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Gradauskaite, Elzbieta; Meisenheimer, Peter; Müller, Marvin; Heron, John; [Trassin, Morgan](#)

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Multiferroic heterostructures for spintronics

Elzbieta Gradauskaite^{1*}, Peter Meisenheimer^{2*}, Marvin Müller¹, John Heron^{2*} and Morgan Trassin^{1*}

1 - Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 4, 8093 Zurich, Switzerland

2 - Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan
48109, USA

*E-mails: elzbieta.gradauskaite@mat.ethz.ch, meisep@umich.edu, jtheron@umich.edu,
morgan.trassin@mat.ethz.ch

Abstract: For next generation technology, magnetic systems are of interest due to the natural ability to store information and, through spin transport, propagate this information for logic functions. Controlling the magnetization state through currents has proven energy inefficient. Multiferroic thin film heterostructures, combining ferroelectric and ferromagnetic orders, hold promise for energy efficient electronics. The electric field control of magnetic order is expected to reduce energy dissipation by 2-3 orders of magnitude relative to the current state-of-the-art. The coupling between electrical and magnetic orders in multiferroic and magnetoelectric thin film heterostructures relies on interfacial coupling through magnetic exchange or mechanical strain and the correlation between domains in adjacent functional ferroic layers. Here we review the recent development dealing with electrical control of magnetism in artificial magnetoelectric heterostructures, domain imprint, emergent physics and device paradigms for magnetoelectric logic, neuromorphic devices, and hybrid magnetoelectric/spin-current based applications. Finally, we conclude with discussing experiments that probe the crucial dynamics of the magnetoelectric switching and optical tuning of ferroelectric states towards all optical control of magnetoelectric switching events.

Keywords: multiferroics, BiFeO₃, Cr₂O₃, magnetoelectrics, artificial multiferroics, spintronics, ferroic domain imprint, exchange bias, magnetostriction, memory and logic

1. Introduction

1. 1 *Magnetoelectric multiferroic heterostructures*

Multiferroic materials, exhibiting multiple order parameters in a single-phase, were first discussed in the 50's [1] and have been in the recent years at the center of interest with the development of experimental techniques for the design and probe of such complex materials [2,3]. Here, we will consider materials exhibiting ferroelectricity and ferromagnetism for spintronic applications [4,5]. When the two orders coexist but are not coupled, so-called multiferroic memory elements can be envisioned [6]. In such memories, the information can be stored independently in each order parameter, increasing the storage density in a given active space. The focus of the scientific community, however, is shifting towards magnetoelectric multiferroic materials, where the magnetic and electric orders are coupled, meaning that a magnetic state can be electrically altered. Magnetoelectric-based device paradigms [7] could solve the current limitations accompanying the magnetic data storage development and the energy costs associated with magnetization reversal, as state-of-the-art magnetization switching processes involve high-density spin polarized currents, which result in extreme heat dissipation and limited energy efficiency. Using an electric field to reverse a magnetic bit could lead to current-less and extremely localized switching events through voltage application to a capacitor.

Technologically relevant magnetoelectric multiferroic materials, i.e. those possessing coexisting and robustly coupled magnetization and ferroelectric polarization at elevated temperature, are scarce. The conditions for the establishment of a polarization and magnetization in a material are often mutually exclusive [8], yet, several mechanisms allow for a polarization to coexist with magnetic order [1]. For example, improper ferroelectric materials, in which the polarization is not the primary order parameter, often exhibit magnetic order. Sometimes the magnetism itself can trigger a polarization, causing an induced ferroelectricity to emerge at low temperature. In this case, however, the polarization values are too small for device integration [1]. Most single-phase multiferroic magnetoelectric materials exhibit a ferroelectric polarization in an antiferromagnetic matrix, the prototypical materials being YMnO_3 and BiFeO_3 . We emphasize here that Cr_2O_3 , discussed in the following sections is not multiferroic, however, its established magnetoelectric effect at room temperature [9,10] brings this material in the focus regarding magnetoelectric-based device research. Hexagonal YMnO_3 belongs to the improper ferroelectric category, in which the ferroelectricity emerges a consequence of steric effects [1,11], it is also antiferromagnetic below ~ 130 K [1,12,13]. The integration of YMnO_3 into thin film heterostructures and the accompanying impact of epitaxial interface on the exotic ferroelectric state has only been investigated recently [14]. Most

of the multiferroic and application relevant advances in hexagonal manganites are dealing with bulk measurements [15–17].

In contrast, BiFeO₃ is the most studied multiferroic thin-film material [1,18]. Its room temperature ferroelectricity with extremely high polarization values, reaching up to 150 $\mu\text{C cm}^{-2}$ [19], and G-type antiferromagnetic order [20,21] offer a unique platform to study the potential applications of multiferroic magnetoelectric materials. We recommend recent reviews dedicated to the material for further reading [22,23].

With the progress in growth techniques, new multiferroic magnetoelectric candidates have emerged as alternatives to BiFeO₃-based heterostructures. For instance, GaFeO₃ [24–26], exhibiting a higher magnetoelectric coefficient than the reference Cr₂O₃ material, can now be deposited as high quality thin films [27]. Similarly, layered materials such as Aurivillius phases [28,29], only recently grown in a single-crystalline epitaxial form [30], show robust ferroelectric properties in the ultrathin regime [30–33] in a structure that is compatible with long-range magnetic order [34,35].

In order to compensate for the current lack of materials exhibiting strong and coupled ferroelectric and magnetic orders, artificial multiferroic heterostructures were introduced to the mix and are now playing a major role [5]. Here, the ferroelectric and magnetically ordered systems are coupled in multilayers, which is triggered via interface-based interactions, as depicted in figure 1. The possibilities in the symmetry of the heterostructures, i.e. two dimensional based interface or involving nano-sized pillar self-assembled architectures have been reviewed in detailed previously [3], thus here we restrict ourselves to the most recent development in the design and integration of these multilayers into emerging technologies discussed in the following sections.

FIGURE 1 | Artificial magnetoelectric multiferroic heterostructures based strain coupling (a) and on interfacial magnetic exchange (b). Reprinted with permission from [1]. Copyright © 2016, Springer Nature.

1.2 Energy efficient spintronics

The demand for smaller and energy-efficient devices is driving the integration of complex oxides into new device architectures with reduced energy consumption. With the technological burst that followed the discovery of giant magnetoresistance [36,37], magnet-based data storage devices are at the forefront of current research. In state-of-the-art device concepts, spin currents replace heat- or magnetic field- assisted switching of the magnetic bit. Spin transfer torque (STT) technology is robust and offers ultrafast dynamics for various applications [38,39]. Spin currents directly generated via the spin Hall effect in heavy metals electrodes, so-called spin-orbit torques (SOT) are also emerging as technology relevant magnetic bit manipulation process [40–42]. Both STT- and SOT-based switching, however, dissipate significant energy through Joule heating, which, ultimately limits their integration into ever-smaller device architectures.

Ferroelectric-based memory devices offer the advantage of a non-volatile polarization state that can be controlled using a low-energy-consuming electric field. Electroresistance then allows the direct reading of the polarization state by monitoring the tunneling current across the ferroelectric [43,44]. Here however, interface related effects can drastically alter the polarization state in the ultrathin regime and hinder the implementation of ferroelectric materials in the required metal-ferroelectric-metal capacitor design. Uncompensated bound charges at ferroelectric epitaxial interfaces trigger a depolarizing field [45], which in return can suppress the ferroelectric behavior in the application relevant ultrathin films [46,47].

The combined ferroelectric and magnetic states in artificial multiferroic heterostructures offer the possibility to control with an electric field a robust and easy to read magnetic state in the ultrathin regime. Here, we review the advances in the field of electrical control of magnetization in such architectures.

2. Acting on magnetic order with electric fields in multiferroic heterostructures

The development focus for the field of multiferroic heterostructures primarily lies in systems coupled through strain and interlayer magnetic exchange [3]. This is because the largest converse magnetoelectric coefficients and most reasonable switching times reported to date are observed in these

systems [48,49]. Single phase multiferroics that are operable at room temperature, such as BiFeO₃, tend to have low converse magnetoelectric coefficients [1,50,51] that need to be enhanced to facilitate real applications.

