CHAPTER 1

INTRODUCTION TO GIANT MAGNETO RESISTANCE (GMR) MATERIALS

1.1 Introduction

Functional Nano-ceramics / nanomaterials of Perovskite manganites have attracted attention owing to their applications in devices for magnetic information storage and retrieval. More studies have been carried out in the last ten years on rare earth manganites with Perovskite structure, driven by the discovery of Giant Magneto Resistance or Colossal Magneto Resistance (GMR or CMR) in these compounds. Many researchers are used of magnetic multilayer with Giant Magneto Resistance as magnetic reading heads has also been reported [1, 2]. These materials exhibit a very huge magneto resistance in a temperature range that lies in closely with the ferromagnetic Curie temperature of the manganites. Despite, co-doped rare earth manganese oxides are also popular due to their potential applications as electrode materials in solid oxide fuel cells [3]. $La_{1-x}Sr_xMnO_3$ is currently used as an electrode material in solid oxide fuel cells (SOFCs) because of its high electronic/oxide conductivity, good chemical stability and compatibility with other cell components even at high temperatures of 1000℃ [4]. Use of nanostructure materials as electrodes for fuel cell cathodes is expected to promote catalytic reactions on the surface as they provide larger specific surface area. Stoichiometric $LaMnO_3$ is an antiferromagnetic insulator; however it is always nonstoichiometric when prepared in air [5]. The presence of Mn^{4+}-O-Mn^{3+} pairs in the Perovskites structure allows double exchange, leading to ferromagnetism, metal-insulator transitions (MIT), and magneto resistance in nominal $LaMnO_3$ [6]. With cationic substitutions like Ca^{2+} or Sr^{2+} on the lanthanum site, it shows paramagnetic-ferromagnetic transition coupled to high magneto resistance ratios [7, 8].

Several methods have been explored for the synthesis of nanoceramics/nano-materials. These processes involve a few physical (like vapor deposition and evaporation-condensation etc.) and chemical methods like (hydrothermal, solvothermal and sonochemical etc.) [9-12]. The development of new functional nano-ceramics/nano-materials for technological applications has opened many doors to innovation in the twenty first century. New electronic and magnetic materials in particular have been helped bring about the information revolution. Technological applications often have strict compositional and micro structural requirements for their materials.

An integrated circuit (IC) for example must have numerous compatible semiconductor, dielectric, and metallic materials with specific properties in precise locations. Improvements using well materials usually increasingly, but potentially much revolutionary method for advancing technologies is to find different materials which have inherent properties superior to those currently in use. There are several known materials which need to be better understood before it would be clear that their use would be important advancement. In some cases unknown class of compounds may have to be discovered for instance (the cuprate superconductors). It is significant to consider other aspects of the nanomaterials, for example availability, thermal stability and toxicity.

The study of new nanomaterials physics can have different emphasis. Many physicists are interested in new materials because they can be used to study a new physical phenomenon. An example of this is the study of heavy fermions metals and superconductors which have little potential application in themselves, but the physics learned from their study may be entirely meaning full. Conversely, one can use physics to help understand new materials for potential applications. The physics may be well established but will give valuable insight into the uses and limitations of the materials. The emphasis of this dissertation is on the latter: what physics can reveal about a magnetic materials science and manganites Perovskites which have at the boundary of technological advancement science for several applications such as memories, data storage, processing and probing. These magnetic materials divided to several groups, depending on their origin and applications. Like the transition metal oxides (TMO) having Perovskites (ABO_3) structures which form an important class of materials from the point of view of fundamental physics as well as technological applications [13]. They have been attracting attention because of their exotic properties such as ferroelectricty of titanates (codoped $BaTiO_3$) [14], high temperature superconductivity of cuprates ($La_{2-x}Ba_xCuO_4$, $HgBa_2Ca_2Cu_3O_{8-\delta}$) [15], Giant Magneto Resistance of manganites (codoped $LaMnO_3$) [16] and unconventional p-type superconductivity of ruthenates (Sr_2RuO_4) [17].

TMO based magneto electronics is fast emerging as future technology, during the last decade. Before the magnetic materials e.g. Fe_2O_3, CrO_2, were used in motors and generators, as permanent magnets followed finally by applications like magnetic media for data storage, read heads, magnetic field sensors etc. The field of magnetism still running to attractive attention for scientist and industrial community [18].

Efforts are focused on the aim of achieving higher areal density for magnetic recording, which is possible to increase the linear as well as track densities. Improvement in the linear density requires advancement in the recording techniques in materials, and in miniaturization of the components. Track densities can be increased by improving the material or magnetic media characteristics. The nanomaterial or media developments overlap a broad range of processes and materials. Recently improvement of deposited metal film media makes it possible to achieve still higher magnetization value having high linear as well as track densities. So that increased attention is paved the way for metal thin films with higher coercivity are required for higher density media. The most challenging issue towards achieving high recording density media is to produce magnetic thin films which have a huge signal- to- noise ratio despite, the smaller size of the bit or data being detected. The flexibility of thin films technology makes it possible to tailor the magnetic properties to meet specific design requirements [19, 20].

Magnetism is still a very competitive technology not only for recording but also for other novel application. Recently, an approach to electronics is emerging that is based on the up or down spin of the charge carriers rather than on electrons or holes as in traditional semiconductor electronics. Devices that depend on electron's spin to perform their functions from the foundation of spintronics or magneto electronics [21-24].

These spintronics devices are being developed for applications such as ultrasensitive magnetic sensors and magneto resistive random access memory (MRAM). The key factor for the growth of magnetism based technology is the increase in the real density. The real density of the state of the art production was 700 Mbit in^{-2} in 1995. In the research to lower the cost and improve the performance, the real density has increased more than 20 million fold in modern disk drives and currently doubles every year (Fig.1.3). Nonetheless, the pursuit of higher a real densities still continues, as is evident in recent laboratory experiments of recording densities beyond 1000G bit in^{-2} [25, 26] and the next big challenge now looming ahead is to achieve 2T bit in^{-2} recording density [27].

The main limitations on the size of the smallest bit rely on the design of read-write head and the intrinsic signal-to-noise ratio of the material. Herein come the next generation devices based on Giant and Colossal Magneto Resistance materials.

Very sensitive magneto resistance materials called Giant Magneto Resistance (GMR) materials and more recently the colossal magneto resistance materials have been rediscovered in the past few years, due to the intense, new materials research. These materials exhibit a resistance change when subjected to a magnetic field and may eventually develop into magneto resistive (MR) heads to achieve the required a real densities. Commercialization of the GMR and CMR effects will require materials which have both high magnetization and low activation fields of the order of few tens of gauss or smaller. Thus, research on magnetic materials and understanding its magnetic properties has the potential to make of significant contribution to information technology.

In this work, our principal motivation is to study influence of co-dopants on transport including magneto resistance in nanostructured samples of the Perovskites based rare earth manganites. These oxides have attracted wide attention as Colossal Magneto-resistance (CMR) in the last decade. Synthesis routes play a major role in improving/ enhancing the physicochemical properties of most of the materials. The characteristics of nano-sized powders are influenced by shape, size, size distribution and nature of the constituting particles, which in turn depend on the nature of synthesis. The processes such as co-precipitation, sol-gel etc. Are not suitable to product directly as they involve a number of tedious and time consuming intermediate steps e.g. repeated grindings and calcinations in solid state process; washing, drying and calcinations of the precursors in co-precipitation and Pechiney processes etc. Hence, exploring a novel direct conversion process, which can produce ultrafine powders of oxide ceramics in a simple and economic way with improved powder characteristics, is of utmost importance. The solution combustion technique is one of such processes. In general, the powder obtained by this process has the high degree of phase purity with improved powder characteristics such as narrow distribution of nano-particles, higher surface area and better sinter-ability.

In this work we have investigated a simple and novel method of synthesizing nanocrystalline strontium substituted lanthanum manganites by solution combustion method using a fuel and oxidizers. It is an important powder processing technique generally used to prepare oxide ceramics. During this work, we have developed the necessary facilities for the measurement of resistivity at low temperature both in low and high magnetic fields.

1.2 Magneto Resistance (%MR) phenomenon

The phenomenon of Magneto Resistance (MR) is a change in the resistance of a material when a magnetic field is applied. The application of a large magnetic field, on the order of 5 Tesla, or cooling the sample to below its Curie temperature T_C results in the macroscopic ordering of a cluster's ferromagnetic moment. This is accompanied by a large decrease in the sample resistance.

The simplest example of magneto resistance (MR) is transverse magneto resistance associated with the Hall Effect as shown in fig.1.1.

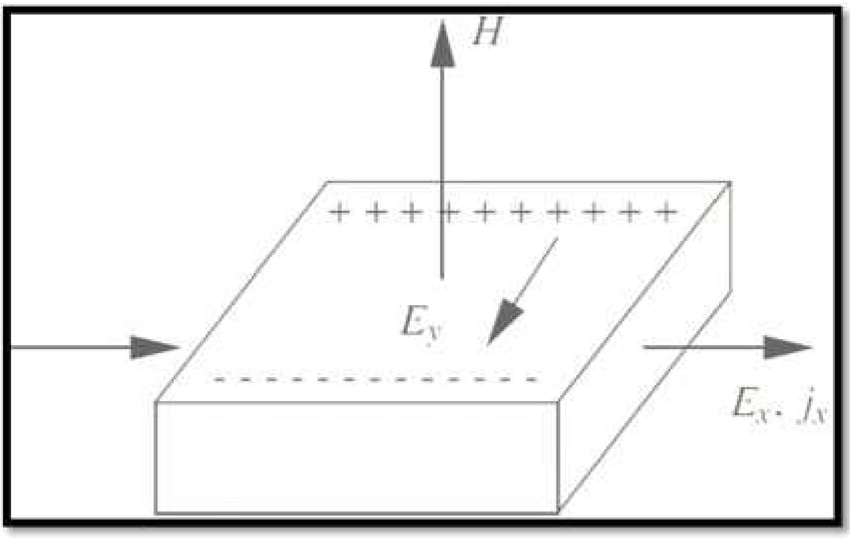


Fig.1.1 Magneto resistance (MR) associated with Hall Effect

When an electrical conductor is subject to an electric field E_x along x and simultaneously, a magnetic field H along z, a new transverse field arises due to the Lorentz force of H on the electrons moving along x. This field E_y acts along y (because the Lorentz force is a cross product) giving rise to the Hall voltage. There is a magneto resistance associated with the transverse field. Such magneto resistance measurements allow the number of free carriers to be obtained experimentally, as well as allow mapping of the Fermi surface etc. An illustration of the ferromagnetic ordering process that gives the codoped manganite system high magneto resistance [28].

The MR effect is characterized not only by its large numerical MR ratio, but also by its negative value and isotropic (independent of field orientation) nature [29].The MR ratio is defined as:

$$MR = \frac{\Delta R}{R_H} = \frac{R_H - R_0}{R_H}$$

Where R_0 the resistance at zero magnetic field and R_H is R with applied magnetic field H**.** This typically corresponds to more than a thousand-fold change in resistivity [30]. The MR ratio also can be expressed in terms of the fractional change to the zero field resistance as given by Von Helmolt et al., [1].

$$MR = \frac{\Delta R}{R_0} = \frac{R_0 - R_H}{R_0}$$

Lord Kelvin was first observed the Magneto Resistance effect (MR) [31] 158 years ago; to be more precise, the phenomenon Lord Kelvin detected was Anisotropic Magneto Resistance (AMR) as discussed in section (1.2.1.2) later. However, MR effect was completely ignored until 1950s. Since 1950s many research efforts have been placed on Colossal Magneto Resistance (CMR) which discussed in section (1.2.1.3) [32, 33]. However, the large magnetic field required to perform the resistance change severely limited its applications.

MR once again attracted intensive investigations because the discovery of Giant Magneto Resistance (GMR) [34, 35] effect in 1988. Before 10 years GMR was used in read heads of magnetic hard disks as shown in fig.1.2. On the other hand Tunnel Magneto Resistance (TMR) (as mentioned in section 1.2.1.4) based devices are gradually replacing their GMR counterparts in different kinds. TMR devices generally exhibit larger changes in resistances compared with similar devices based on the GMR effect; its main drawback is the need of depositing very thin insulating layers. GMR or TMR heads are still the mainstream technologies in the production of digital storage devices and such technologies have grown largely recently [36] as shown in fig.1.3**.**

Fig.1.2 A hard disk with GMR read head [35]

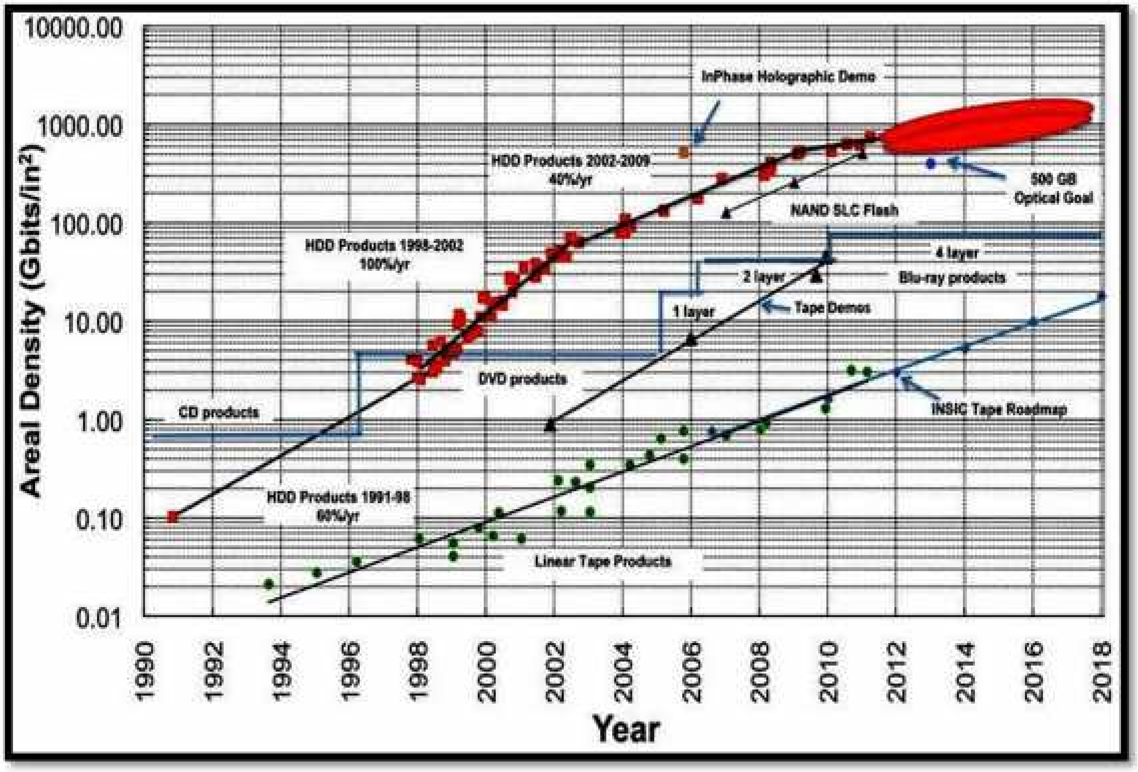


Fig.1.3 Growth of a real density of hard disk drives over years [36]

1.2.1 Family of Magneto Resistance (MR)

Magneto Resistance (MR), where the resistance of the material changes with applied magnetic field, occurs in metals. Classically, the MR effect depends on both the strength of the magnetic field and the relative direction of the magnetic field with respect to the current. Five distinct types of magneto resistance will be reviewed here: ordinary magneto resistance (OMR), anisotropic magneto resistance (AMR), giant magneto resistance (GMR), colossal magneto resistance (CMR) and Tunnel Magneto Resistance (TMR). The materials and mechanism for these five types of magneto resistance are distinctly different [37].

