Giant Magnetoresistance in Electrodeposited Films: Current Status and the Influence of Parameters

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Electrodeposition of some alloys and multilayer which exhibits the giant magneto resistance (GMR) effect, have been the subject of numerous studies. They have great potential for technological applications, such as magneto resistive sensors and magnetic recording devices. GMR effect is more usually seen in multilayer and alloys structure, when two magnetic layers are closely separated by a thin non-magnetic spacer layer. This paper deals with the review of literature available on electrodeposition of alloys and multilayer for GMR application. The effect of thickness of magnetic, non-magnetic layers, number of bi-layers, electrolyte pH, electrolyte temperature, additives and annealing process on GMR properties will be discussed.

Keywords GMR, layer thickness, annealing, electrolyte, magnetic, non-magnetic

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1. INTRODUCTION

In the past few years magnetic multilayers have been the subject of extensive research effort. This effort is mainly based on the very interesting magnetic and electrical phenomena that can be observed in these artificially layered structures, such as the oscillatory exchange coupling between magnetic layers across nonmagnetic spacer layers and the so-called giant magnetoresistance (GMR) effect. The GMR has attracted a great deal of attention for fundamental interest and technological applications. GMR was first discovered in certain Fe/Cr structures, and these materials have been made mostly by sputtering and molecular beam epitaxy (MBE), which require high or ultra high vacuum. For this to be observed a fair control over the deposition parameters is needed, since rough interfaces between subsequent layers can easily destroy the effect. That is why most of the samples which exhibit large coupling strengths and high MR values have been prepared by sputtering, MBE, or other vacuum-based techniques. However, recently electrodeposition has attracted many researchers worldwide for its successful utility as a tool in producing thin films for GMR applications. In 1993 Alper et al. and Hua et al. have reported giant magnetoresistance in Co-Ni/Cu multilayers grown by electrodeposition in a single electrolyte. The concept of multilayer growth by electrodeposition is not a new one. The advantage of electrodeposition over vacuum-based techniques mainly lies in the simplicity of the experimental setup, less expensive apparatus, large area of epitaxial growth, well-controlled film orientation, minimum interdiffusion, flat individual layers and the multilayers with the individual layer thicknesses below 10 Å.

However, growing high quality multilayers that exhibit appreciable giant MR values still remains a challenge. Electrodeposition offers the promising possibility of growing wire-like multilayer structures with very large height-to-width aspect ratios as recently demonstrated by Blonde1 et al. and Piraux et al., which enables the study of the giant MR effect with the current perpendicular to the multilayer planes (the so-called CPP MR). Until recently, this could only be realized either by superconducting contacts, which limits the measurements to low temperatures, or by advanced micro structuring, which results in structures having rather poor aspect ratios compared to the electrodeposited wires. As mentioned above, high quality electrodeposited samples which show giant MR values comparable with those of sputtered or MBE-grown multilayers are scarce, mainly due to a lack of thickness control and growth homogeneity, making the very thin spacer-layer thickness regime of antiferromagnetic (AF) coupling (5-3 nm) not yet accessible. For the CPP MR this is less a problem than for the case where the current is flowing in the planes of the layers (the CIP geometry) because of the different length scales involved for the MR effect.

Reviews on GMR have been published by Fort and Bruno, Levy, and Dieny covering the field up to 1994. Other reviews by Gijs and Bauer, Ansermet, Bass and Pratt, Fert and Piraux, and Gijs are devoted specifically to the CPP GMR. Coehoorn E.Y. Tsymbal and Barthelemy et al. have also reported a review of GMR. The first one highlights the theoretical and experimental results, which are of particular interest for applications of spin valves in read heads. The second one discusses the nature of GMR by accenting the importance of CPP geometry and gives a full list of experimental papers. In the above reviews are discussed the materials prepared by the physical techniques as well as electrochemical techniques. In addition, all the reviews are covering the reports up to 2001 only. Recently, Bakonyi et al. has published a review of GMR in electrodeposited materials.

The present review is devoted to the electrodeposition of giant magnetoresistance materials. We emphasize in this review the experimental data on GMR in magnetic multilayer, alloys and the dependence of GMR on magnetic layer thickness, non-magnetic layer thickness, number of bi-layers, electrolyte pH, electrolyte temperature, additives and annealing process.

2. APPLICATION

GMR applications are very promising, such as the magnetic-field sensors, GMR read heads, random access memory (RAM), etc. The conventional RAM memory is made of transistors and capacitors that are paired to create a memory cell, which represents one bit of data (0 or 1). Like conventional RAM, MRAM is composed of transistors but, instead of electrical charges, it uses magnetic charges to store information. In this way we can get the permanent memory even electrical power is lost i.e. battery backed RAM. An MRAM chip is made up of millions of pairs of tiny ferromagnetic plates (like the one covering hard drives) called memory cells, i.e., magnetic sandwiches consisting of two magnetic layers separated by a very thin non-magnetic layer. Each magnetic layer has a polarity—a north pole and a south pole. These can be oriented in a parallel orientation, meaning that both have their respective poles (or ‘magnetic moments’) in the same orientation, or in an anti-parallel fashion, meaning that their poles/magnetic moments are oriented in opposite directions. These relative magnetic pole orientations correspond to the binary memory states, either 0 or 1.
Originally, induction coils where used in read-out heads, exploiting the fact that a changing magnetic field induces a current through an electric coil. Even though this technology has not been able to keep pace with the demands of shrinking hard disks, induction coils are still in use for writing information onto the disk. For the read-out function, however, magnetoresistance suits better.

The read element consists of MR or GMR sensor between two magnetic shields. The magnetic shields greatly reduce unwanted magnetic fields coming from the disk; the MR or GMR sensor essentially “sees” only the magnetic field from the recorded data bit to be read. In a merged head the second magnetic shield also functions as one pole of the inductive write head.

Giant magnetoresistance sensors are typically designed for maximum sensitivity to the low magnetic fields in magnetic recording readback. However, some applications require sensing of much larger magnetic fields, for example, optimization of electric motors, magnetic levitating trains, position sensors, or synchrotron insertion devices. Magnetic fields from 0 to 20 kG are often measured using a semiconductor Hall probe. Despite widespread use, such devices are limited in thermal stability, frequency range, and accuracy. The performance of common Hall effect sensors typically decreases above approximately 150 °C or 10 kHz, and the sensor Hall effect can cause inaccuracy and difficulty in manufacturing due to fabrication imperfections in the electrical contacts. A GMR-based sensor designed for high magnetic fields could offer advantages over Hall probe limitations. The stability of GMR devices at high temperature can be appreciably greater, with significant GMR up to 200–300 °C. Also, field sensors using GMR can operate at significantly higher frequencies. Despite these benefits, the application of GMR for sensing large magnetic fields is relatively unaddressed, especially in comparison to GMR sensing of low fields.

3. EXPERIMENTAL DETAILS
In this section we mainly overview the experimental results of GMR materials prepared by electrodeposition. GMR was first discovered in 1988 by the group of Albert Fert on Fe/Cr magnetic multilayer and the group of Peter Grunberg on Fe/Cr/Fe trilayer. In both cases the samples were grown using MBE and had [001] orientation of the layers.

The GMR has been observed in many multilayered structures of the form B tB /n∗ (F tF Å/NM tNM Å)/C tC, in which B and C designate a buffer and a capping layer, respectively, F is a magnetic layer and NM is a non-ferromagnetic layer. tB, tF, tNM and tC refers to the thickness of the corresponding layers and n∗ is number of bi-layers. The amplitude of the GMR depends considerably on the pair of F and NM materials and on the thickness of the various layers. The GMR values are calculated from the following formula

\[
\text{GMR(\%)} = \frac{R_H - R_0}{R_0} \times 100
\]

Where, \(R_H\) – resistance in the presence of magnetic field (H) \(R_0\) – resistance in the absence of magnetic field

Techniques for the electrochemical preparation of GMR materials include:

i) Dual bath technique
ii) Single-bath technique

In the dual bath technique, the cathode is transferred between the two different electrolytes which have the metal ion going to be deposited as a multilayer. The idea is to deposit only one metal or alloy form each electrolyte. The cathode should be cleaned before the deposition of each layer in order to avoid the contamination of one electrolyte by the other.

