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Review Article

Multiferroic Memories

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Multiferroism implies simultaneous presence of more than one ferroic characteristics such as coexistence of ferroelectric and magnetic ordering. This phenomenon has led to the development of various kinds of materials and conceptions of many novel applications such as development of a memory device utilizing the multifunctionality of the multiferroic materials leading to a multistate memory device with electrical writing and nondestructive magnetic reading operations. Though, interdependence of electrical- and magnetic-order parameters makes it difficult to accomplish the above and thus rendering the device to only two switchable states, recent research has shown that such problems can be circumvented by novel device designs such as formation of tunnel junction or by use of exchange bias. In this paper, we review the operational aspects of multiferroic memories as well as the materials used for these applications along with the designs that hold promise for the future memory devices.

1. Introduction

With ever-increasing demand, numerous efforts are being made to fabricate the "ultimate memory device" [1], which is simultaneously nonvolatile, dense, robust, fast, and less energy expensive. Ferroelectric or FE (ferromagnetic or FM) materials, owing to their switchable polarization (magnetization) states with remnant polarization (magnetization), have already demonstrated their importance in the data storage industry by allowing storage of binary information in their two polarization (magnetization) states [2]. In the commercially available magnetic memory device (MRAM), data is written by switching the magnetic states ($\pm$M) upon application of a magnetic field while to read data, one exploits variation of magnetoresistance in the magnetic states [3, 4]. Being hard ferromagnets, the materials in the MRAMs possess high coercivity [5] resulting in large magnetic field requirement for switching magnetic states and thus consume large amount of energy. In contrast, ferroelectric memories (FeRAMs) possess faster writing speeds via polarization switching and are energy efficient. However, these have limitations on their size and show slow readability due to their destructive read operation and subsequent reset [1]. Therefore, a memory device with the best functionalities of FeRAMs and MRAMs (ferroelectric write and magnetic read operations) would effectively enhance the writing speed and reduce the specific energy consumption. This is probably the first step toward designing the "ultimate memory device." Moreover, device miniaturization can further lead to reduced energy consumption and higher speeds. Unfortunately, any further improvement in the bit density in the MRAMs/FeRAMs is hampered in the FM/FE materials by presence of only two switchable states. From this perspective, multiferroic and magnetoelectric materials present new possibilities towards enhancing data densities by many folds [6, 7] and thus pave the opportunity towards the fabrication of the "ultimate memory device."

Multiferroics (MF) and magnetoelectrics (ME) with simultaneous presence of electrical and magnetic order parameters (polarization and magnetization, resp.); can make use of both the functionalities of FeRAMs and MRAMs, independently, to store binary data. Further, coupling between electrical- ($\pm$P) and magnetic- ($\pm$M) order parameters in these materials provides a possibility of possessing additional functionalities such as electrical (magnetic) control of magnetization (polarization) [8], enabling design of futuristic multistate memory devices with electrical writing and nondestructive magnetic reading

operations [9, 10]. However, with strong coupling between the electric and magnetic states (ME coupling), the available switchable states, namely, (+P, +M), (+P, −M), (−P, +M), and (−P, −M) are not absolutely independent of each other and only combinations that are independently achievable are either (+P, +M) and (−P, −M) or (+P, −M), and (−P, +M) [1]. Thus, the device is restricted to two states similar to conventional ferroelectric or magnetic memories [1]. However, as recent research has shown, this problem can be circumvented by forming a ferromagnetic-magnetoelectric tunnel junction, where combination of electroresistance and magnetoresistance can result in four state memory effect [11]. In this paper, we will review how multiferroic and magnetoelectric materials can be used to design high-density and efficient nonvolatile memory elements for futuristic memory devices by using variety of novel device designs. Here, we will mainly restrict our discussion to the oxide-based multiferroics. In the process, wherever necessary, we will briefly review the key mechanisms involved in the construction of the multiferroic memory devices.

2. Materials

The drive to create novel and miniaturized devices with multiple degrees of control has led to an extensive research on the multiferroic materials, in which magnetic and ferroelectric degrees of freedom can be coupled. Since ferroelectricity and magnetism tend to exclude each other [12], multiferroism is observed in very few naturally available single-phase multiferroic systems. Moreover, commercial device engineering considerations impose further restrictions on the materials to exhibit ferroelectric/magnetic ordering at room temperature (RT) or close to RT. Initially, most of the focus was on materials such as $BiFeO_3$, which have ferroelectric and magnetic transition temperatures close to or above RT. In recent years after the realization that multiferroism is a rather rare event, the focus has shifted to synthetically generated complex oxides in bulk and thin film forms. Laboratory properties of these materials can be significantly altered by applying perturbations such as epitaxial strain. Close competition between different structural, magnetic, and electronic degrees of freedom usually results in energetically competing ground states with different structure and magnetic ordering. In the following sections, we briefly review the most commonly studied multiferroic materials followed by a brief review of the novel approaches to demonstrate multiferroicity using external stimuli such as strain in hitherto unstudied materials.

2.1. Bismuth Ferrite ($BiFeO_3$). The most promising and most studied material for multiferroic devices is bismuth ferrite ($BiFeO_3$ or BFO), which shows RT ferroelectricity ($T_c \approx 1100$ K) and antiferromagnetism ($T_N \approx 640$ K). The material has a rhombohedral structure (see Figure 1(a)) and shows a large ferroelectric polarization ($P_r \sim 50$–$60\,\mu C/cm^2$) [13] with spontaneous polarization, P_s vector along [111]-axis and significant magnetoelectric coupling [14]. Owing to its large spontaneous polarization, possibly the largest among all known perovskite and nonperovskite multiferroic oxides, coupled with its lead free nature, BFO is also a prospective candidate for next-generation ferroelectric memory applications. However, the major challenges BFO faces, in this context, are its poor leakage characteristics, tendency to fatigue [15] and thermal decomposition near coercive field [16]. These setbacks of BFO have been, at least partly, circumvented by doping both at Bi [17] and Fe sites, [18–21], removing substrate clamping effect, [15], and so forth. Further, BFO has been reported to emit THz radiation [22] when irradiated with a femto-second laser pulse which may have huge potential in telecommunication applications [23]. Moreover, THz emission is dependent on the poling state of BFO and, therefore, ultrafast, nondestructive ferroelectric memory readout is possible. Additionally, high frequency operation in THz range eliminates disadvantages of leakage [24]. However, the major thrust toward the research of BFO and related materials is driven by their prospective applications in magnetoelectric and spintronic devices where they are primarily used as memory elements. The key advantages of BFO-based memory devices are their electrical writing and magnetic reading operations, which can further utilize the advantages of solid-state circuits that is, their low energy consumption, scalability, nondestructive read operations, etc. [24].