1.2.1.1 Ordinary Magneto Resistance (OMR)

Magneto Resistance (MR) is the property of a material to change the value of its electrical resistance when external magnetic field is applied to it. William Thomson (or Lord Kelvin as shown in fig.1.4) first discovered ordinary magneto resistance in 1856, but he was unable to lower the electrical resistance of anything by more than 5%. This effect was later called Ordinary Magneto Resistance (OMR).

William Thomson experimented with pieces of iron and discovered that the resistance increases when the current is in the same direction as the magnetic force and decreases when the current is 90^0 to the magnetic force. He also did the same experiment with the nickel and found that it was affected in the same way but the magnitude of the effect was greater. This effect is referred to as anisotropic magneto resistance (AMR).For ordinary non-magnetic metals, such as Au, the MR are quite small. Both $\Delta\rho_p$ and $\Delta\rho_{ap}$ are positive with $\Delta\rho_{ap}>\Delta\rho_p$, and increase approximately as H_2 without saturation [38, 39].

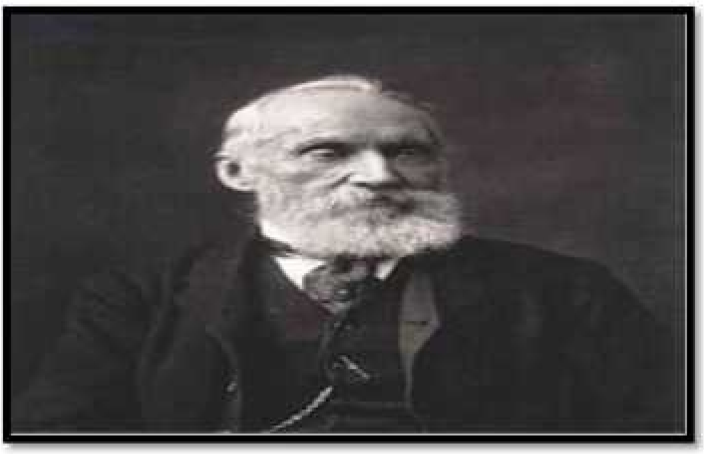


Fig.1.4 William Thomson (Lord Kelvin)

1.2.1.2 Anisotropic Magneto Resistance (AMR)

AMR measures the change in resistance when the current flowing through a magnetic sample changes from being parallel to the internal magnetization to being perpendicular to the sample [40] as shown in (fig. 1.5). The British physicist Lord Kelvin had already reported "That iron, when subjected to a magnetic force, acquires an increase in resistance to the conduction of electricity along, and a diminution of resistance to the conduction of electricity across, the lines of magnetization" [41]. This effect was known as Anisotropic Magneto Resistance (AMR) which appears in ferromagnetic materials, and is the dependency of the resistivity on the relative orientation of the magnetization and the current originated from the spin-orbit interaction. In a thin film where magnetization M makes an angle θ with current I in a film plane as shown in fig.1.6 the resistivity $\rho(\theta)$ is given by:

$$\rho(\theta) = \rho_0 + \Delta\rho\cos^2\theta \qquad (1)$$

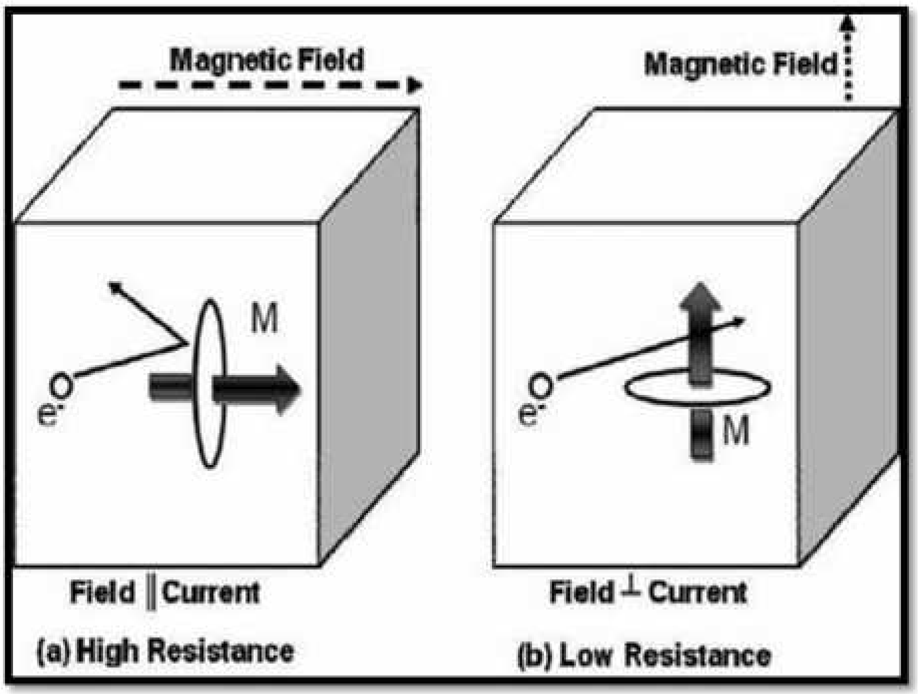


Fig.1.5 (a &b) Physical origins of AMR

When we denote ρ_p and ρ_{ap} as the resistivity for magnetization Parallel and Perpendicular to the current, respectively, Eq. (1) can be written as [42]

$$\rho(\theta) = \rho_{ap}\sin^2\theta + \rho_p\cos^2\theta \qquad (2)$$

Where the anisotropic magneto resistivity is defined as

$$\Delta\rho = \rho_p - \rho_{ap} \qquad (3)$$

AMR can be used to detect changes in magnetization, and it was the basis of hard drive read sensors before the discovery of GMR [43]. However, the magnitude of the AMR effect is usually small, with a resistance change on the order of a few percent. This limits its sensitivity to weak magnetic fields. A review about AMR, containing both theoretical and experimental results has been written by McGuire and Potter [44].

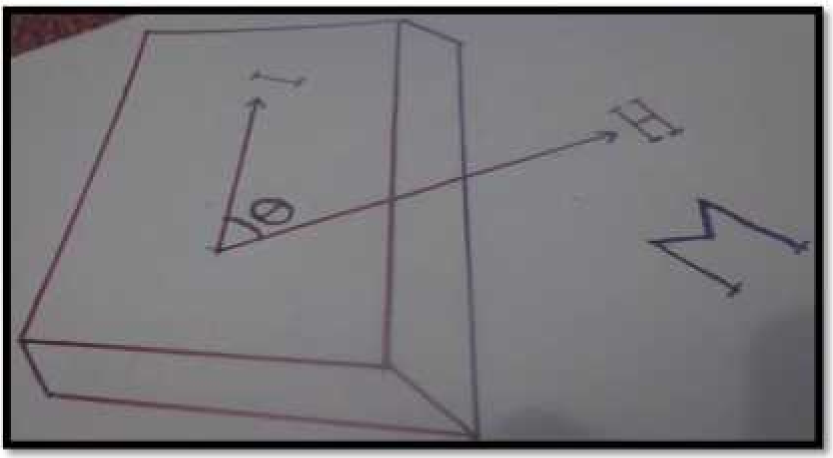
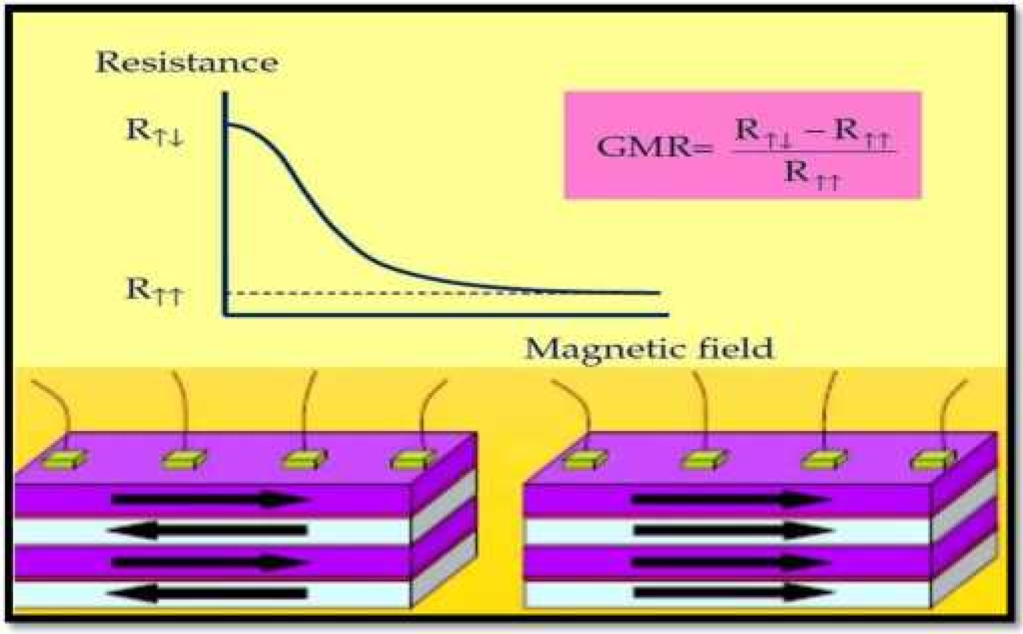


Fig.1.6 Relation between current and magnetic field directions

1.3 Giant Magneto Resistance (GMR)

Since the discovery of giant magneto resistance (GMR) in the late 1980s [45] there has been a lot of work devoted to this phenomenon owing to its immediate technological applications. The GMR was first observed in metallic multilayers composed of ferromagnetic (FM) metals and nonmagnetic metals acting as spacer layers. The GMR effect consists in an important change of the resistivity of the multi-layers depending on whether the FM layers have their magnetizations aligned parallel or antiparallel to each other as shown in fig.1.7. The magnitude of the GMR depends on many factors, being among the most relevant: the thickness of the spacer layer, the spin polarization of the electrons in the FM material, and the spin-dependent scattering at the interfaces. When measuring the GMR with the current in the plane of the samples [current-in-plane (CIP) configuration], the characteristic length of the problem is the mean free path L of the electrons [46]. The GMR was very important not only from the basic research point of view but also from the applied research point of view. In 1997 IBM introduced in the hard-disk technology magneto resistive read heads based on the GMR effect, which has allowed the increase in the density of the stored information in hard disks at a rate much beyond previous technologies [47].



High resistance　　　　　　Low resistance

Fig.1.7 GMR effect

1.3.1 The Discovery of (GMR)

The phenomenon called Giant Magneto Resistance (GMR) is a quantum mechanical magneto resistance effect observed in thin film structures composed of alternating ferromagnetic and nonmagnetic layers. The effect is observed as a significant change in the electrical resistance when apply external magnetic field. In 1988 a more dramatic MR effect, which is called giant magneto resistance (GMR) effect, was discovered [48]. It was a great surprise when two research groups independently discovered materials showing a very huge magneto resistance, which known as Giant Magneto resistance (GMR). These materials are so called magnetic multilayers, where layers of ferromagnetic and non- ferromagnetic metals are stacked on each other as shown in figs. (1.8 & 1.9). The widths of the individual layers are of nanometer size i.e. only a few atomic layers thick. In the original experiments leading to the discovery of GMR one group, led by Peter Grunberg [49] used a trilayer system Fe/Cr/Fe as shown in (fig.1.8), while the other group, led by Albert Fert [50] used multilayers of the from $(Fe/Cr)_{\mathbf{n}}$ where n could be as high as 60 as shown in (fig.1.9). Fert’s and Peter Grunberg’s groups prepared by the Molecular Beam Epitaxy (MBE) method to grow their samples which were the only method available at the time to grow the materials with the required thickness 1nm. Later on sputtering would be used in commercial applications. Both Fert and Grunberg would receive the 2007

Noble prize for their independent discoveries of Giant Magneto Resistance [51] as shown in fig.1.11.

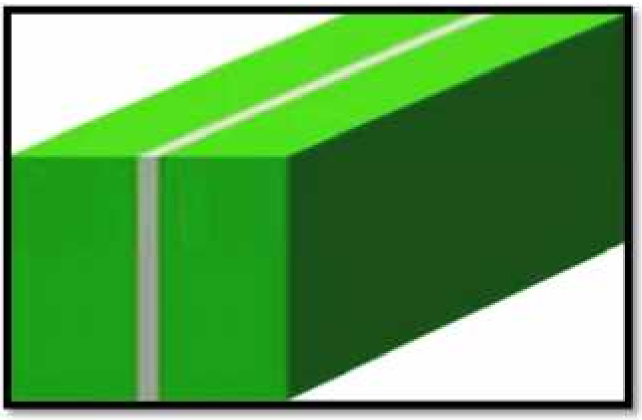


Fig.1.8 Fe/Cr/Fe trilayer, P. Grunberg

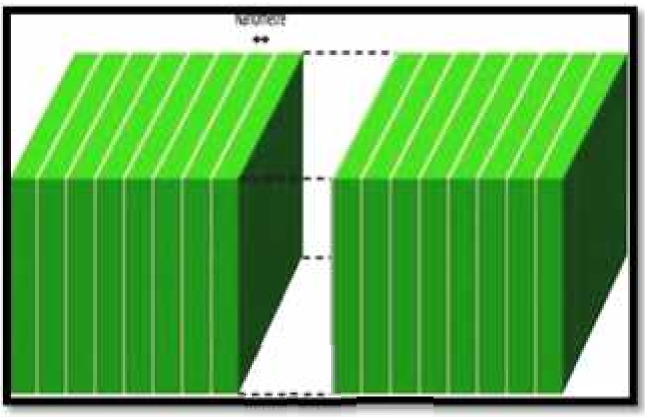


Fig.1.9 $(Fe/Cr)_{n=60}$ ***A. Fert***

Figs. (1.8 & 1.9) Schematic of magnetic multilayers. Nanometer thick layers of iron (green) are separated by nanometer thick spacer layers of a second metal (for instance chromium or copper). The top figure shows the trilayer Fe/Cr/Fe used by Grunberg's group and the bottom the multilayer $(Fe/Cr)_n$ with n as high as 60, used by Fert's group.