2.1 Electric field control of magnetic anisotropy

In this section, we focus on the use of ferroelectric and piezoelectric crystals to modify or switch magnetocrystalline anisotropy in an adjacent magnetically ordered coupled layer, most commonly through the application of strain by the piezoelectric layer and taking advantage of magnetostriction in the ferromagnet. A magnetostrictive ferromagnetic layer is strained by a piezoelectric/ferroelectric crystal [52,53] to produce changes in magnetic anisotropy [54–57] and control the associated energy landscape through magnetostriction, as represented in Figure 2a.

The magnetostriction coefficient, usually denoted as λ_{ijkl} , describes how a material transduces magnetization into strain according to the relation $\epsilon_{ij} = \lambda_{ijkl} \mathbf{m}_k \mathbf{m}_l = -C_{ijmn}^{-1} B_{mnkl} \mathbf{m}_k \mathbf{m}_l$, where C_{ijmn} is the stiffness tensor, B_{mnkl} is the magnetoelastic energy, and $\mathbf{m}_k, \mathbf{m}_l$ are the direction cosines of the magnetization [58,59]. Physically, this originates from changes in the band structure of the material due to the mechanical distortion. Effectively, as a crystal is strained and the atoms move, the band structure will change which can deplete/add to the spin-dependent density of states of a ferromagnet [60–62]. Macroscopically, this is observed as the change in magnetocrystalline anisotropy per change in strain, $B_{mnkl} = \frac{\partial K_{mn}}{\partial \epsilon_{kl}}$, where K_{ij} is the magnetic anisotropy, and ϵ_{kl} is the strain [63]. As this is an effect of the magnetic anisotropy energy, it is proportional to the spin-orbit coupling of the material [62] and ferromagnets with large spin-orbit coupling, like rare earth containing materials, tend to also exhibit large magnetostriction coefficients. Additionally, materials that are mechanically isotropic (i.e. the ratio of components of C_{ijmn} approach 1 or the shear modulus goes to 0) show larger magnetostriction values since λ is proportional to $C^{-1}B$. Experiments with strain-mediated composite magnetoelectrics usually employ conductive magnets with large magnetostrictive coefficients (λ) such as rare-earth containing Terfenol-D [52,64] ($\lambda \sim 1200$ ppm), Galfenol (Fe_{1-x}Ga_x) [65,66] ($\lambda \sim 250$ ppm), FeRh [67] (ferromagnet-antiferromagnet transition), CoFeB [64,68] ($\lambda \sim 50$ ppm), and Ni [69] ($\lambda \sim 34$ ppm).

One static demonstration of this concept has been the imprinting of ferroelectric domains from a substrate onto a magnetostrictive film via strain-mediation (see section 3.2 for more on domain imprint). By depositing magnetostrictive CoFe on a BaTiO₃ substrate, the in-plane strain state of a₁-a₂ domains in the BaTiO₃ create localized easy axes in the magnetostrictive magnet, effectively mapping the polarization

of the substrate directly into a magnetic domain (Figure 2b) [70]. These imprinted magnetic domains have been seen to persist unambiguously through the temperature-driven phase transitions of BaTiO_3 [71] and the effect has been noted with other magnetic films, such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) and CoFe_2O_4 [72]. Beyond this, magnetic domain imprinting has been used to control domain walls in the pre-switching regime, as the magnetic domain will move with the ferroelectric domain [73], and this phenomenon will be discussed further in section 3.

Magnetoelectric switching of magnetic anisotropy with the use of magnetostrictive ferromagnets has been able to achieve energy dissipations per area per switch on the order of $1 - 100 \mu\text{J cm}^{-2}$ [69], making these devices competitive for post-Si memory and logic applications [74–76]. While much of the early work in strain-coupled multiferroics was done using bonded piezoelectric transducers [77,78], scale devices necessitate thin film magnets deposited on high-strain piezoelectric crystals, typically relaxor-type PbTiO_3 (PTO) derivatives such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) [69,79,80] and $\text{Pb}(\text{MgNb})\text{O}_3$ - PbTiO_3 (PMN-PT) [68,81,82]. Strain mediation has widely been used to manipulate the energy landscape in composite materials [83], changing coercive fields and the depth of the potential well along the easy axis, (an example of which is shown in Figure 2c) however full switching of the anisotropy axis is much rarer [49,84] and will be discussed further below.

Strain mediated magnetoelectric coupling is widely used for the production of extremely sensitive magnetic field detectors, particularly for biomedical applications [85–87]. In addition to the directional dependence of magnetization in strain-mediated composites, small changes in linear anisotropy energies can be detected via ferromagnetic resonance (FMR), shown in Figure 2d, and acoustic resonance of a cantilever structure [85,87–89]. These kind of multiferroic antennae have demonstrated frequency tunability in the GHz regime on the order of $\Delta f \cong 6 \text{ GHz}$ [88]. The use of this technology for biomagnetic sensors is extremely promising, with significant work in the field having progressed to devices testable in vivo [90,91].

FIGURE 2| Strain- and exchange-coupled multiferroic composites. (a) Diagram showing how strain-coupled composites operate, where a strain is generated by a piezoelectric layer and transduced into a magnetization by the magnetostrictor. The figure shows both enhancement of uniaxial anisotropy due to strain and a potential switching pathway for a composite structure. (b) Birefringent (top) and magneto-optical Kerr effect (MOKE, bottom) images showing domain mapping from ferroelectric to ferromagnetic domains based on the in-plane strain state. Reprinted with permission from [54]. Copyright © 2012, Springer Nature. (c) Hysteresis of a uniaxial $\text{Fe}_{0.81}\text{Ga}_{0.19}/\text{PMN-PT}$ strain coupled composite, where the magnetic anisotropy is modulated by the application of an electric field. Reprinted with permission from [92]. Copyright 2020 by the American Physical Society. (d) Shift in FMR resonance as a function of applied electric field in $\text{FeGaB}/\text{PZN-PT}$. Reproduced with permission from [88] (copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA). (e) Diagram showing a switching of the exchange bias field from an antiferromagnet, which is driven by the magnetoelectric effect in an antiferromagnetic exchange-coupled heterostructure. (f) MOKE hysteresis loop of exchange biased $(\text{CoPd})_n/\text{Cr}_2\text{O}_3$, where the bias field is switched with a voltage and magnetic field pulse. Reprinted with permission from [93]. Copyright © 2010, Springer Nature.

2.2 Electric field control of exchange bias

Due to the mutually exclusive conditions for the onset of simultaneous ferromagnetic and ferroelectric order in a material (refer to section 1 and [8]), most single-phase multiferroic materials exhibit a ferroelectric order coexisting with an antiferromagnetic state. Therefore, single-phase multiferroic materials, such as BiFeO_3 , tend to have low converse magnetoelectric coefficients due to their small ferromagnetic moment that results from canted antiferromagnetic order [1,50,51,94,95]. Thus, conductive ferromagnetic layers, such as Co [96], CoFe [97,98] and Ni [69] are employed and exchange

coupled to the multiferroic magnetic order. This effectively amplifies the weak magnetic moment of the multiferroic. In so-called exchange coupled multiferroic heterostructures, a single-phase magnetoelectric antiferromagnetic multiferroic is coupled to a ferromagnetic layer through interfacial coupling. The exchange bias, see Figure 2e, is a phenomenon that occurs when a thin ferromagnet is in contact with the surface of an antiferromagnetic crystal. Below the ordering temperature of the antiferromagnetic state, the Néel temperature, the relatively hard spins of the antiferromagnetic surface interact with the soft spins in the ferromagnet, pinning the magnetization direction to that of the surface spins in the antiferromagnetic lattice [99]. This results in a significant broadening of the ferromagnetic hysteresis under magnetic field application, an enhancement in the coercive field, and a shift of the loop along the field direction called exchange bias field. At zero magnetic field, the ferromagnet is robustly pinned into one state by the bias field. Here, a magnetoelectric switching event can trigger a change in the antiferromagnetic state and lead to a net exchange coupled magnetization switch. The efficiency of this switching mechanism has been demonstrated in heterostructures based on prototypical antiferromagnetic magnetoelectric materials Cr_2O_3 [100,101] and BiFeO_3 [97,102–104]. An example of this switching using Cr_2O_3 is shown in Figure 2f.

