03 M Fe2(SO4)3, 0.06 M Ga2(SO4)3, 0.15 M G3H4O7 (citric acid) and 0.50 M H3BO3 was employed to grow Fe-Ga alloy and analogous bath but Ga-free was used to obtain pure Fe film for comparison. The bath pH was adjusted to 3.0 by addition of 5 M NaOH. Electrodeposition was performed in a three-electrode cell connected to a PCSTAT302 N Autolab potentiostat/galvanostat (Metrohm), where a platiniated titanium mesh served as a counter electrode and a Ag/AgCl/KCl0.1M as a reference electrode. Electrodeposition was performed at 25 °C and the solution was stirred at 200 rpm. As it is given by the polarization curve for Fe-Ga electrodeposition (Fig. 1), a constant potential of −1.45 V was applied in order to incorporate about 25 at.% of Ga in the film, which is the percentage close to the maximum in magnetostriction [24]. The estimated deposition rate of Fe-Ga alloy was around 50 nm min⁻¹ which enabled the growth of 1 μm-thick Fe-Ga layer in 20 min. After electrodeposition, the samples were rinsed with acidic water (H2SO4, pH 2) followed by neutral water in order to minimize surface oxidation.

P(VDF-TrFE) powder, (70/30) was dissolved in diethyl ketone to form a transparent solution with a concentration of 2 wt./vol.%. The solution was spin-coated onto Fe-Ga during 60 s at 3000 rpm by using a spinner (Suss Microtech) and the samples were consequently annealed at 125 °C for 12 h in a vacuum oven (DZF-6020, ZKDZ) to increase the crystallinity of P(VDF-TrFE).

Sample morphology was characterized by scanning electron microscopy (SEM) using a Zeiss MERLIN field emission SEM at 5 keV and the elemental composition was estimated by energy dispersive X-ray spectroscopy (EDX) using SEM at an acceleration voltage of 20 keV. The surface was examined at five different locations of each sample and the average atomic percentage of each element was calculated. The XRD patterns were acquired on a Philips X’Pert diffractometer using Cu Kα radiation in θ-2θ configuration while a magnetic field was applied in situ and in the plane of the sample by using a NdFeB permanent magnet (Ø 2 cm, 0.2 T at a distance of 5 mm from the magnet) placed in the diffractometer. Fe-Ga samples with an area of 0.5 cm × 0.5 cm were placed in the middle of the permanent magnet and the xyz position of the sample in the XRD diffractometer was kept the same for the measurements without and with the magnetic field. Although the magnetic field reduces with the distance from the magnet, its value (measured using a gaussmeter) remained always well above the saturation magnetic field of the film. Therefore, the magnetostriction induced by this magnet on the Fe-Ga alloy, which is proportional to the magneti-
The interplanar distances $d_{\text{in}}$ were evaluated by Rietveld refinement [25] using the ‘Materials Analysis Using Diffraction’ (MAUD) software. High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were performed on a JEOL-JEM 2011 operated at 200 kV. The PFM natural domain maps, FE-domain recording experiments and piezoelectric coefficient $d_{33}$ were obtained using a Keysight 5500 atomic force microscope (AFM) and using a full platinum tip with high tip shank length [26], i.e. RMN-25Pt300B (spring constant $k \approx 18 \text{ N m}^{-1}$). The measurements were carried out at low humidity (less than 6%) to avoid unwanted electrochemical phenomena. The FE recording voltages were adjusted at ±7 VDC to polarize the samples while an AC of 3 V was used for reading. For the electromechanical measurements, the tip was located in a single spot of the sample surface while an amplitude vs. frequency sweep was performed to disclose the resonance curve. The equipment was calibrated using a standard procedure based on force vs. distance curve to obtain the deflection sensitivity from which the $d_{33}$ was evaluated. DPFM experiments were carried out by using an ultra-low leakage Transimpedance Amplifier (ADA4530 from Analog Devices Inc.) followed by a voltage-to-voltage amplifier (AD8421 from Analog Devices Inc.). The tip used for scanning was a full platinum tip, i.e. RMN-25PtIr300-H (spring constant $k \approx 290 \text{ N m}^{-1}$). The image was obtained at a constant speed of 84 $\mu \text{m s}^{-1}$ at low humidity environment. The amplifier was calibrated using a known 100 GOhm resistor (RX-1M1009FE). The magnetoelectric coupling in the Fe-Ga/P(VDF-TrFE) films was directly probed using a commercial AFM (NT-MDT Ntegra Prima). PtIr-coated Si probes, i.e., FMG01/Pt (spring constant $k \approx 3 \text{ N m}^{-1}$), were used to acquire local piezoresponse loops in contact mode, as signals ($V_{\text{AC}} = 0.5 \text{ V}$) were superimposed on triangular staircase wave with DC switching from −10 V to 10 V. PFM measurements were performed at room temperature, and a magnetic field of 0.1 T was applied in-plane to the Fe-Ga/P(VDF-TrFE) layer in order to induce the strain in the magnetostriuctive part.

