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ELECTROCHEMICAL SYNTHESIS OF MAGNETIC MATERIALS FOR MAGNETIC RECORDING AND MEMS APPLICATIONS

A Dissertation

Presented to

the Faculty of the Department of Electrical and Computer Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in Electrical Engineering

by

Jinnie George

May 2012

DEDICATION

I would like to dedicate this dissertation to my mummy and daddy whose unending love for me and faith that I was always doing the right thing gave me courage at all times. Thanks for being the most awesome parents!!!

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ABSTRACT

With the increase in the areal density for magnetic recording disks, the bits are becoming smaller so that more bits can be accommodated in a given area of disk. However, there is a certain limit up to which the bits can be made smaller until it reaches the superparamagnetic limit, where bits become thermally unstable. In order for bits to be stable, high coercivity media is needed and the flux coming out from the writer head should be high enough to switch the high coercivity medium bits. Hence Cobalt Iron (Co₃₇Fe₆₃) alloys having the highest magnetic flux density of 2.4 T are used for this purpose. Sulfur containing additives like saccharin are incorporated in the CoFe electrodeposition bath to provide desirable properties like low stress, low coercivity and fine grain size to the deposit. The effect of saccharin incorporation during electrodeposition process on the properties of CoFe films is studied in this research.

In-situ stress measurements were performed to determine the reduction in stress with increasing saccharin concentrations in the bath and an analytical model was developed to explain phenomenological dependence of the maximum stress level in CoFe films as a function of saccharin concentration in the bath. However, saccharin incorporation in CoFe bath lowers the corrosion resistance of CoFe films. The corrosion potential dependence on the sulfur incorporation mechanisms in CoFe films was studied via an analytical model based on the mixed potential theory.

As bit size decreases, new magnetic sensors that provide high sensitivity and increased magnetoresistance ratio have to be developed. As a part of this research, the novel magnetic field sensors were fabricated based on electrodeposited CoFe nanocontacts and demonstrated magnetoresistance ratio as high as 3000%. The CoFe nanocontacts, ~70 nm in diameter, embedded in insulating Al₂O₃ layer which separates two plane parallel ferromagnetic layers represent the basic magnetic field sensor design. The magnetoresistance curves of these sensors displayed properties characteristic of both tunneling and ballistic transport of electrons by domain wall scattering. Hence, low temperature measurements were performed to understand the transport mechanisms of electrons in these electrodeposited magnetic nanocontacts.

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CHAPTER 1

INTRODUCTION

Thin films are widely used in the fabrication of MEMS devices and in magnetic recording technology. As the critical dimensions of the devices scale down to nanometers, controlling the corrosion and stress in thin films play a significant role for device reliability and performance. One of the most popular applications of thin films is in the fabrication of magnetic recording heads. Continuous efforts are being taken to increase the areal density of hard disks and thus controlling the magnetic, corrosion and mechanical properties of these films are critical. In this chapter, we will review the factors or parameters that are crucial in synthesizing thin films for reliable use in magnetic recording and MEMS devices.

1.1. Stress in thin films-Consequences

As scaling of devices advances, feature size becomes smaller and thus the fabrication techniques need to be more precise. Controlling the stress in such nanodevices is of crucial importance. Stress in thin films can be divided into thermal stress and residual stresses [1]. Thermal stress is the one which is caused due to difference in thermal expansion coefficients between films and substrate and residual stresses are the stress developed during the deposition process [2]. Residual stress in thin films causes various detrimental effects such as delamination and blistering in case of compression and film cracking, peeling in case of tension [3]. Figure 1-1 below shows the image of a thin film fabricated by electrochemical deposition technique. We clearly see the cracks in

this film and one of the aims of the project is modifying or synthesizing the bath design by means of additives to control stress in electrodeposited CoFe films



Figure 1-1. Image of cracks in the thin film leading to delamination [4].

1.2. Corrosion in magnetic heads-Consequences

Corrosion in simple terms is the degradation of a material due to chemical reaction with its environment [5]. Corrosion in magnetic heads is a very serious issue, because when the structures are scaled down to nanometer range, reliability is a major concern. When trying to scale down the devices, more emphasis is made on materials that provide better magnetic properties as compared to their chemical properties. $Co_{37}Fe_{63}$ alloys that have been used in fabrication of magnetic recording heads possess a high magnetic flux density but are not very resistant to corrosion as compared to Permalloy (Ni₈₀Fe₂₀) which are chemically more stable. Figure1-2 shows a CoFe corroded pole tip structure.



Figure 1-2. The dark region in figure represents a void due to the corrosion of the electrodeposited CoFe pole tip.

Also, the materials used for the fabrication of magnetic recording heads need to have low stress, low coercivity and a smooth and controlled finish. Sulfur- containing additives like saccharin are incorporated in the electrodeposition bath to provide these properties. However, it was found that addition of saccharin deteriorated the corrosion properties of the electroplated magnetic alloys [6-8]. Thus, most of the times, designing a magnetic alloy is a compromise between obtaining low coercivity, low stress and low magnetostriction on one side and high corrosion resistance on the other.

1.3. Need for better magnetic field sensors

One of the current research trends in the data storage industry is aimed at increasing the areal density of hard drives. In order to achieve this, the bit size needs to be decreased so that more bits can be accommodated per unit length and hence magnetic read heads have to scale down their critical dimensions to below 30nm. At this scale, the SNR (Signal to noise ratio) needs to be very high, and the current read head sensors based on Giant Magnetoresistance (GMR) and Tunneling Magnetoresistance (TMR) does not have sufficient sensitivity. This has motivated the research for a new sensor design to provide high sensitivity and magnetoresistance ratio. This need for higher magnetoresistance (MR) ratio has prompted a shift from the early inductive read heads to the currently used TMR heads with a MR ratio of about 50% as shown in Figure 1-3.



Figure 1-3. Increase in areal density (log scale) between 1985 and 2005. The inserts show schematics of the recording heads at each time point, and list the material used in the reading operation. Courtesy of International Business Machines Corporation.

Garcia et al. [9-11] pioneered a new type of magnetic sensor that demonstrated a MR ratio as high as 700% and was based on the phenomenon called Ballistic Magnetoresistance. This phenomenon is explained by electron scattering from magnetic domain walls. However, there have been reports of MR ratio of about 3000% [12] in Ni nanocontacts which cannot be explained by the above theory. There has been speculation that this unexpectedly large MR ratio could be the effect of a thin magnetic dead layer

during the electrodeposition process[13]. These discoveries and progress have prompted a rapid interest in the research for magnetic field sensors based on electrodeposited nanocontacts.

1.4. Electrodeposited Materials for Magnetic Recording and MEMS Applications

Nowadays, electrodeposition is recognized as mature deposition method for fabrication of magnetic thin film heads [14,15] as well as in microelectronics and MEMS technologies [6,16]. The most recent developments suggest that the electrodeposition becomes an attractive fabrication process for many emerging fields of nanotechnology. The fabrication of the writing pole in magnetic recording heads has been the most important manufacturing step where the electrodeposition has gained its fame as cost effective, reliable, and high throughput operation (Figure 1-4A). Over the years, the development of the magnetic reader technologies, recording media and the geometry of the magnetic recording process have posted many challenges that electrodeposition had to meet in order to stay at par with other alternative deposition methods. The common requirement for alloys used in magnetic pole fabrication is that they need to demonstrate low coercivity (softness), low magnetostriction ($\lambda \approx 0$) and relatively high magnetic moment. The electrodeposition process of these alloys has to be scalable with high throughput manufacturing with minimum efforts in process control and reproducibility. Also, the bath chemistry has to be stable over the time and compatible with other materials and processes used in through mask fabrication.

Initially, the electrodeposited magnetic alloy used for magnetic recording and MEMS application was $Ni_{81}Fe_{19}$ – Permalloy (inductive read heads) with saturation

magnetic flux density $B_s = 1$ T [17]. Further development of electrodeposited soft magnetic alloys proceeded with the introduction of Ni₄₅Fe₅₅ which had 70% higher B_s values (magnetoresistive read heads), and ternary CoFeNi alloys with Co content larger than Ni and Fe and B_s ranging between 1.6 T and 2.2 T [10-12] (GMR read heads). However, the recent introduction of the perpendicular magnetic recording geometry and magnetic media with significantly larger anisotropy and coercivities require soft magnetic alloys with the highest magnetic moment possible. In an attempt to counter this challenge, academic and industrial researchers have demonstrated the electrodeposited soft 2.4 T CoFe films and nanostructures with composition in the range of Co₃₀₋₅₀Fe₇₀₋₅₀ [18].



Figure 1-4. (A) Schematics of perpendicular magnetic recording head with most important parts indicated, (B) 2.4 T CoFe magnetic pole test structure, (C) The FIB cross-section of the ≈ 50 nm wide 2.4 T CoFe magnetic pole test structure [19].

The continued drive to increase the areal density of magnetic recording has driven lithography and other related processes involved in fabrication of magnetic heads to the nanoscale level. Hence, electrodeposition is facing the task of delivering a controlled process to produce soft, high magnetic moment alloys into photoresist features with high aspect ratio and sub-100 nm dimensions (Figure 1-4B). For future devices with >1Tbit·in⁻² recording density it is expected that pole width will scale down to ~ 40 nm in order to meet the magnetic head design requirements, (Figure 1-4C). At this scale, the successful electrodeposition process has to be designed by comprehensively considering all transport limitations through the diffusion layer, the electrochemical interface stability with respect to Fe(OH)₃ precipitation, and the optimum conditions for additive adsorption. These criteria require that the phenomenon that determine the properties of the soft magnetic alloys, for example, the additive and Fe(OH)₃ incorporation, crystal structure, effects of substrate or size effects are to be examined in more details. This will allow the parameters for electrodepositing magnetic alloys and nanostructures with optimum properties and performance.

1.5. Organization of the Dissertation

This dissertation is organized in the following chapters:

Chapter 1 is the introduction which discusses the motivation behind the project. It explains the consequences of stress in thin films and effect of corrosion in magnetic recording heads. A brief outline of the progress in MR head sensor is presented along with the need for their improvement.

Chapter 2 provides a general summary of the kinetics of alloy electrodeposition and in particular about electrodeposition of Soft High Magnetic Moment (SHMM) alloys. The mixed potential theory is explained to understand the kinetics of corrosion process and rise of the corrosion potential phenomenon. Additionally, the origin of stress in thin films is explained along with the source of oxide incorporation during electrodeposition of CoFe alloys.

Chapter 3 describes the various types of magnetoresistance and also explains the theory behind resistance dependence on temperature and how IV curves at low temperature help determine transport mechanism of the magnetic sensors.

Chapter 4 describes the principle behind the various experimental equipments used. Additionally, this chapter also focuses on the experimental procedure for the corrosion, in-situ stress and magnetoresistance measurements.

Chapter 5 gives a detailed description about the fabrication of magnetic sensors based on electrodeposited CoFe nanocontacts.

Chapter 6 explains the results for corrosion measurements of electrodeposited CoFe alloy from solutions with different concentrations of saccharin. This section also discusses the in-situ stress measurements of electrodeposited CoFe alloys and an analytical model. The latter part of this chapter explains the results for magnetoresistance measurements of magnetic field sensors/nanocontacts.

Chapter 7 is the conclusion and also lists some of the possible future work in this area that can aid a better understanding of these magnetic sensors.

This dissertation resulted in the publication of 4 peer reviewed publications and 3 publications in stage as listed below.

 Nanostructure and oxide phase distribution in Co₃₆₋₄₀Fe₆₄₋₆₀ electrodeposited films for magnetic field sensors, S. Elhalawaty, R. W. Carpenter, J. George, and S. R. Brankovic, Journal of Applied Physics, 111, 07A330 (2012).

- Oxygen Incorporation into Electrodeposited CoFe Films: Consequences for Structure and Magnetic Properties, S. Elhalawaty, R. W. Carpenter, J. George, and S. R. Brankovic, Journal of the Electrochemical Society, 158 (11) D641-D646 (2011).
- Critical Parameters of Solution Design for Electrodeposition of 2.4 T CoFe Alloys, S.
 R. Brankovic, J. George, S. -E. Bae and D. Litvinov, ECS Transactions, 16 (45) 75-87 (2009).
- Sulfur and Saccharin Incorporation into Electrodeposited CoFe Alloys: Consequences for Magnetic and Corrosion Properties, Journal of the Electrochemical Society, Jinnie George, James Rantschler, Sang-Eun Bae, Dmitri Litvinov, and Stanko R. Brankovic, 155 (9) D589-D594 (2008).
- Stress Control in Electrodeposited CoFe Films Experimental Study and Analytical Model, Stanko R. Brankovic, Burhanuddin Kagajwala, Jinnie George, Shruti Santanagopalan, Goran Majkic, Gerry Stafford and Paul Ruchhoeft. (Accepted to Electrochimica Acta).

CHAPTER 2

FUNDAMENTALS

2.1. Electrodeposition

Electrodeposition has been a promising deposition technique for many of the emerging applications of nanotechnology. One of the prime advantages of electrodeposition is that there are many parameters like pH, temperature, deposit thickness, and current density which can be adjusted to obtain suitable deposits. Over the years, there have been many studies reporting binary [20-25] and ternary magnetic alloys [26] produced by electrodeposition. In recent years, electrodeposition has also been used to grow multilayered metallic thin films and nano-structures for use in magnetic recording, MEMS and microelectronic applications.

2.1.1. Kinetics of electrodeposition

The thermodynamic equilibrium potential of an electrode surface in contact with it's ions in the solution is defined by the *Nernst* equation,

$$E_{M^{n+}/M} = E^{o} + \frac{RT}{2.303 \cdot nF} \log[a_{M^{n+}}].$$
(2-1)

Here E^0 represents the equilibrium potential of the electrode surface at standard conditions (P°=101 kPa, T°=298 K), R is the universal gas constant, F is Faraday's constant, and T is the absolute temperature. The term $a_{M^{n+}}$ represents the activity of the metal ions in solution with n being their oxidation state. In dilute solutions, the ion activity is approximated by their concentration, *i.e.* $a_{Mn+} \approx C_{Mn+}$ [27]. The above
expression suggests that equilibrium potential of metal electrode shifts by ≈ 0.059 V/n in negative direction if the metal ion concentration in the solution is decreased by a factor of 10. This means that adjusting the concentration of the corresponding metal ions in the solution can effectively change the equilibrium potential. If the applied potential (*E*) to the metal electrode is more negative than $E_{M^{n+}/M}$, ($\eta = E - E_{M^{n+}/M} < 0$) the electrode is at overpotential conditions, and η is called overpotential. Under this condition, the metal electrodeposition occurs, ($M^{n+} + ne^- \rightarrow M$).

During this process, the corresponding cathodic current density is given by the Butler Volmer equation as

$$j(<0) = j_0 \cdot \left(\exp \frac{\alpha_a F}{RT} \eta_s - \exp \frac{-\alpha_c F}{RT} \eta_s \right).$$
(2-2)

In the above expression, j_0 is the exchange current density, α_a and α_c are the anodic and cathodic current density and η is the overpotential. For $\eta_s <<0$, this equation is simplified to give the Tafel equation as

$$j(<0) = -j_0 \cdot \exp \frac{-\alpha_c F}{RT} \eta_s.$$
(2-3)

2.1.2. Electrodeposition of alloys

The generalized thermodynamic condition for electrodeposition of A_pB_{1-p} binary alloy is defined as [28]:

$$E_A + \eta_A = E_B + \eta_B. \tag{2-4}$$

Here, E_i (i = A, B) is the equilibrium potential of the metal-component i in the alloy A_pB_{1-p} defined by modified *Nernst* expression:

$$E_i = E_i^0 + \frac{RT}{2.303nF} \log \left[\frac{a_i^{n+1}}{a_i^{alloy}}\right].$$
(2-5)

The activity of the metal in the alloy is always less than 1 which yields different values of the equilibrium potential for different components in the alloy as compared to the corresponding elemental bulk metal electrode. According to Equation (2-4), in order to form an AB alloy, the applied potential to the electrode surface has to be such, that both components of the alloy are at overpotential conditions with respect to the equilibrium potentials of constituents in the alloy (Equation (2-5)). In practice, the term *overpotential co-deposition* (OPCD) is related to electrodeposition of alloys in the potential range where the applied potential is such that both components of the alloy are at overpotentials of the alloy are at overpotentials of the alloy are at overpotential conditions with respect to the equilibrium potential is such that both components of the alloy are at overpotential conditions with respect to the equilibrium potentials of the resulting composition of the alloy are at overpotential conditions with respect to the equilibrium potentials of the electrodeposited alloys is controlled by the combination of several effects: 1) kinetics of the electrodeposition of each component itself, 2) transport limitations, 3) conditions at the electrochemical interface, and 4) mutual interaction of adsorbed intermediates.