In this technique, the normal rectifier is sufficient for the preparation of multilayer instead of two-wave pulse rectifier. The incorporation of more noble metals on the less noble metal layer will be avoided by using this technique and this one important advantage than the single bath technique. But one major drawback is, there is a possibility of deposit layer surface getting oxidized during the period of transferring the cathode from one electrolyte to another. This may lead to the impurity at the interface of multilayer and suppress the GMR behavior. GMR mainly depends on the interfacial scattering so we should maintain the interface quality as well as sharp which favors high GMR property.

Dual bath technique also requires comparatively complex mechanical apparatus which could limit its applications. Apart from these disadvantages, the dual bath deposition method will be widely used in future because of its ability to deposit two different pure metals or alloys.

The single bath technique is most widely used for the preparation of multilayers due to the simplicity of this technique. All the metals which are going to be deposited as multilayer is present in the same electrolyte so the cathode transfer process can be avoided. At less negative potential, the more noble metals is deposited on the working electrode (say metal A) forming layer A, while at the more negative potential the other metal which is less noble one is deposit and form a layer B. Thus it is possible to deposit metallic superlattices by switching the potentials between the suitable values. Although it is not possible to deposit pure metal in less nobler side because of unavoidable incorporation of more noble metal. For this case, we can tune the potential away form the more noble metal deposit potential to reduce the incorporation. The galvanic exchange process may also be possible when the potential shifts from one to another. This may lead to the rougher interface which is not favored for the good GMR properties.

3.1. Effect of Number of Bilayers
Giant magnetoresistance of multilayers enhances strongly with increase the number of bi-layers. The increase in GMR with rising number of interfaces (increasing overall thickness) might be due to decreasing shunting effect of the metallic
The addition of more bi-layers reduces the total resistance but increases the importance of spin-dependent scattering in the film over spin-independent scattering in the substrate and thus, increases the magnetoresistance. Cyrille et al. explained the increasing the magnitude of GMR with bi-layers number and this is due to the overall increase of coherent interface roughness.

The magnitude of this enhancement in GMR with bi-layer or interface number is greater than that which might be assigned to a shunting effect. The GMR becomes almost double when the number of layers doubled. Whatever the reason it is clear that GMR behaviors are dependent on the number of interfaces. Therefore, it is important to mention the number of bi-layers when GMR effects are reported. For example, Bird and Schlesinger reported 55% GMR in electrodeposited Co/Cu multilayers at 6000 bi-layers. The other groups were not able to achieve 55% GMR for electrodeposited multi-layers. In the light of present data, a 55% GMR for a multilayer consisting of 6000 bi-layers is consistent with GMR effects reported by other groups as their values indicate less than 1% GMR per 100 bi-layers. One the other hand, Weihnacht et al. have accounted 10% GMR in electrodeposited Co (Cu)/Cu multilayers, which consisted of 300 bi-layers. Their results indicate that they have achieved 3.3% GMR per 100 bi-layers which is higher than earlier report.

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### 3.2. Effect of Magnetic Layer Thickness on the GMR

The effect of magnetic layer thickness (Figure 1) on GMR at a fixed non-magnetic layer thickness in electrodeposited multilayer was reported. The results were understood in terms of a gradual morphological transition of the magnetic layer from a granular to a continuous layer pattern as the magnetic layer thickness increases. Dulal et al. reported that the multilayer with the very thin (2 nm) magnetic layer exhibit lower GMR than that of 4 nm. The GMR decreases with further increase in magnetic layer thickness and this is due the fact that 2 nm layer thickness may not be continuous and this may lead to the lower GMR value. Chowdhury et al. reported that the value of GMR increases with $t_{\text{mag}}$, attains a sharp maximum at $t_{\text{mag}} = 0.5$ nm, and then decreases to have a sharp minimum at 0.6 nm, followed by a broad maximum between 1 and 3 nm and decreases thereafter. This variation in GMR with $t_{\text{mag}}$ is unexpected, while the magnetic coupling between layers, which depends on non-magnetic layer thickness $t_{\text{non-mag}}$ is normally a cause of a similar behavior.

The initial change is due to an increase in the amount of ferromagnetic spins in the ferromagnetic layers caused by the ferromagnetic exchange interactions associated with the increase of ferromagnetic layer thickness. The average dimension of magnetic particles and magnetic field efficiency are also increasing as a consequence of increasing $t_{\text{mag}}$. Further observation at higher thicknesses shows a decrease in GMR due to the decrease in the anti-ferromagnetic interactions existing between the two magnetic layers near the non-magnetic layer. An increase of magnetic layer thickness contributes to a different saturation state and its resistance, thus, enhancing GMR.

E.Y. Tsymbal et al. observed the reduction in GMR at large magnetic layer thickness and this is due to the increasing shunting of the current in the inner part of the ferromagnetic layers. The decrease in GMR at low thickness is due to the scattering at the outer boundaries (substrate, buffer layer or capping layer). This scattering significantly affects GMR when the thickness of the ferromagnetic layer becomes smaller than the longer of the two mean-free paths associated with the up- and down-spin electrons.

When the magnetic layer thickness as high as 10 nm or more, the measured MR values are decreased (comparable to alloy system). This fact indicates that at such high magnetic layer thicknesses, the GMR contribution to the total MR from the interfaces is strongly reduced and the AMR contribution from the interior of the magnetic sub-layer dominates clearly. The increasing dominance of the AMR contribution at high magnetic layer thicknesses clearly indicates that the GMR effect in multilayer is mostly connected with spin dependent scattering at the FM/NM interfaces and not in the bulk of the FM layer.

### 3.3. Effect of Non-magnetic Layer Thickness on the GMR

The dependence of MR with non-magnetic layer thickness in multilayers (Figure 2), the MR initially increases with thickness and attains its maximum value for certain $t_{\text{Cu}}$ and decreases for higher thicknesses. The drop of GMR beyond $t_{\text{Cu}} = 1.5$ nm is due to the absence of the sharp low-field GMR contribution in this thickness range. The decrease in GMR is due to the thinnest Cu layers which have pinholes in the layers.

Rafaja et al. observed an increase in the GMR magnitude with increasing thickness of Cu layers in the ED multilayers. Still, the increase in the GMR amplitude was much larger between [Co(4.0 nm)/Cu(2.4 nm)]$_{125}$, [Co(3.3 nm)/Cu(4.0 nm)]$_{91}$ and [Co(3.6 nm)/Cu(9.3 nm)]$_{55}$ multilayers. Still, the increase in the GMR amplitude was much larger between [Co(4.0 nm)/Cu(2.4 nm)]$_{125}$ and [Co(3.3 nm)/Cu(4.0 nm)]$_{91}$ than between...
The thickness of the non-magnetic layer. This is due to the reduction in thicknesses. The GMR values are decreased with increasing the Cu spacer materials is achieved beyond 2 nm average Cu layer thicknesses. The weak or vanishing AF coupling, under the current deposition conditions a complete separation of the magnetic layers by the dipole-dipole interaction between the adjacent magnetic layers. The GMR exhibits oscillations in its magnitude as the thickness of Cu layer was varied. This behavior is observed due to structural imperfections. Pandya et al. attributed this to the higher surface roughness induced in the multilayer by the initial surface roughness of substrate. The magnitude of GMR varies from study to study (probably due to differences in actual layer thickness, preferred texture, substrate material, and other details of the electrodeposition process). The general trend is that (i) a clear GMR effect develops above 1 nm Cu-layer thickness (ii) the GMR magnitude increases monotonically with the Cu-layer thickness. A reduction of Co dissolution and the formation of smoother and flatter interfaces between the Co-Ni-Cu and Cu layers is observed due to structural imperfections. Pandya et al. attributed this to the higher surface roughness induced in the multilayer by the initial surface roughness of substrate. The GMR values are decreased with increasing the thickness of non-magnetic layer. This is due to the reduction of the dipole-dipole interaction between the adjacent magnetic layers.

