Multiferroic Tunnel Junctions: Do TER and TMR effects Coexist ?

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(June 2, 2009)

Recent theoretical and experimental works show that there is a sizable change in the conductance of ferroelectric tunnel junctions (FTJs) due to the polarization of the ferroelectric material. In particular, the electric-field-induced polarization reversal creates the giant electroresistance (GER) effect. In multiferroic tunnel junctions (MFTJs), spin-dependent tunneling can be controlled by reversing the electric polarization and vice versa. The coexistence of tunneling magnetoresistance (TMR) and GER effects in multiferroic tunnel junctions have been predicted theoretically and shown experimentally (although still controversial). In this paper, we will try to review recent developments in FTJ and MFTJs. We describe the largely agreed mechanisms of switching in both tunnel junctions and discuss if coexistence of the TER and TMR is indeed possible by referring to recent first principle calculations and experimental observations.

Contents

"… large changes in electrical resistivity are not associated with reorientations of ferroelectric polarization, and so an electrical analog of a magnetic tunnel junction does not exist." [1]
Nicola A. Spaldin, 2007

"… ferroelectric tunnel junctions, which take advantage of a ferroelectric as the barrier potential…may have a profound effect on the conductance leading to a resistive switching…"[2]
E.Y. Tsymbal

1 Introduction

Some researchers are convinced that ferroelectric tunnel junctions cannot be realized, as the tunneling electroresistance (TER) is not associated to different orientations of the ferroelectric polarization [1]. Yet some others have shown, using first principle calculations, the possibility for these junctions to exhibit hysteretic TER effect[2] due to the dependence of the electric polarization on the biasing voltage, which is similar to its magnetic counterpart – tunneling magnetoresistance effect (TMR). Recent work by Julian P. Velev et al.[3], have indicated the possibility of having both TER and TMR in $SrRuO_3/BaTiO_3/SrRuO_3$ multiferroic tunnel junctions. Using ab initio calculations on $Fe/BaTiO_3/Pt$ and $Fe/BaTiO_3/Fe$ layers, they have shown that the tunneling conductance decreases due to the switching of polarization of $BaTiO_3$ when compared to the high conductance in the unpolarized barrier, thereby witnessing the resistance dependence on the polarization [6,7].

This was also supported by J. Wang *et al.* by utilizing composite ferroelectric-ferromagnetic barrier to get around the problem of scarcity of multiferroic materials. In their report, they have claimed that spin filtering; TMR and TER effects can indeed be obtained. [8]

Using a multiferroic barrier in magnetic tunnel junctions instead of the non polar insulator or a ferroelectric, adds multifunctionality to such devices yielding a four-state resistive memory element [4]. In doing so, one can exploit both TMR and TER effects. This was first demonstrated by Martin Gajek and coworkers in thin films of $La_{0.1}Bi_{0.9}MnO_3$ (LBMO) down to a thickness of 2nm, when used as multiferroic tunnel barrier in spin-filters, acts as a four state resistive system [4,5]. However, for a general accord to be reached, this work has to be

reproduced on other materials and is yet to be reported by other research groups.

Yet the scarce experimental reports have not been sufficiently tested. This is mainly due to the difficulty of growing such devices completely reproducibly. J. F. Scott has pointed out that claims of resistive effect in ferroelectrics may sometimes not be due to tunneling effect [9], especially because direct tunneling should not be observed at a film thickness greater than 10nm, as reported by [31]. Besides to this, scarcity of multiferroic materials, lack of complete understanding of the multiferroic thin films and experimental control at the nanoscale contribute their own share. Much effort should be put in obtaining a clear, unambiguous and indeed significant coupling between TER and TMR effects in single device with four-state memory devices.

This paper tries to review the theoretical and experimental results achieved over the last years on these promising junctions. To that end, I will first discuss analogies and differences between ferroelectrics and ferromagnets to make discussion of multiferroic tunnel junctions easier. Second, I will present the corresponding TMR and TER effects before winding up the paper with multiferroic tunnel junctions. Finally, I will try to explain why these promising devices are so difficult to make and commercialize as far as the theoretical and experimental results are concerned.

2 Ferroelectrics, Ferromagnets and Multiferroics

Beautiful analogies and differences between ferroelectrics and ferromagnets are given by Nicola A. Spaldin [1]. I will here put abridged form of what is explained in the book so as to help me explain the beauty of multiferroic tunnel junctions later in this paper. A ferroelectric has a spontaneous non-zero polarization (P) that can be switched by a strong electric field; a ferromagnet has a spontaneous magnetization (M) that can be switched with a strong magnetic field. The dependence of P (M) with applied field E (H) gives ferroelectrics (ferromagnets) the hysteretic behavior and the existence of two states that can be used as a data bit in memory devices.

In ferroelectrics, for example the ferroelectric perovskites (ABO_3), the displacement of the cation B towards the anions leaves the crystal polarized removing its centrosymmetry and creating a spontaneous polarization. The spontaneous polarization is due to the collective effect in the crystal that can be switched by the application of an external electric field. In ferromagnets, spontaneous magnetization is due to the spin of the electrons that couples with their orbital angular momentum resulting in a magnetic dipole moment and creating a net magnetization even in the absence of an external

field. The exchange interaction between two spins is responsible for the magnetic ordering in ferromagnetic materials and dictates the total behavior of these materials.

In both ferroelectrics and ferromagnets, domain walls form so as to minimize the total energy of the material. One sharp difference, though, is that domain walls in ferromagnetic materials are wide and require less energy to form as compared to ferroelectric domain walls. This is because the polarization reversals at the ferroelectric domain walls require changes in the atomic displacements near the walls, which do not take place at a ferromagnetic wall.

Materials that exhibit these two properties, ferromagnetism and ferroelectricity, are referred to as multiferroic materials. To once dismay, such materials are very scarce in nature duet to the 'contra-indication' of mechanisms causing ferroelectricity and ferromagnetism in a single phase [10].

2.1 Scarcity of Multiferroics

The polarization arises due to the nocentrosymmetric arrangement of ions with respect to the central cation. Hence the origin of this ferroelectricity is the same as the cause for Ferroelectricity is a combined effect of long-range Coulomb forces and short-range repulsive forces. The former favors the ferroelectric state while the later induces repulsion between the electron this ionic off-centering. However, one should note that, although some crystals are intrinsically nocentrosymmetric, they don't possess the property of ferroelectricity. This is because the polarization is not known to be switched by any finite electric field. Most known ferroelectrics have non polar centrosymmetric prototype phases at high temperatures, for example the perovskites. As shown if figure 1, a perovskite will not be ferroelectric in their symmetric case

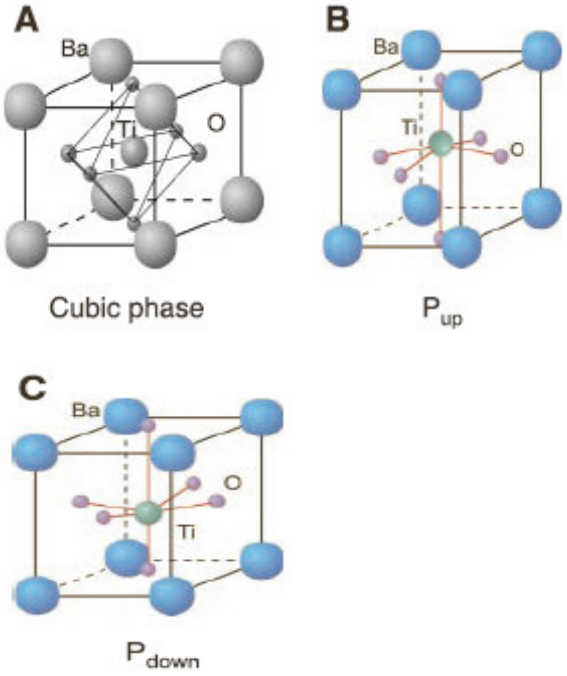


Fig. 1. Crystal structure of the perovskite ferroelectric BaTiO3. (A) Paraelectric, cubic phase. (B and C) ferroelectric, tetragonal phases [11].