The condition for OPCD of CoFe alloy is shown in Figure 2-1. In order to obtain desired composition of $Co_{50}Fe_{50}$ alloy, the concentrations of Co and Fe ions in the solution have to be appropriately adjusted together with the potential or current at which the alloy deposition occurs. Typical approach towards the solution and deposition potential (or current) design involves the experiments where the concentration of more noble metal, Co, is such that $C_{Co^{2+}} < C_{Fe^{2+}}$, so that Co deposition occurs under mixed control for wide range of potentials. The Fe²⁺ concentration is typically taken to be such that Fe deposition occurs under kinetic control for the chosen potential (current). The

deposition potential (or current) is then varied through different runs until the satisfactory composition of the CoFe alloy is achieved.



Figure 2-1. Potential region for CoFe alloy OPCD [29].

The successful application of electrodeposited Soft High Magnetic Moment (SHMM) alloys in the fabrication of magnetic recording heads is dependent on properties like high magnetic flux density, low coercivity, low magnetostriction, and low stress. The electrodeposition of SHMM alloys occur exhibit the phenomenon of anomalous codeposition, where the less noble metal deposits preferentially as compared to the more noble metal. Thus in case of CoFe alloy, Fe which is less noble as compared to Co would deposit preferentially and is represented mathematically as

$$\frac{at\%Fe}{at\%Co} > \frac{[Fe^{2+}]}{[Co^{2+}]}.$$
(2-6)

Equation 2-6 indicates that the ratio of atomic percentages of Fe to Co in ED CoFe deposit is more as compared to the Fe^{2+} and Co^{2+} concentration in the solution. Thus the proper design of the SHMM alloys requires a thorough understanding of the various parameters influencing the electrodeposition process.

2.1.3. Additive effect on electrodeposited SHMM alloys

Many of the properties demonstrated by SHMM alloys useful in magnetic recording and MEMS application are due to the addition of sulfur containing additives like saccharin in the electrodeposition bath. Incorporation of these additives in the electrodeposition bath provides favorable properties like low coercivity, uniform leveling, smooth finish and low stress.



Figure 2-2. SEM of the CoFe deposit surface produced during galvanostatic deposition, j = 4 mA.cm⁻². (A) No saccharin in solution, RMS of the 5 μ m x 5 μ m area is 27 nm, (B) with 10⁻³ mol saccharine in solution, RMS of the 5 μ m x 5 μ m area is 7 nm.

In Figure2-2, on left side(A) is the SEM image of CoFe deposit electrodeposited without saccharin while the figure 2-2(B) shows the surface morphology of CoFe electrodeposited with saccharin. A small addition of saccharin causes the roughness to decrease by a factor of 4 times.

During electrodeposition process, saccharin adsorbs on the metal surface forming some type of condensed phase [18]. The density and the coverage of the adsorbed saccharin phase is dependent on the potential of electrode surface and the concentration of saccharin in the plating solution [30]. Useful information about saccharine adsorption and coverage can be deduced from the impedance spectroscopy [31]. Figure 2-3 shows how the coverage of saccharin and the double layer capacitance varies as a function of the deposition potential for different saccharin concentrations. It is observed that maximum saccharin coverage is obtained at a potential of -1.3 V vs Ag/AgCl.



Figure 2-3. The double layer capacitance vs. potential dependence extracted from the impedance measurements for CoNiFe surface [18]. The corresponding coverage of saccharine is calculated from double layer capacitance measurements are shown as dashed line [18]. The additive coverage is estimated using following expression $[31]:_{\theta = \frac{C_{dl} - C_{dl-min}}{C_{dl-max} - C_{dl-min}}}$.

The two main mechanisms by which additives incorporate into deposit are adsorption-electroreduction and physical incorporation [15,18]. The first mechanism represents the chemical route responsible for incorporating of molecular fragments and formation of intermetallic compounds like metal sulfides, while the second one represents the incorporation of entire molecules of additives. The additive incorporation (saccharin) in the deposit is a function of their concentration in the plating solution and is described within the scope of following analytical model [7];

$$R = K_1 \cdot \frac{b \cdot C_{sac}}{1 + b \cdot C_{sac}} + K_2 \cdot \frac{b \cdot C_{sac}}{(1 + b \cdot C_{sac})^2}.$$
(2-7)

In the above expression, R represents the additive incorporation rate in flux units [mol·m⁻²s⁻¹] and C_{sac} stands for concentration of the additive saccharin in the plating solution [mol·m⁻³]. The first term on the right side represents the additive incorporation *via* electroreduction mechanism and the second term represents the additive incorporation by physical entrapment of the entire molecules. The K_1 and K_2 are the electroreduction and incorporation rate constants expressed in [mol·m⁻²s⁻¹] units and *b* is the additive adsorption constant [m³·mol⁻¹]. The above model from Equation 2-7 can predict the concentration of the different interstitials/inclusions in electrodeposited films originating from incorporated additives and could be used to correlate the additive incorporation effect with the deposit properties [7].



Figure 2-4. (A) Model fit (eq.(2-7) to experimental data on sulfur incorporation rate and atomic % in electrodeposited CoFe alloys. (B) Correlation between the decrease in coercivity of CoFe alloys and incorporation rate of sulfur coming saccharine [7].

Figure 2-4 (A) shows the model fit to the experimentally determined S content in CoFe deposit, and Figure 2-4 (B) shows the correlation between the decrease of CoFe alloy coercivity and incorporation rate of sulfur/saccharin in the deposit. The constants K_1 , K_2 , and b Equation (2-7) are obtained from the fit of the model to data in image (A) and then used to calculate the incorporation rate of sulfur for particular concentration of saccharin in the bath from which CoFe films are deposited. Coercivities of CoFe films electrodeposited with different concentrations of saccharin are correlated to sulfur incorporation rate yielding a linear regression.

2.2. Oxide/Hydroxide incorporation in CoFe films

2.2.1. Source of oxygen incorporation in electrodeposited CoFe films

During the electrodeposition of CoFe alloys, there is a reduction of Co^{2+} and Fe^{2+} ions at the cathode. However, along with the metal deposition, a simultaneous hydrogen

codeposition also occurs. This gives rise to a depletion of H^+ ions in the solution/electrode interface, leading to a local increase of pH. This is one of the main reasons for inclusion of metal hydroxides in the deposit. The formation of of Fe³⁺ and Fe(OH)₃ is attributed to the oxygen form air which oxidizes Fe²⁺ into Fe³⁺ represented as

$$Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + H_2O.$$
 (2-8)

If the concentrations of Fe³⁺ and OH⁻ in the bulk solution is such that the solubility product of Fe(OH)₃ (K_p) is exceeded, i.e. $C_{\infty}^{Fe^{3+}} > \frac{K_p}{\left(C_{\infty}^{OH^-}\right)^3}$, then hydroxide precipitation

in the bulk solution occurs.

Using this relation and expressing C_{∞}^{OH-} in terms of ionic product of water, the equilibrium or limiting concentration of Fe³⁺ can be expressed as [32]

$$C^*_{\infty,Fe^{3+}} = \frac{K_p}{(K_w)^3} \times 10^{-3pH}$$
 (2-9)

The net flux of hydrogen ions towards the electrode surface through the diffusion layer (J_{H+}) is expressed as $J_{H^+} = \frac{j(1-\gamma)}{F}$, where j(current density) and γ (current efficiency) are the parameters of the deposition process. The concentration gradient of hydrogen ions through the diffusion layer is expressed as

$$\frac{\delta C}{\delta x} = \frac{C_{\infty}^{H+} - C_i^{H+}}{\delta}.$$
(2-10)

Using Fick's law of diffusion, and using the same procedure as used for determining $C^*_{\infty,Fe^{3+}}$, the concentration of the hydrogen ions at the electrode/solution

interface, C_i^{H+} and correspondingly the equilibrium concentration of Fe³⁺ at solution/electrode interface $C_{i Fe^{3+}}^*$ is expressed as

$$C_{i,Fe^{3+}}^{*} = \frac{K_{p}}{(K_{w})^{3}} \cdot \left(10^{-pH} - \frac{(1-\gamma)j}{F} \cdot \frac{\delta}{D_{H^{+}}}\right)^{3}.$$
(2-11)

Since $\frac{(1-\gamma)j}{F} \cdot \frac{\delta}{D_{H^+}}$ is always > 0, Fe(OH)₃ precipitation at the solution/electrode

interface is possible even if these conditions are not met in the bulk of the solution.

2.2.2. Heterogeneous nucleation of iron (III) hydroxide at electrode/solution

interface and Fe(OH)₃ incorporation model.

The driving force for nucleation of $Fe(OH)_3$ from solution is the difference in chemical potential of $Fe(OH)_3$ dissolved in solution and its counterpart in the crystalline(solid) phase

 $\frac{\Delta \mu_{s/c}}{RT} = \frac{\Delta G_{s/c}}{kT} = \ln S$, where S is the term called saturation and in this case is defined as

$$S = \frac{C_i^{Fe^{3+}}}{C_{i}^{*}_{Fe^{3+}}}.$$
(2-12)

Where $C_i^{Fe^{3+}}$ is the concentration of Fe³⁺ ions at the solution/electrode interface while $C_{i,Fe^{3+}}^*$ is the concentration of Fe³⁺ ions at the solution/electrode interface at which precipitation occurs. The concentration of Fe³⁺ at the bulk is related to Fe³⁺ concentration

at interface by introducing a parameter p such that $C_i^{Fe^{3+}} = pC_{\infty}^{Fe^{3+}}$, where 0<p<1. The rate of Fe³⁺ electroreduction in terms of the Fe³⁺ concentration at interface is expressed as

$$R_{Fe^{3+},ER} = k_{ER} \cdot C_{i,Fe^{3+}}.$$
 (2-13)

The total rate of Fe^{3+} consumption at the electrode/solution interface is the sum of Fe^{3+} electroreduction rate and $\text{Fe}(\text{OH})_3$ incorporation rate expressed as

$$R_{Fe^{3+},T} = R_{Fe^{3+},ER} + R_{Fe(OH)_3}.$$
(2-14)

Also, the total rate of Fe^{3+} consumption is equal to the flux of Fe^{3+} through the diffusion layer expressed as

$$J_{Fe^{3+}} = \frac{D_{Fe^{3+}}}{\delta} \left(C_{\infty, Fe^{3+}} - C_{i, Fe^{3+}} \right)$$
(2-15)

For the range of Fe³⁺ concentrations that were used for analysis, it can be safely assumed that

 $R_{Fe^{3+},ER} >> R_{Fe(OH)_3}$. Thus, combining the above equations, we obtain [32]

$$\frac{C_{i,Fe^{3+}}}{C_{\infty,Fe^{3+}}} \approx \frac{\frac{D_{Fe^{3+}}}{\delta}}{\frac{D_{Fe^{3+}}}{\delta} + k_{ER}} = p.$$
(2-16)

CoFe electrodeposition occur at significantly lower negative potential (~ -1.19 V vs SHE) as compared to the equilibrium potential for Fe^{2+}/Fe^{3+} redox couple ($\Delta E^{0}_{Fe^{2+}/Fe^{3+}}$ =+0.771 V vs SHE). Hence, there is certain depletion of Fe³⁺ at interface due to reduction of Fe³⁺ to Fe²⁺.

 $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$. Thus, 0 .

On the growing CoFe surface, as soon as the stable nucleus of $Fe(OH)_3$ is formed, it immediately becomes an active nucleation center for arriving Co, Fe adatoms and is instantaneously buried into deposit. The $Fe(OH)_3$ incorporation rate in units of flux(mol/cm²s) is defined as

$$R_{Fe(OH)_{3}} = \langle N_{Fe(OH)_{3}} \rangle J_{Fe(OH)_{3}}.$$
(2-17)

where $\langle N_{Fe(OH)_3} \rangle$ represents average size of stable nuclei and is defined as the ratio of the number of molecules in stable nuclei, n_{molec} and Avagadro's constant, N_A, $\langle N_{Fe(OH)_3} \rangle = \frac{n_{molec}}{N_A}$. $J_{Fe(OH)_3}$ is Fe(OH)₃ nucleation rate.

Assuming the hemispherical nucleus shape, the nucleation rate can be expressed as

$$J_{Fe(OH)_3} = \Xi \cdot \exp\left(-\frac{16\pi\sigma_{hyd}^3 \cdot \Omega^2}{3k^3 T^3 \cdot (\ln S)^2} \cdot \phi\right).$$
(2-18)

Here, the terms σ_{hyd} , k and Ω represent the Fe(OH)₃ crystal/solution interfacial free energy (J/cm²), Boltzman's constant (J/K) and the volume of the Fe(OH)₃ molecule (cm³) and Ξ is the nucleation rate constant.

Thus the total Fe(OH)₃ incorporation rate is given as [32]

$$R_{Fe(OH)_{3}} = \frac{n_{molec}}{N_{A}} \cdot \Xi \exp\left(-\frac{16\pi\sigma^{3}_{hyd} \cdot \Omega^{2}}{3k^{3}T^{3} \cdot \left(\ln\left(pC_{\infty,Fe^{3+}}/(K_{p}/K_{w})^{3}.(10^{-pH} - (1-\gamma)j/F \cdot (\delta/D_{H^{+}})^{3}))\right)^{2}\phi\right)\right).$$
(2-19)

2.2.3. Effect of hydroxide incorporation on magnetic properties-Analytical model

The total B_s is sum of the magnetic flux density of different phases in film. Hence, if an electrodeposited film contains separate phases each with magnetic moment and volume fraction in the film α_i (%), the measured Bs is given as $B_s = \sum_{i=1}^n \alpha_i \cdot B_{s,i}$. At room temperature, Fe(OH)₃ is nonmagnetic and hence the dilution in the electrodeposited CoFe film due to Fe(OH)₃ incorporation can be expressed as $B_{s,film} = B_{s,0} \cdot (1 - \alpha_{Fe(OH)3})$, where $\alpha_{Fe(OH)3}$ is the volume fraction of Fe(OH)₃ in electrodeposited films [32]. Thus the formula for B_s is given as

$$B_{s,film} = 2.41[T]. \times \left(1 - \frac{A \cdot \exp\left(-B \cdot \left(\ln\left(C \cdot C_{\infty}^{Fe^{3+}}\right)\right)^{-2}\right)}{1.63 \times 10^{-8} \, cm \, s^{-1} + A \cdot \exp\left(-B \cdot \left(\ln\left(C \cdot C_{\infty}^{Fe^{3+}}\right)\right)^{-2}\right)} \right).$$
(2-20)

Here, A, B and C are adjustable constants defined as

$$A = \frac{\upsilon_{m,Fe(OH)_3} . n_{molec} \Xi}{N_A}, \ B = \frac{16\pi\sigma_{hyd}^3 \Omega^2}{3k^3 T^3} \text{ and } C = \frac{p}{C_{i,Fe3+}^*}.$$

Where $v_{m,Fe(OH)_3}$ is the molar volume of Fe(OH)₃ phase. The model fit to the experimental data is as shown in Figure 2-5.