Cr_2O_3 is a non-ferroelectric antiferromagnetic material which shows a linear magnetoelectric effect above room temperature [9,10]. It is a uniaxial antiferromagnet pointing along the c-axis of the hexagonal unit cell, and the magnetic cations are arranged in such a way that a c-plane terminated crystal can be engineered to produce a single, global, perpendicular surface magnetization [105]. This out-of-plane antiferromagnet would exchange couple to a ferromagnetic film or multilayer with perpendicular magnetic anisotropy, in contrast to most in-plane AFM/FM systems, creating an out-of-plane magnetized multiferroic heterostructure. Electric-field-driven switching of this configuration was first demonstrated in bulk crystals with out-of-plane ferromagnet $(\text{Co/Pt})_n$, however it required a static magnetic field to achieve full switching of the surface magnetization [101,105]. Linear magnetoelectric switching is defined by a critical energy product of electric field and magnetic field [10], meaning magnetoelectric switching of Cr_2O_3 requires either substantial static magnetic fields [106,107] or extraordinarily large voltages. This presents a significant engineering challenge for scaling of devices, as a Cr_2O_3 thin film must be able to withstand voltages large enough for switching, and significant work is currently focused on increasing the breakdown voltage or decreasing the switching threshold for thin films [108,109]. Thus far, magnetoelectric switching in thin film heterostructures has required substantial magnetic fields on the order of $\sim 0.6\text{--}1\text{ T}$ [93,106,107], but the technology remains promising for scale multiferroic devices.

In room temperature ferroelectric antiferromagnetic BiFeO_3 , the antiferromagnetic structure can cant and result in a weak moment that forms a long-range spin cycloid [110]. With enough epitaxial strain, a uniform canted moment emerges [111]. The antiferromagnetic and canted moment structure have been observed to track the ferroelectric polarization, thus, the moments of an exchange coupled ferromagnet not only amplify the effective moment but also correlate to the ferroelectric domain structure of the multiferroic [21,23,96,98,102,112,113]. This coupling between the magnetic and ferroelectric domain structure then permits the electric field control of the magnetization through the control of the ferroelectric polarization. This has been leveraged in BiFeO_3 -LSMO heterostructures and the sign of the bias field could be reversed after electrical switching [103,104]. In this system, however, the exchange bias field is not large enough to fully switch the magnetization of the ferromagnet, requiring the use of other magnetic layers to realize deterministic switching.

2.3 Electric field induced magnetization reversal

In strain-coupled multiferroics, the use of epitaxy to maximize strain transfer to the magnetostrictive layer has enabled electric field-controlled, non-volatile 90° switching of the ferromagnetic magnetization in a Gallenol (FeGa) film [65] (Figure 3a,b). This, however, may be the limit for purely strain-based devices as symmetry considerations state only 90° switching should be possible with a single voltage pulse. Experimental reports have demonstrated that enough magnetoelastic energy can be generated to drive 90° reorientation of anisotropy [54,65,82], but 180° switching, which is desired for maximum readout, may not be achievable unless sequential voltages are applied [114,115]. As an engineering challenge, this problem can be circumvented if material symmetries are broken by external stimuli or clever architectures utilizing the switching kinetics of the ferroelectric [114]. One way this can be accomplished is through external magnetic fields [116–118] or hybrid magnetoelectric-spintronic devices [119,120], which are discussed in section 4.

FIGURE 3| Magnetoelectric switching of magnetization. a) Magneto-optical Kerr effect (MOKE) micrographs of a strain-coupled composite multiferroic consisting of magnetostrictive $\text{Fe}_{0.81}\text{Ga}_{0.19}$ epitaxially grown on a GaAs substrate and bonded to a piezoelectric transducer. We see that, as the device is cycled through a full ferroelectric loop, the magnetization is deterministically switched between the two strain states. b) Transverse anisotropic magnetoresistance (AMR) showing repeatable resistive switching of the device. Reprinted with permission from [65]. Copyright 2012, AIP Publishing LLC. c) X-ray magnetic circular dichroism photoemission electron microscopy (XMCD-PEEM) images of a CoFe/BiFeO₃ exchange-coupled multiferroic showing deterministic switching of the magnetization that follows the ferroelectric domain pattern of the BiFeO₃. d) Low-field AMR versus applied voltage, showing 180° switching of magnetization under voltage. The upper, middle and lower panels show AMR from the as-grown (as-deposited) state, after -7 V and after +7 V. Reprinted with permission from [97]. Copyright © 2014, Springer Nature.

Full switching of magnetization induced by an electric field has been observed in exchange coupled BiFeO₃-ferromagnetic heterostructures, shown in Figure 3c,d. The magnetization of the ferromagnetic layer is strongly coupled to the antiferromagnetic axis, whose orientation depends on the ferroelectric polarization direction. Deterministic switching has been observed and studied primarily using CoFe metallic ferromagnets [97,102,121,122] using both microscopy [97] and transport measurements [102,122]. This deterministic switching event which requires no external fields has spurred the development of multiferroic computing technologies based on the material system [75,76], as well as

significant efforts to increase its efficiency [122,123]. Its implementation into energy efficient device heterostructures will be described in section 4.

3. Ferroic domains and domain imprint in thin film heterostructures

In multiferroic heterostructures, energy efficient functionalities rely on the ability to alter the ferroelectric domain architecture using an electric field in a controlled fashion once integrated in the ferroelectric/ferromagnetic multilayer. Ferroelectric domain architectures define the switching mechanism, they can also be transferred into an adjacent ferromagnetic layer and therefore drive the magnetoelectric behavior of the multiferroic multilayer. Engineering of domains and corresponding domain walls is the key towards reliable magnetoelectric switching events.

3.1 Ferroelectric domain engineering

Epitaxy - Because of the lattice-polarization coupling in ferroelectrics, the ferroelectric domain configuration in epitaxial thin films is dictated by the geometry and epitaxial strain, imposed by the selected single-crystal substrate. Substrate step edges are often preferential nucleation sites for ferroelectric domains [124], therefore substrate orientation and miscut angle become tuning parameters to control the degeneracy of domains [125,126]. In-plane strain anisotropy induced by the substrate often results in anisotropic stripe domain patterns [127,128]. Epitaxial strain, in extreme cases, can even induce polarity in otherwise non-polar structures, such as SrTiO_3 [129], EuTiO_3 [130], SrMnO_3 [131,132] or BaSnO_3 , SrSnO_3 [133]. Domain engineering in ferroelectric thin films using epitaxial strain has been reviewed in great detail, see [45] for references. Here, we highlight some recent development involving electrostatic boundary conditions and surface symmetry and atomic terminations to achieve a predefined polarization state.

In the particular case of multiferroic magnetoelectric BiFeO_3 thin films, the configuration of ferroelectric domains can be fully controlled by the choice of the crystallographic orientation of the substrate: thin films have one, two or four allowed polarization variants when grown on (111), (110) and (001) orientations of the lattice matching SrTiO_3 substrate, respectively [125]. High interfacial strain gradient can produce mosaic ferroelectric domains in BiFeO_3 that can be turned into stripes upon substrate annealing [134]. It is worth noting that the antiferromagnetic order in multiferroic BiFeO_3 is strongly

correlated with the ferroelectric domain state and also depends on epitaxial strain: spin cycloid can be suppressed by epitaxial strain [135,136]. BiFeO₃ epitaxial films thus provide a unique platform towards the antiferromagnetic order parameter engineering using epitaxial strain in thin films. Its antiferromagnetic-axis orientation can be tuned [137] from in-plane to out-of-plane by compressive and tensile strain, respectively. Furthermore, once stabilized in a single ferroelectric and magnetic domain state, the magnetic polarity in BiFeO₃ domains is inverted upon 180° ferroelectric switching on the macroscopic scale [138,139].

Electrostatics - Depolarizing field emerges with the accumulation of the ferroelectric bound charges at the surfaces of ferroelectric thin films. Oppositely oriented to the polarization direction, it usually has a detrimental impact on the polar properties of the films in the technology-relevant ultrathin regime. The depolarizing field can cause the polarization suppression [47,140,141] and limit the integration of ultrathin ferroelectric materials into devices and is therefore often viewed in a negative light. As most ferroelectric systems grow epitaxially in the ferroelectric phase [141,142], the depolarizing field already impacts the domain state during the design of functional heterostructures based on ferroelectric films [46]. Nevertheless, the progress in epitaxial design and nanoscale ferroelectric domain probe capacity recently allowed the integration of depolarizing field effects into the domain engineering process to tailor ferroelectric domains in a controlled manner with desired electrostatic boundary conditions [143,144].