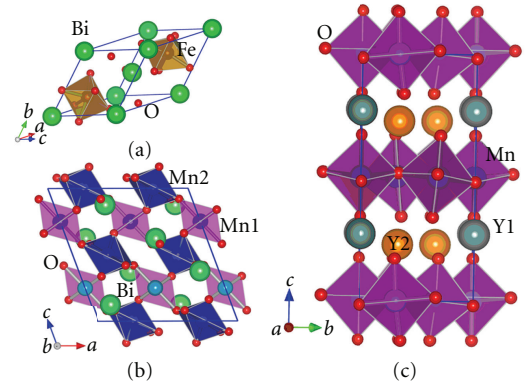

Figure 1: Schematic crystal structures of (a) $BiFeO_3$ with rhombohedral *R3c* symmetry, (b) $BiMnO_3$ with monoclinic *C2/c* symmetry, and (c) $YMnO_3$ with hexagonal $P6_3cm$.

2.2. Bismuth Manganite ($BiMnO_3$). Bismuth manganite ($BiMnO_3$), a perovskite ABO_3-structured compound (see Figure 1(b)) is another interesting multiferroic material with low-temperature ferromagnetic and room-temperature ferroelectric characteristics. The material shows ferromagnetic ordering below 105 K attributed to the orbital ordering of B-site ions that is, Mn^{3+} ions and a magnetization of $3.6\,\mu_B$ per formula unit [25]. The material has a perovskite triclinic structure which changes to monoclinic structure, at ~450 K and then to a nonferroelectric orthorhombic phase at ~770 K [26]. However, poor resistivity of this material in polycrystalline form renders the material unsuitable for device applications. The material in bulk form exhibits multiferroic behavior near 80 K [27] and negative magneto-capacitance effect in the vicinity of magnetic transition

temperature (T_m) with −0.6% change in the dielectric constant near T_m [26]. While preparation in the bulk form requires use of high pressures, thin resistive films of this material can be prepared with much ease [28].

2.3. Hexagonal Manganites ($RMnO_3$). Hexagonal manganites are another interesting class of manganites and are depicted by the general formula $RMnO_3$, where R is typically a rare earth ion such as Y and Ho. These materials simultaneously exhibit ferroelectricity and antiferromagnetic ordering of magnetic Mn ions. In general, rare earth elements having a small ionic radii tend to stabilize hexagonal phase, $RMnO_3$ [29] (R = Sc, Y, Ho, Er, Tm, Yb, Lu) with space group $P6_3cm$ [30] (see Figure 1(c)). In spite of having a chemical formula, ABO_3, similar to the perovskites, hexagonal manganites have altogether different crystal and electronic structure. In contrast to the conventional perovskites, hexagonal manganites have their Mn^{3+} ions with 5-fold coordination, located at the center of an MnO_5 trigonal bi-prism. R ions, on the other hand, have 7-fold coordination unlike the cubic coordination in perovskites. The MnO_5 bi-prisms are arranged in space and are separated by a layer of R^{3+} ions. Crystal field level scheme of Mn^{3+} ions in hexagonal $RMnO_3$ is also different from that of Mn^{3+} ions with octahedral coordination. Here, the *d*-levels are split into two doublets and an upper singlet. As a result, four *d*-electrons of Mn^{3+} occupy two lowest lying doublets and unlike Mn^{3+} ion in octahedral coordination, there is no degeneracy present. Consequently, Mn^{3+} ions in these compounds are not Jahn-Teller ions [31].

Hexagonal $RMnO_3$ are found to possess considerably high ferroelectric transition temperature (>500 K). However, their Néel temperature (T_N) is far below the room temperature, with highest reported $T_N \sim 129$ K for $ScMnO_3$ [32]. The mechanism of ferroelectricity in these compounds also differs from that of the conventional perovskite oxides. In case of $YMnO_3$, it was observed that off-centering of Mn^{3+} ion from the center of the MnO_5 biprism is very small and cannot be considered to contribute toward ferroelectricity [33]. Apparently it turns out that Y ions contribute most towards ferroelectricity by having large Y-O dipole moments. However, in reality, ferroelectricity in these materials has different origin and can be considered as an accidental by-product. Similar to BO_6 octahedra in perovskite oxides (ABO_3), MnO_5 trigonal bi-prism in $RMnO_3$ tilts and rotates in order to ensure closest packed structure. Such tilting of MnO_5 trigonal bi-prism results in loss of inversion symmetry in the structure and brings about ferroelectricity [33, 34]. Since the mechanisms of ferroelectric and magnetic ordering in the above materials are quite different in nature, giant effect of magnetoelectric coupling is understandably not present [31].

2.4. Strongly Coupled Multiferroics. Multiferroic materials belonging to this class show ferroelectricity in their magnetically ordered state and that too of a particular type. Moreover, very strong coupling between ferroelectric and magnetic-order parameters has also been observed. In 2003, Kimura et al. reported [8] presence of spontaneous polarization in the magnetized state of the $TbMnO_3$. $TbMnO_3$ has various magnetic structures: it is an incommensurate antiferromagnet between 27 and 42 K and a commensurate antiferromagnet between 7 and 27 K. It is in the commensurate state between 7 and 27 K that the material shows ferroelectricity. This discovery was followed by an observation of similar effect in $TbMn_2O_5$ by Hur et al. [35]. Subsequently a variety of other materials have also been investigated such as $Ni_3V_2O_8$ [36], $MnWO_6$ [37], and Ca_3CoMnO_6 [38] showing this effect. Magnetic spin structure in these materials has been shown to be either of spiral cycloid type [36, 37] or a collinear type [38].