clouds of adjacent ions that favor the non polar cubic structure [12]. The ferroelectric behavior of a crystal is determined by the balance between these two counteracting forces. Perturbative

expansion over the total Hamiltonian, H, of the electronic ground state as a function of the displacement shows how the contributions from these two forces influence the state of the crystal system. Hence, the energy E(Q) can be written to second order as:

$$E(Q) = E(0) + \langle 0|(\delta H / \delta Q)_o|0\rangle Q + \frac{1}{2}\langle 0|(\delta^2 H / \delta Q^2)_o|0\rangle Q^2 - \sum_n \frac{\left|\langle 0|(\delta H / \delta Q)_o|n\rangle\right|^2}{E_n - E(0)} Q^2 .... \quad (1)$$

Here, E(0) is the energy of the undistorted ground state, E_n is the excited-state energies. The first term that is linear in Q is responsible for the characteristic tetragonal distortions of d^1 & d^4 perovskite structures. It is usually referred to as the first-order Jahn-Teller contribution which is non-zero only for degenerate states that could be lifted by the action of a crystal field in a tetragonal environment. The second term is a positive contribution to a second order Jahn-Teller distortion, which describes the increase in energy due to a distortion that results from the Coulomb repulsion. The third term is a negative. If the second term is larger than the first, then a distortion will cause a second-order reduction in the total energy. M. Atansov and co workers investigated the role of lone pairs on the electronic structure and found out that a noncentrosymmetric distortion results if the contribution from the second term is larger than the first [13].

Magnetism has quite different requirements than ferroelectricity. In a ferromagnet, outer shell electrons must have a net angular momentum. In addition to this, there should be unbalanced number of spin-up electrons to spin-down electrons. Hence unlike ferroelectric materials they demand partially filled *d* or *f* orbitals. Pauli's exclusion principle demands electrons of antiparallel spins to share a single atomic or molecular orbital. This effectively increases spatial overlap of wave function even if that means increasing Columbic repulsive interaction. On the other hand, if they have similar orientation in spin, the cost for energy to place two electrons in a single atomic orbital is larger than putting them in two different orbitals. This reduces the repulsive Coulombic force. It seems thus that ferroelectricity and ferromagnetism exclude one another, especially if the cations involved in off-centering and formation of magnetic moment are the same. That is the main reason why finding a single phase multiferroic material is very difficult [14]

2.2 Magnetoelectric Coupling

Coupled ferroelectric and magnetic properties - magnetoelectric effect can be explained by the well known Landau theory. The free energy of a non-ferroic material can be written in terms of an applied magnetic field H and electric field E. Let H_i and E_i be components of the respective fields. Now assuming that the respective polarization $P_i(T)$ and magnetization $M_i(T)$ be zero in the absence of applied fields and that means no hysteretic nature will be observed. Therefore the free energy can be given as (in SI units) [15]:

$$F(E,H) = \frac{1}{2}\varepsilon_o \varepsilon_{ij} E_i E_j + \frac{1}{2}\mu_o \mu_{ij} H_i H_j + \alpha_{ij} E_i H_j + \frac{1}{2}\beta_{ijk} E_i H_j H_k + \frac{1}{2}\gamma_{ijk} H_i E_j E_k + \ldots \quad (2)$$

The first term is due to contribution resulting from the electrical response to an applied electric field, where ε_o and ε_{ij} are the permittivity of free space and the relative permittivity respectively. Similarly, μ_o and μ_{ij} are the permeability of free space and the relative permeability. α_{ij} is the linear magnetoelectric coupling tensor, β_{ijk} and γ_{ijk} are higher order magnetoelectric coefficients of third order ranks describing the "EHH" and "HEE" responses, respectively. Due to symmetry reasons, the occurrence of the linear and bilinear magnetoelectric effects can be achieved in crystals with ferromagnetic or antiferromagnetic point groups only [1].

From this treatment of non-ferroic materials, the magnetoelectric effect can easily be established using the following two relations from statistical mechanics:

$$M_i = \frac{\partial F}{\partial H_i} \quad (3)$$

$$P_i = \frac{\partial F}{\partial E_i} \quad (4)$$

Substituting the expression for the free energy into the above two equations and by setting both independent parameters to zero yields:

$$P_i = \left.\frac{\partial F}{\partial E_i}\right|_0 = \alpha_{ij} H_j + \frac{\beta_{ijk}}{2} H_j H_k \quad (5)$$

$$\mu_o M_i = \left.\frac{\partial F}{\partial H_i}\right|_0 = \alpha_{ji} H_j + \frac{\gamma_{ijk}}{2} E_j E_k \quad (6)$$

This treatment can be applied to ferroic materials by introducing temperature dependence to the relative permeabity and permittivity. Moreover, accounting for the depolarizing factors in such materials is easier because the coupling constants would then be function of temperature alone, as in standard Landau theory. However, one may try to introduce dependence in the applied field. In that case, rather than using the applied field as a parameter, using the resultant field suffices [15].

Based on the work by Brown et al., [16] multiferroic materials, that are both ferromagnetic and ferroelectric, often possess one interesting property: They have large permittivity and permeability respectively, and α_{ij} is bounded by the geometric mean of the diagonalized tensor ε_{ii} and μ_{jj}, to first order approximation, such that

$$\alpha_{ij}^2 \le \varepsilon_o \mu_o \varepsilon_{ii} \mu_{jj} \tag{7}$$

This allows us to write a simple relationship between the two order parameters in the form of two coupled equations as [7]

$$P = \chi_e E + \chi_{em} H \text{ and } M = \chi_{me} E + \chi_m H \tag{8}$$

Or in a compact matrix form

$$\begin{pmatrix} P \\ M \end{pmatrix} = \begin{pmatrix} \chi_e & \chi_{em} \\ \chi_{me} & \chi_m \end{pmatrix} \begin{pmatrix} E \\ H \end{pmatrix} \tag{9}$$

The magnetoelectric coupling can be understood once the point group symmetry is known and can be measured by recording changes in either magnetization near the ferroelectric transition temperature or recording polarization at the magnetic transition temperature. The properties of the matrix elements hence can be known based on the symmetry considerations.

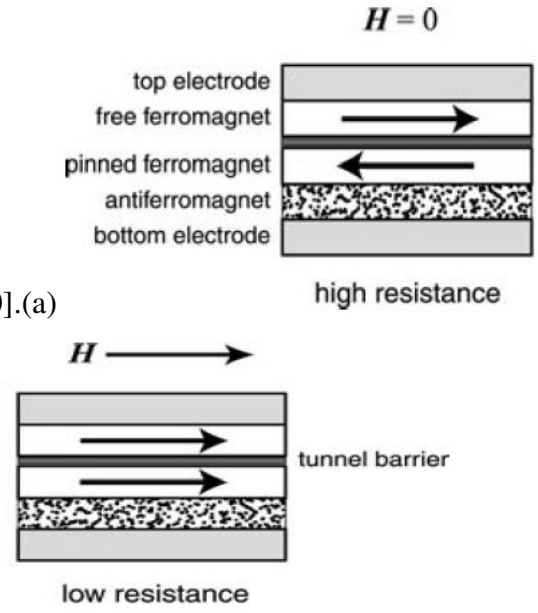
The main difficulty in this research area is the inability to find a material with a significant magnetoelectric coupling constant at room temperature. Recent methods of engineering magnetoelectric coupling can be thought of as targeted in two groups of materials – single phase ($BiFeO_3$, $BiMnO_3$ and $YMnO_3$ etc) and two phase materials (composites or multilayers). One should note that, within the single phase materials, the mechanism of multiferrocity is different from one material to another [14]. Most of the known single phase bulk multiferroic materials do not possess strong magnetoelectric coupling. Besides, they are characterized by a very low Néel or Curie temperatures far below room temperature. Hence this obstacle was circumvented by trying to look for strong coupling in two-phase (composite), laminates and more recently in horizontal (vertical) nanostructured materials. The components in the composite are chosen such that one of the components is highly magnetostrictive, while the other one is highly piezoelectric. In this way the materials are magnetoelectrically coupled though strain. Recently, H.Zheng et al. showed how it is possible to grow multiferroic $BaTiO_3$-$CoFe_2O_4$ with large magnetoelectric coupling [18]. By employing this method, it is possible to obtain thin films with large magnetoelectric coupling coefficients as required by MFTJs and other future multiferroic based microelectronics, magnetic storage, and microwave techniques. A rather new and exciting approach to magnetoelectric interaction is the cross-coupling effect obtained in frustrated magnets. In such materials, the strength of coupling is very large,