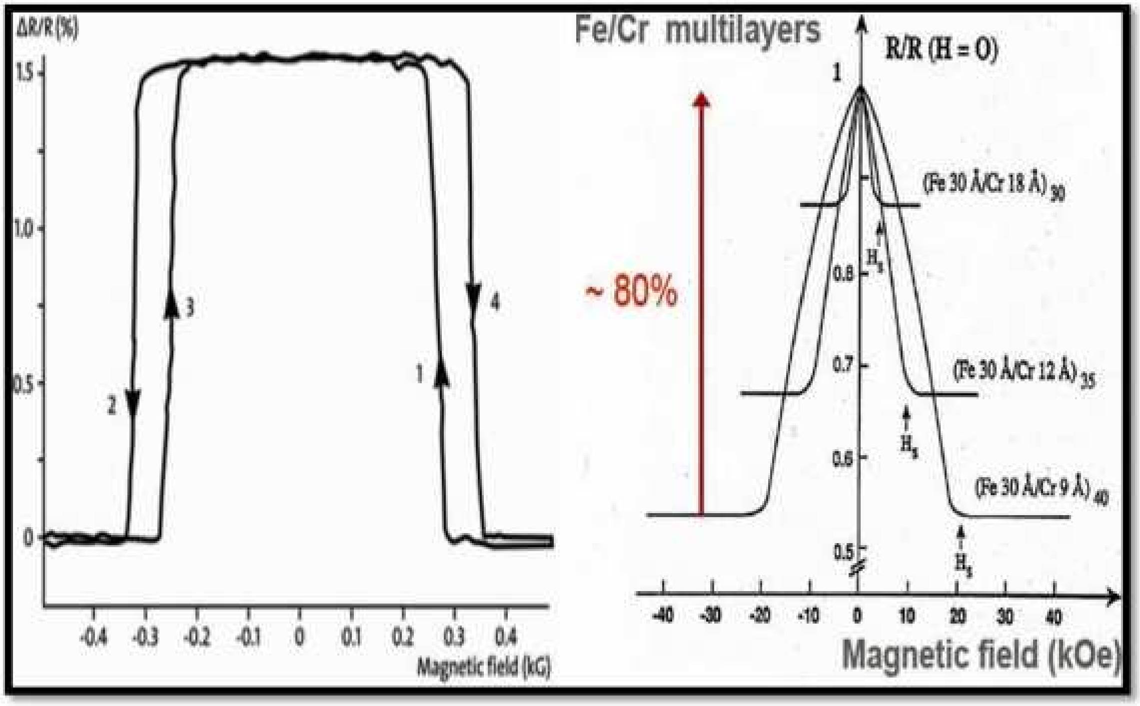


Fig.1.10 Magneto Resistance measurements

To the far right as well as to the far left in fig.1.10 the magnetizations of the two iron layers are both parallel to the external magnetic field. In the intermediate region the magnetizations of the two iron layers are antiparallel. The experiments also show a hysteresis behavior (different 1 and 4 (2 and 3)) typical for magnetization measurements. Right: Magneto Resistance measurements (4.2K) for the multilayer system $(Fe/Cr)_n$. To the far right ($>H_S$, where H_S is the saturation field) as well as to the far left ($<-H_S$) the magnetizations of all iron layers are parallel to the external magnetic field. In the low field region every second iron layer is magnetized antiparallel to the external magnetic field. 10KG=1Tesla [52].

In fig. (1.10) above the measurements of Grunberg's group are displayed (left) together with those of Fert's group (right). The y-axis and x-axis represent the resista-nce change and external magnetic field, respectively. The experiments show a most significant negative magneto resistance for the trilayer as well as the multilayers. The systems to the right, involving huge stacks of layers, show a decrease of resistance by almost 50% when subjected to a magnetic field.

The effect is much smaller for the system to the left, not only because the system is merely a trilayer but also because the experiments led by Grunberg were made at room temperature, while the experiments reported by Fert and co-workers were performed at very low temperature (4.2K).

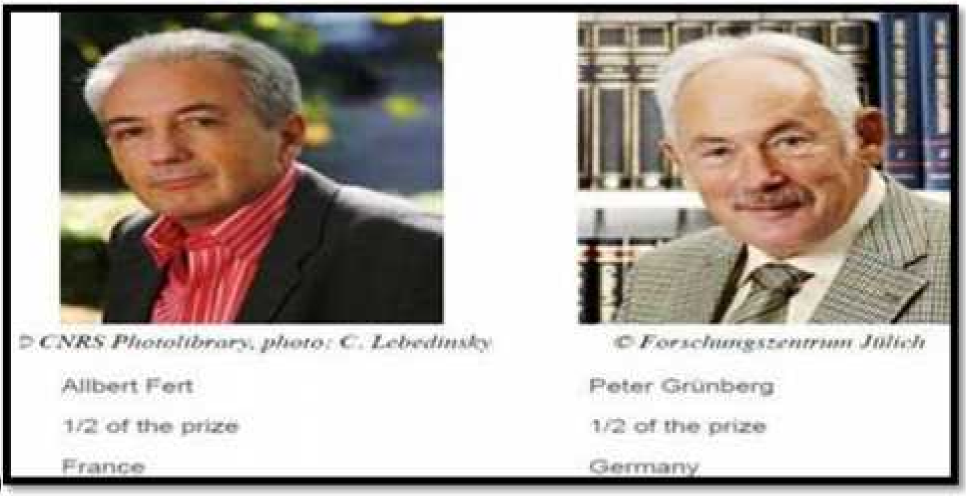
Grunberg also reported low temperature magneto resistance measurements for a system with three iron layers separated by two chromium layers and found a resistance decrease of 10%.

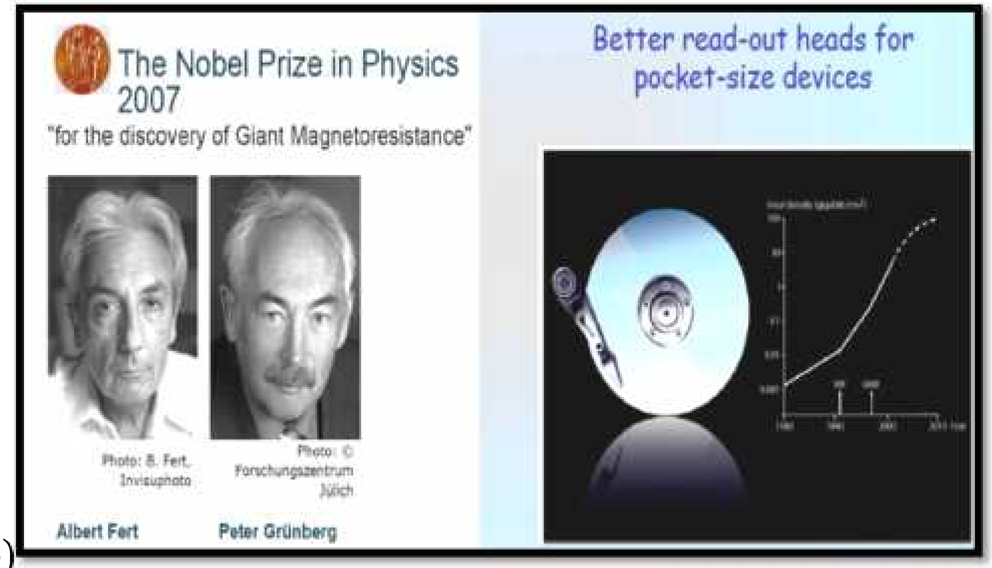
Not only did Fert and Grunberg measure strongly also identified these observations as a new phenomenon, where the origin of the magneto resistance was of a totally new type. The title of the original paper from Fert’s group already referred to the observed effect as Giant Magneto Resistance. Grunberg also realized at once the new possibilities for technical applications and patented the discovery. From this very moment the area of thin film magnetism research completely changed direction into magneto electronics.

The discovery of huge magneto resistance immediately opened the door to a wealth of new scientific and technological possibilities, including a tremendous influence on the technique of data storage and magnetic sensors. Thousands of scientists all around the world are today working on magneto electronic phenomena and their exploration. The story of GMR effect is a very good demonstration of how a totally unexpected scientific discovery can give rise to completely new technologies and commercial products [53]. GMR can be considered to be the first paradigm of the so called spintronics or spin electronics (discussed in section 1.3) where in sharp contrast with semiconductor technology, the spin as well as the change transports is taken into account. This field could be developed thanks to the fine nanometric control of thin films in the growth direction. Mathematically, GMR can be defined as:

$$\mathrm{GMR} = \frac{R_{ap} - R_p}{R_p}$$

Where R_p and R_{ap} are the resistances in parallel and antiparallel states as shown in fig. 1.7(a &b). The Nobel Prize in Physics 2007 awarded to Albert Fert and Peter Grunberg bisection for discovering GMR as shown in fig.1.11 (a &b).

(a) 

(b) 

Figs.1.11 (a & b) The Nobel Prize in Physics 2007

1.3.2 Mechanism of (GMR)

Giant Magneto Resistance (GMR) refers to the change in resistance of a magnetic material as its magnetic state changes, owing to the spin-dependent scattering of spin-polarized current flowing through the material. GMR can be qualitatively understood using the Mott model, which was introduced as early as 1936 to explain the sudden increase in resistivity of ferromagnetic metals as they are heated above the Curie temperature [54]. There are two points proposed by Mott. First, the electrical conductivity in metals can be described in terms of two largely independent conducting channels, corresponding to the up-spin and down-spin electrons, which are distinguished according to the projection of their spins along the quantization axis.

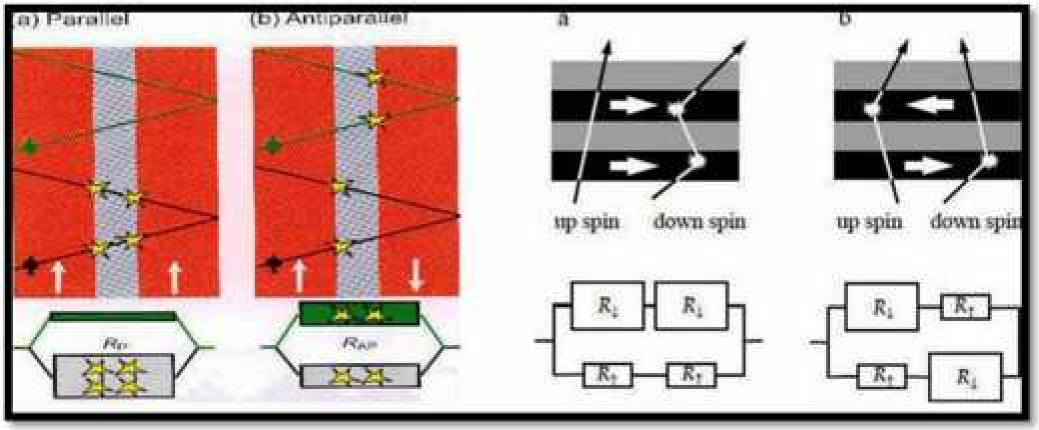
The probability of spin-flip scattering processes in metals is normally small as compared to the probability of the scattering processes in which the spin is conserved. This means that the up-spin and down-spin electrons do not mix over long distance and, therefore, the electrical conduction occurs in parallel for the two spin channels.

Second, in ferromagnetic metals the scattering rates of the up-spin and down-spin electrons are quite different, whatever the nature of the scattering centers is. According to Mott, the electric current is primarily carried by electrons from the valence sp bands due to their low effective mass and high mobility. The d bands play an important role in providing final states for the scattering of the sp electrons. In ferromagnetism the d bands are exchange-split, so that the density of states is not the same for the up-spin and down-spin electrons at the Fermi energy. The probability of scattering into these states is proportional to their density, so that the scattering rates are spin-dependent, i.e. are different for the two conduction channels. Although, as mentioned below, this picture is too simplified in a view of the strong hybridization between the sp and d states, it forms a useful basis for a qualitative understanding of the spin-dependent conduction in transition metals.

Using Mott's argument it is straightforward to explain GMR in magnetic multilayers. We consider collinear magnetic configurations, as shown in fig.1.12 (a & b) and assume that the scattering is strong for electrons with spin antiparallel to the magnetization direction and is weak for electrons with spin parallel to the magnetization direction. This is supposed to reflect the asymmetry in the density of states at the Fermi level, in according with Mott's second argument. For the parallel aligned magnetic layers (the top panel in Fig.1.12 (a) the up spin electrons pass through the structure almost without scattering, because their spin is parallel to the magnetization of the layers. On the contrary, the down-spin electrons are scattered strongly within both ferromagnetic layers, because their spin is antiparallel to the magnetization of the layers. Science conduction occurs in parallel for the two spin channels; the total resistivity of the multilayer is determined mainly by the highly conductive up-spin electrons and appears to be low). For the antiparallel aligned multilayer (the top panel in Fig.1.12 (b), both the up-spin and down-spin electrons are scattered strongly within one of the ferromagnetic layers, because within the one of the layers the spin is antiparallel to the magnetization direction. Therefore, in this case the total resistivity of the multilayer is high [55].

The same argument can be used for understanding GMR in granular materials. In the absence of a magnetic field, the magnetic moments of the ferromagnetic granular are randomly oriented. This implies that both up-spin and down spin electrons are scattered strongly by the granules. The magnetic moments of which are close to antiparallel. The resistance in this case is large. When a saturating magnetic field is applied, the magnetic moments are aligned and the resistance is low, like in the case of the parallel aligned multilayer.

Therefore, as was originally suggested by Baibich et al., [56] spin dependent scattering is the primary origin of GMR.The origins of GMR can be traced to the general interaction between currents and magnetism. It has been known since the 1800s that the resistance of ferromagnetic materials depends on the current flow direction, parallel or perpendicular to the magnetization direction [57].