2.5. Artificially Designed Multiferroic Materials. While the discovery of new materials is dependent on extensive experimentation, more recently, first principle studies have led to quite a few useful suggestions. Such studies theoretically predict the design of a variety of novel compounds, which may exhibit multiferroic behavior and effects such as magnetostructural coupling. For instance, it was predicted [39] that epitaxial strain can lead to a phase that is ferroelectric and ferromagnetic at the same temperature. This strong multiferroic effect is due to the large magnetostructural coupling in $EuTiO_3$, which was later experimentally proven by Lee et al. [40] when they grew strain-tuned thin films of $EuTiO_3$ on single crystal $DyScO_3$ substrates. Although the transition temperatures are quite low, below 5 K, the discovery is indeed remarkable as it creates possibilities of designing multiferroic materials by application of external stimuli such as strain. More recently, similar first principle studies on other compounds have also predicted multiferroicity in compounds such as $SrMnO_3$ [41] and $SrCoO_3$ [42], which are yet to be experimentally studied in detail. Nevertheless, design of materials using these approaches open new opportunities for the tailoring of devices, important from the device perspective because devices use such materials in thin film form and strain in such system can be effectively used to induce hitherto unobserved effects.

3. Device Functionality Considerations

To achieve functionality of multiferroic memory devices, the magnetic state of the memory material should be electrically switchable and magnetically readable. The first prerequisite is easily met by a material such as BFO since the magnetic easy plane of its antiferromagnetic domains is coupled with its polarization direction, that is, [111]-axis and a polarization rotation results in the rotation of sublattice magnetization [14]. However, the major obstacle that BFO encounters is the difficulty in reading the magnetic states due to difficulty of magnetic domain rotation in its antiferromagnetic structure. The problem can be overcome either by using exchange bias mechanism [43] or by tunneling magnetoresistance approach [11].

3.1. Memory Devices Based on Exchange Bias. When the interface between a ferromagnetic (FM) and an antiferromagnetic (AFM) material (Curie temperature (T_C) of the FM phase is higher than the Néel temperature (T_N) of the AFM

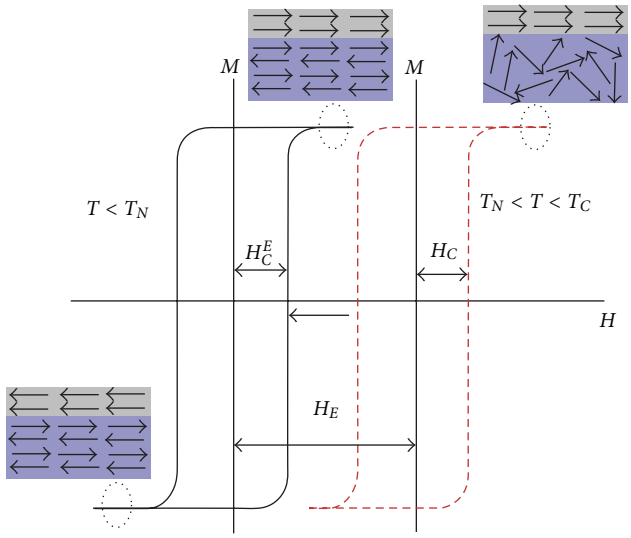

FIGURE 2: Schematic diagram of FM/AFM bilayer showing exchange bias effect. The grey layer has AFM spin structure, while the violet one represents FM layer. M-H hysteresis loop is shifted along the field axis demonstrating exchange bias at temperature $T < T_N$.

phase) is cooled from a temperature T ($T_N < T < T_C$) to temperature $T < T_N$ in presence of a static magnetic field, the M-H hysteresis loop of the system at $T < T_N$, after the field cooled operation, manifests a shift along the field direction. This shift of the hysteresis loop is termed as exchange bias (H_E) [44, 45] and is schematically demonstrated in Figure 2. In general, the hysteresis loop is shifted towards the opposite direction to the applied field direction during cooling [44]. The coercivity at $T < T_N$ is larger than that at $T_N < T < T_C$, $H_C^E > H_C$, suggesting that the presence of AFM material causes the observed anisotropy [44]. Figure 2 also qualitatively explains the exchange bias effect. In the temperature range, $T_N < T < T_C$, if a magnetic field is applied to an FM-AFM bi-layer system, the spins of the FM layer will align themselves along the direction of the applied field, while the spins in the AFM layer will remain random. Corresponding M-H hysteresis loop is characteristic to the FM layer as shown by the dotted line in Figure 2. As the temperature falls below T_N, an application of field will align the spins of the AFM layer at the interface, parallel to the spins of FM layer, while the spins adjacent to the interface in the AFM layer will retain their AFM arrangements. When the direction of applied field is reversed, the FM spins will start rotating so as to align themselves along the field direction. However, due to sizeable AFM anisotropy, the orientation of AFM spins will remain unchanged. As a result, the AFM spins at the interface will exert microscopic torque on the FM spins in order to maintain ferromagnetic coupling. Thus, additional field would be required to rotate the FM spins in order to compensate the microscopic torque. When the applied field direction is again changed to the original field direction, FM spins will rotate again, however, requiring a smaller field owing to the interaction with the AFM spins. The system acts as if there is an additional biasing field, which shifts the hysteresis loop along the field direction, which is manifested by exchange bias, H_E [44]. The direction and magnitude of H_E and the value of H_C^E would depend upon the orientation of the AFM/FM layer, properties of the FM and AFM layers, direction of applied field during FM layer growth, and so on and so forth.