In addition to the impact of the bound charge screening on the ferroelectric polarization state in the ultrathin regime, the electrode material selection and its corresponding work function drastically impact the ferroelectric bulk properties. Any asymmetry in the electronic and chemical environments of a ferroelectric layer results in an internal built-in field [145,146], which affects the polarization orientation and induces a preferred polarization direction and retention problems [147,148]. The insertion of a dielectric material within the ferroelectric capacitor architecture results in reduced bound charge screening efficiency and an onset of the depolarizing field, which induces a domain nucleation and leads to a multi-domain state in ferroelectric layer. It attenuates the built-in field influence on the ferroelectric hysteresis loop. Thickness control of the dielectric layer allows for tuning of the depolarizing field strength and the corresponding domain formation [144]. Furthermore, the existence of domains in an as-grown state and diminished dielectric leakage further improves the switching performance [143,144,147]. Such an approach previously restricted to prototypical tetragonal ferroelectric (BaTiO₃, PZT and PTO) has been used to engineer multiferroic domains in BiFeO₃ films. Chen and co-workers [149] showed that ultrathin dielectric layer of La-doped BiFeO₃ radically alters domain state in BiFeO₃. On DyScO₃ substrates, when a

conducting buffer is used, a uniform out-of-plane polarization state is stable and the BiFeO₃ system exhibits 71° stripe domain architecture. However, the insertion of the dielectric buffer results in the conversion towards a fully 109°-type stripe domain pattern, without any net out-of-plane polarization component and technology-relevant conducting 109° domain walls [150,151] (See Figure 4a-d).

Atomic surface termination and interface chemistry, symmetry - In the ultrathin regime, the polarization direction (up or down in a single domain state) and overall domain architecture can also be controlled by selecting an appropriate atomic surface termination of the substrate or buffer layer. Using chemical surface treatments or thermal annealing, the substrate atomic termination can be engineered. Considering perovskite ABO₃ model system, the thin film (001) oriented growth can take place from either the AO or BO₂ plane. In the case of ABO₃ type ferroelectrics containing charged planes, there is an electrostatic potential step across the interface with the buffer. This results in a deterministic control on the direction of polarization of the film. For instance, because the BiFeO₃ unit cell consists of charged planes, i.e. (BiO)⁺ and (FeO₂)⁻, the polarization can be predefined by selecting the buffer surface termination for the growth. On negatively charged (MnO₂)^{-0.7} planes of LSMO buffer, the growth starts with positively charged (BiO)⁺ planes. The resulting potential sets the polarization in the upwards direction. The deposition on (La_{0.7}Sr_{0.3}O)^{+0.7} plane results in downward oriented films [152]. Because the stacking sequence in atomic plane can propagate during the growth of several successive perovskite materials, the design of multilayer with predefined polarization configuration [141], i.e. with parallel or antiparallel relative polarization state, is possible as shown in Figure 4e-g. Moreover, different interfacial atomic sequences and corresponding electrostatic potential, also results in a modulated magnetoelectric effect and exchange bias in oxide multilayers [153]. The atomic surface termination and symmetry provide a handle on the polarization state from the bottom interface during the multilayer design process itself, adding a degree of freedom for the design of domain architecture and the surface topography of the film [154].

In order to stabilize ferroelectricity in the ultrathin regime, polar metals crystallizing in non-centrosymmetric point groups compatible with ferroelectric symmetries are emerging as a promising alternative to standard metals. Their intrinsically broken parity can even help to surpass critical thickness [155]. They have been proposed as key elements towards the suppression of the critical thickness in ferroelectrics once integrated in technology-relevant capacitors. The scarcity of polar metals, that are structurally compatible with application-relevant ferroelectrics, however, limits their integration into ferroelectric base devices. Alternatively, the chemistry at the top interface of the ferroelectric material can be tuned in order to achieve a deterministic polarization state [156]. The importance of tunable

electrostatics at ferroelectric BiFeO₃ films surfaces was explored in a reversible aqueous switching. Depending on the H⁺/OH⁻ concentration of the solution in direct contact with the film, the formation of polarization-selective chemical bonds at the interface is controlled, as shown in Figure 4h-i.

FIGURE 4 | (a-d) BiFeO₃ domain engineering by insertion of dielectric La-doped BiFeO₃ buffer layer. Out-of-plane (a) and in-plane (b) Piezoresponse force microscopy (PFM) images of BiFeO₃ 71° stripe domain structure in BiFeO₃/SRO/DSO. 109° stripe domains appear upon the insertion of La-doped BiFeO₃ in vertical (c) and lateral (d) PFM images. Reprinted with permission from [149]. Copyright © 2017, American Chemical Society. (e-g) Engineering ferroelectric multilayers with user-defined up/down polarization sequence (e): A-site growth and upwards polarization of BiFeO₃ is achieved by insertion of a TiO₂ monolayer. B-site growth and downwards polarization of BiFeO₃ is achieved by SrO self-termination of SRO buffer, confirmed by PFM scans (f) and (g), respectively. Reprinted with permission from [141]. Copyright © 2017, Springer Nature (h-i) Water poling of ultrathin ferroelectric BiFeO₃: polarization is reversed to the upward (h) and downward (i) after exposing the film to water and acidic solution, respectively. Reprinted with permission from [156]. Copyright © 2018, Springer Nature.

3. 2 Domain imprint

The interface between ferroelectric and ferromagnetic thin films can enable magnetoelectric coupling. In particular, ferroelectric domains can be imprinted into the magnetic state in an adjacent layer. There are three distinct ways to achieve artificial magnetoelectric coupling [5]: via (i) strain, (ii) direct (spin) exchange, and (iii) charge coupling, see section 2. In strain coupled artificial multiferroics, piezoelectric crystal or thin film and magnetostrictive layer are elastically coupled leading to controllable magnetoelastic anisotropy due to propagation of electrostrain [70,157–164] with a key requirement of strong elastic pinning of magnetic domain walls onto ferroelectric domain walls [165]. In exchange-biased multiferroic composites, the interaction occurs between a ferromagnet and intrinsic multiferroic with uncompensated antiferromagnetic order, such as BiFeO_3 [21,98,166,167], YMnO_3 [168] and LuMnO_3 [118]. The electric field changes both the polarization and the direction of antiferromagnetic spin ordering in a multiferroic. This allows a direct exchange effect between antiferromagnetic and ferromagnetic spin ordering. Although the physics of exchange coupling is different from strain coupling, both produce lateral modulations of magnetic anisotropy leading to domain transfer. Note that because strain is uniaxial, the electrical directional control of a magnetic state, i.e. 180° electric-field-induced magnetization reversal, has been restricted to exchange-coupled systems. Charge-coupled artificial multiferroics make use of the ferroelectric field effect: non-volatile bound charges at the ferroelectric interface are screened by the ferromagnetic layer, leading to either accumulation (hole doped) or depletion (electron doped) states in ferromagnet when the polarization is pointing away or towards the ferromagnet, respectively. If the ferromagnet has multiple accessible ground states, this might result in drastic alterations of magnetization and domain imprint [79,169–175]. This mechanism is different from the two mentioned previously, because changes in magnetization are limited to interfaces, up to a screening length [175,176]. However, in the ultrathin regime (especially when superlattices are considered), full domain transfer could be achieved.

Most recent studies on domain imprint have focused on the dynamics investigation aiming to understand the origin of the domain imprint and the domain pattern evolution upon the application of electric field. De Luca and coworkers [177] investigated magnetoelectric coupling dynamics between exchange-coupled BiFeO_3 and ferromagnetic CoFe using optical SHG and magnetic force microscopy (MFM) techniques *operando*; see Figure 5a-f . An electric field in the order of coercive field of BiFeO_3 is required to activate the domain pattern transfer. In another work, magneto-optical Kerr effect (MOKE) microscopy was employed to show that ferroelectric and ferromagnetic domain walls move in unison upon the application of out-of-plane electric field pulses [73,178,179]. These experiments confirmed that the process is reversible and neither magnetic field, nor current are required. The domain wall velocity is hence

fully determined by electric field strength and can reach several 100 m s^{-1} as predicted by numerical simulations [180]. Recent studies on strain-mediated magnetoelectric coupling revealed that rotations of the local magnetization upon electric field pulses are normally smaller than expected 90° due to electrically driven shear strain [181], see Figure 5g-l. This guarantees a deterministic return to the initial magnetization direction with no possibility of magnetization reversal and offers the prospect of writing data both magnetically and electrically [181].