Low Resistance   High resistance   Low resistance   High Resistance

Fig.1.12 Spin-dependent scattering parallel (a) and antiparallel (b) magnetization

Fig.1.12 Simplistic nanostructure of spin-dependent scattering for explanation of GMR effect and illustration of electron transport in a multilayer for parallel (a) and antiparallel (b) magnetization of the successive ferromagnetic layers.The magnetization directions is indicated by the arrows. The solid lines are individual electron trajectories within the two spin channels [58]. It is assumed that the mean free path is much longer than the layer thicknesses and the net electric current flows in the plane of the layers. Bottom panels show the resistor network within the two current series resistor model.

For the parallel aligned multilayer (a), the up-spin electrons pass through the structure almost without scattering, whereas the down-spin electrons are scattered strongly within both ferromagnetic layers. Science conduction occurs in parallel for the two spin channels, the total resistivity of the multilayer is low. For the antiparallel aligned multilayer (b), both the up-spin and down-spin electrons are scattered strongly within one of the ferromagnetic layers and the total resistivity of the multilayer is high.

1.3.3 GMR Materials and its Importance

Importance of GMR materials started since 1988 as a results obtained by many groups workers on Giant Magneto Resistance Ratio (GMR) materials show increases in magneto resistance (when apply external magnetic field) of about a factor of 10 over the Anisotropic Magneto Resistance Ratio (AMR) materials currently in use for magneto resistive memories, read heads for tape, disk drives and sensors etc [59]. In order for these benefits in magneto resistance to be utilized in practical applications, several additional parameters must be considered, such as drive field, impedance level, current capacity, hysteresis, biasing requirements, stability with temperature and environment, magneto-striction , temperature coefficient of resistivity, and manufacturability. These factors are compared for the principal types of GMR structures: sandwiches and multilayers (using vertical and in-plane conduction) and the most recently discovered granular films [60, 61]. A comparison is made between these structures and the incumbent upon sensing methods in present products which use AMR materials and the Hall Effect.

1.3.3.1 Impedance Level

For applications high impedance is required in order to raise the signal levels for a given current and to minimize the effects of lead resistance. This is a decided disadvantage for the vertical GMR orientation where superconducting leads have been used to make the lead resistance tolerable [62]. This orientation, theoretically can have higher GMR than the in-plane orientation, but the device must be a very thick one with many layers and very small with surface area to performance practical room temperature impedance level. On the other hand, the in-plane sheet resistivity of sandwiches is on the order of 10 to 30 Ohms per square, which is quite usable.

While multilayers have potentially higher GMR than sandwiches; they go back part their advantage by having somewhat lower sheet resistivity.

1.3.3.2 Drive Field

May be the most serious constraint regarding the use of GMR materials for most present applications are the required drive field. Multi-layers which have demonstrated the highest GMRs also have had very high anti-ferromagnetic coupling fields, typically in the several hundred to several thousand Oe range. The required sensitivity range for most common applications is on the order of 10 Oe to 50 Oe. Fortunately, the antiferromagnetic coupling field in sandwiches and multi-layers oscillates with thickness and low anti-ferromagnetic coupling have been demonstrated, although the implied thickness control limits perhaps prove difficult to hole in practice. In theory the coupling field for a simple magnetic sandwich is half of that for a multilayer if the thicknesses and moments of the magnetic films are equal and interfaces films are the identical.

Uncoupled magnetic sandwiches are relatively easy to fabricate. The drive field requirements for in-plane and vertical GMR modes of operation are the same [63].

1.3.3.3 Other Factors

All other factors of current capacity, hysteresis, biasing requirement, thermal and environmental stability, magneto-striction, temperature coefficient of resistivity, and manufacturability do not favor a particular GMR structure. Any of the approaches examined could be practical. Significance of Giant Magneto Resistance (GMR) as nature result for its applications industrials in our life for instances:

1.3.3.3.1 Low field sensor

- Magneto-resistance means
  Measuring current <=> measuring magnetic field
- But OMR gives slight shift only
- Sensitivity is restricted

1.3.3.3.2 MR sensors VS inductive sensors

- Magneto-resistance detects the strength of magnetic field

- Though no definite law, but the resistance variation with field strength can be worked out empirically (can calibrate)
- Induction measures the rate of change of the field.
- In other words, the mathematical model of MR sensor is a zero order system. While inductive sensors are of first order in which response depends on the time derivative of magnetic flux density (see section 1.3.5.1).

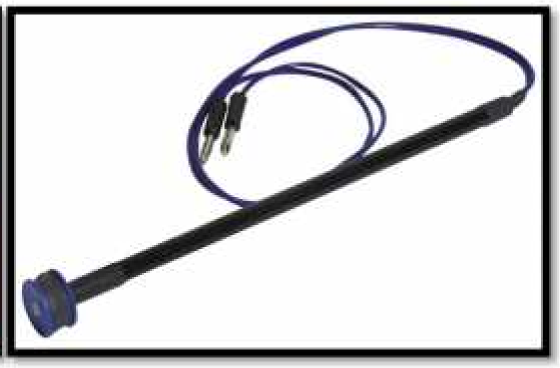


Fig. 1.13 Normal MR sensor ***Fig.1.14 Normal search coil***

1.3.3.3.3 Spin Valve

The magnetic orientation of one layer is pinned in one direction by adding a strong anti-ferromagnetic for details see section 1.3.4.2.

- The magnetic orientation of the unpinned magnetic layer rotates relative to that of the pinned layer under mild magnetic field.
- This flip requires extra energy which generates a significant change in electrical resistance due to the GMR effect.

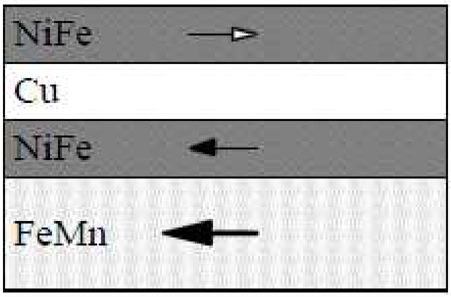


Fig.1.15 Spin Valve structure

1.3.3.3.4 Birth of Spintronics

- Also known as magneto-electronics

- Exploiting both the intrinsic spin of the electron and its associated magnetic moment (instead of charge alone) in solid state devices (see section 1.4).

For-instance

spin, either up or down can be used to encode data as the 0s and 1s of the binary system => MRAM (Magneto resistive random access memory) section 1.3.5.2.

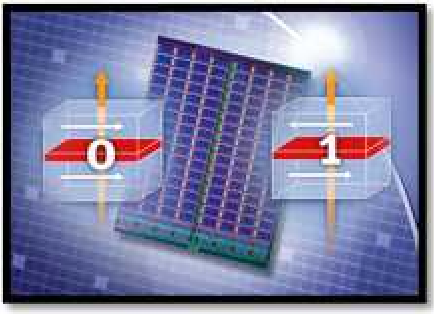


Fig. 1.16 MRAM computer chips

1.3.4 Classifications of GMR Material

1.3.4.1 Magnetic Multilayer

Multilayered structures consist of two or more magnetic layers of a Fe-Cr-Fe alloy, as can be perm alloy, separated by a very thin non-magnetic conductive layer, as can be [64]. In fact the thickness of the nonmagnetic layers can be tuned in such a way that the exchange coupling between magnetic layers through the non-magnetic layer makes adjacent magnetizations anti-parallel [65-67]. A general scheme is shown in figs. (1.17& 1.18). Multi-layered Fe-Cr structures have been developed by Mojika et al., [68] following the early works of Piraux et al., [69] a Blondel et al., [70].Successful applications of multilayered structures in magnetic field sensing include bioelectronics [71] and angle detectors [72].

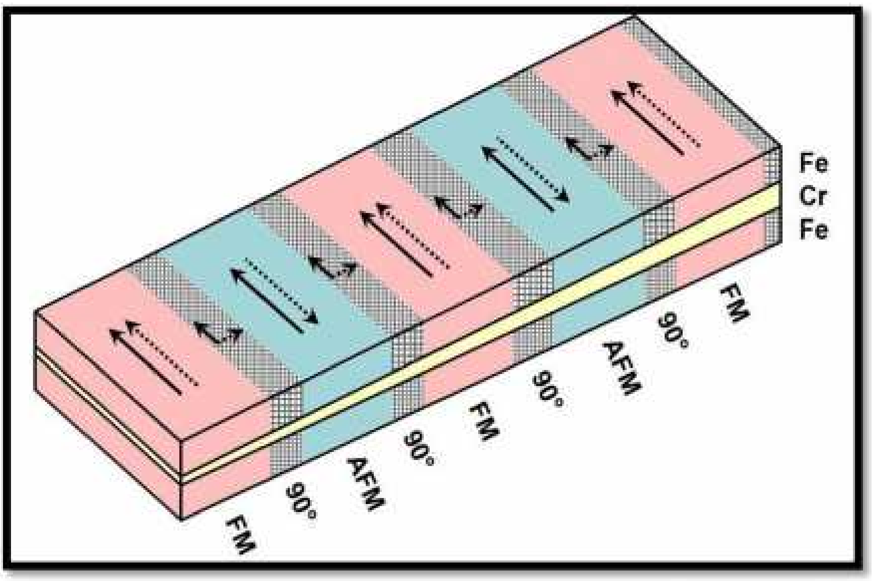


Fig.1.17 Structure of GMR Magnetic Multilayer

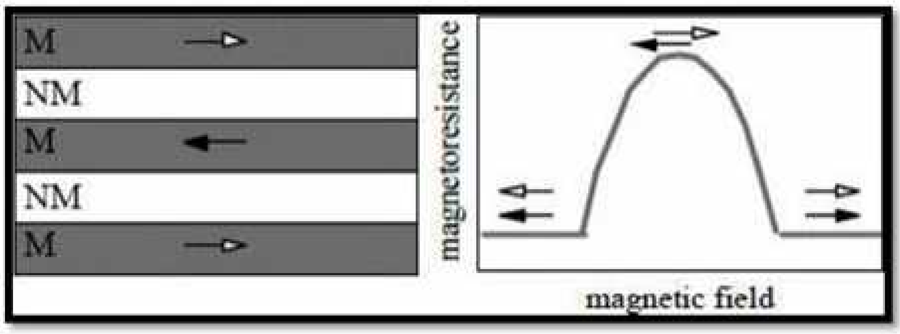


Fig.1.18 GMR nano-structures (left) and magneto resistance behavior (right)

1.3.4.2 Spin Valves GMR

The origin of spin valves are a particular case of multilayered structure [73]. The spin valves; an additional anti-ferromagnetic (pinning) layer is added to the top or bottom part of the structure, as shown in fig.1.19 (a & b). In this sort of structures, there is no need of an external excitation to get the anti-parallel alignment. In spite of this, the pinned direction (easy axis) is usually fixed by raising the temperature above the knee temperature (at which the anti-ferromagnetic coupling disappears) and then cooling it within affixing magnetic field. Obviously, so obtained devices have a temperature limitation below the knee temperature. Typically values displayed by spin valves are a MR of 4%-20% with saturation fields of 0.8-6kA/m [74].

Fig.1.19 GMR Spin Valve Nano-structures (left) and magneto resistance behavior (right)

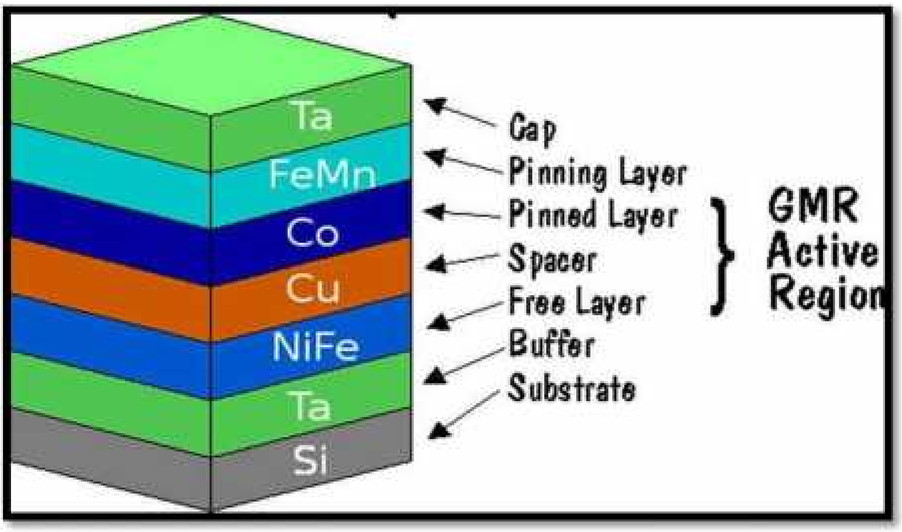


Fig.1.20 Structure of GMR Spin Valves

1.3.4.3 Pseudo Spin Valves

In the pseudo spin valve, the magnetic structure combines a hard and soft magnetic layer; the switching of ferromagnetic layers occurs at different magnetic fields providing a change in the relative orientation of magnetization. MRAM, Spin-Valve [75], tunneling [76, 77], and pseudo-valve [78, 79] nanostructures have all been proposed for high density non-volatile random access memory. The use of GMR materials to replace anisotropic magneto resistive (AMR) materials shows promise to ameliorate one of the most difficult problems which has faced MRAM technology, that of a small signal size, leading to relative long read access times for memory applications. Honeywell was the first to demonstrate an operating memory chip using materials [80] using sense line widths of approximately 2μm.

Submicron GMR memory cells required an improved mode of operation, and one of the more promising proposals is the pseudo spin-valve nanostructures and cell concept shown in fig.1.21 (a&b) where two magnetic films are separated by a thin conducting layer. These layers are etched into stripes sufficiently narrow to constrain the magnetizations in the stripes to lie along the long axis of the stripe. A conductor layer etched into a stripe line is place over the stripe to apply a magnetic field when a current is passed through it. One of the magnetic films switches at a lower magnetic field than the other. This is accomplished either by the two films having different thicknesses or composition. Data is stored in the magnetization layer requiring the larger magnetic field for reversal. The softer film can switch back and forth without the storage film switching. The magneto resistive property is used to read out data by observing whether the resistance increases or decreases when a magnetic field is swept from a negative to a positive value stored ‘1’ and a stored ‘0’ have opposite signs.