In the context of antiferromagnetic (AFM) multiferroic-(such as BFO) based memory devices, the importance of exchange bias is palpable since voltage control of sublattice magnetization in the AFM layer would in turn control the hysteresis in the adjacent FM layer of an FM/BFO exchange bias device. Consequently, variation in the magnetoresistance could be exploited to read the data in a fashion similar to the MRAMs. Exchange bias effect has been, therefore, studied in a number of BFO-based FM/AFM systems because of room temperature and higher antiferromagnetic stability in BFO, crucial for device engineering [43, 46, 47]. Dho et al. [47] reported exchange bias $H_E \sim 50$ Oe and coercivity $H_C^E \sim 65$ Oe in a 5 nm NiFe/300 nm BFO device at room temperature. The observed exchange bias was qualitatively explained in terms of rearrangements of the interface spins of the BFO layer to minimize total magnetic energy during the growth of the NiFe layer resulting in an exchange imbalance at the interface [47]. Subsequently, Béa et al. [43] demonstrated exchange bias effect in BFO/CoFeB system with $H_E \sim 62$ Oe and $H_C^E \sim 42$ Oe at room temperature. The effect of different orientation of BFO and applied field direction during the growth of FM layer, as shown in Figure 3 clearly confirms the existence of the effect. This is further substantiated by the presence of exchange bias with different film thicknesses [43, 48]. Further, exchange bias in the polycrystalline BFO/Co_2FeAl heterostructure has been reported to exhibit a fluctuating characteristic with a cyclical thickness of 60 nm indicating that spiral modulation of BFO (spiral modulation wavelength ~62 nm) has a correlation with exchange bias effect [49]. However, somewhat contrasting result was reported for BFO/CoFeB structure, where H_E reached a saturated value beyond a critical BFO layer thickness, as shown in Figure 4(b) [50]. Interestingly, ferroelectric and antiferromagnetic domain sizes have profound effect on the exchange bias. It was reported that, H_E increases linearly with decreasing domain size as shown in Figures 4(a) and 4(c) [50]. Further it was shown that BFO-based heterostructures with stripe-like (Figures 5(a) and 5(c)) and mosaic-like (Figures 5(b) and 5(d)) ferroelectric domain structure results in improved H_E and H_C^E (Figure 4(c)) with H_E and domain size holds and inverse correlation [51]. It was further demonstrated that presence of large volume of 109° ferroelectric domain walls at the interface of BFO/CoFe layer is primarily responsible for the observed exchange bias effect [51, 52]. Appreciation of such correlation between ferroelectric domains and exchange bias is a crucial milestone towards voltage control of magnetization in the FM state. Finally, Chu et al. presented a compelling evidence of electric control of the ferromagnetism in a STO/SRO/BFO/CoFe (Figure 6) device [51]. Most of the studies on exchange bias effect have been performed on BFO that is inherently leaky which further affects the ferroelectric performance in the BFO films [47]

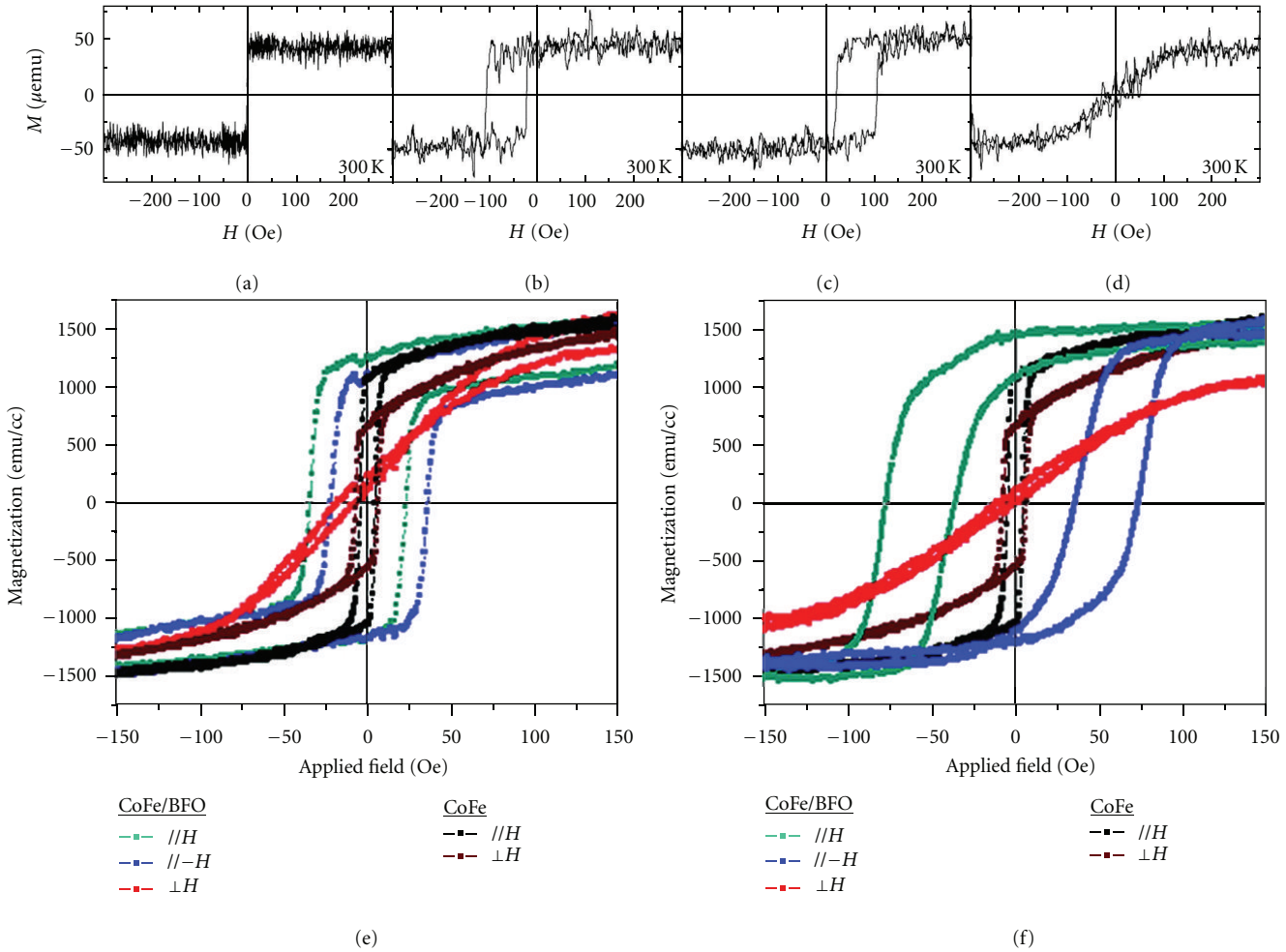

FIGURE 3: Hysteresis loop along (a) [100] direction of CoFeB (5 nm)||Si layer, (b) [100] direction, (c) [$\bar{1}$00] direction, and (d) [010] direction of CoFeB (5 nm)/BFO (35 nm)||STO bilayer. (e) and (f) room temperature magnetic properties of CoFe/BFO heterostructure showing improvement of coercivity and exchange bias, respectively. (a)–(d) were reproduced from Béa et al. [43], and (e) and (f) were reproduced with permission from Martin et al. [48].

and could in turn affect the control of magnetism in the FM layer in the device. Therefore, doped BFO systems with superior leakage and fatigue performance could possibly replace BFO in a commercial device [53]. However, detailed studies are required to appreciate the performance of doped BFO system in exchange bias device.