allowing the switching of the polarization with a magnetic field, but the polarization is two to three orders of magnitude smaller than in typical ferroelectrics and the working temperatures are too low to be used in devices. This type of multiferroics were first observed in orthorhombic rare-earth manganites $Tb(Dy)MnO_3$ and $Tb(Dy)Mn_2O_5$ [19]

Future spintronics based on MFTJs hence eagerly awaits for a breakthrough in good coupling and control of these materials through one of the above mentioned coupling mechanisms. Otherwise, the envisioned multiple state memory devices will remain futile.

3 Magnetic tunnel junctions and tunnel magneto resistance (TMR)

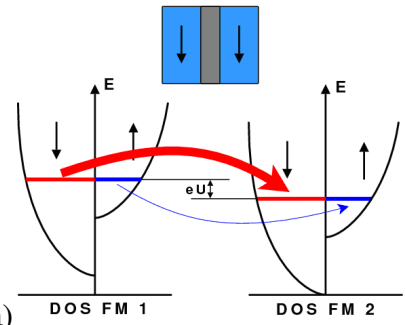
A magnetic tunnel junction consists of two magnetic metal electrodes separated by a nanometer-thick insulating layer (usually aluminum oxide), as shown in figure 2. Electrons, therefore, have a finite probability of tunneling to the other side through the barrier. The first spin dependent tunneling was originally observed 1975 by M. Julliere in Fe/Ge-O/Co junctions at 4.2K [20].(a)



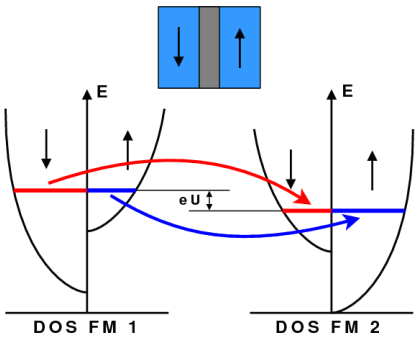
(b)

Fig. 2. Schematic of a magnetic tunnel junction (a) high-resistance (b) low-resistance states [1]

This led to the well known tunnel magnetoresistance effect (TMR), in which a remarkable change of the tunneling current is obtained when relative orientations of magnetization of electrodes are changed. As shown in fig. 2, the magnetization of the lower electrode is pinned by an underlying antiferromagnet, while the orientation of the upper electrode can be switched by applying a magnetic field.



(a)



(b)

Fig. 3. Schematics of the tunneling mechanism for (a) parallel and (b)antiparallel orientations [21]

Under the condition that the spin of electrons is conserved during tunneling, tunneling of up- and down-spin electrons are two independent processes following different channels. Electrons tunnel with ease if they originate from one spin state of the first electrode and find unfilled states of the same spin. If the two ferromagnetic films are magnetized parallel, the minority spins tunnel to the minority states and the majority spins tunnel to the majority states. If, however, the two films are magnetized antiparallel, the identity of the majority- and minority-spin electrons is reversed, so the majority spins of the first film tunnel to the minority states in the second film and vice versa. The relative resistance change, TMR, is defined as:

$$TMR = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\uparrow}} = \frac{2P_1P_2}{1 - P_1P_2} \qquad (10)$$

Where $R_{\uparrow\downarrow}$ and $R_{\uparrow\uparrow}$ are electrical resistances for antiparallel & parallel respectively.

$P_1 = \frac{n_1^{\uparrow} - n_1^{\downarrow}}{n_1^{\uparrow} + n_1^{\downarrow}}$ & $P_1 = \frac{n_2^{\uparrow} - n_2^{\downarrow}}{n_2^{\uparrow} + n_2^{\downarrow}}$ are the spin polarizations of the ferromagnets. (11)

Over the years, the range of insulators used in such devices was not limited only to Al_2O_3 but also $SrTiO_3$, MgO and, recently, ferroelectrics [2] have also been used as a barrier.

4 Ferroelectric tunnel junctions and tunnel electroresistance (TER)

The study of a FTJ as a polar switch started in the 1970s by Esaki [22]. However, it was not possible by then to realize this idea due to technical limitations to fulfill the requirement for thin films as thin as a few unit cells. A ferroelectric tunnel junction is a layered structure in which a ferroelectric is sandwiched in between two metal electrodes. Such metal/ferroelectric/metal structure can be regarded as two Schottky contacts or diodes on both sides of the FE film. Hence we will have at least two interfaces that influence the transport properties and, thus, the resistance of the junction upon inversion of polarization.

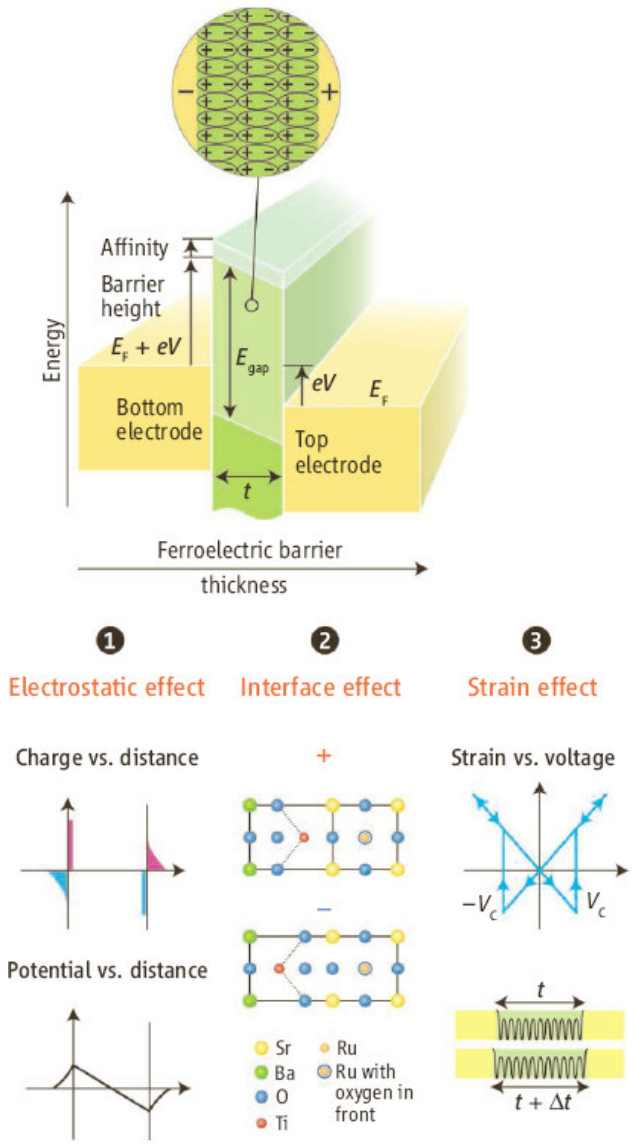


Fig. 4. A schematic ferroelectric tunnel junction (Eg is the energy gap. EF is the Fermi energy, V is the applied voltage [2].