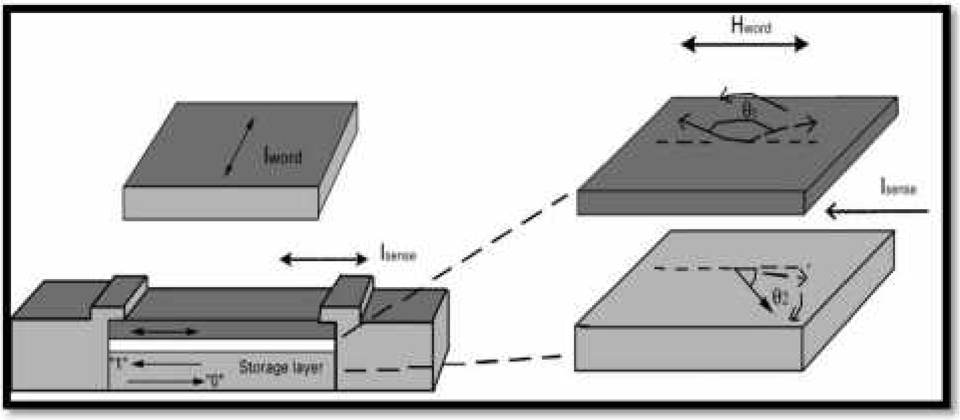


Fig.1.21(a) Pseudo-spin valve concept

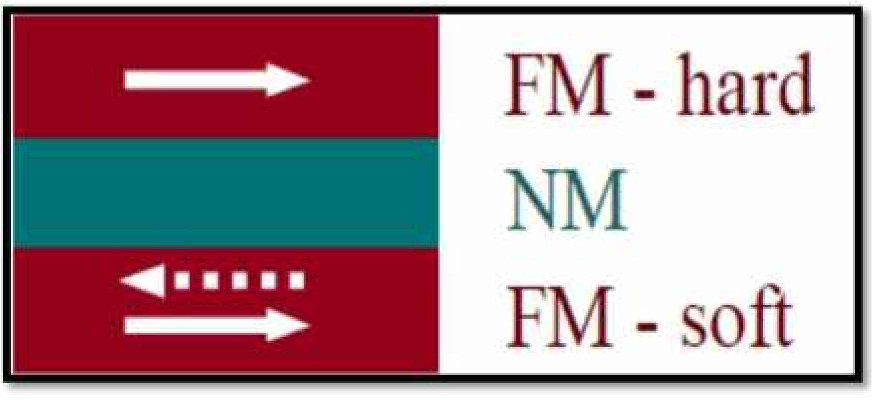


Fig.1.21 (b) Nano-structures of GMR Pseudo Spin Valves

1.3.4.4 Granular Solids

Granular films of Co-Cu and Co-Ag exhibit a Giant Magneto Resistance effect [81]. The giant magneto resistance effect is due to the spin- dependent scattering taking place at the boundaries of Co clusters embedded in the host lattice, as shown in fig.1.22. Because of these binary systems are not miscible, the characteristics of the devices are highly conditioned by the growth condition the post- deposition treatments [82]. In fact, the amount of magneto resistance is accepted to be associated to the size of the Co clusters [83] Vergara et al., obtained granular films of Ag-Co (10%) by pulsed laser ablated deposition [84] this deposition was demonstrated to be compatible with some subsequent micro fabrication processes (lithography, contact deposition and passivation) in order to obtain functional nano-ceramics sensors [85, 86].

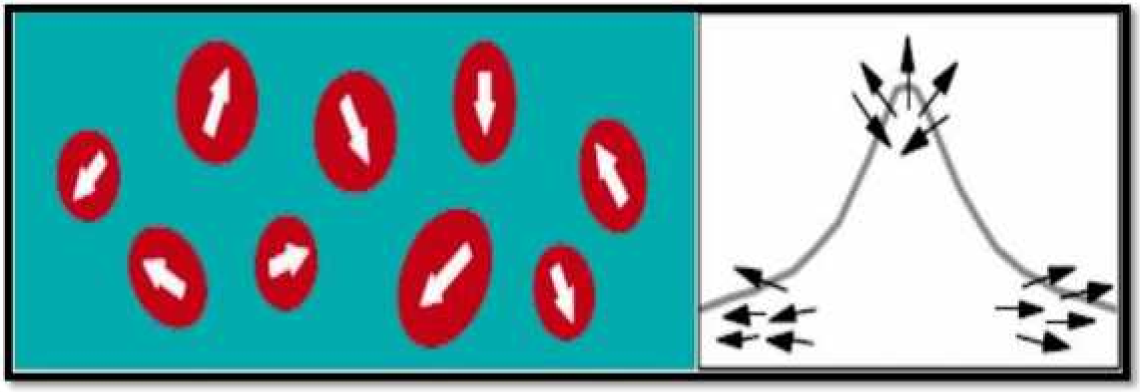


Fig.1.22 GMR nano-structures (left) and its magneto-resistance behavior (right) of Granular Solids

1.3.4.5 Magnetic Tunnel Junctions (MTJ)

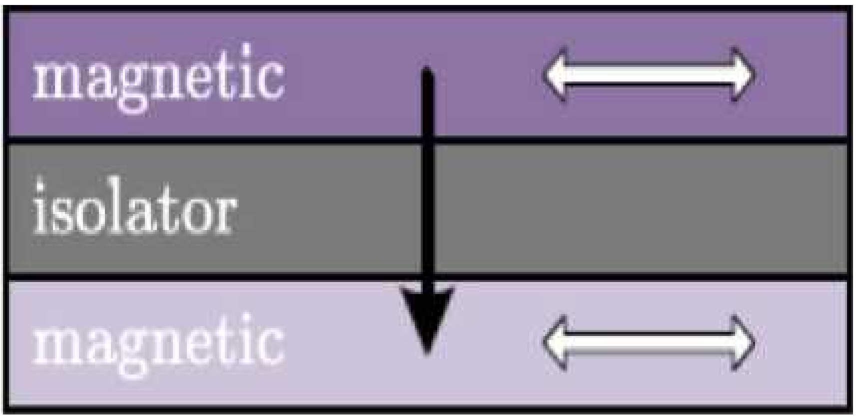


Fig.1.23 Nano-structures of GMR magnetic tunnel junction

The Magnetic layers are separated not by a conductive layer but a very thin isolating one, following a CPP configuration as shown in fig.1.23. Electronics can surpass this thin film by means of the quantum tunnel effect [87].

As deducted from quantum mechanics arguments, the crossing probability is higher when both magnetic moments are aligned in parallel and lower when both magnetic moments are not aligned in parallel. These devices usually make use of the Spin-valve principle in order to fix the easy axis by means of pinning anti-ferromagnetic layer. Typical MR levels of MTJ are above 40% with Al_2O_3 as isolating layer [88]. More recently, MR levels about 200% have been reported for MgO based structures [89]. Saturation fields are in the order of 1-100 Oe.The bases of magnetic tunnel junctions is analogous to that of spin valve. When configured in a crossed axis configuration, ranges suitable for sensors applications can be achieved [90] despite of; the usage of MTJ is still in its initial and is demanding additional research efforts.

1.3.4.6 Organic Magneto Resistance (OMAR)

Today, the new GMR materials based on organic material obtained after allowing for Organic Magneto-Resistance (OMAR) was found in OLEDs (organic light-emitting diodes). This organic material is used as a spacer layer in spin-valve. However, several factors such as spin scattering caused by large atoms of the spacer material and the interface scattering of ferromagnetic with a spacer, will limit the efficiency of spin-valve [91].The new GMR materials based on organic material in form of NiCoFe/Alq_3/NiCoFe. Recently Organic Magneto-Resistance (OMAR) is discovered, which magneto-resistance (MR) values up to 10% at fields of a few mT and room temperature have been reported in difference organic materials. Also effect of organic magneto-resistance was found in organic thin films sandwiched between two conductive electrodes and found that about 70% MR value in NiCoFe/Cu/NiCoFe sandwich [92-94] as shown in fig.1.24.

Currently, organic spintronics is a new and promising research field where applied to mediate or control a spin-polarized signal. The spin-valve consisting of an organic layer sandwiched between two ferromagnetic electrodes considered one of the most widely studied.

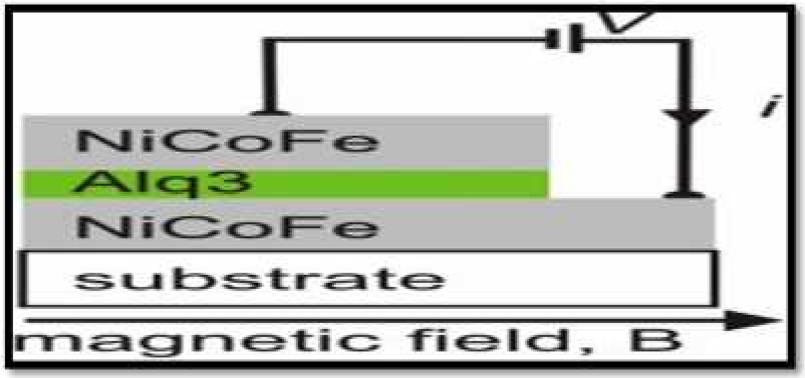


Fig.1.24 Schematic picture of an organic SV device and magneto resistance

The attributes of organic materials include

- Chemical tuning of electronic functionality
- Easy structural modifications
- Ability of self-assembly and mechanical flexibility

  These advantages are exploited for large-area and low-cost electronic applications. Organic spin-valves are particularly attractive for spintronics applications, because of its low cost and flexibility.

1.3.4.7 Other structures

Giant Magneto Resistance is also found in other structures. Pena et al., [95] reported on giant magneto resistance in ferromagnetic/superconductor super lattices. On the other hand, Pullini et al., [96] described GMR in multilayered nano-wires. Svalov et al., reported on successful spin-valve structures with Co-Tb based multi-layers [97]. In any case, a magnetic/non-magnetic interface is required in order to allow the spin-electron scattering producing the effect.

1.3.5 Applications of GMR Materials

The discovery [98] of the giant magneto resistance (GMR) effect has led to many technological applications, especially in data storage devices such as GMR read heads, magneto resistive random access memory, and in magnetic sensors [99,100]. The GMR effect reflects changes in resistivity as result of spin-dependent scattering of two spin channels across the interfaces between the magnetic and nonmagnetic metal layers (i.e., GMR effect) or magnetic and insulating layers (i.e., tunneling magneto resistance effect) [101].

The key property of these materials is the reduction of their electrical resistivity in magnetic field. Tunneling magneto resistance effect (TMR) and industrial applications.

The GMR materials promise some important applications, among others as magnetic sensors. The GMR sensor has many attractive properties, for instance: its electric and magnetic properties can be varied in very wide range, reduction size, low price as compared to other magnetic sensors and low power consumption etc [102].GMR materials appear benefits such as low magnetic sensors technology for example: high sensitivity, low cost, low power and small size. Because of these benefits compare to other magnetic materials, technically it's not difficult and the technique as it was new in the world. Fig.1.27 (a & b) shows some applications of GMR sensors.

1.3.5.1 GMR Magnetic field sensor

The applications integrated the new technology of GMR as a magnetic field sensor as we saw with the previous applications. The field change is turned into a resistance change which can be analyzed by the integrated circuit technology. It currently appears that GMR magnetic field sensors the best device available on the market, because sensors play important role for they have many features for instance, a great sensitivity (they can be used to detect low field whose amplitude is around the Earth's), very small size, small cost, and low consumption; for these reasons they are about to replace the old sensors in all applications and enable to move further away the limitations due to weight, size, power consumption and cost [103]. We can name some applications in brief for examples as mentioned below because the applications areas are numerous.

1.3.5.1.1 Currency validation

The use of iron oxide as a pigment in black ink has provided a method of reading and validating currency and other negotiable documents. The black ink on the bills contains small magnetic particles which act as dipoles and create the magnetic signature of the bill. This will make a low magnetic field sensor react which makes it possible to check whether the currency is a fake or not. GMR devices are useful because it has high sensitivity allows a large gap between the bill and the sensor [104] as shown in fig.1.25 Magnetic signatures from Magnetic Ink Character Recognition (MICR) characters on the bottom of checks.

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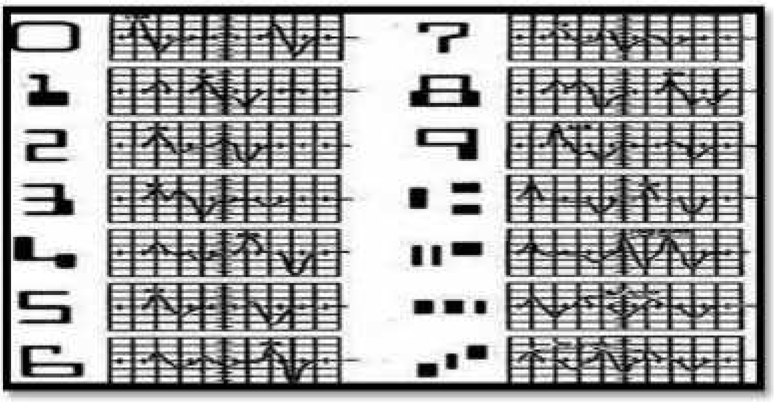


Fig. 1.25 Magnetic signatures [104]

1.3.5.1.2 Eddy current mapping for defect detection/Geophysics

Eddy current detection is a non-contacting method that does not require placing electrodes in the ground. The wide bandwidth of GMR sensors allow both time and frequency domain measurements to be made simultaneously. An ac magnetic field causes eddy currents in the conductive material which oppose the applied field (Lenz's law). The presence of a flaw in the conducting material can change the direction of the magnetic field so that it will be detected by a GMR sensor. Also we can apply that to geophysical exploration by detecting the change in conductivity of the soil due to water. Fig.1.26 shows the relative positions of the sensor and coil for eddy current detection [105].