A novel route towards exact matching between ferroelectric and ferromagnetic domain patterns was proposed by Leo et al. [182] in bulk material. Complete magnetoelectric domain inversion was observed in multiferroic Mn_2GeO_4 and magnetoelectric Co_3TeO_6 : the ferroic order parameter in these materials is fully reversed in each domain, but the initial domain pattern is perfectly reproduced. Figure 5m shows how ferroelectric domains in Mn_2GeO_4 are inverted upon application of magnetic field. The observation is rationalized by the coupling between a complex set of order parameters where one of them is independently switched with an external field, while another retains the memory of the domain pattern. A related effect was observed in $\text{Dy}_{0.7}\text{Tb}_{0.3}\text{FeO}_3$ [183]: here multiferroic domains defined by multiple order parameters can be reversibly converted to multiferroic domain walls and back at a specified location within a non-multiferroic matrix. Such interconversion can be a key to tailoring elusive domain architectures in antiferromagnets. Although both effects have only been demonstrated at cryogenic temperatures, other materials exhibiting similar properties are anticipated to be discovered, owing to the generality of the two effects.

FIGURE 5 | (a-f) Domain transfer from BiFeO₃ to CoFe. The spatially resolved MFM scans show ferromagnetic domains in CoFe with the magnetic field applied along [001]_{DSO} (a,d) and [1 -1 0]_{DSO} (b,c). The pristine CoFe film yields a uniform in-plane magnetization indicating the suppression of the magnetoelectric BiFeO₃/CoFe coupling as shown in (c). After application of an electric field $E \approx E_c$ domain pattern transfer is activated (f). Reprinted with permission from [177]. Copyright 2018 by the American Physical Society. (g-l) Electrically driven shear strain effects in magnetoelectric switching of PMN–Pt/Ni heterostructure. 50- μ m-diameter maps (g,h) showing changes of magnetization direction $-180^\circ \leq \Delta\phi \leq 180^\circ$ of each pixel upon electric field steps ($E_1 \rightarrow E_2$) and ($E_2 \rightarrow E_3$) anticipated to interconvert the hard and easy magnetization directions in Ni. Due to shear strain magnetization rotates by angles smaller than hitherto expected 90° , as shown by the number of pixels N' that undergo a change of magnetization direction $\Delta\phi$, for pixels that are green (i,k) and purple (j,l) with modal angles specified. The data color represents a modal angle on the color wheel. Reprinted with permission from [181]. Copyright © 2019, Springer Nature. (m) Inversion of the ferroelectric domain pattern in multiferroic Mn₂GeO₄ evidenced by sequentially taken SHG images of out-of-plane P_z domains at the given magnetic fields Hz. Reprinted with permission from [182]. Copyright © 2018, Springer Nature.

3.3 Domain wall engineering

Domain architecture is also characterized by its domain walls configuration. Domain walls, separating different region of uniformly oriented order parameter, here ferroelectricity and ferromagnetism, can play an important role in functionalities of thin film heterostructures. The physical properties emerging at ferroelectric domain walls and the corresponding applications have been the subject of several reviews, refer to [184–186]. Here, we place the emphasis on the magnetoelectric systems and applications.

Tremendous progress has been achieved in the field of ferroelectric domain walls over the last couple of years. Ways of injecting ferroelectric domain walls [187–189] and controlling their motion [188,190,191] as well as their speed [192] are now established. Sharma and coworkers [189] have demonstrated a prototype domain wall switch in BiFeO₃ with three distinct states: no domain wall, neutral domain wall and charged domain wall as shown in Figure 6a-f. Domain wall detection is now possible not only via conventional scanning probe techniques [185], but also with optical SHG [193,194], Raman spectroscopy [195] as well as synchrotron X-ray diffraction [196]. Moreover, PZT domain walls were recently identified as optically active objects when interfaced with MoS₂ flakes offering novel tunability of interfacial optical response [197]. All these advances point towards the future development of magnetoelectric devices based on domain walls.

Magnetic domain walls in ferroelectric matrix - Magnetoelectric coupling in heterostructures can alternatively be achieved through the domain walls. The importance of the domain wall role first emerged

upon nanoscale investigation of BiFeO₃ interfaced with CoFe, which showed that exchange-bias directly depends on the type and crystallography of the domain walls in BiFeO₃ [112]. An enhancement of the coercive field is observed regardless of the domain wall type, while exchange bias itself, manifesting by shifted magnetization hysteresis, is ascribed to uncompensated spins at 109° domain walls exclusively [112], as seen in Figure 6g-l. The domain wall dynamics itself influences the domain imprint or domain coupling in artificial multiferroic heterostructures. The application of an electric field can induce a ferroelectric domain wall motion, releasing the imprint or magnetoelectric coupling locally until the domain coupling is recovered at a new ferroelectric domain wall location. This was used to control the magnetic exchange bias and magnetotransport properties in the model system YMnO₃/Py [168] and LuMnO₃/Py bilayers. Antiferromagnetic and ferroelectric domain walls in multiferroic manganites can be unclamped and change the sign of exchange bias after each successive electric pulse [118]. Such clamped domain walls, possessing multiple ferroic order parameters, can in turn be referred to as multiferroic domain walls [1]. They sometimes are the sole reason for magnetoelectric domain coupling, e.g. as in hexagonal manganites h-RMnO₃ [12]. Multiferroic domain walls have also been reported in multiferroics such as MnWO₄ [198,199], RFeO₃ [200,201] or TbMnO₃ [202]. A finite magnetic moment at the domain wall can sometimes accompany polar and antiferromagnetic domains as measured in h-ErMnO₃ [203], oxygen deficient PbTiO₃ [204] or ferroelastic TbMnO₃ [205]. We note that polar domain walls in non-ferroelectric structures, e.g. Néel-like domain walls in iron garnet films [206], ferroelastic domain boundaries [207–209] have also been reported. All of this holds potential for magnetoelectric coupling in heterostructures right at the wall location in a non-magnetoelectric host compound.

Charged-domain-wall in vicinity of magnetic state - Bound charge accumulation at so called charged ferroelectric domain walls [15,150] or ferroelastic boundaries [210] creates another pathway to a magnetoelectric effects at domain walls: localized charge coupling can be induced at interfaces of metallic ferromagnets [170]. This could trigger electrically tunable localized interfacial reconstructions, leading to the ferromagnetic to antiferromagnetic phase transition in colossal magnetoresistive ferromagnets such as LSMO [171,211]. A challenge remains in the stabilization of charged domain walls and their unfavorable electrostatic configuration. The family of improper ferroelectric, i.e. geometric ferroelectrics h-RMnO₃ [15] or electronically-driven improper ferroelectric CsNbW₂O₉ [212] are prominent candidates for the design of functional and stable charged domain walls.

In proper ferroelectric systems, fully in-plane polarized systems may open new avenues towards stable charged domain wall design. In in-plane polarized system, the depolarizing field influence on the domain pattern does not depend on the layer thickness and may be linked to the domain width [30,31].

Stable periodic arrays of nominally charged domain walls have been recently reported in ultrathin Aurivillius films (see Figure 6m-o) [30], putting this class of layered ferroelectrics [29,213] in the forefront of domain wall engineering research. These compounds can further host magnetic ions driving multiferroicity [34,214–216]. However, the impact of layered anisotropic structure [217,218] and B-site doping on the domain wall electronic configuration remains to be explored.

FIGURE 6] (a-f) Tristate conformational domain wall switch in BiFeO₃. Lateral PFM amplitude (a,c,e) and the corresponding c-AFM images (b,d,f): in the absence of domain walls (a,b) and in the presence of neutral (c,d), and charged (e,f) domain wall achieved with the device. Reproduced with permission from [189]. (g-l) Exchange bias dependence on domain wall type in BiFeO₃. Magnetic measurements on BiFeO₃/CoFe heterostructures exhibiting enhanced coercivity (g) and exchange bias (h). (i,j) In-plane and out-of-plane (inset) PFM contrast for typical BiFeO₃ films corresponding to (g) and (h), respectively. Detailed domain wall analysis for (k) stripe-like and (l) mosaic-like BiFeO₃ films. 109° domain walls are directly related to exchange bias, while other domain walls still enhance coercivity. Reprinted with permission from [112]. Copyright © 2008, American Chemical Society. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA. (m-o) Nominally charged domain walls in ultrathin Bi₅FeTi₃O₁₅ Aurivillius films (film structure depicted in m). Lateral PFM contrast (n) recorded for a half-unit-cell film revealing nominally charged head-to-head and tail-to-tail domain walls, sketched in a schematic (o). Reproduced with permission from [30]. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA.