Upon application of a voltage difference across the barrier, one of the diodes will be reversed biased and the other forward biased and, usually, it is assumed that the ferroelectric film is thick enough to avoid overlapping of the two depletion regions [23] and thin enough to allow tunneling. As pointed out by E.Y. Tsymbal and H. Kohlstedt [2], all three mechanisms shown in fig. 4 1, 2 and 3 lead to a resistive switching mechanism at the coercive voltage of the ferroelectric. In (1), due to the piezoelectric nature of the ferroelectric barrier, an applied voltage produces a strain which changes transport characteristics of the barrier such as the barrier width and the attenuation constant. In (2), incomplete screening of the ferroelectric bound charge leads to an electrostatic potential that superimposes to the contact potential in the tunnel junction. In (3), the displacement of the cations affects the atomic orbital hybridizations at the interface, which makes the transmission probability different for the two opposite polarization orientations. These, obviously, in turn influences the tunneling probability of electrons through the ferroelectric barrier, which believed to cause the giant electroresistance effect [24]. But, these do not directly involve the reorientations of the electric dipole upon polarization switch, which only influence the tunnel barrier.

4.1 Ferroelectric/ metal junction

Ferroelectrics have a spontaneous polarization, P_s, that is nonzero even in the absence of applied electric field. When a ferroelectric and a metal make contact, the spontaneous polarization in the ferroelectric is influenced by the screening (shielding) effect due to electrons in the metal.

Consequently, the basic characteristics of the device will change due to the Thomas–Fermi screening length. Usually for most metals this screening length ranges from 0.01 nm to 0.1 nm. I hereby try to present the basics of this kind of junction with an emphasis on the effect that ferroelectricity has on the barrier height, the depletion width, current density and also the causes for resistive switching.

4.1.1 Schottky contacts

When a metal is brought into intimate contact with a semiconductor/insulator ferroelectric, a barrier will be formed at the metal-insulator interface. Electrons are injected from the metal electrode to the ferroelectric. This junction will tend to create asymmetric current-voltage characteristics typical of a diode blocking current in one direction and allowing in the other direction[25].

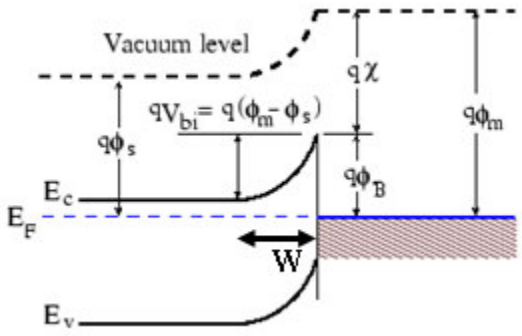


Fig. 5 Metal/ n-type semiconductor contact at thermal equilibrium. Adapted from Sze [25]

However, figure 5 represents an ideal case of a metal/insulator junction. Presence of polarization from a ferroelectric changes the band bending structure, as will be discussed at the end of this section. The barrier height is the difference between the work function of the metal and the electron affinity of the ferroelectric material. Mathematically,

$$\Phi_B^O = \phi_m - \chi \qquad (12)$$

How a ferroelectric should be treated when it makes contact with a metal has been a debatable topic. Treating the ferroelectric material as insulator fails to explain the experimentally observed conduction mechanism. At the same time, if it is treated as a semiconductor, it complicates the already complex system [23]. If a low work function metal is in contact with the ferroelectric, the contact formed will be termed as ohmic. In such junction, the flow of charges in and out of the metal are balanced and the metal-semiconductor contact has a negligible contact resistance relative to the bulk. However, usually ferroelectric device applications demand a higher potential barrier in between contacts.

J. F. Scott et al.[26] pointed out that, although most ferroelectrics turn out to be p-type semiconductors with large band gap of the order of 3.2 – 3.9 eV, in some cases oxygen vacancies at or near interface acts as donor ions, which leads to an n-type behavior of the interface as opposed to the p-type nature in bulk. J. Robertson et al. [27] had investigated the Schottky barrier heights of various metals on the high permittivity oxides

tantalum pentoxide, barium strontium titanate, lead zirconate titanate, and strontium bismuth tantalite and found that the barrier height seen by electrons at a metal/ferroelectric junctions is smaller than that seen by holes, confirming the Schottky diode behavior.

The polarization in the ferroelectric material can be taken into consideration by introducing a sheet of surface charges a distance δ. Therefore, an apparent built in potential can be rewritten as [28]:

$$V_{bi}^{'} = V_{bi} \pm \frac{P}{\varepsilon_O \varepsilon_{st}} \delta \tag{13}$$

where P is the polarization, ε_O and ε_{st} are the free and static permittivity, respectively, and δ is the distance between the polarization surface charge and the metal/ferroelectric junction. V_{bi} is the classical built in potential between a metal/ferroelectric junction, whose value can be found from the expression:

$$V_{bi} = \Phi_B^o - \frac{KT}{q} \ln \frac{N_v}{p(T)}, \tag{14}$$

N_v is density of states in the valence band, T is temperature and p(T) is the concentration of holes at a given temperature.

The abrupt change in the profile of the Fermi energy near the interface results in the formation of a depletion layer. There has been a debate over the size of the depletion width over the years and J. F. Scott insists that the depletion width should not extend beyond the film thickness [28]. L. Pintille et al., have presented unambiguous experimental result for the depletion width [23]. In their report, they have shown that the depletion width is nearly half of the film thickness even in the thinnest films. As calculated by [22], the depletion with can be expressed as:

$$w = \sqrt{\frac{2\varepsilon_o \varepsilon_{st} (V + V_{bi}^{'})}{qN_{eff}}} \tag{15}$$

Similarly, one can calculate the capacitance near the interface by replacing the nominal built in potential by the modified built in potential given in eq. (14). The maximum electric field at the interface will also depend on the polarization of the ferroelectric and it is modified as:

$$E_{\max} = \sqrt{\frac{2qN_{eff}(V + V_{bi})}{\varepsilon_o \varepsilon_{st}}} \pm \frac{P}{\varepsilon_o \varepsilon_{st}} \tag{16}$$

Parameters like $P, V_{bi}^{'}$ & Φ_B^O can be extracted by analyzing the current voltage characteristics of the metal/ferroelectric/metal junction.

By taking in to account the above modifications made for a ferroelectric tunnel barrier, one can investigate the current – voltage characteristics and expect the current density to be dominated by thermionic emission through the barrier at room temperature. Therefore, the current density can be given by [23]

$$J = A^* T^2 \exp\left[-\frac{q}{kT} \left(\Phi_B^O - \sqrt{\frac{qE_m}{4\pi\varepsilon_o \varepsilon_{op}}} \right) \right] \tag{17}$$

where A^* is the Richardson's constant and ε_{op} is the optical (high frequency) dielectric constant. By combining eq. (16) and (17), one can write:

$$\ln(J) = \frac{q^4}{kT}\sqrt{\frac{q^3 N_{eff}}{8\pi^2 \varepsilon_o^3 \varepsilon_{op}^2 \varepsilon_{st}}}\left(V + V_{bi}'\right)^{1/4} \qquad (18)$$

By plotting (11), it has been shown that it is possible to find N_{eff} for ferroelectrics and semiconductors as well. In general, we have seen that, the presence of the spontaneous polarization introduces modification to the barrier height, the built in potential, the current density and the tunneling probability, all influencing the resistance of the device upon switching the polarization.