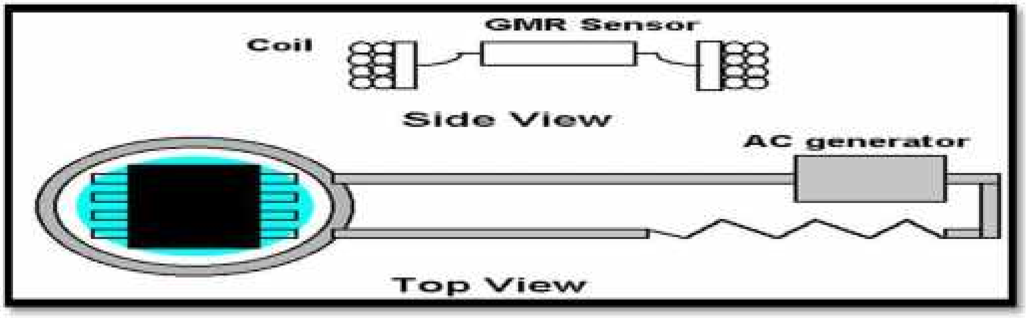


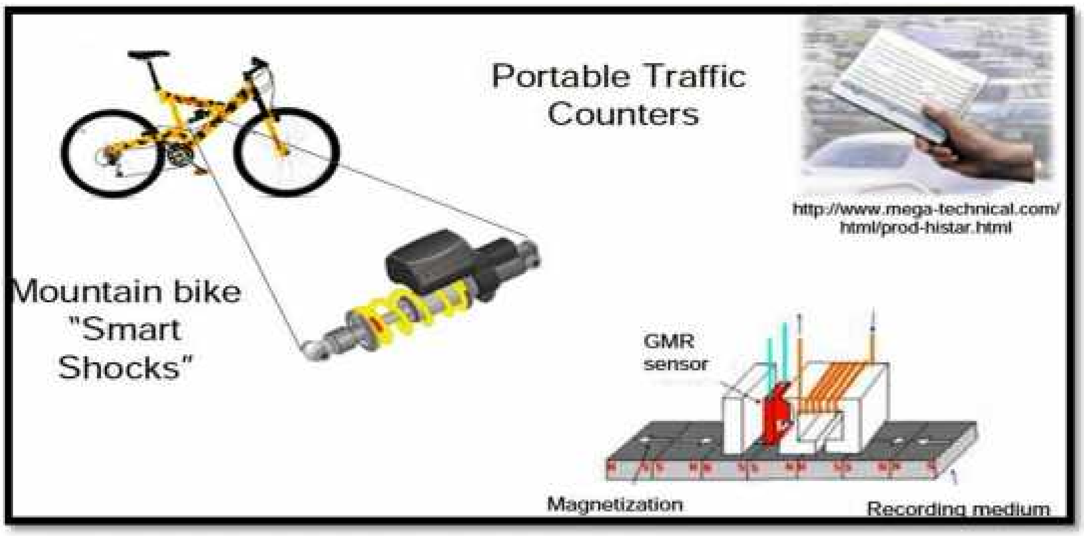
Fig. 1.26 GMR sensors for eddy current detection

1.3.5.1.3 Detection of motor vehicles & traffic control sensor

The earth field acts as a biasing magnet resulting in a magnetic signature from different parts of the vehicle when passing a sensor. This allows detection of stationary and moving vehicles which is important for traffic control. The use of GMR for this application enables the whole device to fit in your hand!

The same system can also be used to detect a train approaching a cross section with a road and optimize the moment to lower the gates. Magnetic sensors also are used for moving traffic, counting and classification of motor vehicles passing over portable or permanent sensors in the road as showing in fig.1.27 (a &b) [105].

(a)



(b)

Fig.1.27 (a& b) Some applications of GMR sensors

1.3.5.1.4 Geophysical Surveying

Airborne surveys of magnetic anomalies are used to locate potential magnetic ore bodies. Ground based magnetic surveys require portable equipment. Low field GMR sensors are ideal for equipment packed into remote survey areas.

The magnetic fields of interest are less than the Earth’s magnetic field. The wide bandwidth of GMR sensors allow both frequency and time domain measurements to be made simultaneously. Arrays of sensors product possibility 2-D imaging simultaneously.

Magnetic low field GMR sensors are also of interest in locating other materials hidden in the soil [103].

1.3.5.1.5 Unexploded Ordnance (UXO)

Unexploded ordnance (or UXOs/UXBs, sometimes acronymized as UO) is explosive weapons (bombs, bullets, shells, grenades, land mines, naval mines, etc.) that did not explode when they were employed and still pose a risk of detonation, potentially many decades after they were used or discarded. While UXO is widely and informally used, munitions and explosives of concern (MEC) is the current preferred terminology within the remediation community. Differential magnetic sensing is conventionally used for maximum sensitivity in the presence of the Earth’s field to avoid confusion of the desired signal with the changing component of the Earth’s field along the sensors sensitive axis. Not all ordnance has ferromagnetic materials in them. Plastic-cased land mines are designed to be difficult to locate and clear. For type of UXO, laboratories have been working with arrays of GMR sensors to look for magnetic anomalies in the background magnetism from the soil. Where there is a hole or absence of magnetic signal is a potential location of UXO. Small, Low power GMR sensors are ideal for such an array of magnetic sensors.

1.3.5.1.6 The sensing of body position

The position data can be correlated with other information such as electro-myogram (EMG) reading to diagnose movement disorders. The position of the magnet plays important a role in various medical evolutions-the tracking of the movements of the eye or a limb for instance. In some cases a small magnet can be attached to the body part to be monitored. For instance, small magnets can be placed in sclera contact lenses. The position of the magnet can then be monitored by magnetic sensors mounted on an eyeglass rime. A 3-D measurement of motion of a limb including vertical inclination and horizontal azimuth has been accomplished using 3 orthogonal GMR sensors measuring vector components of the Earth’s magnetic field together with 3 accelerometers [106].

The system was small enough so it could be used in long-term ambulatory measurements of patients during normal activities.

1.3.5.1.7 Biological Diagnostics

Solid state magnetic sensors now promise to change this picture by facilitation miniaturized magnetic sensor based systems. Including the applications detection of the small magnetic fields created by nerve impulses for monitoring the activity of the heart and brain. By using sensors utilizing GMR and SDT materials, is being overcome insurmountable barrier to the use of solid state magnetic sensors, sensitivity. These highly sensitive near-micrometer sized sensing elements stand at the edge of biological diagnostics research [107]. In the past, the sensors used, such as SQUIDs (super-conducting quantum interference detectors), have limited the deployment of such systems to the field due to their size and power constraints.

1.3.5.1.8 Biological assays

These particles range in size from few nanometers up to a few microns, and in composition from pure ferrite to small percentages of ferrite encapsulated in plastic or ceramic spheres. The beads are coated with a chemical or biological species such as DNA or antibodies that selectively binds to the target analyte. Antibodies are detected by flowing them over a sensor coated with antigens which they bind to. The magnetic particle-labeled antigens then bind to the antibodies providing a magnetic indication of the presence of those antigens which will be sensed by the GMR device. This operation requires extremely small, low-power, low field magnetic sensors, which makes the GMR the ideal solution. Moreover, the use of solid state sensors as GMR facilitates a lot the integration [108] as shown in fig.1.28.

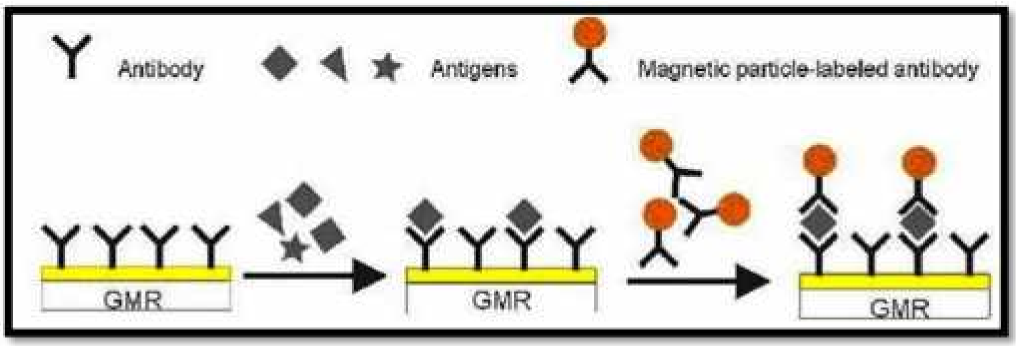


Fig.1.28 Antigen detection process

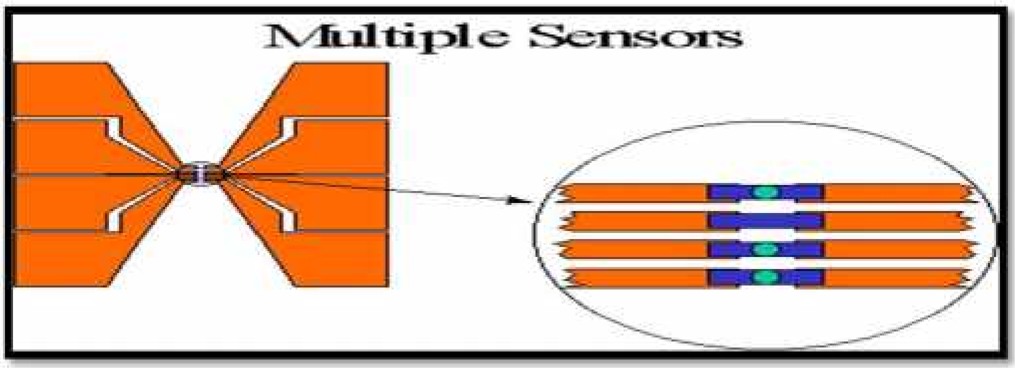


Fig.1.29 Schematic diagram shows beads on three of the four locations

The miniature nature of GMR sensor elements allows an array to simultaneously test for multiple biological molecules of interest as is shown in Fig.1.29 each sensor was coated with different biological molecules that will bond to different materials to be assayed. The magnetic micro-beads were coated with the materials to be analyzed. In a multiple sensor array each location is coated to bond to a different antigen. This schematic diagram shows beads on three of the four locations.

1.3.5.1.9 Arrays of GMR biochips for analysis of Biomolecules

Arrays of GMR magnetic sensors allow rapid scanning of an area for defects in a single pass. The solid state magnetic sensors enable the fabrication of compact arrays of sensors on circuit boards and even on-chip sensor arrays because; they have low power consumption and small size. Arrays have been fabricated with sensor spacing as small as 5 micrometers when fine resolution is required. The sensitivity of GMR sensors increases as its volume decreases. The solution to measure a large area with great precision is to build an array of GMR sensors. It is equivalent to increasing the number of pixel per area for a digital picture: it gives a better result with more precision. GMR sensor elements can be deposited on active silicon substrates facilitating on-chip signal processing and multiplexing. This integration simplifies the sensor-signal-processing interface, minimizes the number of leads, and can reduce the effect of noise.

Can be used sensors arrays in different ways according to the situation. If we take the example of the currency validation (the eddy current mapping), an array of sensors allows to cover a big area of the bill (surface to probe) at once which makes the entire process much faster.

The case of the biological assay gives different antigens at the same time. However, those improved achieve might sometimes come with additional limitations [109].

1.3.5.1.10 GMR/MR Encoder Sensors for Wind Power Energy

As shown in fig.1.30 Hitachi Metals is developing and manufacturing a magnetic sensor utilizing magnetic recording head technologies. Magneto resistive (MR) and giant magneto-resistive (GMR) sensors offer high magnetic sensitivity for a wide variety of markets, such as rotary and linear magnetic encoders. The market is growing for Wind Power Energy as a renewable energy source. A most effective transformation from wind into electric power generation needs to control direction and speed of turbine in the wind power system. Customized Hitachi Metals MR / GMR encoder sensors are well defined to meet these requirements [110].

Fig.1.30 Wind Power Energy [110]

Key Features of our Magnetic Encoders demonstrates a much higher level of magnetic sensitivity than MR sensors Surface-mounted sensors appropriate for miniaturization operates in severe environments within a wide range of temperatures.

1.3.5.1.11 Spin valve GMR Sensors

A spin valve Sensors is a layered structure of two ferromagnetic (FM) electrodes separated by a nonmagnetic spacer [111]. The spacer decouples the two FM electrodes and allows spin polarized carriers to travel through it without much relaxation. This modified GMR structure allows one to obtain good sensitivity and a relatively high magneto resistive ratio. Traditionally, metals and inorganic semiconductors are used as the spacer material in SVs.

Despite, a few factors such as the spin scattering owing to huge atomic radius of the spacer materials and scattering from the FM/spacer interface, limit the efficiency of such SVs to a certain level. One solution to the first problem could be the introduction of spacer materials made from lighter elements, e.g. carbon that will also have spin-transporting capabilities [112]. Spin Valves a key to using this technology in computer products was finding a way to quickly and efficiently locate and identify these tiny magnetized bits on a disk. The solution, again related to the GMR effect, was spin valves, where the very small fields from the tiny bits rotate the magnetization direction in an unpinned magnetic layer in relation to the magnetization direction of a pinned magnetic layer. The resulting change in electrical resistance allows the information stored in the bit to be read by electronics in the disk drive. Another highly desirable feature of SV-GMR as a biomedical magnetometer is the fact that it can operate at room temperature [113]. Their microsize dimensions render them comparable in size to the examined bioobject and create the opportunity to build small portable devices. These thin film structures can be deposited in complex configurations, e.g. to create an array of sensors applied in biomolecular tweezers to increase the throughput of individual molecules for analysis as depicted in Fig.1.31 (a) [114] and Fig.1.31 (b) shows SV-GMR sensor integrated with tapered current lines for biomolecules concentration in recognition process. Current flowing through the narrow parts of current lines induces higher local magnetic fields in the proximity of the sensor capable of attracting the labeled molecules to the sensors region [115] or on a needle to allow for in-vivo measurements inside of the body Fig.1.31 (c) [116-119]. They can be easily integrated into various biochip patterns [120,121] or even to standard CMOS chips to facilitate detection [122].

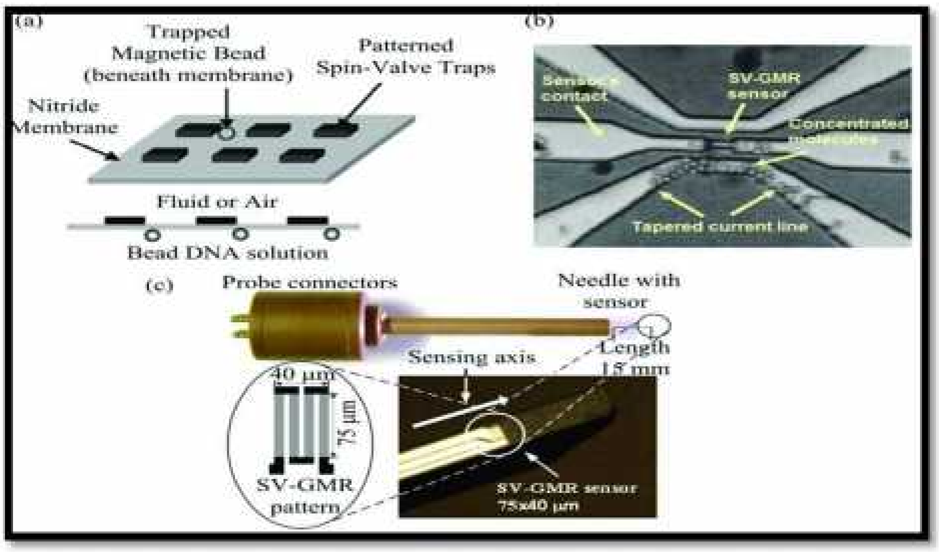


Fig.1.31 (a) Array of SV-GMR (b) SV-GMR system (c) needle type SV-GMR sensor

1.3.5.2 Magneto Resistive Random Access Memory (MRAM)/ Non- Volatile

Fast, non-volatile and random accessed magnetic storage of data was realized in1960s for very early computers in the shape of magnetic core memory. As shown in fig.1.32 the memory cells consist of wired threaded tiny ferrite toroids. With two states of remanent polarization binary 1 and 0 are stored. Now with the development of integrated electronic circuits the bulky ferrite toroids has been replaced by thin magnetic layer elements. This memory has the same writing principle while for reading more sensitive magneto resistive effects are being employed. That's why now it is known as Magneto-Resistive Random Access Memory (MRAM) [123].Magnetic Random Access Memory (MRAM) is a new non-volatile memory technology trying established itself as a mainstream technology.