Figure 2-5. B_s values of electrodeposited CoFe films from solutions with different concentrations of Fe³⁺[32]. Line is the fit of Equation 2-20 to the experimental data.

From Figure 2-5, we observe that CoFe alloys electrodeposited from solutions with very low Fe³⁺, i.e. [Fe³⁺]< 0.00125, yields alloys with B_s ~2.41 T. Thus, in this range, there is no appreciable effect of Fe³⁺ on the magnetic flux density of CoFe alloys. However, with further increase in Fe³⁺ concentration, the magnetic flux density decreases and for solutions with $C_{\infty}^{Fe^{3+}}$ between 0.00134 and 0.0014 mol L⁻¹ the B_s values are slightly lower, decreasing from $\approx 2.41 T$ to $\approx 2.32 T$. The saturation magnetic flux density of Co₄₀₋₄₄Fe₆₀₋₅₆ films is decreasing steeply as the $C_{\infty}^{Fe^{3+}}$ in plating solution is further increased. The solution with $C_{\infty}^{Fe^{3+}} = 0.0020$ mol L⁻¹ yields the Co₄₀₋₄₄Fe₆₀₋₅₆ films which show $\approx 44\%$ decrease in B_s ($\approx 1.35 T$). However, the increase of $C_{\infty}^{Fe^{3+}}$ above the 0.002 mol L⁻¹ does not seem to contribute to the further decrease of the magnetic moment. The *Bs* decreases insignificantly as the Fe³⁺ concentration in the bulk increases further from 0.002 mol L⁻¹ to~0.00275 mol L⁻¹. It is clear that the dilution in magentic flux density depends on the equilibrium concentration of Fe³⁺ at solution/electrode interface $C_{i,Fe^{3+}}^*$ at which precipitation starts. From Equation 2-11, it is observed that the value of $C_{i,Fe^{3+}}^*$ is dependent on parameters like pH, current efficiency (γ), current density(j) and diffusion layer thickness (δ). Thus, it would be interesting to observe how these process parameters affect the magnetic properties of electrodeposited CoFe alloys.

2.2.4. Effect of process parameters on the magnetic flux density.

A. Effect of pH



B. Effect of current density (j)



Figure 2-6. (A) Effect of pH on B_s vs $C_{\infty}^{Fe_{3+}}$ dependence. (B) B_s vs $C_{\infty}^{Fe_{3+}}$ dependence for the films obtained from the solution with different current densities [32].

As shown in Figure 2-6(A), with the increase in pH, the equilibrium concentration of Fe³⁺ decreases to lower concentrations and thus the B_s starts decreasing at much lower values. This is because $C_i^{Fe^{3+}}$ is an exponential function of pH. This illustrates the importance of accurate pH measurement in experiments.

The increase of current density of 20% results in shift of $C_{i,Fe^{3+}}^*$ to ~ 18% smaller value, i.e. the Fe(OH)₃ incorporation and onset of B_s decrease starts for 18% smaller value.

The same conclusion is applied to the effect of diffusion layer thickness δ and current efficiency (γ). Thus the careful optimization of all the deposition parameters is necessary to produce nanostructures with desired magnetic moment.

2.3. Corrosion Potential and Mixed Potential Theory

In corrosion systems, degradation of material occurs via anodic oxidation. The cathodic and anodic sites occupy approximately the same area when the metal is freely corroding. The cathodic reaction is often the reduction of molecular oxygen or hydrogen ions [27]. A schematic of a corrosion cell can be represented as shown in Figure 2-7.



Figure 2-7. Schematic of a corrosion cell. Regions labeled A represent anodic areas where metal is dissolving while C represents cathodic areas. Vectors represent lines of current flow [27].

At pH 7, the concentration of H^+ ions is 10^{-7} M. The concentration of oxygen dissolved in solution from air can be assumed to be approximately 10^{-4} M [33]. Hence the dominant cathodic reaction in this case is the reduction of oxygen which is given as

$$O_2 + 2H_2O + 4e^- \to 4OH^-.$$
 (2-21)

On the other hand, the anodic reaction is the metal dissolution reaction and is given as

$$M \to M^{n+} + ne^{-}, n = 2.$$
 (2-22)

Combining Equation 2-22 and 2-23, the total corrosion reaction in this system is expressed as

$$2 M + O_2 + 2 H_2 O \to 4 OH^- + 2 M^{2+}.$$
(2-23)

The oxygen reduction is a diffusion limited reaction and hence the current density associated with this process is expressed as

$$j_L = \frac{nFD}{\delta} C_b. \tag{2-24}$$

where δ is the diffusion layer thickness, D is the diffusivity of oxygen in water [cm²/s], n is the number of electrons involved in the reaction, and C_b is the bulk (Oxygen) concentration. Thus, from equation the limiting current density (j_L) increases with an increase in the diffusivity, the bulk concentration or with a decrease in δ [5].

The anodic current density associated with metal dissolution (MD) current is given by Tafel's equation as

$$j = j_0 \exp\left(\frac{\alpha F}{RT}\eta\right). \tag{2-25}$$

where α is the charge transfer coefficient, F is the Faraday's constant, T is the temperature (300 K), R is the universal gas constant and η is the overpotential which is the deviation from the reversible potential expressed as $\eta = E_{corr} \cdot E_0$. E₀ is the reversible potential and can be optimized as the electro-oxidation potential. At the

corroding electrode at $E=E_{corr}$, the current in external circuit is zero and thus following condition applies.

$$j_{anodic} = j_{cathodic}$$
(2-26)

Hence, equating Equations 2-24 and 2-25, we obtain an expression for the corrosion potential given as

$$E_{corr} = E_0 + \frac{RT}{\alpha F} \left(\left(\ln \frac{4FD}{\delta} C_{O_2} \right) - \ln(j_0) \right)$$
(2-27)

The relation between E_{corr} and j_{corr} is expressed in Figure 2-8 and it also shows the variation in i_{corr} with the increase in rotation rate (ω) and exchange current density (j_0).



Figure 2-8. Current density as a function of the corrosion potential (E_{corr}) for different rotation rates (ω).

As expressed in Equation 2-23 with higher agitation (ω), there is a decrease in the diffusion layer thickness δ which leads to an increase in j_L. Also, from Figure 2-8, it is observed that increase in agitation causes the corrosion potential to shift to anodic

direction (less negative values) and corrosion current (i_{corr}) to higher values. Conversely, if the corrosion current increases as shown by the shift in red line, the corrosion potential shifts to cathodic direction (more negative values), thus also indicating an increase in the corrosion rate due to an increase in i_0 .

2.4. Stress in Thin Films

Thin films are of utmost importance in device fabrication. They range from a couple of monolayers to a couple of microns in thickness, depending on the type of application. In general, there are three modes of thin film growth based on the affinity between the atoms of the substrate and the atoms of the depositing film. If the adatoms have a greater tendency to attach to the substrate rather than other adatoms, the growth occurs by a layer by layer mechanism known as Frank-van-der Merwe or FM mode. If the adatoms have a greater tendency to attach to each other, then the growth is promoted by the island formation, known as Volmer-Weber or VW growth mode. A growth which prefers both the modes is called as Strankski-Krastanov growth mode or SK growth mode.

According to literature, polycrystalline films are formed by the VW growth mode [2,34,35]. In the case of VW growth mode; initially the material deposits on the substrates and forms clusters or islands, these islands then grow and interact with each other. As the amount of deposited material increases, the islands come into contact and establish an aerial continuity [36]. The polycrystalline films are generally formed through the sequence of steps as illustrated in Figure 2-9.



Figure 2-9. Nucleation, growth and coalescence to form a continuous film [37].

The stress vs thickness curve can be easily understood with the help of a schematic as shown in Figure 2-10. The stress vs thickness curve for most polycrystalline films follow a CTC behavior (compressive tensile and compressive) behavior. The three regions are explained below schematically and explained in detail.



Figure 2-10. In-situ stress as a function of the film thickness during deposition

Region1: Initial compressive region

During the initial nucleation step, as shown in Figure 2-10, the stress in the film is compressive in nature. This initial region of compressive stress can be explained by a combination of two effects. Firstly, the surface stress acting on an unconstrained island induces an equilibrium lattice spacing which is different from its bulk counterpart [38]. The islands start growing with a lattice spacing less than the bulk lattice spacing. This difference results in the force acting on the surface resulting in the stress exerted on the substrate.

To maintain equilibrium there has to be internal stress acting within the crystallite. This stress can also be assumed as a Laplace pressure ΔP , being exerted on a finite size body.

If f is the surface stress and R is the radius of the crystallite, then the equilibrium stress is given by

$$\Delta P = \sigma = \frac{-2f}{R}.$$
(2-28)

Secondly, there is a maximum critical island size above which the island becomes impinged and cannot affect the in-plane lattice spacing. Now, when the film deposits by Volmer-Weber growth mode, initially small nuclei form on the substrate. As the deposition continues, more and more adatoms attach to these nuclei and the crystal grows in size. As long as the radius of the crystallite is less than a critical radius, the nucleation does not affect the internal stress, since it is unconstrained and the lattice constant within the nucleus and the substrate is not the same.

At a critical radius R_{ld} , called as the lock down radius, the nucleus is said to be locked down and the growth of the nucleus is no longer able to change the in-plane lattice spacing, because in order to change the in plane lattice, a large number of bonds have to be disrupted at the island-substrate interface. This lock down radius depends on the bond strength between the particular substrate and the island atoms [30].

When the radius of the crystallite exceeds the lock down radius, the strain due to the mismatch is prevented from relaxing. This strain produces traction at the film substrate interface, which causes the substrate to bend due to the stress given by

$$\sigma = \frac{2f}{R_{ld}} \left(\frac{R_{ld}}{R} - 1 \right). \tag{2-29}$$

As the radius of the cluster grows larger, the ratio $R_{ld}/R \rightarrow 0$. Thus, the compressive peak reaches a maximum value at $\frac{-2f}{R_{ld}}$.

Region2: Tensile stress

As the growth flux increases, the island size grows and they begin to coalesce into each other. The tensile peak has been attributed to this island coalescence phenomenon [2]. Earlier work of Hoffman [35] was based on the theory that when the islands are in the close proximity, they stretch out towards each other to form a grain boundary to reduce the surface energy. Hoffman considered these islands as isotropic cubes and estimated the gap between adjacent crystallites. Using the gap between the islands, biaxial modulus of the film and the crystal size he estimated the stress in the film.

Later, Nix and Clemens [3] imagined the boundary of the crystallites to be elliptical in shape; he postulated that they continue to grow until they touch the adjacent islands, which then eliminated the need for the calculation of the gap between the crystallites. They assume that the crystallites immediately snap on as the grain boundary energy is less than the energy of the free surface. This process was known as the "zipping effect". Thus the driving force for the coalescence is the minimization of energy. The tensile stress is then a function of the average grain boundary formed and the crystal size. The level of the tensile stress is governed by island size at impingement. This generally depends on the process parameters such as growth flux, substrate temperature, and surface diffusivity [35].

Freund and Chason [39] designed a model based on the Hertz contact theory for the prediction of the magnitude of the maximum tensile stress. They assumed that all islands before coalescence are hemispherical in shape and of the same radius *R*, arranged in an array with center to center spacing of 2R. These islands are initially formed with radii smaller than R, and gradually grow to achieve the radii R. Once the islands^{**} radii have reached R, contact areas due to cohesion form spontaneously between the islands as shown in the figure.



Figure 2-11. (a) Islands on the substrate, (b) The tensile peak is due to the zipping of the islands during their coalescence [39].

As a result of this cohesive contact, a tensile force is generated due to the traction between the film-substrate interfaces. This force induces a volume average tensile stress is the film and is given by

$$\sigma_{avg} = \frac{4\Delta\gamma}{R} \Delta\gamma = \gamma_s - 0.5\gamma_{GB}, \qquad (2-30)$$

where $\Delta \gamma$ is the driving force for the grain zipping process. It represents the positive difference between the surface energy of impinging CoFe grains, γ_s and $\frac{1}{2}$ of the energy of the newly formed grain boundary, γ_{GB} . This estimate of the tensile peak should be viewed as the upper bound of the tensile stress, because here the tendency of the substrate to deform the island due to the interfacial constrain has been ignored. Also, the assumption that island coalescence occur throughout the film simultaneously is not true

and the adatoms diffusing at the grain boundaries to relieve the stress has not been accounted for [40].

Region3: Coalesence region

After the tensile peak has been achieved the state of the stress in the continuous film depends on the type of film being deposited. The stress thickness dependence varies depending on the material type. Type1 materials are high melting point material or low adatom mobility refractory metals like Ti, W, and Fe. In this case, the tensile stress increases with increasing film thickness which is a characteristic of columnar grain growth. On the other hand, for the Type 2 material which is a low melting point material with high adatom mobility material and FCC structure like Ni, the resulting film stress is comparatively smaller and tensile, as well as compressive [41].

The atoms of the film having a low mobility, attach to the strained crystal at the point of their arrival, allowing the crystal to grow in a strained state. On the other hand, the atoms with a high mobility are comparatively freer to move and attach at the preferable sites, which results in relaxation, causing a reduction in the stress. The preferable sites for the adatoms to incorporate are the grain boundaries. As the formation of grain boundaries results in elastically strained crystallites, these extra atoms can deposit at the grain boundaries, causing a reduction in the stress. This can be imagined as the formation of misfit dislocation (i.e., extra planes of atoms to relieve the misfit strain) in the case of epitaxial films [3].

CHAPTER 3

MAGNETORESISTANCE

3.1. Magnetoresistance

Magnetoresistance in simple terms is the change in resistance on application of a magnetic field and is expressed as

$$\frac{\Delta R}{R} = \frac{R(H) - R(0)}{R(0)}.$$
(3-1)

This is the definition suggested by Lord Kelvin. Magnetoresistance in metals can be divided into ordinary magnetoresistance (OMR), Anisotropic magnetoresistance (AMR), giant magnetoresistance (GMR) and Tunneling Magnetoresistance (TMR).

3.1.1. Anisotropic Magnetoresistance (AMR)

In AMR phenomenon, the magnetoresistance in the ferromagnet is expected to have a spontaneous contribution that depends on the on the orientation of magnetization [42] and is commonly observed in bulk ferromagnets [43].

In Figure 3-1, the curve ρ II represents the situation where the orientation of magnetization is parallel to the electric current I whereas ρ^{\perp} is the one where orientation of magnetization is perpendicular to the electric current.



Figure 3-1. Resistivity of Ni_{0.9942}Co_{0.0058} at 4.2 K[44].

The 3d metals exhibit maximum resistivity when current is parallel to the magnetization direction ρ and minimum resistivity when current is perpendicular to the magnetization direction, ρ^{\perp} .

$$AMR = \frac{\rho II - \rho \perp}{\rho \perp}.$$
(3-2)

At intermediate angles, the resistivity is given by

$$\rho(\theta) = \rho \perp + (\rho I I - \rho \perp) \cos^2 \theta. \tag{3-3}$$

The phenomenon of spin orbit coupling can be used to explain the origin of magnetoresistance. If the field and magnetization are oriented transverse to the current, then the electronic orbits are in the plane of the current, and there is a small cross-section for scattering, giving a low resistance state. Conversely for fields applied parallel to the current, the electronic orbits are oriented perpendicular to the current, and the cross-section for scattering is increased, giving a high resistance state.

3.1.2. Giant Magnetoresistance (GMR)

The phenomenon of Giant Magnetoresistance was first discovered by Baibich et al [45] in 1988 in FeCr multilayers. The Fe layers were antiferromagnetically coupled through the Cr layers and the antiferromagnetic coupling varies with the Cr layer thickness. The resistivity in this case is larger as compared to the case when the applied magnetic field aligns the magnetic moment.