3.4. Effect of Electrolyte pH on the GMR

The electrolyte pH was found to have a strong effect on the GMR magnitude of electrodeposited materials. Alper et al. has studied the effect of electrolyte pH on the giant magnetoresistance in Co-Ni-Cu/Cu superlattices. Comparison of the magnetoresistances for superlattices grown at high and low pH shows that the GMR is strongly affected by the pH of the electrolyte which is used to deposit the superlattices.

The differences in the GMR values between samples grown at low and high pH as being caused by greater Co dissolution at high pH leading to a greater disruption of the interface structure. Rough interfaces can give rise to ferromagnetic coupling, which will destroy GMR. The lower electrolyte pH leads to a suppression of Co dissolution and the formation of smoother and flatter interfaces between the Co-Ni-Cu and Cu layers. S.M.S. Dulal et al. group reported that the multilayer deposited from the electrolyte pH 3 or less do not exhibit GMR behavior, which is contrary to the work reported by the Alpher et al. It was found that the amount of the magnetic component in the ferromagnetic layer decreased with the lower electrolyte pH.

The influence of the electrolyte pH on GMR magnitude in the Ni-Cu/Cu system is the change of copper content with pH. The copper content in the magnetic layers increases strongly with increasing pH. On the other hand, it is well-known that the Curie point (Tc) of Ni–Cu alloys decreases strongly with increasing Cu content. The lowered Curie temperature implies a reduction of the exchange splitting of the d-band electronic density of states (DOS). This reduction leads to a change in the Fermi level DOS values of the spin-down and spin-up sub-bands. Whereas in pure Ni the Fermi level intersects the spin-down DOS curve only (all the spin-up states lying at lower energies), the effect of strong alloying with Cu is that the Fermi level intersects both d-sub-band DOS curves. The spin asymmetry at the Fermi level which is responsible for spin-dependent transport processes in nanostructures is diminished and, hence, a smaller GMR results for higher Cu contents is observed.

V. Weihnacht et al. reported the magnetoresistance at 8 kOe varied by about 2% when they varied the pH by one unit. Similar results have been published by Alper et al. for Co-Ni-Cu/Cu multilayers, and the dependence of magnetoresistance on bath pH was even more pronounced in their case. The explanation of Alper et al. for the pH effect was that the interface is sharper if the pH is low, but no microscopic background was given. The pH effect on the magnetoresistance lies on the general mechanism of the metal deposition from aqueous baths in the absence of added complexing anions. In this case, the deposition always takes place via an Me intermediate

$$\text{Me}^{2+} + e^- = \text{Me(OH)}_{\text{ads}} \quad [1]$$

and

$$\text{Me(OH)}_{\text{ads}} + e^- + H^+ = \text{Me} + H_2O$$

or

$$\text{Me(OH)}_{\text{ads}} + e^- = \text{Me} + OH^- \quad [2]$$

According to the mechanisms suggested, the higher pH, the higher is the steady-state coverage of the electrode surface with the Me intermediate at a particular reaction rate. In addition, the lifetime of the Me intermediate increases with pH. Both processes 1 and 2 can take place in both the reduction and oxidation direction.
The chemical sharpness of boundary between the Co and Cu layers is expected to depend on the coverage of surface with the intermediates of stepwise deposition process when the high current pulse is switched to the Cu deposition pulse. If the surface coverage with intermediates is small (low pH), the boundary between the layers is sharper than in the case when the surface coverage is high. Hence, the effect of pH, at least partly, can be explained by the stepwise mechanism of both the deposition and the dissolution.

Another aspect of pH effect is the rate of nucleation as a function of pH. When the pH is low, the predominant way of metal deposition is the epitaxial growth along the edges and steps of the crystals with a relatively low nucleation rate and with the retention of the texture developed in the first layers. Nucleation of a new crystal on a defect-free crystal plane requires very high activation energy. However, at high pH the formation of adatoms is less impeded because of the larger size of complexed intermediate, and the complexing agent also serves as a steric hindrance when the metal atom is deposited along a step or an edge. This also leads to a loss in crystal orientation and the texture becomes rather random as the deposit grows. Hence, the low pH results in growth of large crystals and in retention of crystal orientation, which is favored for high GMR.

The OH\(^{-}\) ions may have another effect too. The increased lifetime of the Me\(^{4}\)-containing intermediate leads to a higher coverage of surface with the intermediate. In this sense, the OH\(^{-}\) ion behaves as an adsorbing additive. This additives result in the formation of a deposit with increased structural disorder that leads to a decrease of the GMR.

The materials deposited at different electrolyte pH have the different growth modes. It was found that the copper content of magnetic layers increases with increasing electrolyte pH. The GMR behavior was found to be in granular type alloys which the magnetic regions exhibit superparamagnetism. The estimated lateral size of the SPM regions would allow for a discontinuous multilayer structure. Furthermore, it was found that the films exhibit larger GMR values when they are grown from a low pH electrolyte. It has been shown that structural and compositional effects, both caused by varying pH, can contribute to the observed changes in GMR magnitude with pH.

Pattanaik et al.\(^{191}\) also reported that the pH of electrolyte can have a significant effect on GMR in the case of Co-Cu alloys. The electrolyte pH is increased from 5 to 5.5 and then to 6, the MR of the film increases and reaches a maximum value. Beyond a pH value of 6.0, the MR drastically decreases. The electrolyte pH does affect the magnetoresistive behavior of the electrodeposited films, possibly via the associated changes in the grain size, compositional variation and in the interconnected metal particle network.

3.5. Effect of Electrolyte Temperature on the GMR

Electrolyte temperature has a pronounced effect on GMR of electrodeposited materials. When the electrolyte temperature is increased from 20 to 35 °C, the resulting film show an increase in magnetoresistance, which decreases for the film deposited at a bath temperature of 50 °C. Compositional analysis has revealed that, when increase in bath temperature from 20 to 35 °C, Co concentration in the film decreases from 31% to 26%. Further increase in bath temperature to 50 °C results in a lowering of Co concentration to mere 8%. This implies that suitable control of bath temperature can optimize the Co concentration in the film, and thereby maximize the magnetoresistance.\(^{64,181}\)

The layer thicknesses of the films deposited at 50 °C are expected to be larger\(^{181}\) than the deposits at lower temperature. The layer sizes are nearly an order of magnitude larger, consistent with a lower anti-ferromagnetic coupling effect resulting in a lower GMR. In addition, the average composition of the deposit at 50 °C changed considerably compared to the room-temperature deposits. There is more Cu in the deposit, which would decrease the magnetic moment.

3.6. Effect of Additives in Electrolyte on the GMR

S.K.J. Lenczowski et al.\(^{39}\) studied the effect of adding leveling agent on GMR, thiourea and a polyoxyethylene compound Triton X-100 were used for the study. The addition of additives not only destroys the quality of the multilayer stacking, but also destroys the MR effect, because of the detection of sulphur (thiourea contains sulphur) as impurity for samples grown in electrolytes containing thiourea, because parts of brightener are incorporated at the interfaces as additional defects increasing the rate of spin independent scattering. This is supported by the observation of systematically higher resistivities of samples grown with thiourea. The same influence was found for the other brightener, Triton X-100.