3. Results and discussions

Fig. 2a shows the XRD patterns of electrodeposited Fe and Fe-Ga alloy films. The main peaks located at 44.3° and 81.4° are ascribed to the body-centered cubic (bcc) phase of Fe-Ga, while the peaks at 43.3°, 50.5° and 95.1° originate from the Cu seed layer. No traces of oxide peaks were observed, in agreement with the EDX characterization, which indicates an oxygen concentration ≤ 5 at% (Figure S1). The shift in the Fe-Ga peaks position towards lower 2θ angles, as compared to electrodeposited pure Fe, indicates an increase in the lattice constant. This is explained by the expansion of the bcc Fe lattice with the incorporation of bigger Ga atoms (the atomic radii of Fe and Ga are 0.172 nm and 0.181 nm, respectively [27]) and the corresponding formation of the Fe(Ga) solid solution, which is highly textured along the [110] direction. The SAED pattern shown in the inset of Fig. 2a confirms the polycrystalline nature of the electrodeposited Fe-Ga alloy. The three spots labelled on the image arise from planes with interatomic distances of 2.10, 1.19 and 1.05 Å, which match (110), (211) and likely (220) crystallographic planes of a Fe(Ga) solid solution, in agreement with the XRD results.

The magnetostriiction of Fe-Ga alloys has been the subject of extensive studies and it is found to be strongly dependent on the Ga content and the crystallographic structure of the alloy. In this work, electrodeposited Fe-Ga alloys with 25 ± 5 at% of Ga have been grown since this composition results in a maximized magnetostriective behavior [24]. The maximum magnetostriction has been reported for [100]-oriented Fe-Ga single crystals. Polycrystalline Fe-Ga (such as electrodeposited ones) typically show a less pronounced magnetostriective behavior [28]. To assess the magnetostriiction in thick (1 $\mu \text{m}$) Fe-Ga film electrodeposited in this study, XRD measurements with and without the application of an in-plane magnetic field of >0.2 T were carried out (Fig. 2b). Under the magnetic field, there is a clear shift in (110) Fe(Ga) peak position towards higher 2θ angles (note that the Cu (111) peak has always a fixed position, Figure S2), which is consistent with a decrease of the lattice cell parameter along [110]. Specifically, the corresponding interplanar distance $d_{110}$ decreases by 0.033% as compared with the 0 T field. This change, although very subtle but expected at such magnetic field values [24,29], is consistent with the following competing mechanisms: (i) an expansion along one of the in-plane directions due to the positive magnetostriiction coefficients of Fe-Ga [30], and (ii) compression along the z-axis (out-of-plane compression) to conserve the unit cell volume, as sketched in Fig. 2b. Due to the (110) texture of the polycrystalline Fe-Ga under investigation, the net effect observed by θ/2θ XRD is the compression along the z-axes, that is, a decrease in the distance between (110) planes aligned parallel to the substrate.
Magnetostriiction measurements in thin films (typically 7–60 nm) are usually complicated due to substrate clamping which strongly minimizes magnetostriuctive effects. Here, we are able to observe significant magnetostriuction in a continuous 1 μm-thick Fe-Ga film. As can be seen in Fig. 3a, the SEM image of the top surface of the Fe-Ga alloy reveals a highly polycrystalline structure in the plane of the sample and some residual intergran porosity. The cross-section of the Fe-Ga alloy (Fig. 3b) shows the occurrence of columnar-like grains. The observed nanoporosity between the columns is closely related to electrodeposition conditions. In particular, simultaneous hydrogen evolution which occurs at the cathode upon application of relatively high negative potentials required to attain the desired composition of Fe-Ga alloy (see Fig. 1) may give rise to the porosity in the microstructure [31]. Nevertheless, such microstructure allows for structural relaxation, which presumably becomes more pronounced as the distance from the film/substrate interface is increased, similar to what happens with nanopillars, e.g., in 1D CoFe₂O₄/BaTiO₃ nanocomposite structures [13]. Clamping with the substrate results in a strain gradient along the thickness of the layer in which larger deformations can occur at the outer region of the Fe-Ga layer. Indeed, a recent study on patterned ME heterostructures revealed that the inhomogeneous strain generated in magnetostriuctive nanopillars can be effectively transferred to a neighboring FE causing flexoelectric effects (i.e., strain gradient induced polarization) [32]. Nevertheless, the development of effective strain gradients induced by magnetic field in continuous films has not been experimentally demonstrated previously and was considered only in several highly porous materials operated via converse ME effect [12,33].