The concept of exchange-bias-based multiferroic memory elements was also attempted in other systems such as $YMnO_3$ [49, 54] $BiMnO_3$ and its derivatives [54], and so forth. Laukhin et al. [55] showed a clear evidence of electric field effect on exchange bias in $YMnO_3$/NiFe heterostructure system. The suppression of exchange bias in the system beyond a critical voltage was correlated with the electric field-driven modification of the antiferromagnetic domain structure of $YMnO_3$ [55]. Since their Néel temperatures are far below the room temperature, it is quite unlikely that hexagonal manganite-based multiferroics would demonstrate exchange bias effect at room temperature, and, therefore, they are not lucrative from the device engineering point of view. As a result, there is a lack of literature on exchange bias effects in these materials.

3.2. Tunneling Magnetoresistance-Based Approach. The second approach, based on tunneling magnetoresistance mechanism, carries even more significance for futuristic design of memory elements. In a magnetic tunnel junction (MTJ), two FM layers are separated by a thin (nm or sub-nm length scale) insulating layer. The tunneling resistance (R) of the junction depends on the relative alignment of the spins (parallel or antiparallel) in the FM layers [56]. This is shown schematically in Figure 7. The magnitude of R is larger for antiparallel spin configuration (R_{AP}) (Figure 7(b)) than that of parallel spin configuration (R_P) (Figure 7(a)). Such a variation of resistance relative to the spin orientations in the FM layers is termed as tunneling magnetoresistance (TMR) effect [56]. The magnitude of TMR effect is expressed in terms of fractional change in the resistance and is defined as magnetoresistance ratio or $\%MR = (R_{AP} - R_P)/R_P \times 100$.

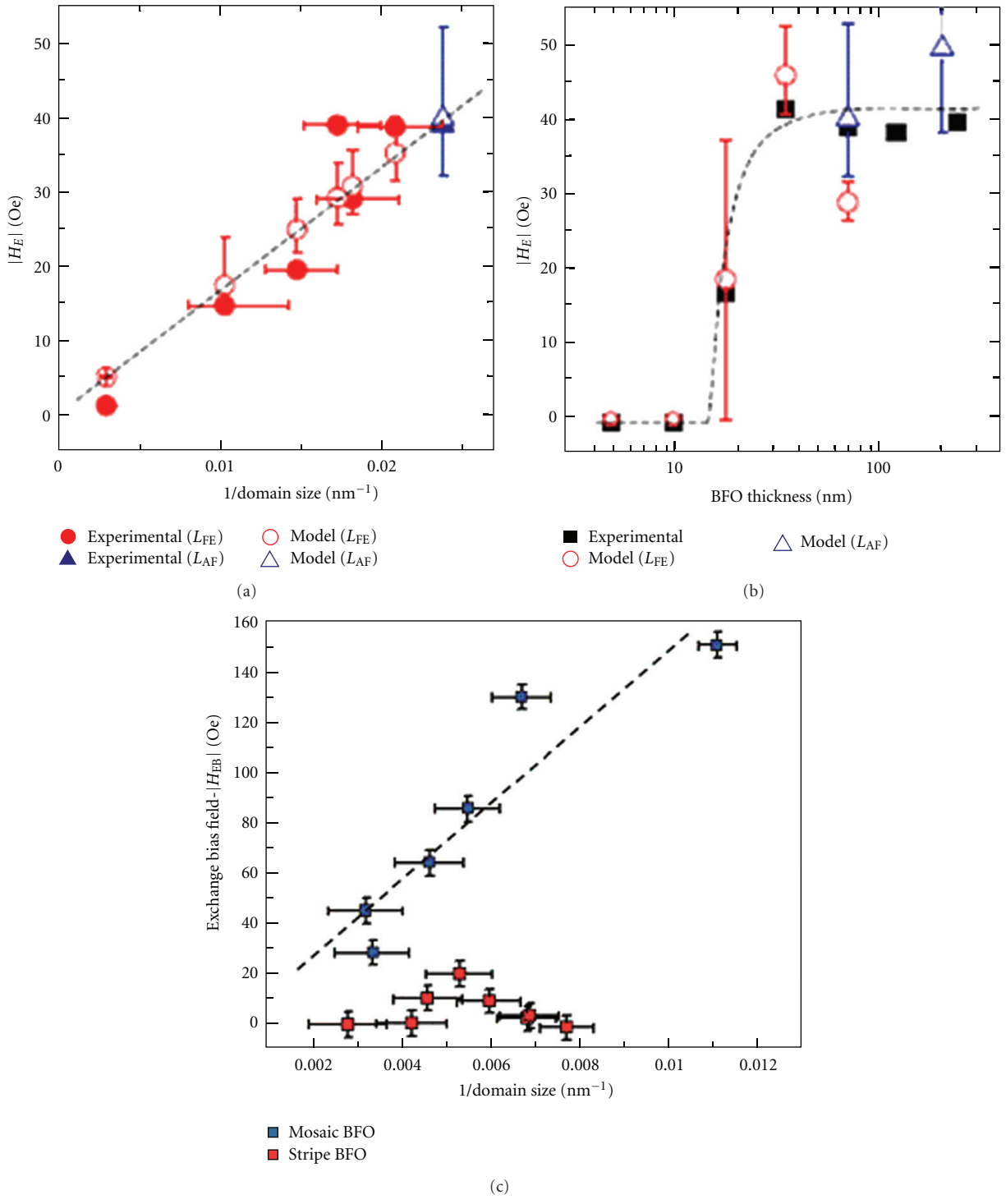

Figure 4: Dependence of exchange bias (a) on domain size in 65 nm BFO thin films, (b) on thickness of CoFeB/BFO stacks deposited on STO (001), and (c) on domain size of CoFe/BFO heterostructure grown on mosaic-like and stripe-like BFO films. Figures were reproduced with permission from Martin et al. [48] and Béa et al. [50].

Phenomenological model proposed by Julliere [57] identifies spin-dependent electron tunneling as the origin of observed TMR effect.