4. Multiferroic heterostructures for spintronics

The coupling between electric and magnetic orders in magnetoelectric and multiferroic heterostructures opens pathways to energy efficient spintronic devices and other novel devices (such as sensors, motors, voltage-controlled RF devices, and reconfigurable electronics) that leverage the electric to magnetic transduction. Over the past 20 years, the embodiment of devices that employ magnetoelectrics or multiferroics has grown from a magnetic memory element to reconfigurable memory-in-logic devices and circuit architectures. Here we will focus on the modern spin-based device concepts that integrate magnetoelectric multiferroic heterostructures and briefly discuss the evolution of the concepts.

4.1 Magnetoelectric/multiferroic memory

The magnetic random-access memory was one of the earliest devices identified where integration of a magnetoelectric or multiferroic could improve performance. This would occur through a reduced write energy via magnetoelectric switching or a multi-state output through independent control of the electric and magnetic polarizations. Here we will focus on the former as it has had the most impact on devices to date.

Spin-based magnetic random-access memory (MRAM) technology uses spin-transfer or spin-orbit torques to convert an electric charge current into a spin current that transfers angular momentum to the magnetization of the free layer in a memory element. From an energy perspective, the conversion of charge to spin current is energy inefficient as the current densities to drive switching are large ($\sim 10^6$ - 10^7 A cm⁻²) and losses from resistive heating (I^2R) are significant. Magnetoelectric switching mitigates the large write currents and dissipation energy as an electric field is applied across a dielectric insulator. The energy dissipation is then dominated by charging of the capacitor or ferroelectric switching and the switching of the magnetization.

For example, the state-of-the-art spin-orbit torque (SOT) switching of a ferromagnetic layer employed low-resistivity AuPt alloys and demonstrated switching at a current density of 1.2×10^7 A/cm². The low resistivity (80 $\mu\Omega$ cm) and high spin Hall conductivity (4.4×10^5 Ω^{-1} m⁻¹) leads to a power dissipation per write operation that is ~ 10 times lower than that using W [219]. Follow-up work has shown that in the Au_{0.25}Pt_{0.75} system has reported sub-50 fJ dissipation (~ 580 μ J cm⁻²) at 1 ns current pulses and less than 10^{-5} error rate [220]. In contrast, the electric field control of magnetism in rather unoptimized multiferroic heterostructures have shown energy dissipations in the range of 1-500 μ J cm⁻² [49]. The primary energy

dissipation comes from the switching of the ferroelectric polarization, or the charging of and leakage in the capacitor in the case of non-ferroelectric magnetoelectrics. Thus, the most immediate embodiment of a magnetoelectric memory element uses the magnetoelectric switching of a layer in a giant magnetoresistance (GMR) or magnetic tunnel junction (MTJ) element, whereby a small current can be used to readout the state of the device (Figure 7).

One of the first materials proposed for such applications was the room temperature magnetoelectric multiferroic BiFeO₃. While the idea was put forward in the 2000's [7,221], it was not until the mid- and late 2010's that reversible magnetoelectric switching of a GMR element was demonstrated at room temperature (shown in Figure 7) [97,222]. By exchange coupling the free layer of the GMR stack to the BiFeO₃ layer, the free layer then becomes controlled by the applied electric field to the BiFeO₃. This is observed in current in-plane resistance measurements of the GMR structure versus applied voltage (Figure 7). Notably, the hysteresis and coercive voltages in the ferroelectric response of the BiFeO₃ agree well with the hysteresis observed the GMR device, demonstrating a clear coupling between electrical and magnetic parameters. In the devices that involve switching the ferroelectric order parameter, the energy dissipation is dominated by that contribution. The energy dissipation (per unit area) can then be approximated by $2P_s V_c$ where P_s is the saturation polarization of the ferroelectric and V_c is the coercive voltage. Thus, the energy dissipation for these pioneering structures is $\sim 450 \mu\text{J cm}^{-2}$ [49,97].

While the pioneering devices have energy dissipation per unit area that is comparable to the leading SOT devices, there are clear routes to tune the magnetoelectric energy landscape for improving performance. La substitution in BiFeO₃ systematically destabilizes the ferroelectric order thereby reducing P_s and V_c . Yet recent work has found that the substitution progressively increases the degeneracy of the potential energy landscape of the system and rotates the polar axis [113,123]. While the magnetoelectric coupling seems preserved, the increased complexity in ferroelectric and antiferromagnetic domain states compared to the undoped BiFeO₃ films demands further investigation.

FIGURE 7 | (a-d) Electric field control of a GMR device using BiFeO₃. (a) Schematic of the magnetoelectric memory element. A voltage is applied across the multiferroic BiFeO₃ which controls the magnetization state of the exchange coupled layer. Current is applied in the plane of the GMR stack for readout. Reprinted with permission from [223]. (b) PFM image of an actual device with the current bar oriented at ~45° from the BiFeO₃ domains. (c,d) Measured GMR (c) and ferroelectric polarization (d) versus voltage applied across the BiFeO₃ layer. The resistance of the GMR device (c) is hysteretic, non-volatile, and with coercive voltages in agreement with that from the ferroelectric switching (d) revealing the magnetoelectric switching of the BiFeO₃ and the reversal of the exchange coupled magnetic layer in the GMR stack. Reprinted with permission from [222].

Recently, the field of antiferromagnetic spintronics has garnered attention due to the new physical insights, probe development of the otherwise inert state, and the new avenues for device implementation. For electrical insulators, the longitudinal and Hall resistance of a spin Hall metal in contact with the antiferromagnetic insulator will depend on the orientation of the Néel vector. This occurs either through spin Hall magnetoresistance or a proximity induced Hall effect. Work by Kosub and colleagues [107] demonstrated a purely antiferromagnetic magnetoelectric memory in a Cr₂O₃/Pt heterostructure (Figure 8). Here the Pt layer couples to the surface magnetization state of Cr₂O₃, which can be readout through a Hall measurement. The surface magnetization state is determined by the antiferromagnetic domain state which can be switched by simultaneous application of an electric and magnetic field with a critical electric and magnetic field product [105]. A few features of this purely antiferromagnetic magnetoelectric memory are particularly noteworthy. First, contrary to the BiFeO₃ based devices discussed previously, the absence of an exchange coupled ferromagnetic layer is expected to decrease the device switching times due to the

faster spin dynamics in antiferromagnetic systems. Second, Cr_2O_3 is not ferroelectric, therefore, energy dissipation is capacitive and ultra-low ($\sim 6 \times 10^{-2} \mu\text{J cm}^{-2}$ – assuming ideal dielectric behavior and neglecting the dissipation associated with the applied 6.3 kOe magnetic field [49]). Finally, extending the idea of coupling to the surface magnetization to quantum materials such as topological insulators, topological ferromagnetic insulators, or spin-valley Hall materials opens doors to electrical control spin-momentum locked phenomena [224,225].

FIGURE 8| (a-d) Cr_2O_3 based antiferromagnetic magnetoelectric memory. (a) Schematic of spin-based memory elements categorized by the writing stimulus and order parameter for readout. (b) The surface magnetization of antiferromagnetic magnetoelectric Cr_2O_3 enables readout of the antiferromagnetic state of a bit through a Hall effect in an adjacent Pt layer. (c,d) Write voltage and Hall signal showing the fundamental write-read procedure (c) and robustness of the device with cycle number (d). Reprinted with permission from [107]. Copyright © 2017, Springer Nature.

4.2 Magnetoelectric/multiferroic Logic

Computation based on complimentary metal-oxide-semiconductor (CMOS) transistors is inherently inefficient due to the volatility of the device and the fundamental losses as the devices are scaled down. In the search for a new materials platform for the next generation of computation, non-

volatile technologies have emerged as promising avenues as the total energy dissipation, write energy, and scalability can be shown to outperform CMOS. Work led by Intel and researchers at UC Berkeley have proposed a Magneto-Electric-Spin-Orbit (MESO) logic as one such technology (Figure 9) [76]. The fundamental device operates with a magnetoelectric write operation that determines the magnetization orientation of a magnetic bit. A supply current injects electrons into the magnetic bit and spin-polarizes them. This spin polarized current is then injected into a spin-orbit layer that uses the interface Rashba-Edelstein effect or the inverse spin Hall effect to create a transverse current that is used for readout or cascading logic devices.