To engineer a magnetoelectric heterostructure, the surface of the Fe-Ga film was covered with a 100 nm-thick P(VDF-TrFE) film (Fig. 3c). Its piezoelectric characterization was performed combining PFM and DPFM techniques. Fig. 4a shows the topology of the P(VDF-TrFE) layer deposited on top of the Fe-Ga film. Its domain structure shows an average size of 20.4 × 10³ nm² (140 nm lateral size), as revealed in Fig. 4b and c by the PFM phase and PFM amplitude images, respectively. It is worth mentioning that the domain size is proportional to the thickness of the FE and the dependence is described by Landau-Lifshitz-Kittel scaling law [34]. Thus, the size of the domains in 100 nm thick P(VDF-TrFE) film studied in this work is larger than the domain size reported by other authors, for instance in [35]. The brighter contrast in the central region in the amplitude image (Fig. 4c) indicates a higher electromechanical response, possibly due to a favorable orientation of β-phase crystals. The formation of the crystalline β-phase was also evidenced from the XRD pattern shown in Figure S3. It is expected to have almost 100% crystallization of the P(VDF-TrFE) after annealing at 125 °C, i.e. between the Curie and melting temperature [36], however, some defects in conformation and molecular packing could be developed during the phase transition and disorder the P(VDF-TrFE) chain orientation, that could impede the polarization reversal [37]. As reported in literature, the presence of β-phase crystals is the key to enhance the piezoelectric characteristics of P(VDF-TrFE) [35,38–40] from which poled and unpoled films have radically distinct piezoelectric properties. To estimate the electromechanical behavior of P(VDF-TrFE), the layer was prepoled by applying a constant DC bias of +7 VDC in a 15 × 15 μm squared area. After completing the frame, a consecutive, concentric square of 8 × 8 μm was performed with a constant DC bias of the opposite magnitude, −7 VDC (Fig. 4d). The square-shaped areas obtained after the poling experiments can be recognized, although the square borders are not as defined as in hard ceramic FE films [15,41]. To quantify the electromechanical behavior of the poled films, the point-spectroscopy curves were recorded in a mode in which the vibration amplitude (PFM amplitude) was captured vs. the applied AC frequency bias. The resonance curves for different AC biases are shown in Fig. 4e, from which the maximum vibration amplitude is extracted for each curve and separately plotted vs. the applied AC bias magnitude. The piezoelectric coefficient d₃₃ of the P(VDF-TrFE) film was then estimated to be of 13 pm V⁻¹ by PFM, in concordance with previously reported values in the literature, which range from 4 to 33 pm V⁻¹ [42–45].

Following the piezoelectric characterization, DPFM was performed to directly measure the piezogenerated charges at the nanoscale. DPFM-Si (signal input) and DPFM-So (signal output) [46] images of a FE P(VDF-TrFE) domain structure are included in Fig. 4f. To obtain the frames, a high spring constant tip (k ≈ 290 N m⁻¹) was used to apply a sufficiently high force to generate enough charge to be measured by the amplifier without plastic deformation of the sample surface. To reduce the pressure exerted to the polymer, a very blunt tip was employed to minimize possible plastic deformation, hence very large contact areas of 280 × 10³ nm² can be expected. The data show a similar current behavior as expected for a scanned FE domain structure, in which the trace (from right to left) image is a mirror from the retrace image (from left to right), confirming the expectation of crossing a FE domain structure [46,47]. The time integral of averaging the current profiles reports the piezogenerated charge, while, with a force vs. distance curve, the exact applied force can be obtained. After performing all the calculations, a d₃₃ DPFM = 56 pC N⁻¹ (1 pC N⁻¹ = 1 pm V⁻¹) was obtained.