Figure 3-2. (A) Magnetoresistance of three Fe/Cr superlattices at 4.2 K [45].(B) Transverse saturation magnetoresistance as a function of Cr layer thickness at 4.2 K [46]

As observed in Figure3-2, the magnetoresistance value is the largest when the Cr thickness is 9 A°, which is the thickness when the antiferromagnetic coupling is strongest. Parkin observed that the interlayer magnetic exchange coupling and magnetoresistance varies as a function of the Cr interlayer thickness [46]. This oscillatory dependence of the magnetoresistance as a function of the Cr thickness is explained by a phenomenon called as the RKKY coupling [46].

Electrodeposited GMR films

Significant research has also been done on electrodeposited GMR films of ferromagnetic/non-magnetic metal superlattices in which individual layers can be as thin as 10 A° or less. There are two main methods of producing electrodeposited GMR structure namely dual bath method and single bath method [47]. In the dual bath method, the substrate is transferred between two separate electrolytes, one for metal A and one for metal B. An alternative to this technique is the single bath method where ions of all the metals to be deposited are present in one electrolyte and the composition is modulated by controlling the deposition parameter, namely current for galvanostatic deposition and potential for potentiostatic deposition. The GMR in granular alloy is a function of the size and spacing between particles. Research in the area of electrodeposited GMR is encouraged because the electrodeposition technique has the advantage of depositing material in high confined spaces which would be inaccessible to techniques like sputtering or Molecular beam epitaxy (MBE) [47].

There are two major configurations for GMR structures shown in Figure 3-3, namely the CIP (Current in plane) and CPP (Current perpendicular to plane)

configuration. The most important difference between these two configurations is that in the CPP geometry, the conduction electrons cross all layers and interfaces, whereas in CIP geometry, the region sampled depends on the spin-dependent mean free paths for elastic scattering [48].



Figure 3-3. Schematic diagram of the principle two geometries of GMR (left) CIP and (right) CPP configuration [49].

In the CIP configuration, the net current direction is in the plane of the layers and it is important that the mean free path of the electrons is longer than the sum of the layer thicknesses so that the electrons sample the different layers. In the second picture, the net current direction is perpendicular to the layers and the critical length scale becomes the spin-diffusion length. In order to experience spin dependent scattering, the electron is supposed to travel or scatter through all layers. This means that in case of the CIP geometry, the effective mean free length should be longer than the thickness of the multilayer. On the other hand, in CPP configuration, where the leads are connected at the top and bottom, the critical length scale is the spin diffusion length which is related to the mean free path as $l_{sf} \approx \sqrt{\frac{\nu F \tau_{sf} \lambda}{3}}$, where v_F is the Fermi velocity, τ_{sf} is the spin-flip relaxation time and λ the electron mean free path.

3.1.3. Tunneling Magnetoresistance (TMR)

Tunneling magnetoresistance is a phenomenon observed in magnetic tunnel junctions (MTJ) that consists of two ferromagnetic electrodes separated by a thin insulating barrier. The insulating barrier is supposed to be extremely thin so that electrons can tunnel through the barrier if the bias voltage is applied between the ferromagnetic electrodes. The tunneling current depends on the relative orientations of the magnetization of the two layers, which can be changed by an applied magnetic field [50]. TMR is due to the spin dependent tunneling and the probability for an electron to tunnel through the barrier depends on the Fermi wavevector. Tunneling magnetoresistance is due to spin dependent tunneling which is the imbalance in current due to spin up and spin down electrons from ferromagnet tunneling through a barrier which in turn is dependent on the fermi wavevector. Thus the implied method to increase the MR ratio would be to use materials where the polarization (P) would be increased. In ferromagnetic metals electronic bands are exchange split, which implies different Fermi wavevectors for the up- and down-spin electrons and consequently a tunneling probability that depends on spin. Another class of materials was half-metallic ferromagnet like CrO₂ that exhibited conducting states at Fermi level (E_t) for majority-spin electrons and semiconductor gap for minority-spin electrons, resulting in a high degree of polarization. Thus the electronic structure of the ferromagnetic electrodes, the insulating layer and the

Ferromagnet/insulator interface are crucial factors in the understanding the phenomenon of TMR [50]. Julliere et al [51] was one of the pioneers in this area and expressed tunneling magnetoresistance ratio in terms of the ferromagnetic layers as $TMR=P_1P_2$ where P_1 and P_2 are the of spin polarizations of the two magnetic layers. This however, is a very simple and general equation which does not consider the structure of the` barrier layer. However, over the years many experiments have been performed and it is seen that TMR depends not only on the ferromagnetic layers, but it is also the structural quality of the barrier layer which helps in improving the spin polarization (P). Progress in the interface layer, namely fabrication processes to produce a pinhole free insulator layer and also the ferromagnet/interface layer resulted in enhancement of the polarization value.

One characteristic feature of the magnetic tunnel junctions is that the TMR decreases with increasing temperature. Shang [52] explained that one of the reasons for the decrease of TMR with increasing temperature is due to the spin wave excitations which increase with increasing temperature and cause the decrease of spin polarization P and the interface magnetization follows Bloch's law, i.e the $T^{3/2}$ law, i.e. $M(T)=M(0)(1-\alpha T^{3/2})$. Vedyayev et al [53] showed that one of the other reasons for this behavior is the sin flip scattering by magnetic impurities in the barrier. The number of electrons contributing to spin flip scattering increases with increasing temperature.

Tunneling Granular Magnetoresistance

In granular magnetic films, the conductivity is due to the tunneling through insulating barrier between ferromagnetic grains [54]. There are various kinds of materials exhibiting tunneling granular magnetoresistance. One of them is granular cermets, where nanometer-sized magnetic metallic particles are embedded in an insulating matrix. In these systems, electrical resistivity (ρ) as a function of temperature (T) at room temperature shows a sharp increase from conducting to insulator [55]. There is an anomalous increase of magnetoresistance observed in insulating granular films at low temperatures and this was suggested to be due to the Coulumb blockade effect which takes place in these Ferromagnet/granular/Ferromagnet junction [56].

3.1.4. Ballistic Magnetoresistance (BMR)

Recent research in the development of data storage industry has focused on the development of new materials and technology for the magnetic heads. With the scaling of bits, there is a greater need for sensors with high signal to noise ratio. This implies researching for new materials and design for sensors with higher MR ratio as compared to the current GMR and TMR devices. Garcia et al reported ballistic magnetoresistance phenomenon in magnetic nanoconstrictions and nanocontacts which demonstrated huge MR values upto 3000% [9]. However, there have also been various controversies surrounding the BMR observance, with some researchers notably Mallet et al [57] who conducted experiments on electrodeposited Ni junctions and concluded that many of the existing geometries were merely a case of the magnetostriction effect assumed to be magnetoresistance change. Another such experiment was performed by Svedberg [58] where he analyzed resistance changes on electrodeposited nanocontacts of Fe, Co and Ni in a classical T configuration geometry as shown in Figure 3-4. In this configuration, if the area between the two electrodes is composed of tiny particles of Fe, they would not only be attracted to each other by the dipole-dipole force among the particles, but there is

also a torque acting on the particles when the magnetic field is swept during the MR measurements given as

$$T_{mag} = \mu_0 H \times M = \mu_0 H M \sin \upsilon, \tag{3-4}$$

where v is the angle between magnetization direction and field direction.



Figure 3-4. (a) Electrodes A and B are used to from a nanocontact, while electrode C is the reference electrode for the potentiostat. D acts as the bulk source of metal during the plating process. (b)The Fe deposit C is shown in the center, partially covering the two electrodes A and B in the areas that have not been protected with an insulator [58].

In the vicinity of the coercive field, the net magnetic moment is zero, which means the resistivity is high. Here, the particles have already begun to align in the new field. This realignment causes a break in the electrically conductive path and resistivity increases. However, when the field is further increased, the particles realign which causes a drop in the resistivity. Thus, this is one configuration in which the mechanical reorientation of the magnetic nanoparticles mimic the BMR effect [58]. Egelhoff et al[59] investigated both thin film and nanowire geometries for both mechanically formed and electrodeposited nanocontacts. Studies were carried out on mechanical contacts between ferromagnetic wires and electrodeposited nanocontact between Ni wires and

ferromagnetic nanocontacts electrodeposited on Cu wires, nanocontacts ED between ferromagnetic films anchored on wafers and nanocontacts formed by focused ion beam etching and via pinholes. Many of the above geometries showed changes in resistance which was due to the magnetostrictive, magnetostatic and magnetomechanical effects which merely mimicked the BMR effect. Thus, the accurate description of BMR is still surrounded by controversies, but the most accepted model is the based on the spin dependent electron scattering from the Magnetic Domain Wall (MDW) existing in the confined geometry of the nanocontact [60-62] (Figure 3-5). According to this model, if the size of the nanocontact containing MDW is the same or less than the spin flip mean free path of the electrons (d, $w \sim \lambda_f$, Figure 3-5), then the electrons passing through the MDW will encounter a high reflection probability due to the poor matching of the Fermi surfaces of spin-up and spin-down electrons. This would manifest as a higher resistance state than in the case when both electrodes have the parallel magnetizations pointing along the same direction (non-existing MDW in nanocontact). The best results reporting "BMR" ($\Delta R/R_{min} = 300\% - 3000\%$) involve nanocontacts created by electrodeposition [9]. These experiments, however, did not offer a clear manufacturing approach that can be further extended towards device design. In addition, the poor characterizations of the nanocontact size and structure have left room for extensive discussions regarding the true origin of magnetoresistance.



Figure 3-5. Geometry of the nanocontacts between two ferromagnetic electrodes. Mutual orientations of the electrodes' magnetizations are 180° (left) and 90° (right). The insets show the schematics of the high resistance state related to nano-confinement of the MDW.

One of the key issues related to experiments reporting the electrodeposited nanocontacts with large magnetoresistance is the possibility of oxide presence in the nanocontact. This idea has been introduced as "magnetic dead layer" and the implications of this effect was considered experimentally and theoretically [63]. The support for oxide presence comes from the fact that all challenging results are reported from experiments where nanocontacts were produced by electrodeposition using potentiostatic control (three electrode cell, directional growth). The cathode (depositing electrode) was grown into an anode (counter electrode) until the nanocontact was formed. The nature of the potentiostatic control in the electrochemical cell [64] requires that during Ni, Co, or Fe electrodeposition on the cathode side, the oxidation of the same metal serving as an anode has to occur simultaneously in order to have the continuity of charge flow through
the cell. The broad region of passivity and trans-passivity for Ni, Co or Fe metals at more positive potentials [65] provides the situation where, in the moment of the nanocontact formation, the metallic cathode surface is connected with an anode covered by the certain form of oxide. This fact has been carefully studied by Mallet et al. [57]. The authors have shown that, if there is no oxide on the anode surface before the nanocontact is formed, no significant magnetoresistance is observed. The importance of oxide in nanocontact geometry has been also pointed out by Tsymbal et al. [66]. In this work, the authors showed that presence of an incoherent metal oxide layer, with disorder or impurities between two ferromagnetic nanoelectrodes gives a rise to the phenomenon called "resonant inversion of tunnelling magnetoresistance". This phenomenon can explain the origin of the positive and negative magnetoresistance observed in some electrodeposited nanocontacts [63]. The tunnelling phenomenon occurring within the metal-metal oxide nanocontact has been elaborated also by Garcia theoretically [61]. In this work, the emphasis was to show that phenomenological distinction between tunnelling in ballistic nanojunctions and ballistic magnetoresistance cannot be achieved by experimental measurements and low temperature measurements were suggested for the same.

The additional contribution that presence of oxide in nanocontacts might have on large values of magnetoresistance could be expected from the point of antiferromagnetic coupling. This effect has been studied already in GMR-spin valves. It was shown that antiferromagnetic (AFM) semi conducting or insulating NiO, CoO or α -Fe₂O₃ oxides present either as a bottom or topmost AFM pinning layers in the GMR stack, can give an additional rise to observed values of magnetoresistance [67,68]. In the situation where the nanocontact geometry is considered, one can envision that metal oxide can act as pinning

AFM entity on the surrounding ferromagnetic matrix. This could contribute to the additional compression of MDW when the external magnetic field is applied, resulting in large values of magnetoresistance [62].

Thus, one of the objectives of this work is to explore the influence of the metal oxide and nanocontact geometry and see its influence on the magnetoresistance while avoiding any artifacts.

3.2. Resistance vs Temperature Dependence

3.2.1. Temperature dependence on resistivity of metals

The electrical resistivity of most metals at room temperature is dominated by collisions of conduction electrons with lattice phonons. However, collisions with impurity atoms and mechanical imperfections in the lattice dominate at low liquid helium temperatures of about 4 K, [69]. The net resistivity is given by

$$\rho = \rho_L + \rho_i. \tag{3-5}$$

where ρ_L is the resistivity caused by thermal phonons and ρ_i is the resistivity caused by scattering of the electron waves by static defects that disturb the periodicity of the lattice. ρ_L is independent of the number of defects when their concentration is small and ρ_i is independent of temperature. Thus the resistance at low temperature will help in understanding the contribution of defect and lattice imperfections in the total device resistance [69]. Low temperature I-V measurements and resistance measurements also serve to estimate the relative ratio between physical dimensions of the nanocontact and the electron mean free path.

3.2.2. Transport mechanisms of MR sensors

Low temperature measurements are an excellent technique to determine the transport mechanism of the nanocontact devices. Ballistic and Tunneling magnetoresistance devices depend equally on the spin polarization (P) of the ferromagnetic electrodes. Here, the electron transport through thin domain walls is analogous to tunneling through pinholes. These two mechanisms depend equally on the spin polarization (P) of the ferromagnetic electrodes [61].

For a MTJ displaying tunnel dominated transport, $\frac{dR}{dT} < 0$ and for a MTJ displaying

metallic like behavior, $\frac{dR}{dT} > 0$ [70].



Figure 3-6. Temperature dependence of the electrical resistance of parallel (R_P) and antiparallel(R_{AP}) states of MTJ1 and MTJ2 denoting (A)tunnel and (B) metallic dominated transport. Insets display corresponding MR [70].

It is known in general that the resistance of MTJ decreases with increase in temperature. Julliere [51] was one of the first to show this dependence. Moodera et al [52] suggested a theory where the maximum conductance at parallel magnetization of the two magnetic electrodes is given by

$$G_{\max}(T) = G_T(T)[1 + P(T)^2] + G_S(T).$$
(3-6)

The minimum conductance is when the magnetizations of the two ferromagnetic electrodes are antiparallel and is given as

$$G_{\min}(T) = G_T(T)[1 - P(T)^2] + G_S(T).$$
(3-7)

G_T(T) is the conductance due to direct elastic tunneling and is given as

$$G_T(T) = G_0 \frac{CT}{\sin(CT)},\tag{3-8}$$

where G_0 is the conductance at 0 K and C is a material constant depending on barrier thickness and barrier height .



Figure 3-7. Temperature dependence of the relative change of conductance $\frac{\Delta G}{G} = TMR$

The spin polarization P depends on the temperature by the relation

$$P(T) = P_0(1 - BT^{3/2}).$$
(3-9)

Previous research has been done on the tunneling granular magnetoresistance and is found that the resistance and magnetoresistance ratio increases with decrease of temperature [71]. An anomalous increase of magnetoresistance ratio was reported in insulting granular films with decreasing temperatures. Correspondingly the resistance increases with decreasing bias voltage and is more prominent at low temperatures and was suggested to be due to the Coulomb blockade effect. Figure 3-8 shows the resistance and MR ratio dependence on temperature for 2 MTJs with different tunneling mechanism.



Figure 3-8. Temperature dependence of the resistance (A) and the MR ratio (B) for junctions [56].

It is observed that both Rs and the MR ratio increase significantly at low temperatures. However, the increase of S2 is low as compared to that of S3, which implies that the tunneling process in both MTJs is different.