The GMR of multilayer is about three times smaller when the electrolyte contains the additives than in the basic electrolyte.\(^{95}\) Though the planarity of the interfaces has been shown to be better in the presence of saccharin,\(^{193}\) the transport properties are smaller. It is likely that decomposition products of the additives are adsorbed at the interfaces and, even in small amounts; they may have a detrimental effect on the magnetoresistance as already observed in the presence of Triton or thiourea.\(^{39}\) The authors attribute the decrease to less perfect crystalline structures.\(^{179}\)

When the additives are added, the crystalline size will be reduced and this can shift the film behavior to either ferromagnetic (FM) or super-paramagnetic (SPM) at room temperature. Superparamagnetic grains are finer in size as compared to FM grains. For MR to occur, SPM particles require higher magnetic field to align for interaction across the non-magnetic region within the spin diffusion length. Therefore, in such granular samples, the size of the magnetic granules, their morphology and spatial distribution with respect to other are responsible for spin-dependent interface scattering. Probably, a combination of these effects is responsible for the lower MR.\(^{179}\) S.K. Ghosh et al.\(^{211}\) reported the presence of additives leads to FM grain
growth suppresses and results in more SPM grains. Thus, the need to employ free-additive electrolyte to prepare alloys and multilayers for GMR applications. 213

3.7. Effect of Annealing Temperature on the GMR

The effect of annealing on the GMR ratio is due to the following two factors. One is the improvement of the overall crystallographic structure (such as, the disappearance of the lattice defects, the reduction of the structure disorder, the increasing of the packing density, etc.) and reducing the parasitic scattering, which results in decrease of resistivity and an increase in the GMR ratio. Another important factor is the precipitation of additional magnetic particles90 from matrix and growth of all the GMR ratio. Another important factor is the precipitation of additional magnetic particles90 from matrix and growth of all magnetic particles and correspondingly, the interfacial sharpness increases and the spin-flip scattering due to magnetic fluctuation reduces, which favors to increase the GMR ratio. With increasing the annealing temperature (T_a), the size of the magnetic particles increases172,176,194–197 up to an optimum value, which may also contribute to a larger GMR ratio. However the further growth of magnetic particles decreases the GMR ratio. The reasons are as follows: first the magnetic particle would become larger than the mean free path within particles. Second, when the particles are no longer single domain, the interaction of the conduction electron spin with varying the magnetization distribution in the particles produces a state in which the conduction electron channels are mixed176,194

H. Zaman et al.195 reported that the GMR ratio of Co-Cu films increases when the films are annealed, but the GMR values of Co-Ag and Fe-Cu decreases. The reason of increase in MR ratio for Co-Cu films after annealing seems to be the Co particle sizes increases to a appropriate value for exhibiting large GMR ratio, but decrease of MR ratio for Co-Ag and Fe-Cu films after annealing is probably due to the Co particle sizes becoming larger than the optimum particle size required to show highest MR ratio.

Based on J.G. Torres et al.196 results, the Co–Ag films were annealed under mild conditions (150 °C for 30 min). Although a decay of the MR was observed, it was not as sharp as in the earlier annealing process, the GMR value decreasing from 5.75% to 1.04% after the annealing. The numerical analysis indicates a lesser FM contribution when deposits were annealed at lower temperatures. The annealing effect was also observed on the morphology. Irrespective of the thermal treatment conditions, granular morphology was observed. However, coarser grains were detected after the annealing. The increasing atomic diffusion by raising annealing temperature gives rise to the increment in contact area between the particles and subsequent formation of the neck between them. Finally, the coalescence between the particles takes place leading to the formation of bigger particles.

Annealing time plays a crucial role104,174,197–201,211 as it controls the extent of Co-particle segregation or growth. Increasing the annealing time from 10 to 60 min at annealing temperature of 425 °C gives raise in MR ratio. Further increase in annealing time results in subsequent lowering of the MR. But the increase in annealing time from 5 to 15 min at a higher temperature (475 °C) resulted in continuous lowering of MR. The increase in MR with annealing time for the films annealed at 425 °C could be ascribed to the gradual reduction of defects and stress accompanied with segregation of more number of fine Co particles with lesser grain growth. Annealing for prolonged time at this temperature eventually results in growth of segregated Co particles causing MR to decrease. But at the relatively higher annealing temperature of 475 °C, the defects are almost annealed out in a short time and with increasing time, the growth of segregated Co particles continues predominantly and hence, the MR decreases continuously.

V.M. Fedosyuk et al.183 reported the GMR value increases when the alloy is annealed upto 600 °C. GMR is determined by magnetic cluster sizes, their distribution and also by the sharpness of the composition profile in vicinity of the particle-matrix boundary; these factors are strongly dependent upon annealing. The MR is not completely saturated up to 600 °C of annealing temperature. This may be ascribed to the existence of very small magnetic clusters that remain superparamagnetic.187

The decrease in MR value after annealing at high temperature is thought to be due to the disruption of the multilayer structure by dilution of atoms. One part of this dilution is restricted to the interfaces and increases the roughness while another part could result in material from one layer penetrating into the bulk of a neighbouring layer. Dilution of ferromagnetic atoms through the non-magnetic spacer layers can also create a ‘bridge’ between the neighbouring magnetic layers giving ferromagnetic coupling, which would destroy the GMR. Annealing the sample at 600 °C for another 6 h still gave AMR, but the GMR behavior appears after a further 15 h anneal at 600 °C and this revealed transition to granular GMR.144

The GMR ratio increases almost steadily from 9.8% to 23.7% over the range of 27 to 400 °C, followed by a rapid fall beyond this point and this was observed by S.B. Sakrani et al.29 This can be attributed to the recrystallization of Co and Cu occurring during the early state of annealing, and both species become soluble to each other as they reach 400 °C. In this condition, the Co atoms gradually precipitate from the Cu matrix and form Co clusters. When the annealing temperature exceeds 400 °C, Co particles become larger and result in the appearance of ferromagnetic interactions between larger Co particles. The results obtained in this study are similar to those predicted using Monte-Carlo simulation, where an optimum GMR occurred at around 400 °C.202–203

For small particles, the value of GMR is small and increases slowly with applied magnetic field. In this case, GMR arises from non-aligned superparamagnetic or ferromagnetic single domain particles. For larger but still single-domain particles, the GMR increases more rapidly with applied field.204 When the particles size becomes larger, the material behaves progressively as a bulk ferromagnetic with multi-domain particles and magnetic interactions between them and consequently the GMR
decreases. S.K. Ghosh et al. reported the annealing process at high temperature helps in transition from SPM to FM Co-regions locally separated via Cu spacers due to phase separation.

4. RESULTS REPORTED ON ELECTRODEPOSITED FILMS

4.1. Co–Cu/Cu Multilayer Films

Most of the papers reported on GMR of ED multilayer films were dealing with Co–Cu systems only.11,26–27,30,33–34,37–39,48,53,55–56,58,61,66–69,70–123,188,211 The dynamic force for this research effort was the fact that, among physical deposited (PD) materials, the Co/Cu system exhibited the largest GMR being as high as about 50% at room temperature.54,60,124 Unfortunately, the GMR magnitude of electrodeposited (ED) Co–Cu/Cu multilayer films has reached 20% only (except from some rare reports33,111,114 which could not be reproduced by other research groups). Due to the differences in the electrochemical behavior of Co and Cu as well as the immiscibility of the two elements, the multilayer growth process appears to be especially unfavorable for achieving appropriate GMR characteristics in this system by electrodeposition.

Bird and Schlesinger37 electrodeposited Co–Cu/Cu multilayer films from a sulfamate/sulfate bath. The Co layer thickness was kept constant at 3.2 nm and the Cu layer thickness was varied from 0.5 to 8 nm with bilayer repeat numbers between 800 and 6000. The total multilayer thickness was at least several micrometers and in many cases it may have exceeded even 20 μm. The saturation GMR values were displayed for ten different Cu layer thicknesses up to \( t_{Cu} \approx 4.3 \text{ nm} \) and this is due to the expected oscillatory (RKKY-type) behavior as a function of Cu layer thickness. A maximum room temperature GMR of 55%, equal to that reported for sputtered Co/Cu multilayers,54,60,124 was obtained for \( t_{Cu} \approx 0.75 \text{ nm} \), with the second and third GMR maximum being around 2 nm and 3.5 nm, respectively. Unfortunately, because of lack of sufficient details about the preparation conditions and the magnetoresistance measurements, especially the shape of the MR(H) curves, one cannot properly assess the validity of these results, which could not be reproduced in subsequent studies.