4.1.2 Conduction mechanisms in FTJs

The study of conduction mechanism through the ferroelectric barrier proves to be important in order to understand the "giant electroresistance effect". It is obvious from the device structure that the interface conduction mechanisms and the tunneling through the barrier are the most dominant mechanisms. Hence conductions mechanism can be classified as being surface limited (Schottky current, direct tunneling and Fowler-Nordheim currents) or bulk-limited (Poole-Frenkel and Space-Charge limited currents). Below is given a simple description of what these conduction mechanisms mean for the ferroelectric tunnel junction.

4.1.2.1 Schottky Emission

It is an interface-limited process that can be expressed by the modified Schottky equation presented in the previous section (eq. 17). As seen above, this conduction mechanism highly depends on the potential barrier shape, height and width at the ferroelectric-electrode interface. The current voltage characteristic is determined by the imager force lowering of the barrier height when a potential is applied.

4.1.2.2 Space Charge Limited current

When charges become immobile and reside in the ferroelectric, space charge is produced. When the sample is biased in one direction, the space-charge-limited currents are seen to dominate. Child and Mott have shown that the space charge limited current takes a quadratic dependence with the applied voltage. When the voltage is increased; it starts to dominate as a result of charges filling up the gap between the cathode and anode. This injected charge retards the transmission of the next injected electrons. As mentioned in the previous sections, plotting the lnJ against the applied voltage shows different functionality of the current density and with that the conduction current can be identified.

4.1.2.3 Poole – Frenkel

It is uninterestingly difficult to differentiate the Schottky emission conduction from the Poole-Frenkel mechanism due to their similar nature.

Pool-Frenkel, unlike Schottky emission, is a bulk-limited conduction mechanism that involves field-assisted variable range hoping from one defect to another. However, for a uniformly doped film, Poole–Frenkel and Schottky currents can easily be discriminated by changing the film thickness or by introducing an asymmetric set of electrodes for the ferroelectric tunnel junction - both of which differentiate between the bulk limited and surface limited conduction mechanisms [29].

4.1.2.4 Fowler – Nordheim

This conduction mechanism arises in a thin film through the potential barrier and not through the ferroelectric barrier in the ferroelectric tunnel junction. The tunnel barrier thickness is estimated to be as low as 3-7nm [28]. It occurs when the voltage applied to the electrode is very low but not greater than 5V.

J. F. Scott gave an explanation about the different regimes of domination of these different conduction mechanisms: At low voltage, the leakage current is exactly ohmic, the high field leakage current is trap-dominated (Frenkel-Poole) in the interior of the film, and the polarity dependence of the current is still Schottky-like and it is quite different from the Frenkel-Poole mechanism.

4.1.2.5 Ultrathin Direct tunneling

This is a tunneling mechanism that, in contrast to Fowler-Nordheim tunneling, occurs through the ferroelectric barrier itself. The observation of direct tunneling through a ferroelectric barrier is claimed by some groups [30] but it is still debatable. This is so because the film is too thick for tunneling to occur. J. F. Scott has commented on the work of Rodriguez Contreras et al.[31], who have claimed the observation of direct tunneling or phonon assisted tunneling through the ferroelectric barrier, that their results are not consistent with their own calculation of the small barrier height extracted using a direct tunneling model.

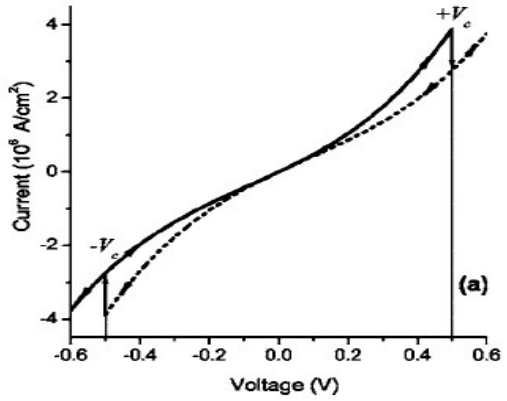
4.2 Resistive Switching in Ferroelectric tunnel junctions

Metal –insulator –metal junctions that exhibit a resistive switching are bound to feature in future memory devices due to the successful study of ferroelectric films as a resistive memory device rather than capacitors [2]. Resistive switching not only arises from direct tunneling [31] through the barrier but also due to some other ordinary effects [9]. The work by H. Kohlstedt et al. suggested strain, depolarizing field, interface and other microscopic effects near the interface as possible sources for resistive switching.

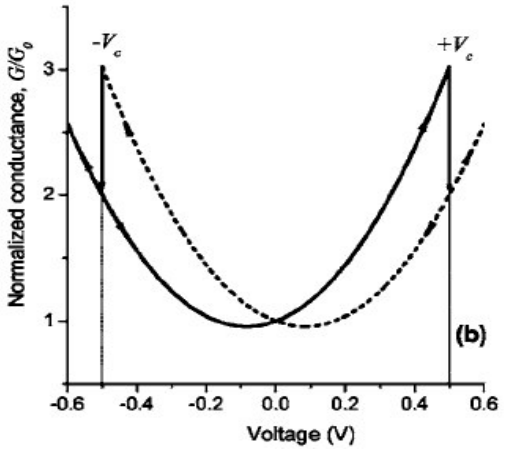
4.2.1 Strain effect

Lattice mismatch between the film and the electrode on which the film is grown puts the film under strain. In their work, they have shown how the presence of strain at the interface highly

influences the current – voltage characteristics of the FTJ (figure 6).



(a)



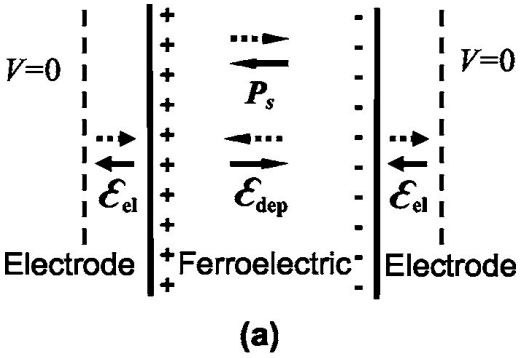
(b)

Fig. 6. Influence of strain on the current-voltage characteristics (a) and on the conductance (b) [32]

The change on current – voltage characteristics as a cause for resistive switching can be explained well with the conductance – voltage measurement. At both negative and positive coercive voltages, a change in the barrier conductance is observed. It is shown in figure 6 (b) that the hysteretic behavior in the conductance – voltage curve allows for resistive switching, in which the high-resistance state corresponds a polarization orientation in the direction of applied field, whereas the low resistance state takes place when the orientation is antiparallel. In an asymmetric tunnel junction, the bottom and top electrode will induce different strain on either side of the film, giving extra flexibility in FTJ engineering. This shows the possibility of resistive switch due to the strain but not due direct tunneling through the barrier.

4.2.2 Depolarizing /electrostatic field effect

The depolarizing electric filed is caused by the polarization charges on the surface of the ferroelectric thin film. The depolarizing field and the spontaneous polarization are oriented in opposite direction as shown in figure 7 (a). Due to the screening effect of the metals, the depolarization field inside the barrier smears out in a symmetric FTJ [33]. In principle, as shown in figure 4 (2) and 7 (b), when a ferroelectric barrier is placed in between two metals, the potential barrier gets modified, which in turn modifies the tunneling current as well as the current – voltage characteristics.