Magnetism contributes to the aim of storing information for long time periods (10years), in the form of hard disk drive and magnetic simulate storage systems. In following instances data access time will be limit by the fact that these are mechanical systems. Only solid state memories like Dynamic Random Access Memory (DRAM) and the Static Random Access Memory (SRAM) are able of ns access times in both read and writes operations [124].These memories are volatile and data is stored only as long as power is supplied to refresh the capacitor charge in DRAM and to keep the transistors in SRAM. The need for a non-volatile memory is reflected in the increasing demand for Flash memory, fuelled by its use in digital consumer products.

However, Flash technology suffers from slow write access time in the μs range and poor bit cyclability limited to 10^6 write events. Magnetic random access memory is one technology proposing to close the achieve gap between existing volatile memory technologies. Other alternatives are ferroelectric random access memories (FeRAM) based on ferroelectric materials and phase change based Ovonyx unifield memory (OUM). MRAM devices have already been demonstrated based on Giant Magneto-Resistance (GMR) elements [125] and more recently using magnetic tunnel junctions (MTJ) [126-128].

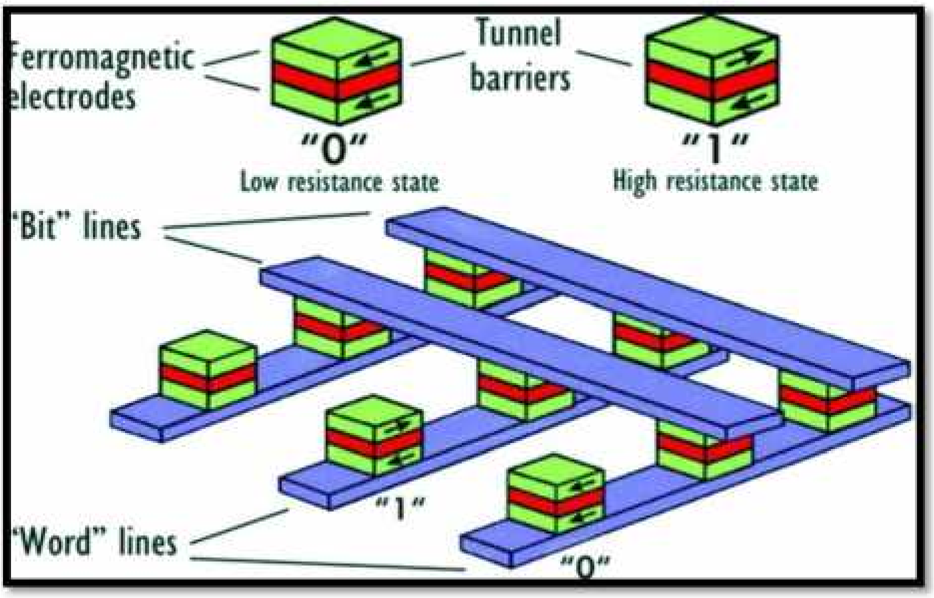


Fig.1.32 Schematic diagram of MRAM architecture [125]

The memory cells are shown at the top to be magnetic tunnel junctions with the two memory states represented by parallel and anti-parallel alignment of the ferromagnetic layers. The bits are assembled and connected in an array as shown in fig.1.32 creating 'word lines' and 'bit lines'. The voltage across a single bit can be read by connecting to the array appropriately and the magnetization orientation of the bits changed by the magnetic field created from the passing of a write current.

1.3.5.3 GMR Magnetic Hard Drive (read head)

Magnetic hard drives store information on a magnetic disk, which spins at high speed. Each data bit corresponds to the magnetization of one region of the disk, and the data are written using a small electromagnet material on the disk as shown in fig.1.33.

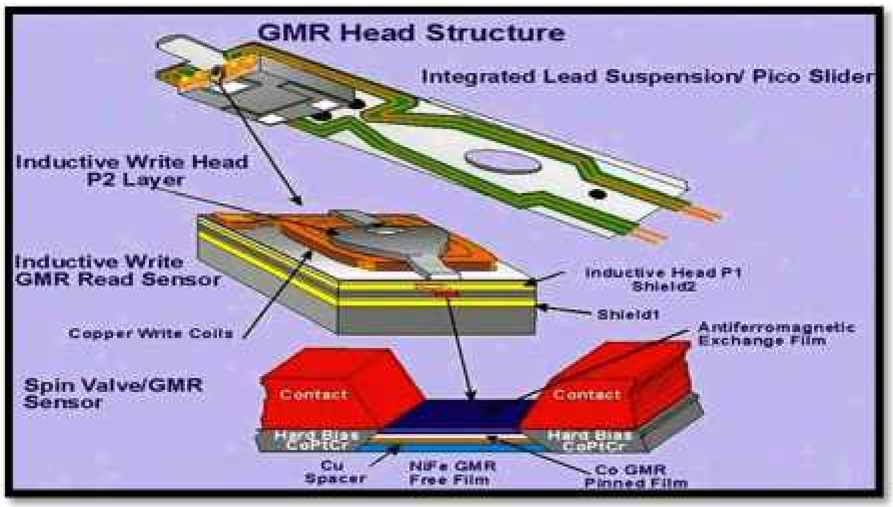


Fig1.33 Schematic diagram of a read–write head

Fig1.33 shows the relative orientations of the inductive writer and the GMR read element. The bottom figure shows the detail of a spin-valve head construction including the contacts and the hard-bias. The technology of the read head in a hard disk recording has developed since the invention of the hard disk in 1956 and the first GMR hard drives were developed as shown in figs. (1.34 & 1.35) duration ten years of the discovery of GMR [129]. GMR is responsible about the huge increases in hard drive capacity which started on the late 1990s to the nowadays. Can we utilize the GMR effect as magnetic field sensors in the read heads of magnetic hard disk drives? This has played an important role in the emergence of the Internet and digital video and our life [130]. The GMR technology has become the dominant technology for hard drives, and a natural evolution is to take advantage of the high TMR values in MTJs.

For the read head, the GMR effect is used as a magnetic field sensor and the basic multilayer structure is shown in bottom of fig.1.33 above. The bottom three layers are Cu/Co/NiFe trilayer which exhibits MR due to the GMR effect. For a sensitive magnetic field sensor, a material having a low coercivity is chosen for the bottom layer (free layer).This ensures that the magnetization direction will track the applied magnetic field. A typically candidate for the free layer is perm alloy (Ni_{81}), which has a very low coercivity of about 1 Oe (similar to the Earth's magnetic field). At the time that GMR was discovered, both the read and write components of the recording head used inductive technology. The inductive reading mechanism was the limiting factor to the increase in data density; compromised by lower magnetization, smaller dimensions and the faster data rate presented by the decreasing bit size.

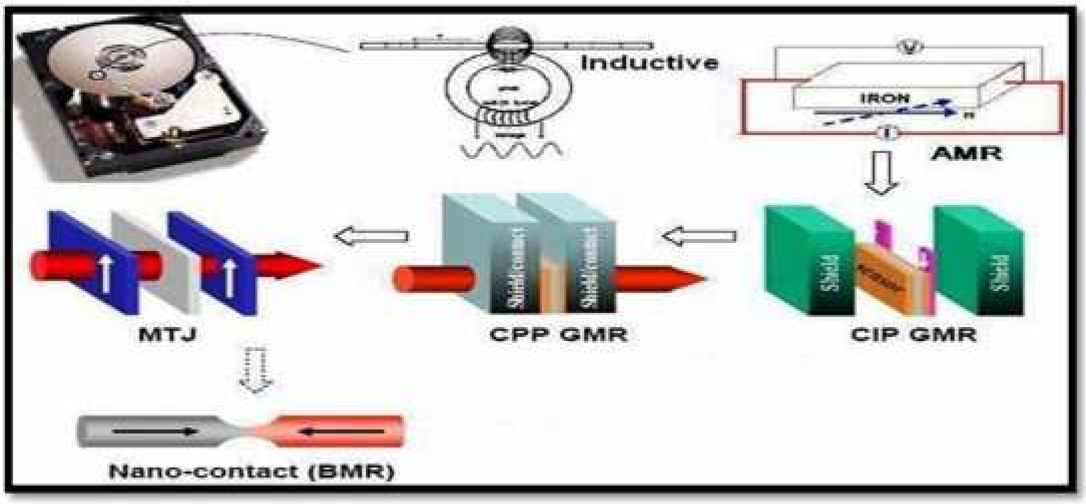


Fig.1.34 Development of the read head technique

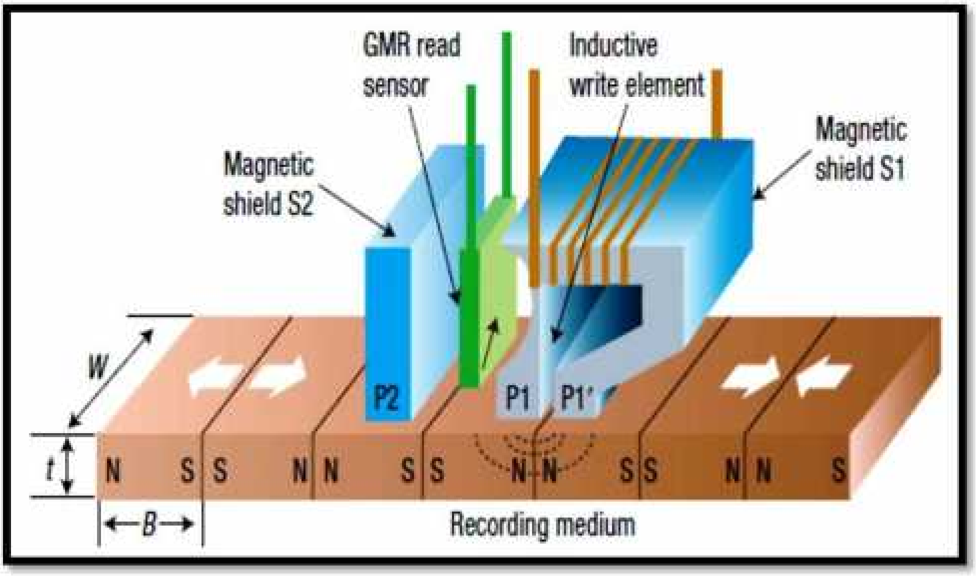


Fig.1.35 Schematic structure of the magneto resistive head (IBM 1991)

1.3.5.4 The digital isolator (Galvanic Isolator)

The digital isolator (Galvanic Isolator) is a device that transfers a signal between elements of circuit, typically a transmitter and a receiver, while keeping them electrically isolated.

Currently the most common device produced is the optical isolator which uses an optical transmission path to do the transfer. On the other hand, the incoming of the GMR things are changing and GMR digital signal isolators [131] are now beginning to appear: they are smaller, faster, yet cost-competitive compared to the optical isolators. These isolators can eliminate or reduce ground noise in communications carried out by wire and ideally suited for industrial data bus, analog to digital conversion, and telecommunications applications [132].

Optical isolators transmit a signal with light where the distance of light between the light-emitting diode and photon-sensing device provides the signal isolation. GMR devices transmit the signal via magnetic field. This provides many design advantages such as:

- A faster transfer rate: GMR isolators transmit data 4 to 20 times faster
- Lower power consumption: GMR isolators draw half power at maximum
- Smaller footprints: GMR isolators are 20% smaller
- Greater noise immunity and temperature stability

The current induced at the input by the signal to be isolated flows through the coil windings, and the GMR structure senses the magnetic field that the windings generate across a thick dielectric film: this is shown by a resistance change in the GMR material. Internal active circuitry boosts the sensed-field signal, in terms of the resistance change, to generate a standard-level, isolated output as shown in fig.1.36.

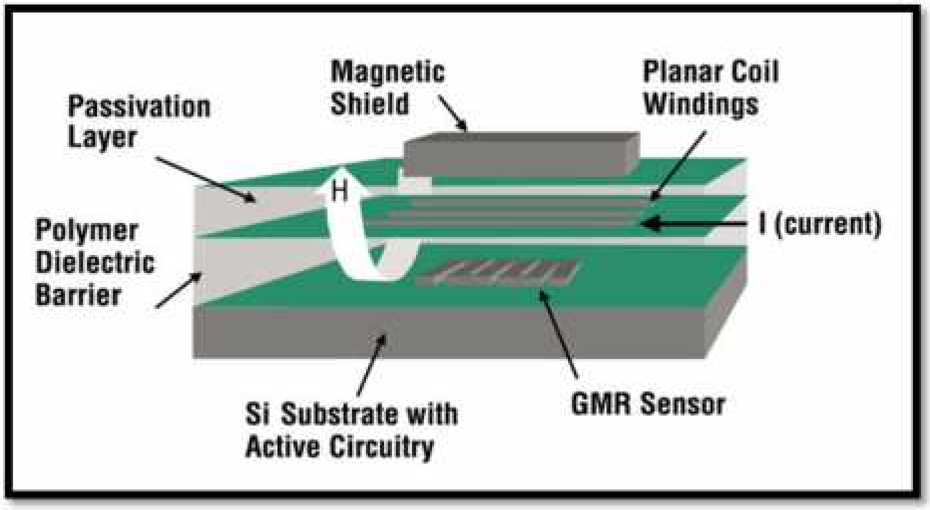


Fig.1.36 Structure of GMR Galvanic Isolator

1.3.7 GMR Future

Twenty five years after the discovery of GMR materials, products using GMR materials are being produced. Wider applications of these materials would benefit from continued advances in understanding and development of GMR materials. Besides the never-ending quest for high magneto-resistance ratios and lower saturation fields, there are several developments which would aid in the commercialization of GMR materials which may not be obvious to researchers concentrating on GMR material development. These were discussed along with GMR materials and their applications. Materials which have little or no hysteresis would be very valuable for magnetic field sensors [80].The GMR has provided us with a new viewpoint both for understanding the electronic properties of solids and for exploiting these properties to generate new effects. These effects will soon be the basis for electronic devices in the new field of spin electronics [133]. The spin valve GMR heads are one of the key technologies for the realization. The new read heads with higher field sensitivity, however, may be required for the higher areal density than 40 GB/in2.