Remarkably, after the full converse and direct piezoelectric characterizations, dissimilar d₃₃ values for the piezoelectric characteristics of the P(VDF-TrFE) film were obtained. This arises from the fact that PFM probes the electromechanical behavior of the entire FE film, which is partially affected by the large electrostrictive coefficients of PVDF, that cannot be neglected at this scale [48]. Moreover, due to electric field penetration into the film, the
electromechanical behavior of the P(VDF-TrFE) can be significantly clamped by the underlying layers [49,50]. Conversely, DPFM is sensitive to the direct piezoelectric effect and only collects the charges generated at the surface where clamping is minimized and, thus, this explains why the $d_{33}$ is larger when determined using this technique.

The magnetoelectricity in Fe-Ga/P(VDF-TrFE) heterostructure was directly probed using PFM under an external in-plane magnetic field of 0.1 T. The magnetic field applied during the PFM measurements was lower than for the Fe-Ga magnetostriction measurements (>0.2 T). Note, however, that Fe-Ga becomes magnetically saturated already at 500 Oe (0.05 T) (Figure S4), and, therefore, the magnetostriction remains nearly constant with the magnetic field from this value onwards. The obtained amplitude vs. bias curves show a typical “butterfly” shape dependence of a piezoelectric material (Fig. 5a). The asymmetry of the loops might originate from different factors such as interphase effects, work function differences between bottom (Fe-Ga) and top electrodes (Pt-coated Si probe) or internal electric fields [5,51]. In absence of external magnetic field, the coercive voltages for the heterostructure are ~6.0 and 4.8 V (i.e., average coercive electric field of 54 MV m$^{-1}$, comparable to the copolymer bulk counterpart [6]), while under magnetic field, the coercive fields shift towards ~5.6 and 3.6 V, respectively (average coercive electric field of 46 MV m$^{-1}$).

The reduction of the coercive field of the P(VDF-TrFE) under the action of the external magnetic field indicates a reduction in the FE domain switching barrier due to the induced magnetostri- cive strain in the FM Fe-Ga phase. Simultaneously, the local ME coupling coefficient can be estimated from the change in the asymmetry of the piezoresponse loops due to the applied magnetic field (contrary to the procedure based on determination of $d_{33}$ [52]) via: $d_{33} = \frac{\Delta E}{\Delta H}$, where $\Delta H$ is the increment in the external magnetic field that causes a change in the internal electric field, $\Delta E$, in the ferroelectric counterpart. Taking into account the offset of the center of the loops upon application of the magnetic field due to the created internal electric field [6,51], the local ME coefficient in the Fe-Ga/P(VDF-TrFE) heterostructure can be estimated as [(1.2 – 0.4)/2/100 nm]1000 Oe = 40 V cm$^{-1}$ Oe$^{-1}$. This value is lower than in free standing Fe-Ga/P(VDF-TrFE) core-shell nanowires [6]. However, it is comparable to that reported in bilayered Terfenol-D/PMN-PT [51] and BiFeO$_3$-CoFe$_2$O$_4$ thin film composites [53]. It should be noted, though, that the PFM is a local technique which allows to probe an area with a lateral resolution of a few nanometers only [42]. Considering the polycrystalline nature of underlying electrodeposited Fe-Ga alloy, it is expected that the coercivity in FE can either increase or decrease with the magnetic field depending on the orientation of the underlying Fe-Ga crystal, which will transmit either tensile or compressive stress to P(VDF-TrFE). Similarly, the transmitted stress (induced by magnetic field) can either increase or decrease the polarization in the P(VDF-TrFE) film, and can even cause FE domain switching under DC magnetic field [6,32]. An example of a different piezoresponse of the P(VDF-
TrFE), and without the applied magnetic field, is shown in supplementary Figure S5. Furthermore, the decrease in the amplitude with the magnetic field (Fig. 5a) could also be indicative for the compression of the underlying magnetostrictive Fe-Ga [54], in agreement with the XRD data. The phase switching angle is close to 180° (Fig. 5b), pointing to a major contribution of the electromechanical response over the electrostatic one [55]. The polarization reversal and changes in piezoresponse under an applied external magnetic field indicate that the strain generated in the magnetostrictive Fe-Ga layer is effectively transmitted to the neighboring P(VDF-TrFE). This is a direct evidence of a strong strain gradient mediated ME coupling in the Fe-Ga/P(VDF-TrFE) heterostructure.