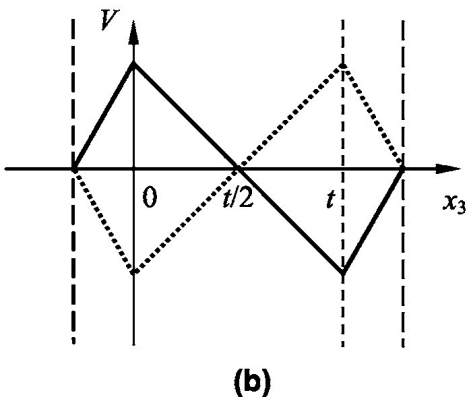


Fig. 7. Influence of the depolarizing field in FTJ [32]

However, in an asymmetric system the story is different. When a FTJ is made of two different metals with nearly same work function but different screening length [33], the electrode's screening ability to screen the depolarizing field will be different. Theoretically calculating the effect of the depolarization field on the conductance of the FTJ, it has been shown that there is an enormous change in the resistivity at V= 0 for the two different switching states, which can be detected experimentally. One should note here that, asymmetric FTJ are not always due to different screening length but also due to different microscopic interfaces, even if the electrodes are similar. For example, C. L. Jia et al. [34] have been able to show the different junctions observed in $SrTiO_3/BaTiO_3/SrTiO_3$ heterostructures leading to an asymmetric FTJ.

So far we have seen some polarization reversal associated resistive mechanisms which are not associated to any form of direct tunneling through the barrier. Hence, based on these evidences, electroresistance is not unambiguously associated to direct tunneling through the barrier, unlike its magnetic counterpart.

4.3 Giant Electroresistance effect in Ferroelectric tunnel junctions

As mentioned in the first page of this paper, there are different outlooks on the cause and existence of 'tunneling electroresistance effect' in FTJs. Some theoretical predictions have been able to show that the giant electroresistance effect can indeed be observed in FTJs, although not many experimental works have witnessed the tunneling induced electroresistance effect in FTJs.

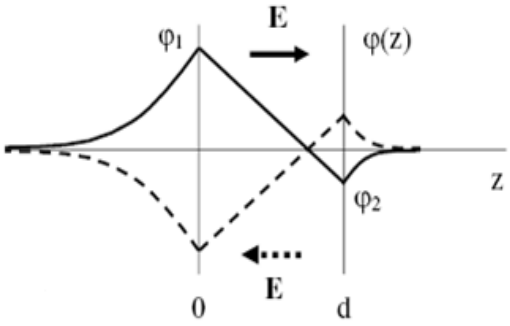


Fig. 8. Potential profile seen by electrons for different polarization [32]

For better understanding, it is worth mentioning how the electroresistance effect is treated theoretically in a FTJ by Zhuralev et al [24]. They investigated the change in resistance during polarization reversal in an ultrathin ferroelectric barrier accounting for the screening of

polarization charges in metallic electrodes and direct quantum tunneling across a ferroelectric barrier. They found a few orders of magnitude change in the conductance for metallic electrodes with sizable difference in screening lengths. They attributed the cause for this giant electroresistance effect to the different potential profile seen by transport electrons for the two opposite polarization orientations (fig. 8). The dashed line in the figure shows the potential profile seen by electrons when the polarization P in the ferroelectric is switched. According to their calculations, the conductance of the tunnel junction per unit area A was found using the expression:

$$\frac{G}{A} = \frac{2e^2}{h} \int \frac{d^2 k_{//}}{(2\pi)^2} T(E_F, K_{//}) \qquad (19)$$

where $T(E_F,k_{//})$ is the transmission amplitude evaluated at the Fermi energy. J. P. Velev and co workers [33] have also carried out density functional theory calculations on $Pt/BaTiO_3/Pt$ tunnel junctions in order to understand the effect of ferroelectricity on the electroresistance effect. The presence of ferroelectricity in $BaTiO_3$ is seen to produce a significant shift in the position of the density of states maxima at the interface, resulting in a change in the conductance for the different polarization directions. Hence, the giant electroresistance ratio (GER) can be obtained after calculating the conductance for the two different polarization directions (right or left) using Eq. 19. Mathematically, the GER ratio is given as:

$$GER = \frac{G_R}{G_L} \text{ or } GER = \frac{G_{\leftarrow} - G_{\rightarrow}}{G_{\leftarrow} + G_{\rightarrow}} \qquad (20)$$

where $G_{\leftarrow} \& G_{\rightarrow}$ are the conductances measured for the electric polarization of the barrier pointing towards the left (right) electrode respectively.

The way in which polarization affects the interface transmission function is schematically shown in figure 4 (1), (2) and (3). For an asymmetric junction, the effect of polarization on the transmission probability can be expressed as the function of the surface transmission functions [3]:

$$T(K_{\|}) \approx t_L(k_{\|}) t_R(l_{\|}) \exp[-2\kappa \cdot d] \qquad (21)$$

where $t_L \& t_R$ are the interface transmission coefficients. They denote the different transmission at the two interfaces. The tunneling mechanism in FTJ and MFTJ depends, therefore, on this value. In conclusion, the film thickness, the interface transmission coefficients and the nature of the interface largely affect the conduction mechanism in such devices.

5 Multiferroic tunnel junctions

Multiferroic spintronics plays a crucial role in the future of non-volatile memory devices. The objective is to be able to control and manipulate the spins of carriers in a ferromagnet by electric field. Multiferroic tunnel junctions are no much different from the ones discussed above. A

multiferroic tunnel junction is a magnetic tunnel junction with the insulating barrier replaced by a multiferroic material. A typical multiferroic tunnel junction is envisioned to switch the ferroelectric polarization by the application of an electric field which in turn, due to the coupling with the ferromagnetism, changes the orientation of the ferromagnet. When realized, one can access the four states of the resistive memory element shown in figure 9.

However, the experimental control of such devices is very problematic. First, the multiferroic tunnel barrier must be so thin (< 3nm) that tunneling can occur through the barrier, but at the same time the stability of both magnetization and polarization of the film has to be maintained at such thickness. Second, epitaxial growth of thin-film multiferroics with high structural quality is problematic and requires further development.

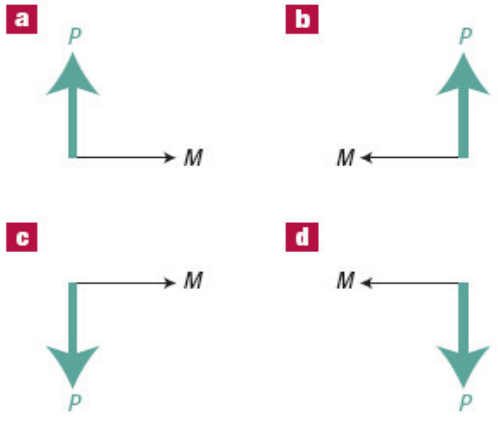
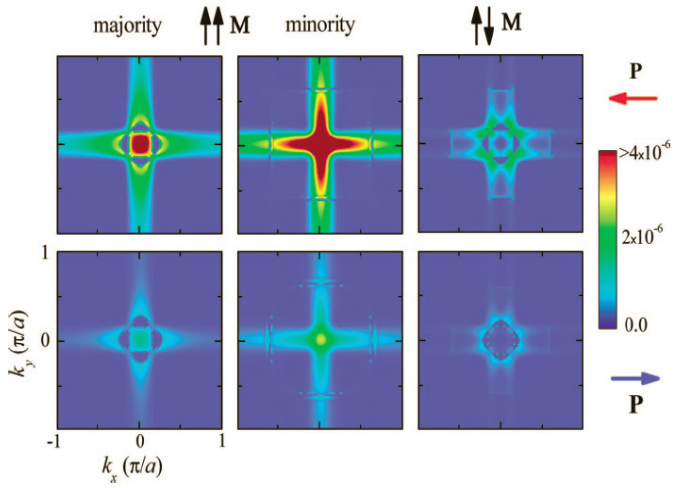
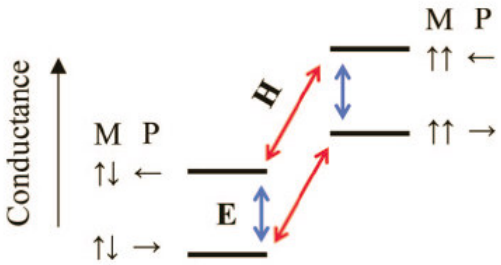


Fig. 9. Four degrees of multiferroic order with polarization P and Magnetization M in a multiferroic memory device [9].