The relevance of the TMR effect in the context of BFO- (or any other multiferroic) based memory device is that, if the insulating spacer layer in the MTJ is replaced by a multiferroic with significantly large magnetoelectric coupling such that a polarization rotation induced by an applied electric field can bring about rotation of sublattice magnetization in the multiferroic layer, this in turn can

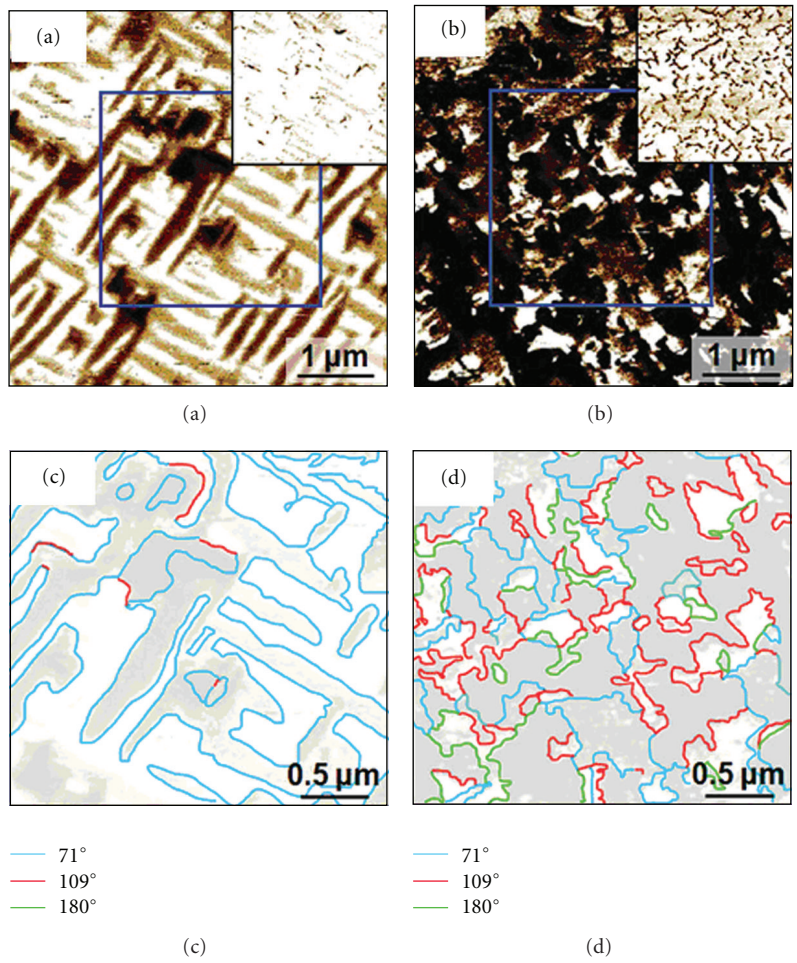

FIGURE 5: (a) and (b) in-plane and out-of-plane (inset) piezo force micrographs (PFM) of BFO films showing improvement of coercivity and exchange bias, respectively. Domain wall study of (c) stripe-like and (d) mosaic-like BFO films. Figures were reproduced with permission from Martin et al. [48].

change the spin configuration in the FM layers of the MTJ, for example, from parallel to antiparallel, resulting in resistance change from small to large and the data could be read using the variation of magnetoresistance in a fashion similar to MRAMs. The additional advantage is that magnetic bit can be written electrically with lower power consumption unlike conventional MRAMs. For such type of device application, the primary requirements are that BFO should be reasonably insulating, robust, and switchable ferroelectric down to tunneling thickness. Fortunately BFO demonstrates all these characteristics down to a thickness of ~2 nm [58]. As a result, BFO has been used in fabrication of TMR-based memory devices where significantly high positive % MR value was recorded for BFO layer thickness of 2–5 nm [43] at 3 K in LSMO/BFO/Co MTJ (see Figure 8(a)). However, TMR effect vanishes beyond 200 K, a much lower temperature than the T_C of the FM layer (LSMO). This issue of vanishing TMR at a significantly lower temperature than the T_C is not fully understood. It has been conjectured that oxygen defects in the BFO/LSMO interface reduce the T_C of the interface to 200 K at which the TMR vanishes [54]. Indeed a protective STO layer on LSMO improves the % MR to ~100% at 3 K and TMR remains upto 300 K (see Figures 8(b) and 8(c)) [54]. However, to the best of our knowledge, MTJ junctions with other FM layers and BFO have not been studied, which could result in even more interesting outcome.

As discussed earlier, one of the very few systems showing ferroelectricity and ferromagnetism in the single phase is $BiMnO_3$ (BMO), whose potential is limited by its rather low ferromagnetic Curie temperature (~105 K) and difficulties in the synthesis of pure BMO (use of high pressure and temperature is needed). As a result, studies have been made on its derivative $(La,Bi)MnO_3$ (LBMO), which possesses nearly similar magnetic and electrical properties to BMO [54]. BMO and LBMO based MTJ demonstrated large TMR effect due to spin filtering [59, 60] by the ferromagnetic BMO- and LBMO-layers, respectively [11, 54]. More importantly, these systems demonstrate electroresistance effect, which is a manifestation of modulation of the tunneling current by ferroelectric polarization of the L(BMO) layer [11, 54]. Ferroelectric polarization is related to the charge

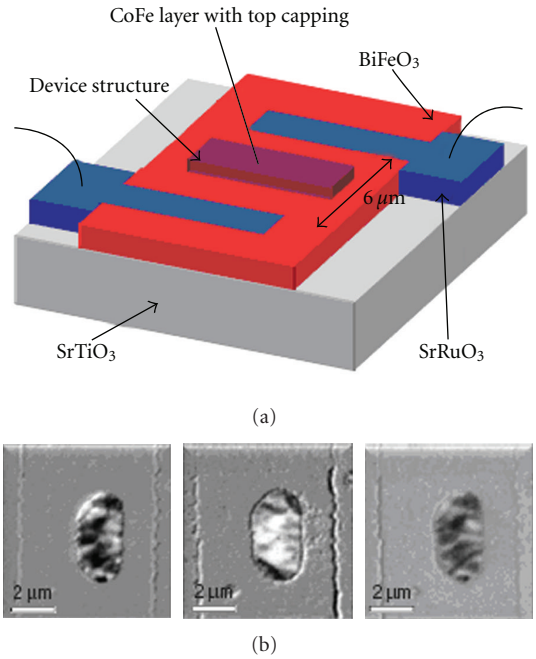

FIGURE 6: (a) Schematic diagram of device that would allow controlled ferroelectric switching in BFO layer and electrical control of ferromagnetism in the CoFe layer, and (b) XMCD-PEEM images acquired at Co L edge showing the ferromagnetic domain of CoFe layer in the as grown, after first electrical switching and after second electrical switching. Figures were reproduced with permission from Chu et al. [51].