CHAPTER 4

EXPERIMENTAL

Chapter 4 is separated into two sections covering the methodologies and setups used in the experimental studies of this research. The first part discusses various experimental methods and techniques used for the characterization and fabrication of the samples. The basic principles underlying the working of the instruments are described briefly. The latter part of this chapter deals with the setup and experimental conditions utilized for the measurements used in our analysis.

4.1. Experimental Methods

4.1.1. Chronoamperometry

Chronoamperometry, also known as the potential step measurement, is the technique used to measure the variation of current response with time under potentiostatic control. It can either be single step or double step measurement. In this work, chronoamperometry was used to perform potentiostatic electrodeposition of nanocontacts. For a simple reaction $O + ne^- \rightarrow R$, where initially only O or R are present [72], the current resulting at t=0, i.e. the step from where there is no electrode reaction to the one corresponding to mass-transport limited current is given by the Cottrell equation [64] stated as

$$I_f = \frac{nFAD^{1/2}C_{\infty}}{(\pi t)^{1/2}}.$$
(4-1)

Where n is the number of electrons, F is the Faraday's constant, A is the surface area of electrode, C_{∞} is the bulk concentration and D is the diffusion coefficient. The Cottrell equation is derived from Fick's second law of diffusion and predicts variation of current with time when a potential step is applied [73]. This equation is only valid, if the current is limited by diffusion of ions to the electrode surface, such that the process is controlled by diffusion to the electrode. For small values of t (t<50 ms), the total current also includes the charging current(I_c) along with the Faradic current (I_f), $I=I_f+I_c$. The charging

current is given as $I_c = \frac{E}{R_s} e^{\frac{-t}{RC_{dl}}}$ [74]. In this equation, E is the potential step applied, R_s

is the solution resistance and C_{dl} is the double layer capacitance.

The potential, concentration gradient and current waveforms for a chronoamperometry experiment is shown in Figure 4-1.





Figure 4-1. Chronoamperometric experiment: (a) Potential-time waveform (b) Change in concentration profile as time progresses (c) the resulting current-time response [74].

Figure4-1 (a) indicates the potential step during a chronoamperometry experiment with E_1 being the initial potential where no reaction takes place and E_2 is the potential value at which the ions that reach the electrode react. Figure 4-1(b) is the change in concentration as a function of the distance from the electrode with increasing time. The concentration change is according to the formula expressed as

$$C = C_{\infty} \left(1 - \operatorname{erfc}\left[\frac{x}{x(Dt)^{1/2}}\right] \right).$$
(4-2)

Figure 4-1(c) shows the decay in faradic current at the electrode over time. In addition there is also a capacitive current due to the double layer charging. This variation in current is according to the Cottrell's equation where I varies as $t^{1/2}$.

4.1.2. Linear Sweep Voltammetry

Linear sweep voltammetry is an electrochemical technique used to detect the current change due to the sweeping potential applied to the working electrode. The potential of the working electrode is varied linearly with time between two values i.e. the initial (E_i) and final (E_f) potentials. The linear sweep voltammetry depends on the rate of the electron transfer reaction, the chemical reactivity of the electroactive species and the voltage scan rate [64]. In this case, the linear sweep voltammetry is used to measure the film thickness and parameters of corrosion experiment like electro-oxidation potential, charge transfer resistance and exchange current density as described in details in Section4.2.

Determining Film Thickness

The film thickness can be determined by using the linear sweep voltammetry technique and is called as the charge stripping measurements. It is based upon the hypothesis that the total mass deposited is proportional to the charge passed or the number of electrons transferred. Also, during metal deposition, along with the metals, there is always a case of hydrogen codeposition, which leads to a drop in current efficiency (γ <1). Thus, by the linear sweep voltammetry technique, we determine the

current efficiency which is the ratio of charge during stripping to the charge during deposition,

$$\gamma = \frac{Ch \arg e \ during \ stripping}{Ch \arg e \ during \ deposition}$$
(4-3)

Total charge during the film stripping is given as,

$$Q_{(strip)} = \int \frac{I \cdot dE}{Scan \ rate} \,. \tag{4-4}$$

Similarly, the charge during film deposition is the product of current density applied (galvanostatic electrodeposition) or constant current density observed for the applied deposition potential (Potentiostatic electrodeposition) over the deposition time.

Thus the total film thickness is expressed as

$$Film \ Thickness = \frac{I \cdot \gamma \cdot t \cdot \upsilon_m}{A \cdot n_e \cdot F} \cdot$$

$$(4-5)$$

Where, I=the current density during deposition, γ is the current efficiency ,t is the deposition time, v_m is the molar volume, n_e is the number of electrons transferred during reaction, A is the surface area of electrode and F is the Faraday's constant.

4.1.3. Energy Dispersive X-Ray Spectroscopy (EDX)

Energy dispersive X-ray Spectroscopy is the analytical technique used for compositional characterization in this research. The principle for characterization techniques in electron microscopy lies on the principle of Moseley's law $v = 2.46 * 10^{15} (Z-1)^2$ which relates the frequency of the emitted X-Ray radiation to the

atomic number of the element. The basic schematic for the EDX principle is as shown in Figure 4-2.



Figure 4-2. Schematic of EDX principle

When a high energy electron beam hits the sample, the electrons from the inner energy level shells are excited and get ejected from that shell. The vacancy so formed is filled by an electron from a higher energy level (Figure 4-3) which causes an energy release. This energy difference between the two levels is released in the form of X-rays and is detected by the EDS detector attached to the SEM. The detector typically used for this purpose is a Lithium drifted Silicon solid state Xray detector.



Figure 4-3. Principle of X-ray generation in an EDS system [75].

The specific energy of each characteristic peak is compared with the reference peak information. One of the main advantages of EDX is that the whole spectrum of interest which includes the whole family of X-rays from 0.1 to the beam energy (approx 20 keV) is acquired in a short time. However, the relatively poor energy resolution of the EDS as compared to the WDX causes frequent spectral interference problems and also the inability to separate the members of the x-ray families that occur at low energy(< 3 keV). For elements having the peak energy above 3 keV, the energy separation of the family members is such that despite the peak broadening, it is possible to recognize more than one peak, even if they are not completely separated [76] as shown in Figure 4-4.



Figure 4-4. Tantalum family showing greater separation of peaks resolved while Silicon K family, showing only one peak with K α and K β unresolved [76].

The following spectrum is obtained for Permalloy films during analysis for $Ni_{80}Fe_{20}$ composition which shows peaks for different elements corresponding to different energy levels.



Figure 4-5. EDX spectrum for Permalloy electrodeposited with additive N-Acetyl L-cysteine.

In Figure 4-5, the peak corresponding to energy of 6.3 keV is Iron while that of 7.5 keV is Nickel. Thus, EDX detects all the elements present in the alloy and an approximate counting time of 100secs. The results for EDX analysis are displayed in the following format.

		Spectrum	Apparent			k Ratio
Element	Line	type	concentration	Stat. Sigma	k Ratio	Sigma
				2.80729029	1.58207	
Fe	Κ	ED	110.6564879	3	6	4.01E-02
					13.2448	
Ni	Κ	ED	331.7436934	4.49744463	8	0.1795607
Fit						
Index	Inten	. Corrn.	Std. Corrn.	Element %	Sigma%	Atomic %
Fe		1.236572	1	22.6139	0.50338	23.50076
Ni		1.083326	1	77.38611	0.50338	76.49924

Table 4-1. EDX results for Permalloy electrodeposited with saccharin showing Ni-Fe(80-20) composition.

The X-ray energy level is characteristic of a particular element which helps to identify the element present [75]. The intensity of the peak is used to determine the composition or the atomic percentages of elements present.

4.1.4. Wavelength Dispersive X-Ray Spectroscopy



Figure 4-6. Schematic representation of Wavelength Dispersive Xray Spectometer and associated electronics [76].

Wavelength dispersive x-ray spectrometry, as the name suggests, determines the contents of the elements based on the wavelength of X-rays generated from the sample due to the bombardment by electrons. The use of a finely focused beam enables a very small selected area to be analyzed. Normally a spatial resolution of around 1 micron is obtained. The intensities of the x-ray lines from the specimen are compared with those from standards of known compositions. The composition at the analyzed point is calculated from the corrected intensities by applying 'matrix corrections' like 'ZAF' corrections which are commonly employed for factors depending on atomic number, absorption, and fluorescence that affect the relationship between intensity and composition [77].

Figure 4-6 shows a schematic of the WDX spectrometer. The electron gun consists of a tungsten filament which is heated to about 2700 K in order to obtain thermionic

emission of electrons. The filament is held at a negative potential (typically 10-30 keV) which accelerates the electrons through an aperture in the earthed anode plate. High vacuum (10^{-4} Torr or better) is required in order to prevent oxidation of the hot tungsten filament, breakdown of the accelerating voltage, and scattering of the electrons in the beam.

The electron beam is further focused by means of the magnetic lenses. For microprobe analysis a probe diameter of 0.2-1 micron is typical, with a current of 1-100 nA [77]. In order to obtain the required demagnification, two lenses are needed, though three may be used if high resolution scanning images are required. The main parts of the electron microprobe are X-ray spectrometers, specimen stage and optical microscope.

WDS analysis uses a diffracting crystal which acts as a monochromator, selecting one wavelength at a time, depending on the angle of incidence of the X-rays. The crystal is curved so that the angle subtended at the point source is constant. Most instruments have two or more spectrometers with crystals covering different wavelength ranges, contained in a chamber which is evacuated in order to prevent absorption of the X-rays in air [77].

The specimen stage usually holds several specimens and standards which can be round or rectangular with dimensions typically on the order of 2-3 cm. The specimen holder is electrically isolated and can be connected to a meter so that current in the incident beam may be measured. For microprobe analysis, flat polished specimens are required and the holder is so designed that the front surface of the specimen is located in a fixed plane. The selected area is clearly seen with the help of an optical microscope which makes the analysis easier especially if the areas are not polished properly or are out of focus.

4.1.4. X-Ray Diffractometer

X-Ray diffractometer is a tool which uses X-rays of known wavelength to determine the unknown spacings of crystal planes and gives information about the orientation and grain size of the crystal [78]. Consider for example a crystal which has a thickness *t* measured in a direction perpendicular to a set of reflecting planes. Let there be (m+1) planes in the set. We will regard Bragg angle θ as a variable and θ_B is the angle which satisfies the Bragg law for particular values of d and λ such that

$$\lambda = 2d\sin\theta_B. \tag{4-6}$$

Thus for any given crystal, the Bragg law can be satisfied by varying either λ or θ . From Figure 4-7 below, we see that ray A, D make exactly this angle θ_B with the reflecting planes. Thus ray D' scattered by the first plane below the surface is one wavelength out of plane with A' scattered by the mth plane below the surface is *m* wavelengths out of phase with A. The angle between the diffracted beam and transmitted beam is the diffraction angle, which is always 2 θ . Hence, at a diffraction angle $2\theta_B$, rays A', D' are completely in phase and form a diffracted beam of maximum amplitude i.e. maximum intensity since intensity is proportional to square of amplitude.



Figure 4-7. (left) Effect of crystal size on diffraction and (right) Effect of particle size on diffraction curve [78].

The width of the diffraction curve increases as the thickness of crystal decreases and is expressed as B [78]. The diffraction width is usually measured at an intensity that is equal to half the maximum intensity. Consider from Figure 4-7(B)

$$B = \frac{1}{2} \left(2\theta_1 - 2\theta_2 \right) = \theta_1 - \theta_2. \tag{4-7}$$

The path difference for these two angles θ_1 and θ_2 is given by

$$2t\sin\theta_1 = (m+1)\lambda, \tag{4-8}$$

$$2t\sin\theta_1 = (m-1)\lambda. \tag{4-9}$$

Subtracting these two, we get

$$t(\sin\theta_1 - \sin\theta_2) = \lambda. \tag{4-10}$$

$$2t\sin\left(\frac{\theta_1 - \theta_2}{2}\right)\cos\left(\frac{\theta_1 + \theta_2}{2}\right) = \lambda.$$
(4-11)

But θ_1 and θ_2 are very nearly equal to θ_B , hence

Hence $\sin\left(\frac{\theta_1 - \theta_2}{2}\right) = \frac{\theta_1 - \theta_2}{2}$

$$2t\left(\frac{\theta_1-\theta_2}{2}\right)\cos\theta_B=\lambda.$$

 $\theta_1 + \theta_2 = 2\theta_B$..

Hence, $t = \frac{\lambda}{B\cos\theta_B}$ [78]. A more exact formula involves putting the shape factor,

commonly assumed as 0.9 [78] and thus the formula becomes

$$t = \frac{0.9\lambda}{B\cos\theta_B}.$$
(4-12)

This is known as the Debye Scherrer formula [78] and is very commonly used for determining the grain size of the crystal. The grain size determination is used in developing an analytical model for the maximum tensile stress in electrodeposited CoFe films as a function of saccharin coverage θ .

4.1.5. In-situ stress measurement and cantilever Bending Method

Geometric conversion of deflection of cantilever into stress using small angle approximation.

The sensitivity of any system can be defined as the smallest change in measurement the system can resolve. Using Stoney's equation [79] the stress in the film can be expressed as

$$\sigma_f = \left(\frac{E_s}{1-\nu}\right)_s \frac{t_s^2}{6rt_f}.$$
(4-13)

The product of the stress and the thickness gives the force exerted per unit width of the cantilever. Thus we get

$$F_{W} = \sigma_{f} * t_{f} = \left(\frac{E_{s}}{1-\nu}\right)_{s} \frac{t_{s}^{2}}{6} \left(\frac{1}{r}\right).$$

$$(4-14)$$

where r is the radius of the curvature, formed by the cantilever due to the internal stress in the film. The schematic is shown in the Figure 4-8.

If we assume that the angle formed between the stressed state and the relaxed state of the cantilever is α , then the angle between the incident ray and the reflected ray from the cantilever (Ray i) is 2α . Let η_{air} , η_{glass} , and $\eta_{solution}$ be the refractive indices of air, glass, and the electrodeposition solution respectively. Let us assume the length of the cantilever to be *L* and the distance between the PSD and the cantilever to be D_{psd} . Now since α is very small, we can assume $\sin \alpha = \alpha$, thus the radius of curvature can be written as



Figure 4-8. Schematic of the reflected laser beam from the cantilever and the geometry used for the conversion of the radius of curvature 'r' to measureable entities.

Now, by using Snell's law of refraction between Ray i and Ray ii we get

$$\frac{2\alpha}{\theta_i} = \frac{\eta_{glass}}{\eta_{solution}}$$
 (4-16)

where θ_i (not shown in figure) is the angle between Ray ii and the normal. Similarly, using Snell's law between the Ray ii and Ray iii we get

$$\frac{\theta}{\theta_i} = \frac{\eta_{glass}}{\eta_{air}} \,. \tag{4-17}$$

Combining equations 4-15 and 4-16 we get

$$\alpha = \frac{\eta_{air}}{2*\eta_{solution}} \theta \,. \tag{4-18}$$

Substituting this value of α into equation 4.15 we obtain

$$r = \frac{2*L*\eta_{solution}}{\eta_{air}*\theta}$$
(4-19)

where θ is the ratio of the displacement by the laser spot on the PSD (d_{psd}) to the distance between the distance between the cantilever and the PSD (D_{psd}). Thus, the radius of curvature can be expressed as

$$r = \frac{2 \cdot L \cdot \eta_{solution} \cdot D_{psd}}{\eta_{air} \cdot d_{psd}}.$$
(4-19)

Substituting this into equation 4.13 we obtain

$$F_{W} = \left(\frac{Y}{1-\nu}\right)_{s} \cdot \frac{t_{s}^{2} \cdot \eta_{air} \cdot d_{psd}}{6 \cdot 2 \cdot L \cdot \eta_{solution} \cdot D_{psd}}.$$
(4-20)

The typical values of the parameters in the above equation for our setup are, L = 40 mm, $D_{psd} = 300$ mm, $\eta_{air} = 1$, and $\eta_{solution} = \eta_{H_2O} = 1.33$. The resolution of the PSD is 1 µm (d_{psd}) . For the substrate; the Young's modulus Y = 72.9 GPa, Poisson's ratio v = 0.208, and the thickness $t_s = 0.21$ mm. Thus, theoretically the maximum radius of curvature r we can measure is 31.92 km and the smallest value F/w = 0.0211 N/m, but practically the resolution of the setup for F/w is about 0.5 N/m.