4. Conclusions

Direct ME coupling has been observed in Fe-Ga/P(VDF-TrFE) heterostructures grown onto a rigid Si/Cu substrate. Fe-Ga layers with minimum amount of incorporated oxygen (<5 at.%) were prepared by electrodeposition and their composition and thickness were adjusted to 25 ± 5 at.% Ga and 1 μm, respectively, by selection of appropriate electrochemical conditions. It has been demonstrated that the distance between (110) planes in the textured polycrystalline Fe-Ga decreases by 0.033% when subjected to an external magnetic field in the plane of the sample, which indicates a compression of the layer along the z-direction (that is, an expansion along the in-plane axis parallel to the magnetic field). Thus, the magnetostrictive Fe-Ga becomes strained in spite of the fact that the bottom of the layer is clamped by the rigid substrate. Therefore, the experimental results suggest that a significant strain gradient develops along the columnar grains in the Fe-Ga film due to the presence of some residual intergrain nanoporosity. To design the magnetoelectric heterostructures, the surface of the Fe-Ga films was covered with a thin P(VDF-TrFE) layer (<100 nm) whose FE properties were thoroughly characterized using PFM and DPFM. Surprisingly, two dissimilar values of $d_{31}$ coefficient were obtained: 13 pm V$^{-1}$ from PFM, and 56 pm V$^{-1}$ from DPFM, probably due to the distinct material volume probed using these techniques. Furthermore, the ME coupling in the Fe-Ga/P(VDF-TrFE) heterostructure was studied by means of PFM under a magnetic field. The polarization reversal and changes in piezoresponse of the neighboring P(VDF-TrFE) when subjected to a magnetic field indicate a strong strain gradient mediated ME coupling in the Fe-Ga/P(VDF-TrFE) heterostructures. The local ME coefficient in the investigated heterostructure has been estimated from the shift in piezoresponse loops and was found to be comparable to certain core-shell and ceramic-based ME composites. The relatively high ME coefficient observed in Fe-Ga/P(VDF-TrFE) layered heterostructures grown onto rigid substrate underscores the importance of the strain gradient in the design of high-performance magnetic field-actuated MEMS (with magnetoelectric properties), integrated on silicon.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that support the findings of this study are available from the corresponding authors on request.

Acknowledgements

This work was supported by the Spanish Government (MAT2017-86357-C3-1-R and associated FEDER), the Generalitat de Catalunya (2017-SGR-292), the European Research Council (ERC) under the SPIN-PORICS 2014-Consolidator Grant (Agreement N 648454) and the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement n°665919. Authors also acknowledge networking support by COST Action MP1407-STSM grant COST-STSM-MP1407-43917. J.F. acknowledges the “Juan de la Cierva” (IJCI-2015-27030) contract by the Spanish Government. S.P. acknowledges support from the ERC-2017-CoG HINBOTS Grant No. 771565.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at https://doi.org/10.1016/j.apmt.2020.100579.