Third, and most importantly, single phase multiferroic materials are very scarce in nature and most of them hardly show multiferroic properties at room temperature.

Multiferroic tunnel junction can be thought to be made from two kinds of systems: single phase systems and two-phase systems. Two–phase systems are composed of composite layered ferroelectric/ferromagnetic structures, whereas a single-phase multiferroics uses a material that show both properties in a single phase as in $BiMnO_3$ and $BiFeO_3$. The number of theoretical works on two-phase systems is by far larger than experimental works. Julian P. Velev and co workers, based on of first-principles calculations, have shown the possible coexistence of TER and TMR effects in a $SrRuO_3/BaTiO_3/SrRuO_3$ [3]. In their work, they have assumed different junctions at both ends of the $BaTiO_3$ barrier. In doing so, they have observed a significant change on the resistance of the MFTJ with the reversal of polarization. Similar effect was also observed when the magnetizations of the electrodes are switched from parallel to antiparallel.





G (10^{-7} e^2/h)	↑↑	↑↓	↑↑:↑↓	TMR (%)
→	3.76	0.83	4.6	**64**
←	11.82	1.69	7.0	**75**
← : →	3.1	2.1		
TER (%)	**52**	**35**		

Fig 10 TER and TMR effects in SrRuO3/BaTiO3/SrRuO3 (a) Transmission in the 2D Brillouin zone, top panel for ← Polarization and bottom panel for → polarization. (b) four conductance states[3].

In the above figure, it can be seen that the control over four resistance states can be achieved by either electric or magnetic field. Upon polarization reversal, the transmission probability of the electron gets modified and in turn changes the conductance of the MFTJ. This is the fundamental nature of the tunnel electroresistance effect. The asymmetric nature of the junction added to the tetragonal distortion in $BaTiO_3$ and $SrRuO_3$ favors an electric polarization perpendicular to the layers which can be switched by an electric or magnetic field. Using such hypothetical arrangement the previous authors have been able to show the possibility of coexistence of TER and TMR effects. In their calculation, they have let the MFT barrier to be six unit cells of $BaTiO_3$ (≈ 2.5 nm) which is in the regime of tunneling. Since the critical thickness for ferroelectricity in $BaTiO_3$ can be as low as 1.2nm [35], it is also possible to further lower the thickness of the barrier and see if the result can be duplicated. An earlier first principle electronic structure and transport work by J. P. Velev et al. [7] also demonstrated the impact of the electric polarization on electron and spin transport in Fe/BaTiO3/Fe MFTJs.

Despite these theoretical predictions, experimental work is yet to be reported on the coexistence of TER and TMR effect based on a two-phase MFTJ. Rather, most experiments are aimed to obtaining large coupling in such composite layers. Although the objective of the report by S. Sahoo et al. was to show the so called converse electromagnetic effect (the effect a ferroelectric $BaTiO_3$ substrate on magnetization of thin Fe film) [36], they have demonstrated how electrical and thermal control of the magnetic anisotropy of

thin Fe deposited over $BaTiO_3$ is possible by allowing the substrate to undergo a structural phase transition. Analogous to figure 2, one may replace the tunnel barrier with BTO or another ferroelectric and study the evolution of the resistance upon phase transitions of the ferroelectric. Such systems might be potential candidates for electromagnetic memory devices. However, as far as I know, no experimental report is yet published on such orientation dependence.

An alternative approach to MFTJs is to use a single-phase multiferroic barrier in magnetic tunnel junctions or even in conventional tunnel junctions – even though multiferroics are scarce and hardly maintain their property at room temperature. Two typical examples of current interest are $BiFeO_3$ and $BiMnO_3$ – the former being antiferromagnetic while the later being ferromagnetic – that can be used as a tunnel barrier in MFTJs. Recently, M. Gajek and co-workers have been able to prepare a $BiMnO_3$ based MFTJ shown to have a four resistance state at cryogenic temperatures[4]. They prepared a 2nm thick epitaxial thin film of LBMO as a tunnel barrier for spin-filtering devices. Spin filters are tunnel junctions in which the tunneling of electrons through a barrier is dependent on the spin orientation. By applying an external magnetic field, both TMR and TER effects have been observed in their devices, as shown in figure 11, consistent with the works of Julian P. Velev [3].

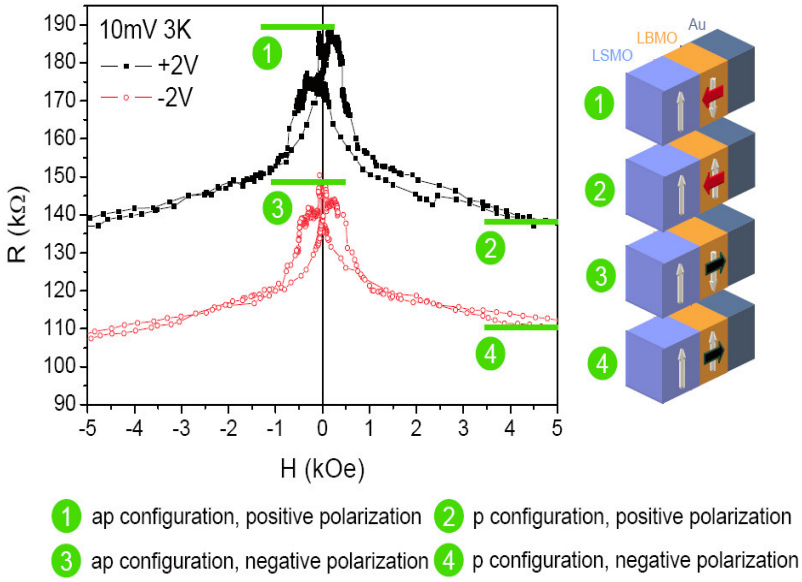
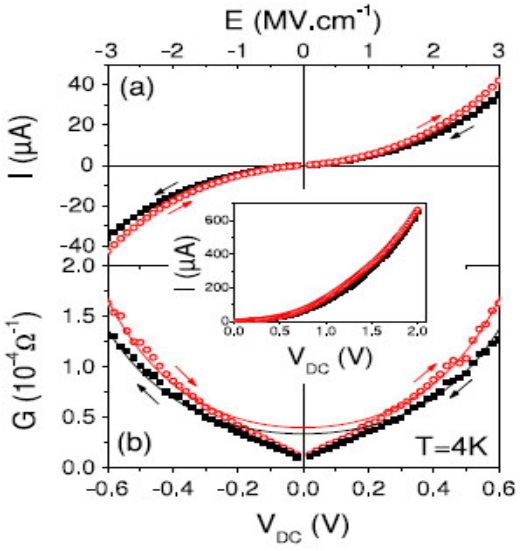


Fig. 11: Four resistance Levels (ap – antiparallel and p-parallel orientation of magnetization) in an Au/LBMO(2 nm)/LSMO junction as a function of the magnetic field and previously applied bias displaying four resistance states whose magnetic and electric configurations are represented on the right-hand side[4].