4.1.6. Four Point Probe Measurements/ Magnetoresistance Measurement Setup

The resistivity of a sample is expressed as

$$\rho = \frac{1}{q\mu_n n + q\mu_n p} \ \Omega \text{cm.} \tag{4-21}$$

The resistance measurements can be done by means of just two probes, however, there is contact resistance associated with the probes and current spreading problems around the probes. The schematic of a 4 point probe measurement is as shown in Figure 4-9.



Figure 4-9. 4 point probe measurement setup [80].

The outer two probes force a current (I) through the sample while the inner two probes measure a voltage (V) across the sample [80]. In this geometry, when the constant current that is used allows us to force the current through the outer two probes, there will still be contact resistance and current spreading problems, but it measures the voltage drop with two inner probes using a high impedance voltmeter. The advantage of this kind of measurement is that problems with probe contacts are eliminated in the voltage measurement since no current flows through these contacts as explained below. The following is the equivalent circuit diagram for 2 point and 4 point probe measurement.



Figure 4-10. Equivalent circuit for (left) 2 point and (right) 4 point probe measurement. From Figure 4-10 (left), the resistance will be the product of voltage across Rx and current through it.

$$Rx_{meas} = \frac{V}{I} = \frac{V(R_x + 2R_c)}{V} = R_x + 2R_c.$$
(4-22)

Hence, for a two point probe, the sample resistance will be off by a huge margin if the contact resistance is high since along with the sample resistance, one also measures the probe resistance or the resistance of contact wires to the sample as expressed in Equation 4-15. Typically, the contact resistance is small and can be neglected, however if the sample resistance is large, then the error cannot be ignored. This error due to contact resistance is overcome by using 4 point probe measurement. The circuit diagram is shown in Figure4-10B.

In the 4 point probe measurement,

$$R_{x,meas} = \frac{V_{Rx}}{I}$$
, where V_{RX} is the voltage across $R_x, V_{RX} = I_x \cdot R_x$

Using the current divider rule for I_x and calculating $R_{x,meas}$,

$$R_{x,meas} = \frac{R_x \cdot I.(2R_c + R_m)}{(2R_c + R_m + R_x)I}.$$

 R_m is the resistance of the voltmeter which is very high and hence the ratio $\frac{2R_c + R_m}{2R_c + R_m + R_x} \sim 1$, indicating that the source of error in the 4point probe measurement is

very small, i.e. R_x~R_{x,meas}.

A constant current flows through the outer two probes while the voltage is measured through the inner two probes. The value of the resistance of sample R_x is given by the ratio of the voltage across the variable current source. The resistance across the voltmeter is very high and hence current through it is neglected.

This four point probe measurement was used to determine the magnetoresistance. The sample is placed in between a magnetic field and is used to determine the variation of resistance with change in magnetic field. The clips were connected to a Keithley 2400 source meter for current supply and voltage measurement. The setup for the magnetoresistance measurement is as shown in Figure4-11.



Figure 4-11. Magnetoresistance measurement setup

A Labview program was designed to record the measurements where the user is able to vary the maximum magnetic field, the number of loops and the frequency. The magnetic field in this case was varied between -700 Oe to +700 Oe. The MR measurements were performed in two ways, either by keeping I constant and measuring V or by keeping V constant and measuring I as the magnetic field was varied. A screenshot of the Labview program is as shown in Figure 4-12.



Figure 4-12. Labview screenshot for Magnetoresistance measurement.

4.1.7. Vibrating Sample Magnetometer (VSM)



Figure 4-13. Block Diagram of Vibrating Sample Magnetometer [81].

The Vibrating Sample Magnetometer operates on the principle of Faraday's Law of Induction which states that an electric field is produced in a changing magnetic field. In the VSM tool, the sample is vibrated perpendicular to the magnetic field. The oscillating magnetic field of the vibrating sample induces voltage in the stationary detecting coils. The voltage induced helps in determining the magnetic properties of the sample. This voltage is compared with a second voltage from a similar set of reference coils by a reference sample [82]. Ideally the VSM should be calibrated with a known standard that has the same shape and size as that of the sample to be measured. Typically a high purity Nickel sample is used as a standard. The mass of the sample is known and the voltage induced in the coils is measured. This helps us to find the magnetic moment of the sample and a calibration constant in terms of Am²/V is determined. This

calibration constant is then used to determine the magnetic moment of the unknown sample by using the calibration constant and the voltage induced in the coils [83].

4.2. Experimental Setup

4.2.1. Corrosion Potential Determination

The experiments to understand the additive influence on the rate of corrosion of electrodeposited CoFe alloys was divided into two parts. The first part involves determining the corrosion potential of the CoFe alloy and the latter part involves determining the different parameters which helped in developing an analytical model for the theory of corrosion.

4.2.1.1. Determination of Corrosion potential and effect of stirring

The corrosion potential of CoFe alloys was determined by measuring its Open Circuit Potential in 0.05M NaCl. The CoFe alloy was first electrodeposited for an hour to obtain a CoFe film of about 0.5 µm. The working electrode (WE) in this case was Au gold electrode with diameter=4 mm. The Au electrode was first polished using sand paper and then further mechanically polished on polishing pads of 6µm, 3µm and 0.5µm to obtain a flat and smooth working electrode. This electrode is then sonicated in ultrapure water for 1minute and then rinsed in 1:1 HNO₃ solution for 30 sec. The solution design and process parameters for electrodeposition of CoFe alloy are listed in Table4-2.

Solution Design	Value	Process parameter	Value
CoSO ₄ .7H ₂ O	15 g/L	γ	0.12
FeSO ₄ .7H ₂ O	31 g/L	J	4 mA/cm^2
H ₃ BO ₃	25 g/L	Deposition time	1 hour
NH ₄ Cl	16 g/L	рН	2.03
Saccharin	0-2.5 g/L	ω	220 rpm

Table 4-2. Table indicating the Solution Design and Process parameters used for

 CoFe Electrodeposition.

The electrodeposited CoFe film is rinsed in water for 30 sec and the corrosion potential (E_{corr}) is recorded in a testing solution of 0.05 M NaCl solution of pH7. The setup for the corrosion measurement is the similar to the electrodeposition (ED) setup except that the working electrode now is the ED CoFe alloy, Pt wire is the Counter electrode and SCE is the RE. The corrosion potential is the Open circuit potential (OCP) and it was recorded until $\frac{dE}{dt} < 5 \ mV/min$.

In the second part of the experiment, in order to understand the effect of agitation or diffusion layer thickness on the corrosion potential, the OCP was recorded at a rotation speed of 300 rpm and 1000 rpm. All electrochemical deposition experiments were carried out on EG&G 263A Potentiostat/ Galvanostat. The composition of CoFe films were determined via EDX and found to be in the range $Co_{35-40}Fe_{60-65}$. The experimental setup is as shown in Figure 4-12.



Figure 4-14. Setup for electrodeposition experiments with the RDE for corrosion tests.

4.1.2. Determination of Electro-oxidation Potential (Eox), Charge Transfer

Resistance (**R**_{ct}) and **Exchange** Current density (j₀).

The parameters E_{ox} , R_{ct} and i_0 are determined via LSV technique. The testing solution is a neutral solution of 0.05 M NaCl with pH 7, which was deareated for 1hour. The initial part of CoFe electrodeposition is the same as Section 4.1.1. After electrodeposition, LSV was performed in the testing solution and the potential was swept from -700 mV to 600 mV with a scan rate of 5 mV/s. The LSV was carried out using EChem Potentiostat and the software used was eDAQ.

A. Determination of Electro-oxidation Potential.

The potential at which the current just starts to increase with positive values is the electro-oxidation potential. It is considered as an approximation of the reversible potential for CoFe alloy. As shown in Figure, the electro-oxidation potential is -600 mV.



Figure 4-15. Determination of electro-oxidation potential.

B. Determination of charge transfer resistance.

 R_{ct} is determined via extrapolation from Linear Sweep Voltammetry. The initial region after the electro-oxidation potential, i.e. first 20 mV shows a linear dependence in the form $\eta = i \cdot R_{ct}$. The linear region from Figure 4-16 (a) is zoomed to show the linear region as seen in Figure 4-14(b). The inverse slope of the initial region of first 20 mV after E_{ox} determines the R_{ct} .



Figure 4-16. LSV of CoFe alloy (inset) linear region showing the first 20 mV after E_{ox}.

C. Determination of exchange current density

The exchange current density was calculated from the initial linear region of the linear sweep voltametry by using the equation $R_{ct} = \frac{RT}{Fj_0}$, where j_0 is the exchange current density.

4.2.2. Thin Film Thickness Determination

The CoFe alloy electrodeposition rate was determined by the charge stripping method using linear sweep voltammetry technique and the film thickness was further verified by milling a cross section using Focused Ion Beam (FIB).

A. Determining CoFe alloy deposition rate via Linear sweep voltammetry

The CoFe alloy that was deposited by galvanostatic electrodeposition is then stripped in the same plating solution electrolyte by applying a potential from -700 mV to +600 mV with a scan rate of 5 mV/s. The solution design and process parameters for CoFe alloy

electrodeposition are as shown in Table 4-2. The Linear sweep volatmetry is carreid out in Echem Potentiostat and the software used to record the voltammetry curves are eDaQ Chart.



Figure 4-18. CoFe film stripping curve via Linear Sweep voltammetry

The film thickness is expressed as

Film Thickness =
$$\frac{I \cdot \gamma \cdot t \cdot \upsilon_m}{A \cdot n_a \cdot F}$$
 (4-23)

Where γ is the current efficiency determined by linear sweep voltammetry.

Current efficiency is the ratio of charge during stripping to charge during deposition.

$$\gamma = \frac{Ch \arg e \ during \ stripping}{ch \arg e \ during \ deposition} \cdot$$
(4-24)

As explained in section 4.1.2, the stripping charge is the integral of the curve shown in Figure 4-18. The CoFe alloys are electrodeposited galvanostatically and hence the deposition charge is the product of current density applied (4 mA/cm²) and deposition time. For the stagnant CoFe electrodeposition, the current efficiency was 0.67.

B. Film Thickness Verification by Focused Ion Beam (FIB).

The film thickness measurement is verified by making a cross section on the film using FIB. The FIB used for our measurements is FEI with gallium (Ga⁺) ion source. In order to measure the thickness, we need to record a cross sectional image and this starts with milling an area of 15X15 μ m² on the sample. For this step, we use a high ion beam current of 20 nA. The next step in this process is to do a cleaning cross section by using a slightly lower beam current of about 100 pA. In order to be able to distinguish the image and make measurement clear, we deposit a thin layer of about 10 nm of Platinum as shown in Figure 4-19. In case of the FIB, the electron and ion beam column are at an angle of 52°, so it is necessary to do the tilt angle correction while measuring the dimensions. An online program called Annotate automatically compensates for the 52° tilt and gives the correct dimensions.



Figure 4-19. Film thickness verification by FIB.

Figure 4-19 is a SEM image of CoFe film with a thickness of 4.9 μ m. The deposition rate of the alloy was calculated using Charge stripping measurement and hence the alloy was deposited accordingly to produce a thickness of 5 μ m. This shows that the error in our film thickness analysis is about 2%.

4.2.3. X-Ray Diffractometer

The Siemens D5000 Powder X-ray Diffractometer is used for the calculation of the grain size of these CoFe alloys. The current used was 30 mA and a voltage of 40 KeV was used. The Cu-K α radiation of wavelength 1.5418 A° was used and step size was 0.04 rad and the scan was from 40° to 52°. The θ -2 θ scan for one such CoFe sample electrodeposited with C_{sac} =0.12 g/L of saccharin is as shown in Figure 4-20.



Figure 4-20. (a) XRD θ -2 θ scan for electrodeposited CoFe alloy with C_{sac}=0.12 g/L of saccharin and (b) CoFe BCC (110) peak along with the corresponding Gaussian fit.

As shown in Figure 4-20, the XRD scan is performed from $2\theta=40^{\circ}$ to $2\theta=50^{\circ}$, with a step size of 0.04°. From the ICDD database, it was known that the CoFe BCC<110> peak (2 θ) appears at around 44.5°. Using the Table Curve 2D software, the curve for each of the scans was fitted using the Gaussian equation as shown in Figure 4-20B to find the FWHM of the curve. The corresponding grain size was determined by the Debye Scherrer formula $D = \frac{0.9\lambda}{B\cos\theta}$. Here, λ is the wavelength of Cu-K α radiation and θ is the position at which the CoFe BCC 110 peak appears and D is the grain size. The Gaussian fit for the 2 θ peak is as shown in Figure 4-20(b).

4.2.4. Compositional Characterization by EDX, WDX

A. Energy Dispersive XRay spectroscopy (EDX)

EDX analysis was used to determine the Co and Fe content in CoFe films electrodeposited with varying saccharin concentrations. A magnetic flux density of 2.4 T is obtained with composition of Co of 36-40 and Fe of 64-70. The instrument used for
this analysis was JEOL JSM 6330 Field Emission Scanning Electron Microscopy. The accelerating voltage used was 15 KeV and the imaging and measurements were carried out at a working distance of 15 mm. The final composition was selected to be the average of measurements that were performed at 4 different positions in the sample. The signals were collected for 100 secs at each position in the sample.

C. Wavelength Dispersive XRay Spectroscopy

WDS measurements were carried out on Electron Microprobe to measure the atomic percentages of oxygen in CoFe alloys electrodeposited with varying Fe³⁺ ions. The electron microprobe used was JEOL JXA 8600 SuperProbe. In a WDS measurement, it is very essential to know beforehand the elements present and for this reason, normally EDS measurement is done wherein a spectrum indicating all the elements present is obtained. The signal at each point was collected for about 30 minutes. The typical WDS spectrum for a particular element is shown in Figure 4-21.





Thus the crystal for oxygen is measured on Spectrometer 1 while the crystal for Iron is measured in spectrometer 3. The peak positions are recorded and compared with previously calibrated values. An important indication of the accuracy is the k-ratio. A kratio greater than 1 indicates that it is calibrated properly while a k-ratio less than 1 means it needs recalibration. The crystals used for the measurements are LiF, PET (Pentaerythritol), LDEB, LDE1. It was known beforehand that the elements present are Fe, Co and the approximate peak positions are as shown in Table 4-3.

Element	Spectrometer	Crystal	L(mm)
Fe	3	LiF	134.65
Со	3	LiF	124.4
S	2	PET	172.239
В	4	LDEB	129.3
N	1	LDE1	147.2
Cl	2	PET	151.6
Cu	3	LiF	107.2
0	1	LDE1	110.0

Table 4-3. Peak positions of all elements calibrated for O measurements.

Chemical analysis was performed using a JEOL JXA 8600 electron microprobe analyzer using 15 keV accelerating voltage and 30 nA beam current. For major elements, peaks were counted for 100 s and backgrounds on two sides for 50 s each. Data were analyzed using an online Gellar $\varphi(\rho z)$ program. Minor element concentrations were measured by combination of sequential 100 seconds peak and two 50 seconds background measurements. This is done to minimize the influence of machine drift. After determining the total count rate, another $\varphi(\rho z)$ correction was performed to determine element concentration

4.2.5. Vibrating Sample Magnetometer

Magnetic measurements were performed on Lakeshore 7400 series Vibrating Sample Magnetometer to determine the coercivity of CoFe alloys electrodeposited with different concentrations of Fe^{3+} . Before the measurements were performed, the calibration was done using a Nickel standard. This step is very important especially for the calculation of magnetic flux density. The next step is saddling of the sample to ensure that the sample is accurately placed in the centre of the magnetic field. This point is obtained by locating the saddle point in the X, Y and Z axes by locating the position where the maximum attainable signal is obtained. Saddling is done via the three screws for X, Y and Z axes as shown in Figure 4-17.