References

[1] X. Zhao, J. Wen, B. Yang, H. Zhu, Q. Cao, B. Wang, Z. Qian, Y. Du, Electric field manipulated multilevel magnetic states storage in FePt(011) PMN-PT heterostructure, ACS Appl. Mater. Interfaces 9 (2017) 36038–36044, http://dx.doi.org/10.1021/acsami.7b01105.
[2] H. Ahmad, J. Atulasimha, S. Bandypadhay, Reversible strain-induced magnetization switching in FeGa nanomagnets: pathway to a re writable, non-volatile, non-togg lif e extremely low energy straintronic memory, Sci. Rep. 5 (2015), 18264, http://dx.doi.org/10.1038/srep18264.
[3] S. Bhatti, R. Shua, A. Hirobata, H. Ohno, S. Fukami, S.N. Piramanayagam, Spintronics based random access memory: a review, Mater. Today 20 (2017) 530–548, http://dx.doi.org/10.1016/j.mat tod.2017.07.007.
Heterostructures, Limburg, heterostructures microelectromechanical properties, E. C. D. H. (2015)
Aimon, Z. in-plane anisotropic converse magnetoelectric coupling effect in FeGa/polyvinylidene fluoride hydroelectro films, J. Appl. Phys. 113 (2013), 17C705, http://dx.doi.org/10.1063/1.4793780.
D. Chen, A.N. Bud’ko, L.T. Schelhas, H.Y. Kang, S. Robbenwolf, J.P. Chang, S.H. Tolbert, Tuning magnetoelectric coupling using porosity in multilayer nanocomposites of ALD-grown PbZrTiO3 and templated mesoporous CoFe2O4, J. Appl. Phys. 109 (2011), 112504, http://dx.doi.org/10.1063/1.4692536.
S. Tuomi, T. Vepsäläinen, A. Schwartz, A. Mäkinen, E. Hämäläinen, R. Rokka, T. Aromaa, N. Hult, R. Paatero, and M. Tuominen, Semiconductor nanomagnetism, Adv. Mater. 20 (2008), 3070–3100, http://dx.doi.org/10.1002/adma.200703866.
K. Nakamura, T. Kuroda, Y. Okazaki, and Y. Haga, Electric-field-induced magnetization switching in a CoFe2O4–BaTiO3 nanocomposite tuned by magnetic fields, Nat. Commun. 4 (2013), 2051, http://dx.doi.org/10.1038/ncomms3051.
W. Wu, Y. Wang, Y. Zhang, J. Wang, J. Wu, High-performance piezoelectric nanogenerators, Adv. Mater. 24 (2012), 2584–2590, http://dx.doi.org/10.1002/adma.201200876.
J. Guo, J. Zhang, Y. Wang, H. Li, J. Tian, and X. Li, Fabrication of high-performance piezoelectric nanogenerators using designable multilayered nanocomposite films, Mater. Lett. 179 (2016), 219–222, http://dx.doi.org/10.1016/j.matlet.2016.09.038.
S. Chen, Q. Li, X. Chen, X. Gu, Y. Chen, C. Liu, and X. Pan, Giant magnetoelectric coupling in the BiFeO3 nanowire system, J. Nanosci. Nanotechnol. 16 (2016), 7334–7339, http://dx.doi.org/10.1166/jnn.2016.11155.
X. Liu, J. Wang, X. Zhao, X. Chen, J. Xing, and Y. Shi, Piezoelectric properties of FeCoBi–BaTiO3 nanocomposite films, J. Phys. D: Appl. Phys. 48 (2015), 195305, http://dx.doi.org/10.1088/0022-3727/48/19/195305.
T. Yasuda, A. Hasegawa, and K. Tanaka, Ferroelectric field effect on a single TiO2 nanowire, Science 335 (2012), 1335–1338, http://dx.doi.org/10.1126/science.1215477.
[50] Y.Y. Choi, T.G. Yun, N. Qaiser, H.S. Roh, J. Hong, S. Hong, S.M. Han, K. No. Vertically aligned P(VDF-TrFE) core-shell structures on flexible pillar arrays, Sci. Rep. 5 (2015) 10728, http://dx.doi.org/10.1038/srep10728.

[51] H. Miao, X. Zhou, S. Dong, H. Luo, F. Li. Magnetic-field-induced ferroelectric polarization reversal in magnetoelectric composites revealed by piezoresponse force microscopy, Nanoscale 6 (2014) 8515–8520, http://dx.doi.org/10.1039/c4nr01910e.

[52] G. Caruntu, A. Yourkhani, M. Vopsaroiu, G. Srinivasan. Probing the local strain-mediated magnetoelectric coupling in multiferroic nanocomposites by magnetic field-assisted piezoresponse force microscopy, Nanoscale 4 (2012) 3218–3227, http://dx.doi.org/10.1039/c2nr00064d.

[53] F. Yan, C. Chen, L. Lu, P. Finkel, J.E. Spanier. Local probing of magnetoelectric coupling and magnetoelastic control of switching in BiFeO3-CoFe2O4 thin-film nanocomposite, Appl. Phys. Lett. 103 (2013) 42906, http://dx.doi.org/10.1063/1.4816793.

[54] T. Zheng, Z. Yue, G.G. Wallace, Y. Du, P. Martins, S. Lancers-Mendez, M.J. Higgins. Local probing of magnetoelectric properties of PVDF/Fe3O4 electrospun nanofibers by piezoresponse force microscopy, Nanotechnology 28 (2017) 65707, http://dx.doi.org/10.1088/1361-6528/aa5217.

[55] S.V. Kalinin, D.A. Bonnell. Imaging mechanism of piezoresponse force microscopy of ferroelectric surfaces, Phys. Rev. B 65 (2002), 125408, http://dx.doi.org/10.1103/physrevb.65.125408.