L. Piraux et al. reported multilayered Co/Cu nanowire with approximately 7 nm Co rich and 3 nm Cu rich layer with MR 19% at room temperature.165 Co/Cu multilayer is deposited with cobalt layer thickness in the range of 2 to 22 nm exhibits GMR up to 12 to 14%. GMR was found to increase with increase in \( t_{Co} \) in the range 5 to 20 nm. The saturation field values were also found to increase with the increase in Co layer thickness. Comparison of GMR measurement of Co-Cu and Ni-Cu multilayer shows the replacement of Ni by Co on multilayer significantly enhance the GMR effect.33 The Co-Cu system has 8 times greater GMR value than Cu-Ni system.

S.K Ghosh discussed the dissolution of Co-layer during pulse switch over occurs due to both cell capacitance effect and galvanic displacement reaction (so-called electroless process) by Cu\(^{2+}\) ions. These can be minimized by:

(a) Larger the difference in applied potentials, more is the dissolution of the Co-layers due to cell capacitance effect. This kind of destructive process can be prevented by applying the Co-deposition potential very close to the onset of Co-deposition allowing more control over the individual layer thickness and interface roughness.

(b) The Co-layer deposited at lower pH is more porous and undergoes more dissolution compared to layer deposited at higher pH. Upon allowance, the extent of electroless displacement reaction can be many times the individual Co-layer thickness rendering the breakdown of the multilayer structure to granular alloy.

Weinhoos et al.34 reported that the following conditions were to be most favorable for a pronounced GMR effect on Co-Cu multilayer.

i) Large negative current density for Co deposition eg. 106 mA/cm²

ii) Low negative potential for Cu deposition, e.g., −0.25V

iii) Relatively thin Cu layer eg. A nominal thickness of about 2 nm

The GMR results of the some Co-Cu systems are presented in Table 1. Among the all Co-Cu system, the maximum 55% of GMR at 0.45T was reported by K.D. Bird et al. with 6000 bi-layer.

4.2. Ni-Cu/Cu Multilayer Films

Kubota et al.60 reported the GMR of sputtered Ni/Cu multilayers is nearly by an order of magnitude smaller than for corresponding Co/Cu multilayers. This may be explained by the fact that much less efforts were devoted to the study of GMR of Ni-Cu/Cu multi layers by electrodeposition33,40,46,47,65,125–135 in comparison with the available literature on electrodeposited Co–Cu/Cu multilayers.

In Ni-Cu system at room temperature when the applied magnetic field is up to 7 Koe, AMR was formed for alloy deposited by DC plating, where as both GMR and AMR were formed for Ni-Cu/Cu multilayer.46

The GMR value of Ni/Cu multilayer system is 2.5% with current flowing in plane of the multilayer and the applied magnetic filed was 0 to 1.5 T at 50K.65 The GMR behavior of Ni(Cu)/Cu was obtained at \( t_{Ni} \) above 2nm for the constant current/constant potential sources, where galvanostatic and potential control was used for the deposition of magnetic and non-magnetic layer.

The electrolyte pH,46 orientation of the deposits52,127,143 and crystalline sizes97 have influence on the GMR properties.135 The two factors may significantly influence the GMR of electrodeposited multilayer41

i. The position and orientation of the investigated sample section on the cathode surface during deposition.

ii. The deterioration of the particular citrate/sulphate electrolyte used.
<table>
<thead>
<tr>
<th>System</th>
<th>No. of bilayers</th>
<th>MR %</th>
<th>Field strength °C</th>
<th>Temp</th>
<th>Electrolyte CoSO₄, CuSO₄ and X</th>
<th>pH</th>
<th>E&lt;sub&gt;cu&lt;/sub&gt;/E&lt;sub&gt;co&lt;/sub&gt; or I&lt;sub&gt;cu&lt;/sub&gt;/I&lt;sub&gt;co&lt;/sub&gt;</th>
<th>Reference</th>
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<td></td>
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<td>−0.96V/1.42V Vs SSE</td>
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<td>−0.8V/−1.5V Vs</td>
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<td>200</td>
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<tr>
<td>No.</td>
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<td>Current (mA/cm²)</td>
<td>Material</td>
<td>Electrolyte</td>
<td>Time (s)</td>
<td>Potential Range (V)</td>
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<tr>
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<td>Cu/Glass</td>
<td>Na₃C₆H₇O₇, NaCl</td>
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<td>-20mA/cm²</td>
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4. Co-Cu alloy

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<th>Temp (°C)</th>
<th>Current (mA/cm²)</th>
<th>Material</th>
<th>Electrolyte</th>
<th>Time (s)</th>
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<td>&quot;</td>
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<td>30mA cm⁻²</td>
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### Table 2
Consolidated GMR data’s for Cu-Ni system

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<th>System</th>
<th>No. of bilayers</th>
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<th>Electrolyte</th>
<th>pH</th>
<th>E_cu/E_co or I_co/I_co</th>
<th>Reference</th>
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<td>168</td>
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<td>2.5</td>
<td>15 RT Cu/Si</td>
<td>X</td>
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<td>RT Cu</td>
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<td>H₂BO₃, Ni(SO₃NH₂)₂</td>
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<td>-0.2V/-1.7V Vs</td>
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<td>Na₃C₆H₈O₇</td>
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<td>RT Ti</td>
<td></td>
<td>Na₃C₆H₈O₇, NaCl</td>
<td>2mA cm⁻²/</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20mA cm⁻²</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>1700</td>
<td>6</td>
<td>4.2K Cu</td>
<td></td>
<td>Na₃C₆H₈O₇, NaCl</td>
<td>2mA cm⁻²/</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20mA cm⁻²</td>
<td></td>
</tr>
</tbody>
</table>

The GMR results of some Ni-Cu/Cu system are presented in Table 2. In Cu-Ni system, the maximum of 7% GMR was achieved at 0.45T by K.D. Bird et al. when the total number of bi-layer 6000.

#### 4.3. Co–Ni–Cu/Cu Multilayer Films

The GMR study of electrodeposited Co–Ni–Cu/Cu multilayers has been carried out intensively. This broad interest was forced mainly by the fact that the addition of Ni to the magnetic layers of Co/Cu multilayers was found to diminish the GMR, the deleterious exchange reaction and magnetic metal dissolution is less effective in the case of using Ni as magnetic metal when preparing GMR multilayers by electrodeposition as compared to the case of Co. Bakonyi et al. has found a successful compromise between reduced GMR and better control electrochemistry during multilayer preparation.

The Co-Ni-Cu/Cu multilayer had a significantly higher GMR than Co-Cu/Cu multilayer deposited with galvanostatic control. The composition of Ni on Co-Ni-Cu alloy layer have beneficial effect on the GMR, Co-Ni(3.5)-Cu/Cu system has 11% GMR.

The GMR value of Co-Ni-Cu/Cu multilayer increases with the Cu layer thickness in the 1–2.3 nm range. The same observation was observed for Co-Cu/Cu multilayer system.

Co-Ni-Cu/Cu multilayers are electrodeposited on n-GaAs substrates with two different crystallographic orientations. The GMR in multilayer grown on n-GaAs (111) is suppressed for t_cu <30 Å but it is suppressed only for t_cu <20 Å in multilayer grown on n-GaAs (001), probably as consequences of the multilayers grown on GaAs (001) favors the structural defects to cause ferromagnetic coupling. The influence of structural defects on GMR is expected to become less as t_cu increase and this could be explained why the multilayer on GaAs (001) and (111) have approximately same GMR for large t_cu. For t_cu <20 Å, the GMR is suppressed for both substrate orientation. The similar suppression has been observed for Co-Ni-Cu/Cu on GaAs (111), Co-Ni-Cu/Cu on n-Si and Co-Cu/Cu on Cu. For Co-Ni-Cu/Cu electrodeposited on Cu, largest GMR values are measured for t_cu <10 Å. Suggesting that the electrodeposition of multilayer on this substrates are structurally more perfect.