Figure 4-22. Lakeshore 7400 Vibrating Sample magnetometer

The saddling is done by first finding the saddle point for Z axes, because unless a saddle point is determined for Z axes, a maximum signal is not obtained for X, Y axes.

The saddle point is determined by making sure that we obtain the following graphs for each of the axes.



Figure 4-23. Variation in magnetic field vs distance between gap between poles in X,Y and Z axes [83].

As shown in Figure 4-21, saddle point is the position where the sample is located symmetrically with respect to the detection coils and a maximum signal is obtained for the Z and Y axes and a minimum signal is obtained for the X axes [84].

After obtaining the saddle point, the measurements are performed by placing the sample onto the end of a sample holder rod mounted in an electromechanical transducer. The transducer was driven by an oscillator at a frequency of 90 Hertz, causing the sample to vibrate along the Z axis perpendicular to the magnetizing field. The MH loop for one such CoFe alloy electrodeposited with 0.12 g/L of saccharin is as shown in Figure 4-24.



Figure 4-24. MH loop for CoFe alloy electrodeposited with 0.12 g/L of saccharin.

As seen in Figure 4-24, the magnetic field is scanned form -500 Oe to +500 Oe with a step size of 10 Oe.

4.2.6. In-situ Stress Measurement setup.

An in-situ stress measurement system was designed to measure the stress evolving during electrodeposition of CoFe alloys with different concentrations of saccharin. We use the Stoney's equation [79] to calculate the in-situ stress from the measurements of the bending of cantilever. This system is based on an earlier optical system developed by Stafford et al [85]. The substrate is glass cantilever deposited with 10 nm of Titanium and 100 nm of Gold by thermal evaporation. The system is assembled on an optical bench as shown in Figure 4-25.



Figure 4-25. In-situ stress measurement setup.

The LASER source in this setup is the JDSU 1.5 mW 632.8 nm He-Ne (Red) linear laser which is incident on a 1" Circular reflecting mirror at an angle of 45° to the laser beam. After reflecting from the mirror it falls on the collimator. The use of the iris is to select the part of the laser beam carrying the highest intensity of the light and thus to minimize the noise level that comes from the source [86].

The beam splitter we use is a cube beam splitter. It splits the beam into two parts. One part of the beam falls on the electrodeposition cell while the other part of the beam is not used. The part of the beam falling on the cell is reflected from the cantilever again passes through the beam splitter and one part of it falls on the photo-sensitive detector (PSD) and the other part is blocked by the collimator. All the optical stages are mounted on standard translational stages for the ease of fine adjustments [86]. The bending of the glass cantilever due to stress evolution in growing CoFe films was tracked by laser spot displacement along the vertical axis of the PSPD. The geometry of our system allowed us to use a small angle approximation in order to estimate the curvature of the glass cantilever directly from the laser spot displacement on PSPD, d_{PSPD} [86].The curvature of the cantilever was calculated as

$$\frac{1}{R} = \frac{n_{air}}{2*L*n_{solution}}*D_{PSPD} \cdot d_{PSPD}.$$
(4-25)

In respective order, L, n_{air} , $n_{solution}$, D_{PSPD} represent the length of the cantilever from the fixture to the place from which the laser beam is reflected, refractive index of air $(n_{air} = 1)$, refractive index of the plating solution $(n_{solution} \approx 1.33)$, and distance of the cantilever to the PSPD. Using the typical values, L=40 mm, D_{PSD}=300 mm, $\eta_{air}=1$ and $\eta_{solution}=\eta_{H2O}=1.33$, R can be expressed as a function of d_{PSD} and is given as $\frac{1}{R}=31.33 \times d_{PSD}m^{-1}$. The Stoney's equation [79] was used to calculate force per width (F/w) acting on the cantilever by the CoFe film during the electrodeposition process directly from the measured curvature of the glass cantilever, 1/R [87]. The electrochemical cell used for stress/electrodeposition measurements was made out of quartz with 0.002 m wall thickness. It had rectangular shape and 0.125 L volume. The electrochemical cell used in these measurements is as shown in the Figure 4-26.



Figure 4-26. Picture of the electrochemical cell for electrodepositing CoFe alloy.

This volume ensured that no compositional or temperature change of electrolyte have occurred during our measurements. The lid/top of the cell was custom made from Teflon (PFA) block to prevent any corrosion damage during the solution spillover. The three electrode cell configuration was used for insitu stress/electrodeposition measurements. The working electrode – gold coated glass cantilever, was vertically held in the solution from the top by a special holder made out of Titanium to provide a good electrical contact. The cantilever holder was built-in as the integral part of the cell cover ensuring the maximum mechanical stability and integrity of stress measurements. The reference electrode was saturated calomel (SCE), and all potentials in this work are quoted with respect to SCE. The counter electrode was Ni foil with area approximately 20 times larger than the area of working electrode [87]. The plating solution and process parameters are the same as listed in Table 4-1 and the films were deposited via galvanostatic electrochemical deposition to obtain a film thickness of 0.1 µm and 0.5 µm.

All signal outputs from the PSPD (stress measurements) and from current/potential measurements (electrodeposition/thickness data) were simultaneously acquired using a *National Instruments* PC board (NI PCI 6143 S-Series) integrated with *LabView* data acquisition software which provided real time recording and analysis of experimental data [86].

CHAPTER 5

MAGNETIC SENSOR DESIGN AND FABRICATION

This chapter focuses on the steps for fabrication of magnetic field sensor. It describes comprehensive aspects in fabrication process such as the various deposition layers, lithography, electrodeposition of CoFe into nanoholes to form nanocontacts and the 4-point probe testing of the electrodeposited contacts.

Magnetic Sensor Fabrication

The ferromagnetic oxide (CoFeO) nanocontact is embedded in the insulating oxide (Al_2O_3) which separates two plane-parallel ferromagnetic layers. The ferromagnetic layers are fabricated to facilitate the formation of the magnetic domain wall within the nanocontact geometry. For this purpose, the bottom wire is fabricated from magnetically harder material as compared to the upper one, for example Co_{bottom} *vs.* NiFe_{top}. The magnetic sensor fabrication is divided into three steps.

- 5.1. Deposition of the bottom ferromagnetic electrode and insulating layer along with patterning of the nanocontact area.
- 5.2. Formation of the nanohole by using Focused Ion Beam.
- 5.3. Formation of the nanocontact by CoFe electrodeposition and deposition of the top ferromagnetic electrode along with contact leads.

5.1. Steps involved in deposition of the bottom ferromagnetic electrode and insulating layer along with patterning of the nanocontact area.

5.1.1. Wafer Cleaning and oxide etch

The starting substrate is 3" antimony doped n-type Si (100) wafer from Silicon Quest Co., with a resistivity of 0.01-0.02 ohm-cm. The most important step is to prepare H terminated and contamination free substrate to make sure that chemically grown or native oxide and contaminants on the wafer do not affect the characteristics of the sensors. The contaminants are a major source for pinholes and hence careful cleaning of the wafer before further processing is very essential. With the requirement for increased device performance and reliability in the VLSI and ULSI circuit technology, more emphasis is given to the steps required for generating clean wafer substrate [88]. Wafer cleaning is one of the most repeated steps in IC device fabrication and careful measures should be taken at every step of fabrication to keep the wafer away from impurities. Although there are many methods of wafer cleaning, we adopt a wet cleaning approach.

The wafer is first rinsed with acetone and then dipped in 10% buffer Hydrofluoric Acid for about 15-20 seconds. The Buffer HF etches away the native oxide and any other contaminants on the wafer. HF is a very strong acid and should be handled with extreme care and precaution. Protective clothing and goggles must be worn while handling it. HF corrodes glass and hence HF should never be stored or poured into glass containers. The wafer is next rinsed thoroughly with deionized (DI) water. It is very essential to have a proper rinsing with DI water. A wetting test is performed to check if the wafer is free of the oxide. Oxide is hydrophilic and pure silicon is hydrophobic. On rinsing the silicon wafer with water, if the water beads up and rolls off, the surface is hydrophobic and water will not wet it, indicating a hydrophobic surface, meaning that the oxide layer has been removed. The test to check if the wafer is devoid of oxide or contaminants is to see if there are any droplets of water sticking to wafer, since clean Silicon wafer is hydrophobic. The next step is to blow dry the Si wafer with nitrogen.

1. Initial starting wafer 2. Rinse with buffer HF and DI water

Figure 5-1. (left) Silicon wafer with native oxide and (right) Si wafer after rinsing with buffer HF and DI water.

In Figure 5-1, on the left is a schematic of bare Si wafer with native oxide and on right is the Si wafer after oxide is removed.

5.1.2. Multilayer Sputtering

The sputtering tool used is AJA Ultrahigh Vacuum DC magnetron sputtering system. The base pressure for sputtering used was $1*10^{-8}$ Torr. Table 5-1 lists the chamber pressure and sputtering rate for all the layers deposited by sputtering.

Layer	Percent Power	Sputtering Rate
Copper	30 %	2.5 A°/s
Cobalt	20 %	0.59 A°/s
Alumina	30 %	1 A°/s
Permalloy	20 %	0.6 A°/s

Table 5-1. Sputtering rates for the various layers used in chip fabrication

The first metal layer deposited is Cu of thickness 100 nm that works as the seed layer. Cu sputtering is done in two stages. The first step is called Cu pre-sputtering. In this step, the plasma is turned on and the target is heated. This step also helps in removing the impurities trapped in the gun. Another reason for using the pre-sputtering step is that, when the sputtering is started, the target takes some time to heat and thus the desired thickness might not be obtained especially if thin layers of about few nm need to be deposited. The pre-sputtering stage is normally carried out for about 30 seconds. The actual sputtering takes place only in the second stage. In order to obtain 100 nm thick copper, the sputtering time is 400 seconds.

The next step is sputtering of Co, which is the hard magnetic material of 200 nm thickness. The cobalt sputtering also follows two stages. Stage 1 is Co pre-sputtering and the second stage is Co sputtering.

The third step is deposition of the insulator layer Alumina. In the first stage, 300 nm of Alumina was sputtered. There are two methods of sputtering Alumina.

Traditionally, many researchers have sputtered Alumina by RF sputtering. However, here we adopt DC sputtering. Alumina is deposited by passing the Oxygen gas to flow and mix with Aluminum ions to form Al_2O_3 .



Figure 5-2. Si wafer with Cu (100 nm)/Co (200 nm) and Alumina (500 nm).

Optimization for quality of Al₂O₃ layer

The quality of the Alumina film was approved by electroplating the $Cu/Co/Al_2O_3$ film in a CoFe plating solution as described in Table 5-2. The CoFe fills the pinholes in a very short time and forms mushrooms. The pinhole density is expressed as the ratio of the number of mushrooms to the total area.

The working electrode is the film, Nickel plate is the counter electrode and SCE is the reference electrode. Electrodeposition is carried out in an EChem potentiostat, since it can measure current in the range of pA. The electrodeposition is carried out in a Faraday's cage which is used to block out external static and non-static fields.

Solution Design	Value	Process parameter	Value
CoSO ₄ .7H ₂ O	15 g/L	γ	0.12
FeSO ₄ .7H ₂ O	31 g/L	Е	-1.1 V
H ₃ BO ₃	25 g/L	Deposition time	~10 minutes
NH ₄ Cl	16 g/L	рН	2.03
Saccharin	0-2.5 g/L	ω	0 rpm
Fe ³⁺	0-0.1 M	Deposition rate	48 nm/minute

Table 5-2. Solution Design and Process Parameters for electrodeposition of CoFe nanocontact.

In order to obtain a pinhole free $Cu/Co/Al_2O_3$ layer, we performed many iterations involving variation in the alumina layer thickness, oxygen gas flow, gas pressure and the way the alumina layer (continuous or intermittent) is sputtered and then a quality check was performed using the electroplating solution in Table 5-2 to record the current density and pinhole density.

(1) Alumina Thickness

We tried 4 different films of $Cu/Co/Al_2O_3$ (100 nm), $Cu/Co/Al_2O_3$ (200 nm), $Cu/Co/Al_2O_3$ (300 nm), $Cu/Co/Al_2O_3$ (400 nm). The chamber pressure, oxygen flow rate, type of sputtering and rate of sputtering remained the same. Analysis on these films was done by observing the density of CoFe electroplated mushrooms after

electroplating. We observed a trend in that the deposition current goes on decreasing with the increase in Alumina thickness and the pinhole density also decreases, however the pinhole density is still large. So we decided to vary one parameter at a time, we chose the Alumina thickness to be 400 nm and then the next step was varying the oxygen flow rate.

(2) Oxygen flow rate

The current oxygen flow rate used was 6 SCCM (standard cubic centimeters per minute). Oxygen flow rate means the rate at which the oxygen mixes with the Al ions to form Al_2O_3 . We decided to vary the flow rate by trying 4 SCCM and 8 SCCM. The SEM images are shown in Figure 5-4.



Figure 5-4. Images for Cu (100 nm)/Co (200 nm)/Al₂O₃ (500 nm) with (A) 4 SCCM (B) 8 SCCM (C) 6 SCCM.

From Figure 5-4, we observe that the pinhole density is less for films deposited at an oxygen flow rate of 6 and 8 SCCM as compared to 4 SCCM. We find a lot of CoFe mushroom growth in Figure 5-4A. However, in image B, there are ~15 mushrooms in an area of $100 \times 100 \ \mu\text{m}^2$, while in Figure C, the CoFe film with a pinhole density of 6 in $100 \times 100 \ \mu\text{m}^2$. However, there was more reproducibility for films with oxygen flow rate of 6 SCCM. The next modification that was made in the sputtering cycle was to deposit Al_2O_3 in on-off cycles of 50 nm each and the SEM image is shown in Figure 5-5.



Figure 5-5. SEM image of Si wafer coated with $Cu/Co/Al_2O_3$ after CoFe electrodeposition where Al_2O_3 was intermittently sputtered at intervals of 10 nm after every 50 nm Al_2O_3 sputtering.

In order to make the quality of films still better and durable and the pinhole density still less, the Al_2O_3 cycle was repeated after every 20 nm and the SEM image of one such film after it is electrodeposited in a CoFe plating solution is shown in Figure 5-





Figure 5-6. SEM image of Si wafer coated with $Cu/Co/Al_2O_3$ after CoFe electrodeposition where Al_2O_3 was intermittently sputtered with intervals of 10 nm after every 50 nm Al_2O_3 sputtering.

Performing all the above iterations, we devised a recipe for pinhole free Alumina film. Thus, the Alumina layer of thickness 300-400 nm with an oxygen flow rate of 6 SCCM was sputtered in intermittent cycles of 20 nm and then allowing oxygen gas to flow for a time of 10 minutes after every 20 nm. This film gave us the least number of pinholes.

5.1.3. PMGI and Photoresist Coating

After the layers are sputtered, the next step is PMGI SF6 (polydimethylglutarimide) coating. PMGI SF6 from Microchem is a polymer resist that is mostly used in liftoff applications [89]. A more detailed description about the thickness vs spin speeds for PMGI SF6 is found in Ref [89]. The process parameters for spin coating PMGI SF6 of thickness 500 nm is as shown in Table 5-3.

Table 5-3. Recipe for spin coating PMGI SF6.

Speed (rpm)	Acceleration	Time (seconds)
500	200	5
3000	1250	55

In Table 5-3, 500 rpm is the initial dispense speed and 3000 rpm is called as the terminal spin speed. The graph for PMGI SF6 for various speeds is as shown in Figure 5-7.



Figure 5-7. PMGI film thickness as a function of the spin speed [89].