Ferromagnetic tunnel junctions are one of the most promising candidates, owing to they have high field sensitivity and a simple structure, and submicron size is possible with junction resistance and low-power dissipation. Even higher field sensitivity is to be expected for the ferromagnetic tunnel junctions with higher spin polarization materials such as half metallic ferromagnetism AMnSb with A=Ni and Pt and doped/co-doped Perovskites manganites $R_{1-x}B_xMnO_3$ with R=rare earth element and B=alkaline earth element [134]. GMR has had a successful run in the industrial market place and its time has ended, but we still see its legacy, and will continue too. GMR researches gave birth to TMR, CMR, and in generate Spintronics. Tunneling Magneto resistance has allowed us to see the price per gigabyte fall below 1 dollar. As of this writing Western Digital has announced the world’s first 2 TB hdd [135].

1.4 Emergence of a new field: Spin Electronics (Spintronics)

The newly emerging field of Spintronics depends on new materials that have magnetic properties. Gaining a deeper understanding of different ferromagnetic materials, and in particular their spin dynamics, is important for today’s quickly evolving technology.

Although, the birth of Spintronics can only be traced back to late 1980s when giant magneto-resistance (GMR) effect was first observed in magnetic multilayer systems, a great amount of work since has been done in this area to further develop it [136].

Spintronics is based on the spin of electron, which is a fundamental property that originates from electron's spinning around its axis. Relining on the direction of the angular momentum that this spinning cause, electrons can have spin up or spin down states. GMR technology uses this unique property of electrons to detect a high or low current signal which later is respectively interpreted into one or zero digits to be used in data processing units. The first spacers have been used as separators of top and bottom ferromagnetic layers, had a conducting nature however shortly after, thin insulating spacers were introduced in order to provide more spin injunction. Utilizing this mechanism has led to the so called Tunneling Magneto Resistance (TMR) effect which is at least one order of magnitude more sensitive in translating the electron current into digital signal compared to GMR.Fig.1.37 (a) the configuration by which we can see the GMR or TMR effect if the space between two ferromagnetism is a metal or insulator, respectively. Here the current is flowing in y-direction through the device.

First ferromagnetic layer polarizes the electrons which are injected into the spacer. If the magnetization of second ferromagnetic layer is parallel to that of polarizer, electrons encounter minimum scattering from the interfaces while they are traversing through the stack. On the other hand, if the magnetization of second ferromagnetic layer is directed opposite to that of polarizer, electrons face a greater spin-dependent scattering. Considering the fact that this device can show a large or small resistance for anti-parallel or parallel orientations of the magnetizations of ferromagnetism, respectively, it can work as a valve and that is why this device is sometimes called Spin Valve. Fig. 1.37 (b) shows a simplified representation of dependence of magneto resistance on external applied magnetic field. In the left-hand side of this figure, magnetization directions of both ferromagnetism are pointed to the left and therefore resistance of the device shows a minimum.

We follow the blue arrows by decreasing the magnetic field down to zero, then switch the direction of the applied magnetic field and increase it until we change the magnetization direction of one of the ferromagnetic layers. At this moment we see a huge resistance in the device.

By further increasing the external magnetic field we change the magnetization direction of the other ferromagnetic layer and we again see a small resistance in the device. We can repeat the same kind of experiment by following the red arrows from the far right in figure 20.b, i.e. by reducing and then reversing the direction of applied magnetic field [137].

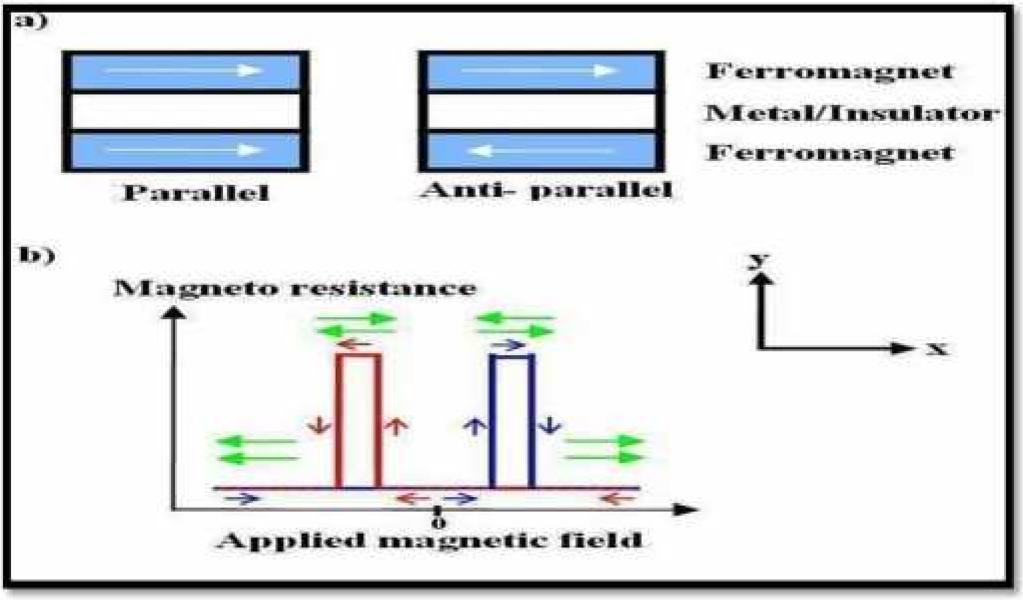


Fig.1.37 (a) Configuration of either GMR or TMR (b) Nanostructure of TMR ratio versus external magnetic field

In the result of the discovery of the giant magneto resistance, a tremendous research activity has been initiated, both in academic and industry institutes, involving several thousands of researchers worldwide, in order to exploit the potential revealed by Fert and Grünberg. A number of important discoveries, which will be briefly reviewed below, followed rapidly. This new field of research has been named spin electronics (also magneto electronics, or spintronics). In its most precise definition, spin electronics refers to new phenomena of electronic transport, in which the spin of the electron plays a central active role (in contrast to conventional electronics, for which the electron spin is essentially irrelevant).

In practice, a somehow looser definition is frequently accepted (including new phenomena not directly related to transport). While it is fair to mention that some of the topics listed below already started before 1988, the discovery of the GMR undoubtedly contributed in a decisive manner to reveal their great potential and to reach their full impact [138].

1.4.1 Advantages of Spintronics

- Non-volatile memory
- Performance improves with smaller devices
- Low power consumption
- Spintronics does not require unique and specialized semiconductors
- Dissipation less transmission
- Switching time is very less
- Compared to normal RAM chips, spintronic RAM chips will increase storage densities by a factor of three
- Have faster switching and rewritability rates smaller

1.2.1.3 Colossal Magneto Resistance (CMR)

The reader may have a first introduction to this topic by reading a recent article in Physics World [139]. A complete survey of the practical understanding of this system and the state of the art in their synthesis can be found in the critical review of Coey, Viret and von Molnar [140]. The topic is related to GMR for historical reasons. The Perovskites that display the so-called colossal magneto resistance were studied in the 1950s [141]. In the 1990s the search for any kind of giant magneto resistance was fiercely under way. In 1994 a group showed that it was possible to tune the structure of manganite Perovskites so that the apparent metal to insulator transition that is affected by magnetic field would occur around room temperature [142]. In terms of magneto resistance ratio as used for AMR or GMR, this transition would represent 100,000% or more. Hence, the authors named it colossal. In fact, at this point of the understanding of CMR, the connection with spin-dependent transport in nanostructure relates to the notion of spin injection and tunnel experiments. These materials appear to be half metallic ferromagnetic, meaning that only one spin band crosses the Fermi Level, hence are expected to have very strong tunnel magneto resistance. At a more fundamental level, the connection between spin transport and CMR arises in the mechanism called the double exchange. The following quote from a Science paper may suffice in giving a favor of the current thinking as to the mechanisms of CMR [143]. Although the theoretical understanding of the CMR phenomenon is still incompleted, double exchange (DE) mechanism [144], electron-phonon coupling [145], and orbital ordering effects [146] are commonly adopted as the main ingredients.

The DE mechanism links the electronic to the magnetic transition and describes the hopping of electrons in e_g orbital. The DE mechanism links the electronic to the magnetic transition and describes the hopping of electrons in $\mathbf{e_g}$ orbital between neighboring Mn^{3+} and Mn^{4+} sites with strong on-site Hund's coupling by an O^{2-} ion. This charge transport is enhanced in the ferromagnetic state when the local Mn d-shell spins are parallel. In turn, the hopping electrons promote ferromagnetic order because they tend to preserve their spin direction [147].

The random spin disorder in the crossover regime around T_C can be removed at least partially by applying a magnetic field. This shifts T_C to higher temperatures and causes CMR. However, the DE mechanism alone is insufficient to correctly describe the high-temperature transport properties and to quantify the giant resistance drop [148]. At such temperatures, the insulator-like behavior results from electron localization caused by electron-lattice coupling, originating from local Jahn-Teller distortions at the Mn^{3+}site see chapter 2.These distortions also lift the degeneracy of the e_g orbital order (and disorder) into play [149].

Negative magneto resistance is the term given to the large decrease in the electrical resistance when certain systems are exposed to a magnetic field. The (negative) magneto resistance is usually defined as a percentage ratio:

$$\mathrm{MR} = -\left[\frac{\rho_0 - \rho_H}{\rho_0}\right] \times 100\%$$

Where ρ_H is the resistivity in the presence of a magnetic field of strength H and ρ_0 is the resistivity in the absence of a magnetic field.

1.2.1.3.1 Applications of CMR materials:

There are many applications of CMR used in magneto electronics, spintronics, sensors, bolometers, and read head devices etc as shown in fig.1.38.

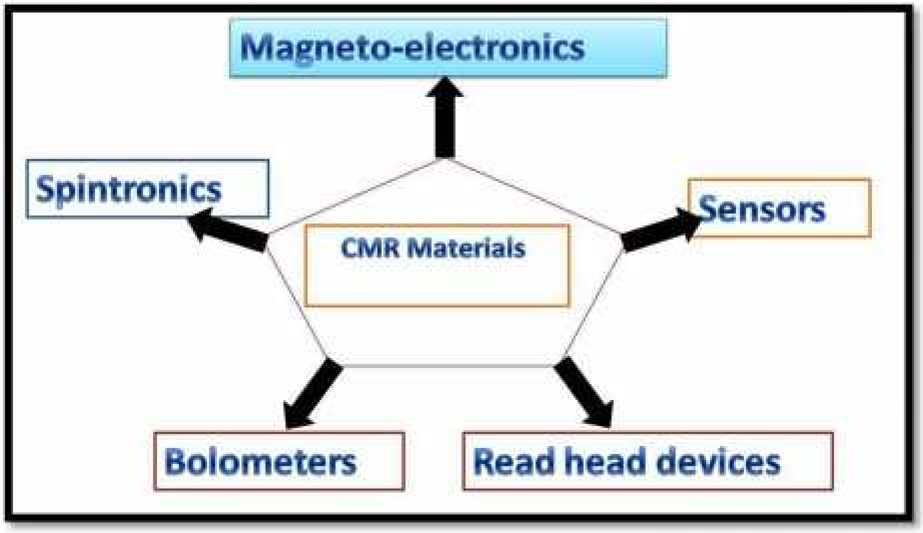


Fig.1.38 Schematic of CMR applications

1.2.1.4 Tunneling Magneto Resistance (TMR)

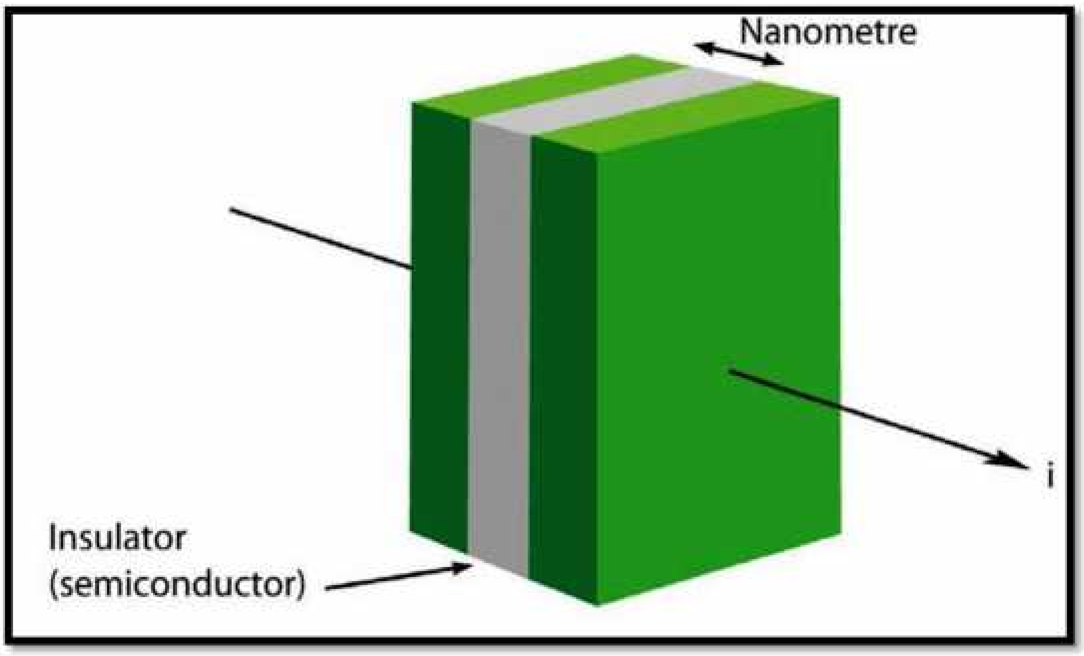


Fig.1.39 Schematic of tunneling magneto resistance (TMR)

Another important phenomenon leading to very giant magneto resistance ratios has attracted much interest in recent years: the tunnel magneto resistance effect (TMR). The TMR effect was proposed by Julliere in 1975 [150] but it was not actually developed until the late nineties [151]. Basically it consist of tow ferromagnetic layers (electrodes) separated by a thin nanometric insulating layer (barrier) as shown in Fig.1.41 two ferromagnetic layers separated by an insulating layer (i = electron current).

The conduction proceeds via electron tunneling and the electrical resistance of such a device is different if the ferromagnetic layers have parallel or antiparallel magnetizations. The origin of this effect lies at the different tunneling probability of spin-up and spin down electrons.

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