screening effect, which controls the depolarizing field across the junction and thus the magnitude of barrier potential that the tunneling electrons encounter [11]. Selecting different electrodes with different screening lengths would allow developing different barrier heights at the two electrode-multiferroic interfaces [11]. Combination of electroresistance and magnetoresistance in such junctions' results in four resistance states, as shown by Gajek et al. [11]. These four resistance states can further be accessed both electrically and magnetically and thus the concept of multiple state memory becomes a reality.

4. Multiple-State Memory Devices at Room Temperature

Discovery of multiple-state memory device based on LBMO is undoubtedly a milestone in the research on multiferroic memories; [11] however, significant memory effect in this device could only be appreciated at a very low temperature. Consequently, its application in the commercial memory device is limited. First-principles study by Velev et al. [61], on the other hand, has shown that the above four resistance states can also be feasible in MTJs with ferromagnetic electrodes and ferroelectric barrier. Their study clearly demonstrated the existence of four resistance states in $SrRuO_3/BaTiO_3/SrRuO_3$ junction owing to the combined effects of electroresistance and magnetoresistance [61].

Therefore, room temperature FM/FE/FM tunnel junctions could, in principle, demonstrate four state memory effect, which would be important from application point of view. Moreover, as explained by Scott [1], strong magnetoelectric coupling in single-phase multiferroics could make the four polarization states interdependent and only two of them would be available at a point of time. As a result, research has been started on such artificial composite multiferroic tunnel junctions, where compelling evidence of four memory states has been demonstrated at room temperature in Co/PZT system [6]. In a further advancement, Yang et al. [7] presented a model showing eight logic memory states based on multiferroic tunnel junction, where the eight states are argued to be generated by considering the screen filtering effect [59] and the screening of charges between the FM electrodes in a complex device, as shown in Figure 9. However, experimental demonstration of such effect is challenging and there are no reports, till now.

5. Recent Advances

Concurrent with the developments in the TMR and exchange-bias-based multiferroic devices, there are a few ideas that have appeared recently and are worthy of further examination in the expanding research activities on the design of multiferroic-based memory devices. One such approach is reported by Vopasaroiu et al. [62] on the design of a laminated multiferroics-based recording head that directly generates voltage signal without the requirement of test current, necessary for conventional TMR-based read back operation. The authors argued that this design would allow further miniaturization of the read head sensor and reduced power consumption without losing the sensitivity [63]. In another report, Tiercelin et al. [63] proposed a composite-type design of magnetoelectric memory cell using piezoelectric matrix embedded with magnetic elements, which can have a data density of 40 Gbits/cm^2 with reduced dimension and power consumption. The device operates on the principle of generating an anisotropic stress in the magnetic elements induced by the piezoelectric matrix when subjected to an external electric field. The anisotropy in the magnetic media is controlled by the applied electric field in the piezoelectric matrix due to inverse magnetostrictive effect. Subsequent switching of the magnetic states is used to store binary data [63]. Another design proposed by Li et al. [64] demonstrated, electric field induced two different coercive states ($\pm H_C$), instead of conventional magnetization states ($\pm$M) which can be exploited to write data. A final example is based on another novel device, where it was demonstrated that the magnetoelectric coupling is not limited in insulators and a few unit cell thick metallic thin film could be used as an electrically controlled memory device, just like multiferroic memory devices, whose functionality is in accordance with magnetoelectric coupling effect [65, 66]. As a result, a new field of research emerges, which would go in tandem with traditional research of multiferroics-based memory cell to achieve the ultimate memory device.

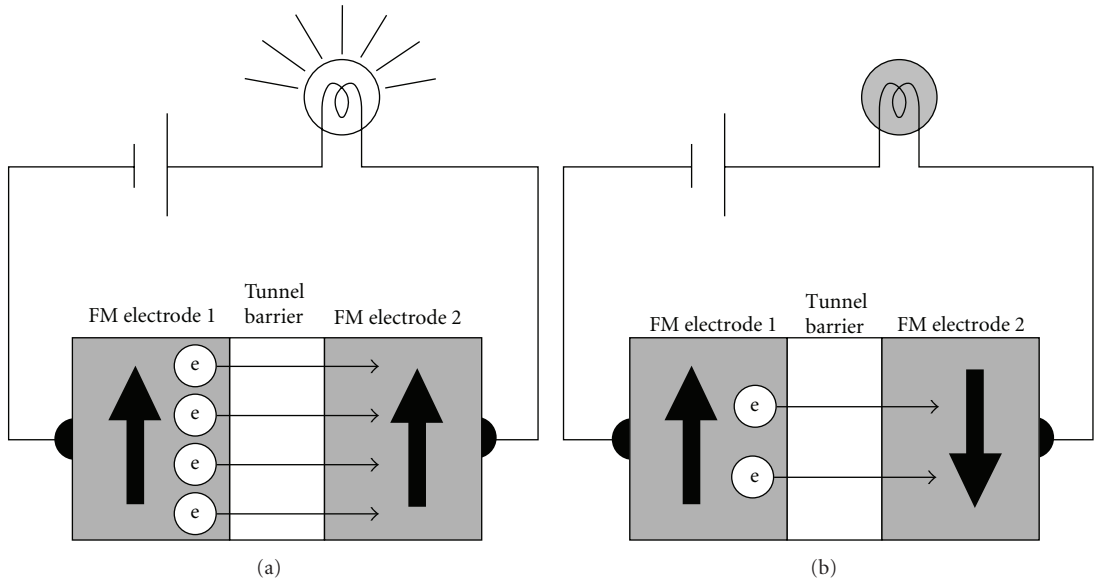

Figure 7: Schematic description of tunneling magnetoresistance effect in a magnetic tunnel junction. Spins in the two electrodes are aligned (a) parallel and (b) antiparallel. Figures were reproduced with permission from Yuasa and Djayaprawira [56].