Based on the current-voltage characteristics measurement, a slight noticeable hysteresis due to different tunneling current for a given voltage was observed. Although the film thickness is in the region of tunneling, they attributed the cause of the ER effect to the different screening lengths of Au and $LaSrMnO_3$ that resulted into different tunnel barrier heights at the two interfaces. Hence, the authors avoided using the term "TER" as it does not involve tunneling directly through the barrier. Figure 12 (a, b) shows current-voltage

characteristics and the dependence of the conductance on applied voltage. One ambiguous measurement is their observed hysteresis in the I-V curve. They have associated the hysteresis to the resistance dependence on the polarization. However, it could also be due to other effects mentioned in the previous section. Indeed, in another paper, they examined the slight electrical hysteresis separately and concluded that it could not only be due polarization reversal but also to other resistive switching mechanisms [9, 37].

As shown in figure 11 (c), the plot of ER with respect to applied voltage shows an electroresistance effect of 22%. In the bias dependence of this ER phenomenon, at low applied voltage regime, the ER is roughly constant whereas, on the other hand, at high voltages, the ER effect decreases rapidly to zero.



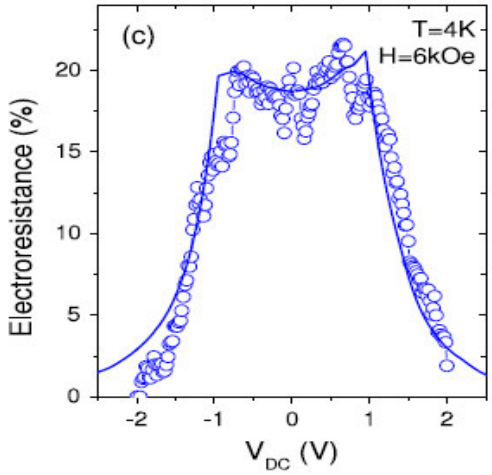


Fig. 12 (a) Hysteresis on I-V curve (b) conductance – voltage and (c) ER effect [37]

This study of M. Gajek et al. has indeed shown the coexistence of ER and TMR effects in a single phase MFTJs. Moreover, they have claimed direct tunneling mechanism based on the shaped of the G(V) curve. However, as pointed out by different works [1], this ER effect is not an equivalent to TMR due to previously mentioned pedestrian mechanisms.

Future works by other researchers on different materials have the task to unveil if TER and TMR can indeed be integrated in one device with no ambiguity before these MFTJs are commercialized. Another bit of concern in this work is the super paramagnetic effect, by which, below a critical thickness thermal fluctuation randomly orients spins, reducing or precluding the net magnetization. It remains to be reported yet if,

at the thickness of 2nm, it could be possible to achieve a multiple state device.

6 Conclusions and Discussions

The coexistence of the electroresistance and magnetoresistance was reviewed in this paper. The main question was if the tunneling electroresistance effect exists in a FTJ or MFTJ. Based on the experimental observations, it is not possible to unambiguously establish if such an effect occurs, as claimed by first principle calculations. Because, in the experimental observations reviewed in this paper; either the tunnel barrier is too thick for tunneling to occur or other resistive switching mechanism may have been responsible even if the film thickness is in the tunneling regime. Hence clear and unambiguous reports are yet to confirm the direct tunneling claimed by M. Gajek and coworkers as the main mechanism for switching and conduction mechanism in such thin multiferroic films. Rather interface effects, strain effects and the electrostatic effects, in addition to other pedestrian effects, ultimately modify the tunnel probability giving rise to large change in conductance upon switching. Hence the problem demands successful distinguishing between direct tunneling and other switching mechanisms to figure out the origin of the tunnel electroresistance effect, leaving the future of FTJ and MFTJ hanging in the balance.

Control over epitaxial thin multiferroic films at the nanoscale, stability at room temperature, stability of both magnetic and ferroelectric properties at film thicknesses of 1-2nm, understanding mechanisms of switching, domain formation and nucleation, finding strong magnetoelectric coupling, looking for high temperature multiferroic materials and realizing multiple memory devices are the future and fascinating challenges.

Although there are so many problems and open questions that need immediate solutions before such device are commercialized, the realization of FTJ RAM, MFTJ RAM and electrically controlled MRAM will largely depend on the successful commercialization of MFTJ, which ultimately will give rise to a multiple state memory device.

7 Acknowledgments

I would like to thank my supervisor Prof. B. Noheda for her critical and constructive comments as well as for her responsiveness that made working on this paper easier for me.

8 Bibliography

1. Rabe, Karin M., Charles H. Ahn, and Jean M. Triscone, eds. Physics of Ferroelectrics: A Modern perspective. p**19**7 Verlag Berlin Heidelberg: Springer, 2007.
2. E.Y. Tsymbal and Hermann Kohlstedt ; Science **313**, 181 (2006)
3. Julian P. Velev et al, Nano Lett., Vol. **9**, 427-432, (2009)
4. Martin Gajek et al., Nature Materials **6**, 296 - 302 (2007)

5. H. Bea and P. Paruch, Nature Materials **8**, 168–169 (2009)
6. Duan et al, Physical Review Letters, **97**, 047201 (2006).
7. Julian P. Velev et al., J. Appl. Phys. **103**, 07A701 (2008)
8. J. Wang and Z. Y. Li, Appl. Phys. Lett. **93**, 112501, (2008)
9. J. F. Scott, Nature Materials **6,** 256 - 257 (2007)
10. R. Ramesh and N. A. Spaldin, Nature Mat. **6**, 21, (2007)
11. C. H. Ahn, K. M. Rabe, J.-M. Triscone: Science **303**, 488 (2004).
12. Ronald, E. Cohen, Nature **358**, 136-138 (1992).
13. M. Atanasov, D. Reinen,J. Phys. Chem. A **105**, 450–5467 (2001).
14. N.A.Hill, Annu. Rev. Mater. Res...**3**2:1-37 (2002).
15. W. Eerenstein, N. D. Mathur & J. F. Scott, Nature **442**, 17 (2006).
16. Brown, W. F. Jr, Hornreich, R. M. & Shtrikman, S. Phys. Rev. **168**, 574-577 (1968).
17. G.T. Rado et al., Phy. Rev. Lett 13335 (1964).
18. H. Zheng et al., Science **303**, 661–663 210(2004)
19. Kimura T., et al, Nature **426**, 55-58 (2003)
20. M. Julliere, Phys. Lett. **54A**: 225–226, (1975)
21. "TMR"www.wikipedia.org , (2008)
22. L. Esaki, R. B. Laibowitz, and P. J. Stiles, IBM Tech. Discl. Bull.**13**, 2161,(1971)
23. L. Pintiliea, M. Alexe,Journ., Appl. Phys. **98**, 124103, (2005)
24. M.Ye. Zhuravlev et al. Physical Review Letters, **94**, 246802 (2005)
25. S. M. Sze, Physics of Semiconductor Devices 2nd ed., John Wiley and Sons, (1981).
26. Dawber, Rabe and Scott, Rev. Mod. Phys., **77**, No. 4, (2005)
27. J. Robertson and C. W. Chen, App Phys Lett **74** 1168 (1999)
28. J. F. Scott, Ferroelectric Memories, Advanced Microelectronics-3, Berlin Heidelberg Springer, (2000)
29. J.F. Scott, J. Phys. Condens. Matter **18** (2006) R361–R386, (2006)
30. V. Garcia, et al. Unpublished, Cambridge university & Unite Mixte de Physique CNRS/Thales, Palaiseau, France, (2008)
31. Rodriguez et al., Appl. Phys. Lett. 8, 4595 (2003)
32. H. Kohlstedt et al.,Physical Review Letters B, **72**, 125341 (2005)
33. J. P. Velev et al., Phy. Rev. Lett. **98**, 137201 (2007)
34. C. L. Jia et al., Journal of Cryst. Growth **247**, 381 (2003)
35. G. Gerra et al., Phys. Rev. Lett. **96**, 107603 (2006)
36. S. Sahoo et al., Phy. Rev. Lett. B **76**, 092108 (2007)
37. H. Beá et al, J. Phys.: Condens. Matter **20** , 43422 (2008) 1