The Co-Cu-Ni/Cu multilayer deposited by flow cell method has the GMR value of approximately 7.2%. If the multilayer have ideally smooth and flat interface, it reduces the ratio of t_cu to electron mean free path in Cu region and it increases the GMR. Co-Cu-Ni/Cu deposited in a cell without forced convections reached 25% when t_cu was reduced from 35-7 Å. However the sample grown in flow cell, the GMR decreased for...
layer structure by suppressing the dissolution of Co. The be explained by the fact that Ni addition improves the multi-systems enhances the GMR, that is, the CoNiCu/Cu multilayers exhibit a GMR larger than CoCu/Cu systems. This result can arise from the fact that the antiferromagnetic coupling between the Ni layers is weaker than the coupling between the Co layers.

The addition of Ni up to 0.2 M to CoCu/Cu multilayer systems enhances the GMR, that is, the CoNiCu/Cu multilayers exhibit a GMR larger than CoCu/Cu systems. This result can be explained by the fact that Ni addition improves the multilayer structure by suppressing the dissolution of Co. The maximum value of the GMR is obtained for CoNiCu/Cu multilayers produced from the electrolyte containing 0.02 M Ni concentration. For the samples with more than 0.2 M Ni ion concentration, the GMR decreases and also the anisotropic magnetoresistance (AMR) effect begins to appear. For high Ni concentrations, even though increasing Ni concentration improves the multilayer structure, the decrease of the GMR effect may be as a result of a high pH value of the electrolyte because in Ni-Co-Cu/Cu multilayers with high Ni concentrations, the GMR is strongly affected by the electrolyte pH. In addition, the Cu content decreases with increasing Ni concentration and as a result of this, the GMR weakens and this was reported by Hua et al. The GMR results of some Co-Ni-Cu systems are presented in Table 3. The maximum 25% of GMR at 0.8 T was achieved for Co-Cu-Ni/Cu ML System by Nabiyoui et al. These multilayers were prepared by using copper substrate from the electrolyte consisting of CoSO4, CuSO4, Ni(SO4)2(NH2)2 and H3BO3.

4.4. Fe–Co–Cu/Cu Multilayer Films

Kakuno et al. reported the GMR of electrodeposited Fe–Co–Cu/Cu multilayers prepared with 20 bilayers on Si(111) substrate covered by copper. Due to the magnetic softness of Co–Fe alloys, the MR(H) curves of electrodeposited Co–Fe–Cu/Cu multilayers saturated in magnetic fields around 0.5 kOe for sufficiently thick (2 to 4 nm) magnetic layers. At low Cu layer thicknesses (below 3 nm), the measured magnetoresistance is so small (0.5–1.5%) that it may arise even from an AMR effect.

4.5. Fe–Ni–Cu/Cu Multilayer Films

Attentborough et al. reported the GMR of electrodeposited Fe–Ni–Cu/Cu multilayers prepared onto textured Cu(1 0 0) and single-crystalline Cu(1 0 0) substrates from a sulfate-based electrolyte. They found the identical sign of LMR and TMR components and it indicates a GMR effect of the order of 1%. Due to the magnetic softness of the magnetic layer consisting predominant by Fe and Ni, there is an extremely sharp MR component saturating in small magnetic fields (well below 1 kOe) which can arise from a GMR term. In addition, one can clearly observe also a component not saturating up to 8 kOe which can certainly be ascribed to a GMR term.

Chassaing et al. deals with the GMR of electrodeposited Fe–Ni–Cu/Cu multilayers prepared in P/P mode. The MR(H) curves measured for a [Fe–Ni–Cu(3 nm)/Cu(1.5 nm)]30 multilayer at 77 K were nearly linear for the LMR and TMR components, both being negative, and did not show a sign of saturation up to the magnetic field applied (2 kOe) where the GMR was about 1%. Chassaing et al. also reported the LMR(H) and TMR(H) curves for a [Fe–Ni–Cu(1.3 nm)/Cu(1.2 nm)]20 multilayer at T = 4.2 K. Both components were again negative and around −3% for magnetic fields around 10 kOe; however, still no saturation of the magnetoresistance was observed. Due to the non-saturating character of the MR(H) curves, it should be concluded that the [Fe–Ni–Cu(3 nm)/Cu(1.5 nm)]30 multilayers studied by Chassaing et al. having GMRPM type behavior. The GMR results of some Fe–Ni–Cu/Cu system presented in Table 4. The Maximum 20% of GMR at 1T were achieved for Co-Ni-Fe-Cu/Cu nano-wire system by Davis et al. These nano-wires were prepared by using AAO template from the electrolyte consisting of CoSO4, FeSO4, NiSO4, CuSO4, Na.K-Tartrate and Sulphamic acid.

4.6. Co–Zn–Cu/Cu Multilayer Films

Peter et al. prepared electrodeposited Co–Zn–Cu/Cu multilayers with several hundred bilayers on mechanically polished Ti sheets both in the G/G and the G/P modes. By measuring the LMR and TMR components of the magnetoresistance, a GMR of about 3% was obtained at 8 kOe for multilayers in which the magnetic layer contained about 6% Zn. However, the GMR of the Co–Zn–Cu/Cu multilayers was only about half of the GMR value obtained for similar samples free of Zn. The decrease in GMR can be attributed to an increase of the resistivity of the magnetic layer due to the codeposition of a third element (i.e., Zn), a change in the electronic structure of the deposit and also to the presence of a Zn-rich layer at the interfaces. This Zn-rich zone produced by the anomalous codeposition results in an interface...
TABLE 3
Consolidated GMR data’s for Co-Ni-Cu system