At the heart of the device is the magnetoelectric write operation which takes the voltage input and controls the orientation of the magnetization which is hysteretic, non-volatile, and 10 to 1000 times more energy efficient than SOT or STT switching [49]. Critical for applications is the efficiency of the device at scale. The authors, using accepted bulk and thin film material parameters, find that MESO will operate at 1-10 aJ dissipation and sub-100 mV per operation at $20 \times 30 \text{ nm}^2$ nanomagnet and $10 \times 10 \times 10 \text{ nm}^3$ magnetoelectric dimensions. Proposed MESO logic circuits compare favorably to CMOS fanout-4 inverter, two-input NAND adder, 32-bit ripple-carry adder and 32-bit ALU logic circuits. Particularly when compared to the inverter in 2018, MESO shows a 10-100 fold switching energy reduction in a non-volatile technology.

FIGURE 9 | (a-e) The MESO device and connectivity. (a) Shows the fundamental mechanisms employed in the MESO devices from an input signal to output. (b) Schematic of the MESO device. Input, output, supply and spin currents are represented by I_c (input), I_c (output), I_{supply} , and J_s (with polarization direction σ), respectively. The electric field (E_{ME}) applied to the magnetoelectric at the input and the effective magnetic field (H_{ME}) generated that couples to the ferromagnetic bit are shown. (c,d) Normalized magnetization direction (c) and output current (d) versus input current. The output is hysteretic and non-volatile. The output current is proportional to the orientation of the magnetization which is controlled by the input to the magnetoelectric layer. (e). Schematic showing the connectivity to form logic structures. Reprinted with permission from [76]. Copyright © 2018, Springer Nature.

The estimations are impressive, and the race is on to realize such a device. Yet, several materials challenges remain to be tackled. While great progress has been made to realize the electrical switching of

magnetism, demonstrating this at technologically relevant scale and solving defect pinning at metal-oxide interfaces remain largely untackled. The observation of application-compatible spin Hall resistivities in material systems compatible with oxide magnetoelectrics has been unexplored.

4.3. Neuromorphic devices

Biologically inspired computing mimics the neural structure of the brain and is highly efficient at difficult tasks. Of current interest is the development of neuromorphic circuits that are able to analyze videos and images for recognition and filtering applications. While such neural networks can be realized using CMOS technology, the inherent inefficiencies of CMOS devices leave room for non-volatile beyond-CMOS technologies to enhance the performance and parallelization. Spin-based neurons have been proposed and simulated. While showing promise, many rely on magnetic tunnel junctions, which makes readout challenging due to the nature of resistance and spin Hall and spin torques which are unideal due to resistive heating [226].

Building on the MESO device, simulations of a cellular neural network with inverse Rashba-Edelstein magnetoelectric (IRME) neurons and CMOS synapses performing a low-pass filtering have been reported to be fast and efficient [227]. In this case, the IRME neuron state is written with a voltage across the antiferromagnetic magnetoelectric layer, which controls the magnetization state of an exchange coupled ferromagnetic layer. Readout is done with a supply current that is spin polarized by the ferromagnet and injected in the inverse Rashba-Edelstein heterostructure, which converts the injected spin current into a transverse voltage. Assuming materials parameters for CoFe as the ferromagnet, magnetoelectric coefficients comparable to BiFeO₃, and an inverse Rashba-Edelstein parameter for that found in LaAlO₃/SrTiO₃ polar interface [228], the IRME performs state transitions in ≈ 100 ps, network operations with a per-neuron energy cost on the order of ≈ 1 fJ, and is non-volatile [227]. The IRME device has several notable features that lead to enhanced performance. Beyond the energy efficiency of the IRME neuron and its non-volatility which are enabled by the materials, the IRME network is parallelized as each neuron operates simultaneously and performs both write and read operations at the same time.

4.4. Hybrid magnetoelectric-spin-orbit torque heterostructures

Composite magnetoelectric multiferroic heterostructures are relatively easy to realize and

demonstrate large magnetoelectric effects at and above room temperature. While such heterostructures have displayed robust coupling and even 90° switching of the magnetization, a full magnetization reversal is often desired to maximize readout signal. Thus, hybrid magnetoelectric-spin-orbit torque heterostructures have emerged to mitigate the weakness of SOT and composite magnetoelectric switching and leveraging their respective strengths. One embodiment of this concept is the hybrid magnetoelectric-spin-orbit torque (ME-SOT) heterostructure, which consists of a composite magnetoelectric with a spin-orbit torque active layer.

The main steps to switching in such a heterostructure first involve a voltage applied to the piezoelectric layer to drive the 90° switching of the magnetization. Then a current is applied to the SOT layer to drive the remaining 90° switch. Simulations of this two-step hybrid switching process indicate that the current pulse width for reliable spin-orbit torque switching may decrease by a factor of ~ 10 -1000, depending on the anisotropy and damping parameter of the magnetostrictive layer [119]. The faster switching times is the result of the reduced precessional motion of the magnetization as the magnetoelectric has already initialized it to the peak of the magnetic anisotropy barrier (assuming a uniaxial anisotropy). The device demonstrates some key advantages, in particular high temperature operation, simple materials synthesis, deterministic 180° magnetization switching at a ~ 10 -1000 times improved energy-delay performance.

Other manifestations of hybrid ME-SOT heterostructures have been explored to break critical symmetries and lift degeneracies in SOT switching [229–232]. For instance, SOT switching of a perpendicular magnetic anisotropy (PMA) magnet by the spin Hall effect of isotropic heavy metals is complicated by non-deterministic switching. The symmetry of the system can be changed to realize deterministic switching by applying an in-plane magnetic field, switching in the presence of an in-plane exchange bias [232], but also by magnetoelectrically induced changes to the magnetic anisotropy and electric field gradients [233,234].

5. Future perspectives and concluding remarks

The current achievements dealing the electric field control of magnetism have been reviewed. Let us now address one of the main challenges limiting the insertion of multiferroics into spintronic devices, i.e. the determination of the magnetoelectric switching dynamics. Switching dynamics are typically estimated from Landau-Lifshitz-Gilbert-Slonczewski (LLGS) simulations and have seen little experimental

work. Therefore, despite all the progress, the competitiveness of magnetoelectric-based devices with respect to established spin current based technology is still under debate. We review emergent probes of the dynamic of multiferroic antiferromagnetic states in thin film heterostructures. We finally present some new avenues in the field, highlighting the potential of light to probe and even assist multiferroic switching.

5.1 Magnetoelectric switching dynamics

Magnetoelectric random-access memories or magnetoelectric spin-orbit logic devices with strong charge-to-spin coupling promise attojoule switching energies. If those concepts shall become reality, the scientific community needs to intensify efforts towards a deeper understanding of multiferroic and interlayer exchange dynamics. The lack of existing data on multiferroic switching dynamics partly originate from the difficulty to simultaneously and operando probe two order parameters, i.e. electric polarization and net magnetization. The direct observation of the ferroelectric-ferromagnetic domain correlation during a magnetoelectric switching event is a prerequisite to the understanding of the switching mechanism and its dynamics.

In the model system, BiFeO₃/ferromagnetic heterostructures, the electric field induced magnetization reversal involves a two-step switching process. Within the unit cell, the polarization projection onto the interface plane rotates twice by 90° [97]. The resulting 180° reversal of the polarization projection and the corresponding antiferromagnetic configuration in BiFeO₃ in the final state thus leads to the 180° switch of the exchange coupled magnetization in the ferromagnetic layer [97,102]. While the ferroelectric switching has been unambiguously demonstrated, the dynamics of the magnetic order in BiFeO₃ and in the magnetically coupled ferromagnetic layer have remained unexplored.

On the one hand, several experimental techniques allow probing of the ferroelectric switching and domain dynamics, even in a buried state. Beyond the investigation of the remnant hysteresis using positive-up negative-down (PUND) method, hard X-ray diffraction [235,236], hard X-ray photoemission spectroscopy [237], second harmonic generation [177,238], X-ray photon correlation spectroscopy [239], and piezoresponse force spectroscopy [126,240] provide direct access to the polarization with time resolution and are compatible with operando analysis. On the other hand, antiferromagnetic states, dominating the magnetoelectric switching mechanism, lack a net magnetization and have therefore remained difficult to address. Over the last few years, the following techniques have emerged as efficient probe of antiferromagnetic state in thin film heterostructures.