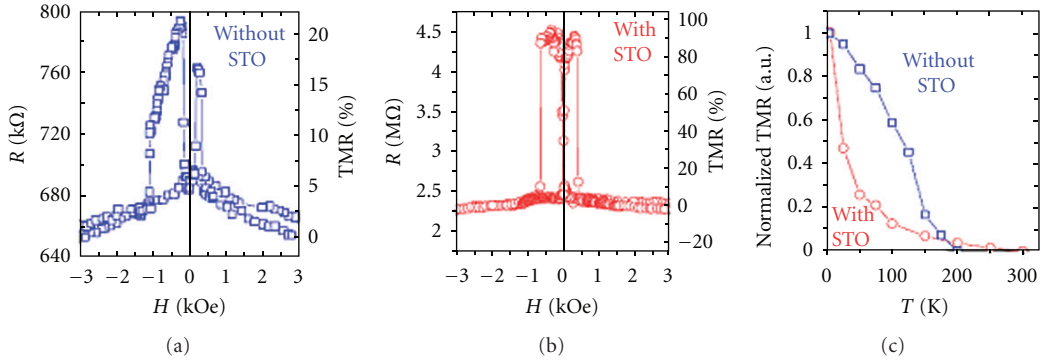

Figure 8: Resistance plotted as a function of magnetic field in magnetic tunnel junctions having Co and LSMO ferromagnetic electrodes and multiferroic BFO layer. The measurements were performed at 3 K and 10 mV: (a) BFO (5 nm) single barrier, that is, without STO, (b) BFO (2 nm)/STO (1.6 nm) double barrier, that is, with STO, and (c) Evolution of the TMR with temperature for these two junctions. Figures were reproduced with permission from Béa et al. [54].

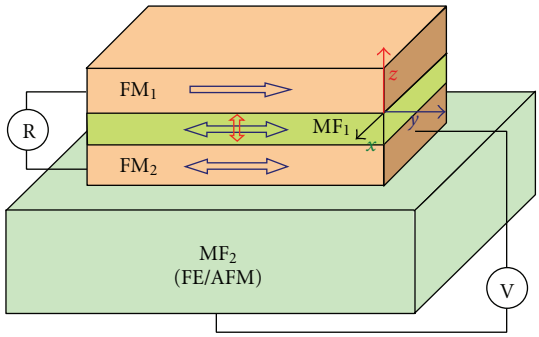

Figure 9: Schematic design of the proposed eight-logic memory cell. MF indicates multiferroic and FM represents ferromagnetic layers. Figures were reproduced with permission from Yang et al. [7].

6. Future Outlook

While the search for ideal multiferroics occurring either naturally or synthesized in the laboratory goes on, device development has to rely on novel designs and new architectures for futuristic memory devices. In the past, approaches such as use of exchange bias, tunnel junctions, and composite architectures have demonstrated working of memory devices using multiferroics. In recent times, many exciting materials with the possibility of multiferroism have been predicted and some have also been examined. This back and forth synergy between theoretical and experimental demonstrations has given new impetus to the research on multiferroics. While existence of multiferroic behavior can be innate to certain materials like $BiFeO_3$, it can also be imparted by application of external parameters such as strain

[39] as experimentally demonstrated by Lee et al. in $EuTiO_3$ [29], which was attributed to strong spin-lattice coupling in the material. It is approaches like these that are likely to demonstrate multiferroic effect in yet-unknown materials and subsequent development of new device designs and architectures. From the perspective of commercially viable technology development, it would be essential that the future materials have their ferroelectric and magnetic transition temperatures close to or above room temperature to exploit the full potential of this technology.

Another aspect against which the development of multiferroic memories needs to be tested is the development of materials and processes, which are compatible with existing semiconductors processing methods. Usually most oxide-based materials are less sensitive to changes in their properties due to small changes in defect density or doping while semiconductor properties alter significantly even with minute doping, levels of parts per million. The integration requirements are far more stringent when memory is fabricated and tested standalone and when it is fabricated as one of the steps during fabrication of complete semiconductor chip. This is one of the aspects that proved detrimental against a few promising ferroelectrics such as $SrBi_2Ta_2O_9$ [67] because of deterioration of functional behavior upon hydrogen exposure, which is a key step in the embedded memory device fabrication. Processing related issues led to very little commercial interest in the development of nonvolatile FeRAM (Ferroelectric Random Access Memories) technology, which had excellent advantages such as very fast switching speeds coupled with high bit density and radiation hardness over conventional magnetic memories [2, 68]. Since all the known multiferroic materials are oxides, these would be a key requirements for their integration.

Another issue that needs to be tackled is thin film growth temperature of these oxides. While growth of BFO requires much lower temperatures than typical ferroelectric oxides, same may not be true for all the materials. Higher growth temperatures increase the thermal budget besides leading to damage to other parts of the circuitry. For instance, platinized silicon substrates may undergo severe interfacial reactions and disruption of the morphology at higher temperatures (readers can refer to Chapter 7 in [68] for a detailed discussion). Further, with more increased emphasis on 300 mm semiconductor technology, research may need to develop methods that result in smooth films with desired microstructure, least particle count and controlled thicknesses. So, in this sense, in addition to material discovery, process development would essentially govern the future development of multiferroic memories.

7. Summary

In this paper, we have reviewed recent developments on the memory devices based on multiferroic and magnetoelectric materials. A brief discussion was provided on the principles of exchange bias and tunneling magneto-resistance effects, which are primarily utilized towards working of the multiferroic memory devices. We also provided an account of currently used multiferroic materials in these memory devices. Finally we discussed a few very recent developments such as those on laminated and composites memory devices, which may further research to realize their potential. At the moment, the device designs are limited by availability of desirable multiferroic materials. However, novel approaches based on invoking of multiferroic effect in materials using external stimuli, such as strain in epitaxial films, can lead to significant changes the way applications of multiferroics will develop. Another important aspect of the development of future technology will be governed by the characteristics transition temperatures. Finally, process development and more importantly process integration with the semiconductor technology will be of utmost importance for any successful commercial realization.

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