<table>
<thead>
<tr>
<th>System</th>
<th>No. of bilayers</th>
<th>MR %</th>
<th>Field strength</th>
<th>Temp</th>
<th>Substrate</th>
<th>Electrolyte CoSo₄, CuSo₄ and X X</th>
<th>pH</th>
<th>E&lt;sub&gt;cu&lt;/sub&gt;/E&lt;sub&gt;co&lt;/sub&gt; or I&lt;sub&gt;cu&lt;/sub&gt;/I&lt;sub&gt;co&lt;/sub&gt;</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Co-Ni-Cu/Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>400</td>
<td>14</td>
<td>0.8</td>
<td>RT</td>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>2.</td>
<td>100</td>
<td>18</td>
<td>0.8</td>
<td>RT</td>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
<td>136</td>
</tr>
<tr>
<td>3.</td>
<td>400</td>
<td>10</td>
<td>1</td>
<td>RT</td>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
<td>63</td>
</tr>
<tr>
<td>4.</td>
<td>150</td>
<td>16</td>
<td>0.8</td>
<td>RT</td>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
<td>138</td>
</tr>
<tr>
<td>5.</td>
<td>50</td>
<td>9</td>
<td>—</td>
<td>RT</td>
<td>GaAs</td>
<td></td>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>6.</td>
<td>30</td>
<td>7</td>
<td>0.2</td>
<td>RT</td>
<td>Cr/Au/Glass</td>
<td>H&lt;sub&gt;3&lt;/sub&gt;BO₃, Ni(SO₃NH₂)₂</td>
<td>1.9</td>
<td>—0.5V/−1.8V Vs Pt</td>
<td>50</td>
</tr>
<tr>
<td>7.</td>
<td>200</td>
<td>2.1</td>
<td>0.9</td>
<td>RT</td>
<td>Ti/Au/Quartz</td>
<td>NiSO₄, Na₃C₆H₅O₇</td>
<td>4.5</td>
<td>−0.6V/−1.8V Vs Cu</td>
<td>149</td>
</tr>
<tr>
<td>8.</td>
<td>2000</td>
<td>11</td>
<td>10</td>
<td>RT</td>
<td>Cu</td>
<td>NiSO₄, H₃BO₃, Na-Saccarin, Triton X-100</td>
<td>5.2</td>
<td>—</td>
<td>150</td>
</tr>
<tr>
<td>9.</td>
<td>—</td>
<td>5</td>
<td>0.9</td>
<td>RT</td>
<td>Ti</td>
<td>NiSO₄, H₃BO₃, Ni(SO₄NH₂)₂</td>
<td>3.2</td>
<td>−0.585V Vs SCE/45mA cm⁻²</td>
<td>151</td>
</tr>
<tr>
<td>10.</td>
<td>400</td>
<td>2.5</td>
<td>0.9</td>
<td>RT</td>
<td>Au/Quartz</td>
<td>NiSO₄, Na₃C₆H₅O₇</td>
<td>4.5</td>
<td>−0.6V/−1.8V Vs Cu</td>
<td>28</td>
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<tr>
<td>11.</td>
<td>100</td>
<td>6</td>
<td>0.6</td>
<td>RT</td>
<td>Ni/Glass</td>
<td>NiSO₄</td>
<td>4.5</td>
<td>−0.2V/−1.6V Vs SCE</td>
<td>177</td>
</tr>
<tr>
<td>12.</td>
<td>100</td>
<td>18</td>
<td>0.8</td>
<td>RT</td>
<td>Cu</td>
<td>NiSO₄, Ni(SO₄NH₂)₂</td>
<td>2</td>
<td>−0.15V/−1.8V Vs SCE</td>
<td>136</td>
</tr>
<tr>
<td>13.</td>
<td>100</td>
<td>25</td>
<td>0.8</td>
<td>RT</td>
<td>Cu</td>
<td>NiSO₄, Ni(SO₄NH₂)₂</td>
<td>—</td>
<td>−0.2V/−1.6V Vs SCE</td>
<td>52</td>
</tr>
<tr>
<td>II. Co-Ni-Cu alloy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>0.6</td>
<td>1</td>
<td>1</td>
<td>RT</td>
<td>Si</td>
<td>NiSO₄, H₃BO₃, Na₃C₆H₅O₇</td>
<td>6</td>
<td>−1.075V Vs Ag/Agcl</td>
<td>164</td>
</tr>
<tr>
<td>2.</td>
<td>1.2</td>
<td>1.2</td>
<td></td>
<td>RT</td>
<td>Al</td>
<td>NiSO₄, HSO₃NH₂, NaOH, CoCl₂, H₃BO₃, Na₃C₆H₅O₇</td>
<td>—</td>
<td>5mA cm⁻²</td>
<td>180</td>
</tr>
<tr>
<td>III. Co-Ni/Cu Nano wire</td>
<td>23</td>
<td>1</td>
<td>1</td>
<td>RT</td>
<td>AAO</td>
<td>Ni(SO₃NH₂)₂, H₃BO₃</td>
<td>2.2</td>
<td>−0.2V/−1.0V Vs Ag/Agcl</td>
<td>43</td>
</tr>
<tr>
<td>System</td>
<td>No. of bilayers</td>
<td>MR %</td>
<td>Field strength</td>
<td>Temp</td>
<td>Substrate</td>
<td>Electrolyte</td>
<td>pH</td>
<td>$E_{\text{Cu}}/E_{\text{Fe-Co-Ni-Cu}}$ or $I_{\text{Cu}}/I_{\text{Fe-Co-Ni-Cu}}$</td>
<td>Reference</td>
</tr>
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<td>-----------------</td>
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<td>-----------------</td>
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<td>---------------------------------------------------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Co-Ni-Fe-Cu/Cu</td>
<td>—</td>
<td>20</td>
<td>1 RT</td>
<td>AAO</td>
<td>Na.K-Tartrate, Sulphamic acid</td>
<td>4</td>
<td>$-0.4V/-1.4V$ Vs SCE</td>
<td>181</td>
<td></td>
</tr>
<tr>
<td>Co-Ni-Fe/Cu Nano wire</td>
<td>—</td>
<td>4.5</td>
<td>0.5 RT</td>
<td>AAO</td>
<td>Na.K-Tartrate, H$_3$BO$_3$</td>
<td>4</td>
<td>$-0.2V/-1.5V$ Vs SCE</td>
<td>182</td>
<td></td>
</tr>
<tr>
<td>Fe-Co-Ni-Cu/Cu ML</td>
<td>730</td>
<td>6</td>
<td>5 RT Au/Cu</td>
<td>Na.K-Tartrate, Sulphamic acid, Na-Saccarin, Triton X-100</td>
<td>2.5</td>
<td>3.5mA cm$^{-2}$/70mA cm$^{-2}$</td>
<td>158</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-Co-Ni/Cu</td>
<td>50</td>
<td>9</td>
<td>0.4 RT Si</td>
<td>H$_3$BO$_3$</td>
<td>Na.K-Tartrate, Sulphamic acid</td>
<td>2.8</td>
<td>$-0.6V/-1.9V$ Vs SCE</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td>Fe-Ni-Co-Cu/Cu</td>
<td>730</td>
<td>3</td>
<td>0.6 RT Au/SS</td>
<td>Na.K-Tartrate, Sulphamic acid, Na-Saccarin, Triton X-100</td>
<td>2.8</td>
<td>$-0.35mA cm^{-2}$ $-35mA cm^{-2}$</td>
<td>159</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
with high resistivity, thus lowering the mean free path of electrons and leading to the loss of spin memory while the electrons are transferred from one magnetic layer to the adjacent one.

4.7. Fe–Co–Ni–Cu/Cu Multilayer Films

The best soft magnetic properties (low coercivity and high induction) among the alloys of the iron-group metals with each other are exhibited by some ternary Fe–Co–Ni alloys, the attempts to produce electrodeposited multilayers having all three ferromagnetic metals and to investigate their GMR behavior. Huang and coworkers\textsuperscript{158–159} studied the GMR of electrodeposited Fe–Co–Ni–Cu/Cu multilayers prepared with a bilayer number of 730 in G/G mode. The room-temperature MR(H) curves in most cases had a rapidly varying component apparently saturating around 10 kOe whereas in several cases usually a slowly saturating component also survived up to magnetic fields around 90 kOe. The GMR magnitude was typically as high as 5% in the maximum magnetic field. At 4 K, the central component of the magnetoresistance strongly increased, reaching about 15% at around 10 kOe whereas there remained also a non-saturating component up 90 kOe. The overall behavior of the MR(H) curves indicates a strong superparamagnetic type contribution to the GMR and this speaks for a very disordered or even granular multilayer structure as suggested already by the results of structural studies (small grain size, lack of superlattice reflections, presence of both fcc and bcc phases). This may probably be ascribed to a large extent to the presence of deleterious additives in the bath used. Gong et al.\textsuperscript{160–161} studied the GMR of electrodeposited \([\text{Fe–Co–Ni–Cu/Cu}]_{30}\) multilayer in P/P mode. Gong et al.\textsuperscript{160–161} achieved a room-temperature GMR of 8% in magnetic fields as low as a few hundred Oersteds, by establishing, through the control of the Fe\textsuperscript{2+} concentration in the bath, the Fe-content in the magnetic layer which yielded the largest GMR and smallest coercivity. Nevertheless, the lack of a significant AF exchange coupling between adjacent layers was also concluded from the splitting of the MR (H) curves and the large relative magnetic remanence. This finding agrees well with the analysis given for electrodeposited Co–Cu/Cu multilayer, together with the similar overall evolution of the GMR with layer thicknesses in both multilayer systems. Gong et al.\textsuperscript{160–161} also tried to estimate, from an analysis of the MR (H) behavior and GMR magnitude, the minimum thickness of magnetic and nonmagnetic layers in electrodeposited Fe–Co–Ni–Cu/Cu multilayer which provide a continuous coverage of the previously deposited layer. These minimum layer thicknesses were found to be 1.5 to 2.2 nm for ferromagnetic layer growth on Cu and >3.5 nm for the Cu layer growth on the ferromagnetic layer. The difference of these values was interpreted as implying a different nucleation behavior for the two kinds of layers, a feature also observed for evaporated Co/Cu\textsuperscript{162} and electrodeposited Co–Cu/Cu\textsuperscript{163} multilayer.