The single-spin magnetometer scanning probe technique – Based on a point-like impurity nitrogen-vacancy (NV) defect in diamond mounted on a scanning tip [241–243], this technique provides an outstanding magnetic sensitivity (down to a few femtotesla) with a spatial resolution comparable to the one achieved with atomic force microscopy. It has been used to spatially resolve the local magnetic order in multiferroic antiferromagnetic BiFeO₃ thin films [244]. The periodic modulation in the magnetic response corresponds to the spin cycloid in the films. Such a measurement allows the correlation of the antiferromagnetic domain state with the ferroelectric domain architecture obtained by PFM.

Magnetoelectric force microscopy (MeFM) – The MeMFM is another scanning probe based technique. A magnetically tip is used to probe the magnetoelectric response of the material exposed to an AC voltage. It is based on the lock-in detection of the magnetic force microscopy signal from the electric-field-induced magnetization in magnetoelectric materials. First developed in order to probe magnetoelectric domains in hexagonal ErMnO₃ crystals at low temperature [245], its efficiency to monitor the magnetoelectric response of the Cr₂O₃ crystal model system has been recently demonstrated [246], see Figure 10a-b. The MeFM requires the magnetoelectric material to be integrated in a capacitor to trigger the magnetoelectric response. On one hand, such capping may prevent simultaneous piezoresponse based ferroelectric domain imaging. On the other hand, the use of heavy metals for the electrode might provide a platform for the investigation of hybrid magnetoelectric STT, SOT type of heterostructures, see section 4.4.

Optical second harmonic generation (SHG) – SHG can be sensitive to the reduction of symmetry through the magnetic ordering of spins. We refer the reader to several reviews dealing with the potential of SHG to probe ferroic states in bulk and thin film materials [238,247,248]. Here we highlight the seminal demonstration in antiferromagnetic magnetoelectric Cr₂O₃ crystal, in which the SHG was employed to image antiferromagnetic domains [140], see Figure 10c-d. Such an optical based technique further offers time resolution matching the ultrafast dynamics of the ferroic switching speed. The potential of time-resolved SHG to determine antiferromagnetic ultrafast dynamics has recently been revealed [249]. In bulk YMnO₃, the spin ordering modulation upon coherent magnon excitation could be tracked using a combination of Faraday rotation and SHG. In multiferroic thin films systems, SHG has been used to identify the antiferromagnetic domains in epitaxially strained BiFeO₃ [250]. Furthermore, taking advantage of the optical rectification process in intense light fields, 100 fs light pulses were used to generate electric pulses in the antiferromagnetic resonance regime of BiFeO₃. The corresponding change in the antiferromagnetic domains were imaged by SHG after the optically induced electric pulses, see Figure 10e-f. This work suggests new avenues towards the optical control of multiferroic and magnetoelectric switching. We address the non-invasive optical control of such switching events in the next section.

FIGURE 10| (a-b) Cr_2O_3 crystal imaged using optical second harmonic (a) and magnetoelectric force microscopy (b). Reprinted with permission from [246]. (c-d) Optical second harmonic generation images with right (c) and (d) left circularly polarized light. The sample is 6 mm long. Reprinted with permission from [140]. Copyright 1995, AIP Publishing LLC. (e-f) Optical second harmonic generation based reconstruction of the antiferromagnetic configurations of the patterns in BiFeO_3 thin films in virgin state (e) and after sub-coercive picosecond electric pulses delivered by rectification of intense laser pulses (f). Reprinted with permission from [250]. Copyright © 2017, Springer Nature.

5.2 Towards all optical magnetoelectric switching

Light, which has been mainly used to probe materials [247,248], now appears to act on ferroic states. Its potential to induce magnetization reversal in thin films was recently demonstrated [251,252]. The long working distance and ultrafast timescale of optical processes render it further compatible with device integration. The light-matter interaction in ferroelectrics however drastically differs from the ferromagnetic analogs. The light induced processes in ferroelectric materials span from local heating [253] to photo-induced flexoelectric effect [254], photovoltaic effect [255] or photostriction [256]. In particular, photo-induced charge carriers may migrate towards domain walls or to the film surface and act on the bound charge screening at the ferroelectric surfaces. Considering the depolarizing impact on domain state in epitaxial thin ferroelectric films, see section 3 and [46,144], light irradiation on thin films may therefore emerge as an efficient approach towards the domain modulation in ferroelectric and multiferroic magnetoelectric systems.

A pioneering work dealing with light-induced polarization changes investigations focused mainly on bulk materials and led to local domain wall motions or phase transitions [255,257–259]. The direct monitoring of an optically induced domain wall motion and domain configuration change in ferroelectric material opened new avenues for tuning macroscopic polarization states by means of a non-contact

external control. Using in-situ XRD measurements, the BaTiO₃ in-plane oriented a-domains reorient in an orthogonal axis point either in-plane or out-of-plane upon irradiation under polarized light as shown in Figure 11a-c. The process is fully reversible and the domain state returns to its original configuration in the dark.

In highly strained multiferroic BiFeO₃ films, the flexophotovoltaic effects [260], combining strain gradient and light sensitivity has been revealed as a potential degree of freedom for all optical multiferroic magnetoelectric switch. The strain induced morphotropic boundary in BiFeO₃ films grown on highly compressive epitaxial strain leads to a rhombohedral and tetragonal phase coexistence. Upon illumination with a coherent light source, the balance between the two phases can be controlled, as illustrated in Figure 11d-e. The mechanism involves a combination of flexoelectricity and thermal heating. Most importantly, the first experimental data further indicate that the light induced changes in the film domain state are accompanied by an alteration of the antiferromagnetic state.

Finally, photocurrents generated via the bulk photovoltaic may be engineered in order to achieve local ferroelectric switching event. Using a tip enhanced electric field created by increased photocurrent density at the tip, the light irradiation induces an electric field surpassing the coercive electric field, as shown in Figure 11f-g. The bulk photovoltaic effect depends on the crystallographic direction and on the light polarization such that an all-optical light polarization dependent switching can be achieved in multiferroic BiFeO₃ films by simply changing the light polarization. Because strain strongly impacts the photocurrent generation [261], the recent development in epitaxial design might further support the development of optically induced functionality in magnetoelectric multilayers.

FIGURE 11| (a-c) Reversible optical control of macroscopic polarization in BaTiO₃. Sequence of synchrotron radiation high-resolution XRD patterns of (002)/(200) reflections corresponding to the off (a)–on (b)–off (c) light succession. The contribution of the c domains enhances when the light is on as a consequence of light-induced domain wall motion and is reversible. Reprinted with permission from [258]. Copyright © 2017, Springer Nature. (d-e) Deterministic optical control of phase distribution in mixed-phase BiFeO₃. Topography images of mixed-phase BiFeO₃ after illumination of areas marked with a triangle (d) and circle (e). Reprinted with permission from [254]. Copyright © 2019, Springer Nature. (f-g) Light-induced reversible switching of ferroelectric BiFeO₃ polarization via tuning illumination area. (f) Schematic showing photoelectric atomic force microscopy (Ph-AFM) setup and illumination areas resulting in photocurrent flow in different directions and hence reversed electric-field polarity under the tip leading to a reversible switch shown in PFM image (g). Reproduced with permission from [255]. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA)

Conclusion

In this article, we reviewed the most recent developments in the field of magnetoelectric heterostructures. More complete review articles dedicated to artificial multiferroic heterostructures [4,5] or domain manipulation [45,262] can be found elsewhere. Magnetoelectric heterostructures have first emerged as an alternative to the scarcity of single-phase multiferroic magnetoelectric materials [8]. They now play a major role in the pursuit of low energy consuming devices paradigms.

New probing tools are pushing the understanding of domain coupling and domain imprint in the multilayers [2]. In particular non-invasive, operando investigations [177,238] are key towards the determination of the magnetoelectric switching dynamics.

Finally, the compatibility of magnetoelectric architecture with SOT or all optical switching schemes allows realization of hybrid devices with expected ultra-fast dynamics and ultra-low energy consumption.

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