4.8. Co–Ag Multilayer Films

The GMR studies of electrodeposited Co–Ag multilayer are comparatively few reports.\textsuperscript{89,89,93,208,209,213} The differences in the crystal structures of Co (hcp) and Ag (fcc) metals accompanied with a large atomic size difference are very unfavorable factors for growing defect-free multilayers. The unsatisfactory structural quality is certainly one of the major reasons for the low GMR. Ueda and coworkers\textsuperscript{89,208} used a sulfate-based electrolyte to prepare Co–Ag multilayers by electrodeposition on glass plate with an evaporated Cu substrate layer. The GMR measured at room temperature in a magnetic field of 21 kOe increased from about 5% to 9% with the Co-rich layer thickness between 0.4 nm and 1.6 nm, respectively. When the GMR was studied as a function of the Ag-rich layer thickness in the range of 0.3 nm to 1.8 nm, a GMR maximum of about 9% was found at about 1.2 nm. This GMR maximum increased to about 13% at 5 K.\textsuperscript{89}

Fedosyuk et al.\textsuperscript{91} reported the electrodeposition of multilayers in Co–Ag system on amorphous Ni-P substrates. The magnetic layer contained some 10 to 15 at.% Ag and the GMR of about 0.7% was measured at room temperature in a magnetic field of about 8 kOe for a multilayer. Garcia-Torres et al.\textsuperscript{49} studied the GMR of electrodeposited Co–Ag/Ag multilayers prepared from quiescent electrolytes containing Co(ClO\textsubscript{4})\textsubscript{2}, AgClO\textsubscript{4} and NaClO\textsubscript{4} on Si(1 0 0)/Cr(5 nm)/Cu(20 nm) substrate. The pH of the electrolytes was between 2.0 and 2.5, depending on the concentration of the metal salts. The number of bilayer repeats was varied in a manner as to maintain a nearly constant total multilayer thickness of about 800 nm. The room-temperature magnetoresistance measurements of electrodeposited Co–Ag/Ag multilayers with layer thicknesses ranging from 2 to 10 nm yielded MR(H) curves with splitting and not saturating up to 8 kOe, the maximum field applied. The GMR exhibited a shallow maximum around 3 nm to 4 nm. The temperature dependence of the GMR for a Co–Ag(3 nm)/Ag(6 nm) multilayer exhibited very similar features as reported for electrodeposited Co–Cu/Cu alloys. The GMR achieved was about 1% at room temperature and 2.5% at 24 K.

In a most recent work by Garcia-Torres et al.,\textsuperscript{196} he studied the temperature dependence of the magnetoresistance of Co–Ag granular films prepared by electrochemical techniques. A continuous increase in the magnetoresistance was observed while temperature was decreased to 20 K, so that GMR values are double at low temperature. The MR(H) curves measured at different temperatures were characterized by a non-saturating behavior. The decomposition of such curves into its superparamagnetic and ferromagnetic contributions revealed that the superparamagnetic contribution was retained even at cryogenic temperatures. This fact was explained by the dipolar interaction among the superparamagnetic particles. A sharp decrease in the GMR values was observed at all the annealing conditions tested.
which was attributed to a pronounced increase on the size of the cobalt granules. Such increment led to observe a more saturating behavior on the MR(H). On the other hand, the ferromagnetic contribution increased from less than 10% up to around 50% after the annealing.

4.9. Co–Au/Au Multilayer Films

Ueda and coworkers deposited Co$_{95}$Au$_{5}$/Au multilayers from the electrolyte containing CoSO$_4$, KAu(CN)$_2$, Na$_3$-citrate and NaCl on glass plate with an evaporated Cu substrate layer. The GMR values exhibited a maximum as a function of both the Co–Au and the Au layer thickness in the range 0.5 to 2.5 nm. The maximum GMR values varied between 2% and 5%, being definitely smaller by about a factor of two in comparison with the electrodeposited Co–Ag/Ag multilayers. In lack of structural characterization, the strong similarity of the magnetic and magnetoresistance data to the electrodeposited Co–Ag/Ag–Co and the electrodeposited Co–Au/Au multilayers might suggest that the GMR originates also for the latter system from a granular magnetic behavior instead of a clear multilayer GMR effect.

4.10. Co–Ru/Ru Multilayer Films

Electrodepositions of Co$_{98.5}$Ru$_{1.5}$/Ru multilayers were prepared on polished Ti substrates by using an electrolyte at 50°C which contained CoSO$_4$, RuCl$_3$, Na$_2$SO$_4$ and HCOOH. The nominal layer thicknesses were varied between 0.2 and 1.2 nm for Ru and 3.5 and 7 nm for Co–Ru. The layered structure could be observed from cross-sectional and partly high-resolution TEM. From the room-temperature longitudinal and transverse MR(H) curves, it was found that the AMR behavior at low Ru thicknesses gradually transformed into a GMR type behavior with the increase of the Ru layer thickness. At sufficiently large Ru layer thickness, both the LMR and TMR components were negative, indicating a clear GMR effect in spite of the small GMR magnitude.

5. CONCLUSION

In this review, an attempt was made to give an overview on the current status of electrodeposited multilayer films exhibiting GMR. Nearly 160 reports have been published on electrodeposition GMR multilayer films since the first paper in this field. These reported results were critically evaluated for each multilayer system accessible for preparation by electrodeposition. The following conclusions can be drawn from the above reviews:

1. Giant magnetoresistance of the multilayer increases strongly with increase the number of bi-layers.
2. The multilayer with the very thin magnetic layer display lower GMR. When the magnetic layer thickness increases, the GMR values are also increases since the layer thickness reach to optimum value. Further increase in magnetic layer thickness, leads to reduction in the GMR values.
3. The MR initially increases with thickness and attains its maximum value for certain f$_{Cu}$ and shrink for higher thicknesses. The oscillation behaviors of GMR with thickness of non-magnetic layer reports are also available.
4. The electrolyte pH does affect the magnetoresistance of the electrodeposited films, possibly via the associated changes in grain size, compositional variation and in the interconnected metal particle network.
5. The electrolyte temperature affects the magnetoresistive behavior of the electrodeposited films, possibly via the associated changes in compositional variation. This implies that suitable control of bath temperature can optimize the Co concentration in the film, and thereby maximize the magnetoresistance.
6. The GMR of multilayer is smaller when the electrolyte contains additives than in the basic electrolyte. The additives are adsorbed at the interfaces and, it may have a detrimental effect on the giant magnetoresistance. The crystalline size will also reduces by adding additives and this can shift to either ferromagnetic or super-paramagnetic in nature at room temperature. The size of the magnetic granules, their morphology and spatial distribution with respect to other are responsible for spin-dependent interface scattering. Perhaps, a combination of these effects is responsible for the lower MR.
7. The GMR values were dependent on the annealing process. When rising the annealing temperature, the size of the magnetic particles increases up to an optimum value, this may also contribute to a larger GMR ratio. However the further growth of magnetic particles decreases the GMR ratio.
8. Among the electrodeposited alloys and multilayer system, the Co–Cu multilayer system exhibits the higher GMR values than the other systems.
9. Reproducibility is still a problem: whereas the basic GMR features appear to be roughly the same when comparing the results of various authors for a given system, some outstanding results reported definitely are not reproduced by other researchers. It has also been the experience that due to some still unknown details the GMR magnitude cannot always be reproduced under identical preparation conditions.

Finally, the authors hope that this review will kick off new research to improve the GMR properties of electrodeposited alloys and multilayer films and this can promote their application in the future.

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