Comparing the values in Table 5-3 and Figure 5-7, we estimated that the PMGI thickness is ~300 nm in our chip. For a clean lift-off processing, the PMGI layer should be thicker than the metal layer, approximately 1.2-1.33 times the metal layer. According to the PMGI datasheet, spin speeds between 2500-4000 rpm generate the maximum uniformity and hence we used a speed of 3000 rpm.

Prebake

Prebake step has a great influence on the final undercut. The primary function of this step is to dry the PMGI film and to fix the development and undercut rate. The prebake temperature that was used in the fabrication of our sensors was 180° on a hotplate for 2 minutes.

Photoresist Coating

Prebake of PMGI is followed by the positive photoresist (AZ 1512) coating. The process applied for this photoresist coating is the same as that for PMGI. The spin curve speed for AZ 1512 is shown in Figure 5-8.



Figure 5-8. AZ 1512 film thickness as a function of the spin speed [90].

Further details about the photoresist AZ 1512 can be found in the AZ Electronics Material datasheet for AZ resist [90].

Hotbake

After photoresist coating, the next step is hotbake. The wafer is baked on a hotplate at 120° for 2minutes and then at 90° for 2 minutes. A schematic showing the wafer after PMGI and AZ 1512 coating is shown in Figure 5-9.



Figure 5-9. Si wafer with Cu(100 nm)/Co(200 nm)/Alumina(500 nm)/PMGI/AZ 1512.

5.1.4. Optical lithography

Optical lithography was performed using a mask aligner from Myriad Semiconductor Co. The exposure time was 35 seconds. The chrome on mask pattern is as shown in Figure 5-10.



Figure 5-10. Chrome Mask used for making patterns.

A schematic of the exposure to the photoresist covered wafer by UV light through the pattern on mask is as shown in Figure 5-11.



Figure 5-11. UV light exposure to chrome on mask to the Si wafer.

5.1.5. Resist Development

After the resist exposure, the resist is developed by using AZ 300 for 1 minute. Since AZ 1512 is a positive photoresist, the areas that are exposed to UV light are washed away. One way to confirm if the squares are developed is to measure the step height using an ellipsometer. After development, the feature would be as shown in Figure 5-12.



Figure 5-12. UV light exposure through chrome mask to the Si wafer.

The next step is sputtering another layer of Alumina. In the second step, we deposit only 200 nm of alumina. However, one important step here is to perform sputtering without putting it in run mode as this facilitates the liftoff process. This process increases the sputtering rate and also does not allow uniform depiction. Thus, the possibility of metal film getting deposited on side walls decreases which aids in a better liftoff.



Figure 5-13. Si wafer after development using AZ300.

5.1.6. Liftoff

Liftoff is an additive technique unlike the other method of creating patterns via the etching technique. First a layer of photoresist is spun over the whole wafer and then an inverse pattern is created. After this step, the metal layer is deposited. The liftoff is performed using acetone and now the area of the metal layer which has the sacrificial layer (photoresist) below it are washed away along with the resist (PMGI and AZ 1512) and the desired pattern is obtained. The wafer is sonicated in acetone for about 30 minutes. During the liftoff process, parts of the metal and resist may stick at undesired

locations and hence fresh solvent (acetone) is poured periodically to ensure a clean wafer. Figure 5-14 is the schematic of the wafer after the liftoff process.



Figure 5-14. Wafer after the liftoff process.

5.1.7. Making Ohmic contact

Contacts have to be made to the Silicon wafers to improve the electrical conductivity. The ohmic contact is applied to the wafers by applying Indium paste. Indium metal is heated at 180°C and evenly spread at the bottom of Si wafer. The wafer was left on the hotplate for another 15 minutes. The baking process helps In to penetrate the silicon wafer and improve Si conductivity.

The devices that are produced by this technique have few pinholes. However, one issue is their reliability over a larger period of time. Durability of the wafers is an important step. Ideally, the wafers should be pinhole free even after extended period of time. This is achieved by means of patterning by negative resist using the same mask as shown in Figure 5-10, so that areas other than the pattern are protected by the insulating negative resist.

The negative photoresist SF 2000.5 is spun by the application of the process parameters as shown in Table5-4.

Speed (rpm)	Acceleration	Time (seconds)
500	100	10
3000	300	30

Table 5-4. Process Parameters for spin coating AZ1512.

Figure 5-15 shows the thickness for varying spinning speeds of SU8 2000.5



Figure 5-15. SU8 2000 spin speed vs thickness [91].

After spinning the resist onto the wafer, it is heated at 95°C for 1minute. It is then exposed to UV light using mask aligner for 35 secs. The wafer is heated at 95°C for 2 min and then developed in SU8 developer for 1 minute. These specifications are in accordance with the parameters specified in SU8 datasheet [91]. Figure 5-16 shows the schematic of the wafer after spin coating SU8 2000.5 negative photoresist.



Figure 5-14. Wafer after spin-coating SU8 2000.5 negative photoresist.

5.1.8. Mask Aligner

The mask aligner positions the mask over the sample so that the pattern created would be in the correct position. The important parts of a mask aligner are:

- a) Mask Holder: This is typically a flat piece of metal that holds the photomask in position. The mask holder has a large hole in its center through which a wafer will be placed in contact with the mask. The mask holder has vacuum holes around its edge that keep the photomask securely in place during the alignment procedure.
- b) Wafer Chuck: Wafer chuck hold the wafer in place using vacuum holes throughout its surface. It moves up and down to bring the wafer into contact with the photomask.
- c) Microscope: This is required to do high-resolution alignment. Most aligners have at least 20X microscope objectives to allow for alignment resolutions down to 1 micron.

- d) Microscope Positioner this allows the microscope to be moved to different x-y positions over the surface of a mask or wafer as well as different angle rotations. Movement is usually done using a joystick or switch controller with different controls for the x-y movement and angle rotation.
- e) Wafer/Mask Positioner This is used to position the wafer to correct alignment with the pattern on the mask. In some aligners the mask is held still while the wafer is moved below it and in other aligners the wafer is held still and the mask is moved above it. Movement is usually done using a joystick, switch controller, or micrometers with different controls for the x-y movement and angle rotation
- f) Exposure Timer This allows the user to set the exposure time for the aligner (how long the wafer and mask will be exposed to UV light).
- g) Expose Command This command begins the exposure process and UV light is flooded over the mask and wafer for the exposure time set by the user.

Getting to the correct alignment between patterns developed by negative resist and that using positive resist is a crucial step. The first step is to overlap fully the alignment marks using the optical microscope and then adjusting the 50×50 µm pools. Still it is very difficult to get 100% overlap, and in most cases a 50% overlap on the square is observed as shown in Figure 5-17.



Figure 5-15. UV light exposure to wafer coated with negative photoresist SU8 2000.5.

After exposure, the wafer is then rinsed in SU8 2000.5 developer. Since SU8 is a negative resist, the areas that are not exposed will be removed and the resulting pattern is shown in Figure 5-16.



Figure 5-16. Wafer exposed to UV light after developing with SU8 developer.

5.3. Optimization of Nanohole Fabrication using Focused Ion Beam.

In order to test if the film is insulating, the films are electrodeposited in a CoFe plating solution for about 10 minutes and then checked under microscope to observe the pinhole density. The nanoholes are made using milling by Gallium (Ga⁺) ions using FEI

FIB. In order to develop an optimum milling time and beam current, we developed a checkerboard pattern with different time and current as shown in Figure 5-17.



Figure 5-17. SEM image of the checkerboard with i_{beam}=10 pA for varying times.

The nanoholes are not supposed to be too deep neither should it be too shallow. If the hole is shallow, it will just cut through the Alumina layer and not reach Cobalt. Thus there would not be any electroplating, since Alumina is an insulator. Also, if it is a pinhole area and electrodeposition does take place, then one ferromagnetic electrode would be permalloy which will be deposited later and the other end would have alumina, which does not serve the purpose.

On the other hand, if the hole is deep, then one side of the nanocontact will have Cu, since it will not cut through Co. Hence, an optimum beam current and time is designed. On the basis of these iterations, we designed two different recipes. The first recipe is a hole produced by 10 pA Ga^+ current for 5 sec and the other method is using 30

pA Ga⁺ current for 3 secs. In order to determine, the cross section of the nanocontact, we did a slicing cross section and determined the nanocontact size as shown in Figure 5-18.



Figure 5-18. SEM image of (A) CoFe mushrooms for holes milled with ibeam=10pA and t~5sec (B) Cross section of one of the nanocontacts and (C) CoFe mushrooms after the cross sectioning.

Both the Ga^+ beam currents produced a hole of ~70 nm. A schematic of the hole is shown in Figure 5-19.



Figure 5-19. Wafer after milling using FIB to form holes.

5.2. Fabricating Nanocontacts via CoFe electrodeposition and deposition of top ferromagnetic electrode

5.2.1. Optimization of formation of CoFe nanocontacts by electrodeposition

One disadvantage of producing holes by means of the FIB is that Gallium (Ga⁺) ions get deposited on the wafer surface. Hence, during electroplating of CoFe onto the holes, first the electrode is held at 100 mV positive of the Open Circuit potential for about 30 seconds to remove the gallium deposit and then a step potential of -1.1 V is applied which is the CoFe depositing potential. This was Method1 for developing the nanocontact. However, on developing cross sections of these films, we observed lots of voids which was due to the layer getting corroded due to the application of potential positive of OCP as shown in Figure 5-20.



Figure 5-20. Corrosion due to electrodeposition by Method1.

In order to avoid corrosion of the films, we directly applied a potential of -1.1 V for about 10 minutes. This is Method2 for CoFe electroplating. Thus sensors having

nanocontacts with different saccharin and oxide concentrations are produced. Before electroplating, the edges and back area of the chip are covered with an insulating layer (nailpaint) so that the only area where electrodeposition takes place is the hole developed by the ion beam and the current transient is reflective of the nanocontact deposition. The solution design and process parameters for the CoFe nanocontact electrodeposition is as shown in Table 5-5.

Solution Design	Value	Process parameter	Value
CoSO ₄ .7H ₂ O	15 g/L	γ	0.12
FeSO ₄ .7H ₂ O	31 g/L	Е	-1.1 V
H ₃ BO ₃	25 g/L	Deposition time	~10 minutes
NH ₄ Cl	16 g/L	рН	2.03
Saccharin	0-2.5 g/L	ω	0 rpm
Fe ³⁺	0-0.1 M	Deposition rate	48 nm/minute

Table 5-5. Solution design and process parameters for CoFe nanocontacts.

One such current transient for electrodepositing CoFe into the hole is shown in Figure 5-21.



Figure 5-21. Current transient for a hole which is electrodeposited with CoFe with 2 g/L saccharin and 0.01 M Fe^{3+.}

After the electroplating is performed, the chip is rinsed with acetone to remove the nailpaint and sonicated in acetone for about 30 minutes to remove the SU8 2000.5 photoresist. The schematic for the chip after the CoFe electroplating is as shown.



Figure 5-22. Wafer after electrodeposition of CoFe alloy onto the holes to form nanocontacts.

Various concentrations of saccharin and Fe^{3+} are added to the CoFe electrodeposition bath to understand the effect of stress and variation of oxide content on magnetoresistance value. The various concentrations are as shown in Table 5-6.

Saccharin (g/L)	Fe³⁺ (M)	
0	0, 0.0025, 0.05	
0.12	0, 0.0015, 0.0025, 0.005, 0.01	
2	0.01	

Table 5-6. Various concentrations of saccharin and Fe³⁺ added in CoFe electrodeposition bath for fabricating CoFe nanocontacts

5.2.2. Deposition of second Ferromagnetic electrode

The next step is depositing permalloy, which is the second ferromagnetic electrode. Before this process, it is necessary to do a flush sputtering to remove the oxide and also clean the top layer. Flush sputtering is done by allowing just argon gas to flow through the sputtering chamber. This step cleans the top layer and then we can deposit the soft magnetic material which is Permalloy in this case. Permalloy can be deposited in two ways. In the first method, Permalloy is deposited by DC sputtering. There are two steps in Permalloy sputtering. In the first step, the Permalloy target was heated up and plasma turns on. Here, the Permalloy sputtering rate was about 0.6 A°/sec and the pressure used was 5 mTorr and 20 % of maximum power was used. In the second method, Permalloy was deposited by thermal evaporation. In both cases, about 200 nm of Permalloy was deposited.

5.2.3. Deposition of contact Pads/Au Pads

After the second ferromagnetic electrode was deposited, the contact pads were deposited, which is Gold in this case. Gold of about 20 nm was deposited. The deposition of gold was done by thermal evaporation. Ideally we use a metal with a very low resistance and the purpose of the Gold layer is to protect the permalloy layer from oxidation. The final sensor design is as shown.



Figure 5-23. Schematic of the cross section of the final sensor design.

Fabrication processes are followed by testing of the wafers for the magnetoresistance by 4 point probe method. During sputtering, the metal layers get coated even at the edges and hence the edges are brushed off using sandpaper to make sure there is no electrical shorting between the top and bottom layers. This is the final magnetic field sensor that is tested for magnetoresistance measurements as shown in Figure 5-24. As we observe, the I and V connecctins are made by 4 copper alligator clips.


Figure 5-24. Final device used for magnetoresistance measurement.

CHAPTER 6

RESULTS AND DISCUSSIONS

The current research in development of magnetic alloys is aimed at increasing the areal density of magnetic recording and improvement in the reliability of MEMS devices. It is driven by the need for soft high magnetic moment (SHMM) alloys with high magnetic flux density, good corrosion resistance and low stress [92]. The general approach to electrodeposit SHMM alloys with good properties is to use different additives in formulation of the plating solutions. The most frequently used one is saccharin and its derivatives [6,15,93] which provide properties like reduction of stress and low coercivity. However, one of the drawbacks of additive incorporation in magnetic alloy is poor alloy corrosion resistance. In this research we try to understand the effect of additive incorporation on the properties of electrodeposited CoFe alloys. The corrosion mechanism of electrodeposited CoFe alloys was discussed as a function of the sulfur incorporation mechanisms in the alloy and the maximum growth stress is studied as a function of saccharin concentration in the CoFe electrodeposition bath.

6.1. Corrosion Potential of CoFe alloys

6.1.1. Open Circuit Potential Measurements

The corrosion potential of an alloy is its Open Circuit Potential and is recorded in a neutral solution of 0.05 M NaCl with pH=7. The open circuit potential of CoFe alloys electrodeposited with different concentrations of saccharin and measured at rotation rates of ω =0 rpm, 200 rpm and 1000 rpm are represented in Figure 6-1. The open circuit potential of the alloy was monitored at each of the rotation rates (ω) for 10 minutes.





Figure 6-1. Measurement of the OCP of CoFe alloys electrodeposited with different saccharin concentrations vs time for rotation rates (A) ω =0 rpm (B) ω =300 rpm (C) ω =1000 rpm. The testing solution is 0.05 M NaCl. The highlighted region indicates the stable range from where E_{corr} for each alloy is determined.

The corrosion potential is determined from the OCP measurements shown in Figure 6-1 at the range when $\frac{dE}{dT} < 5 \ mV/min$. The CoFe alloys were electrodeposited with varying saccharin concentrations and for three different rotation rates of 0 rpm, 300 rpm and 1000 rpm. It is observed that the corrosion potential of electrodeposited CoFe alloy shifts by about 250 mV in the negative direction with the addition of saccharin in the plating bath. The shift in the OCP to less negative values is understood with the help of Evans Diagram explained in Section 2.2.The limiting current density (j_L) for oxygen reduction reaction (ORR) is given by

$$j_L = \frac{nFD}{\delta} C_{O_2} \tag{6-1}$$

where δ is the diffusion layer thickness, n=4 is the number of electrons involved in the reaction, D is the diffusivity of O₂ in solution, C_{O2} is the bulk oxygen concentration and F=96500 C/mol is the Faraday's constant. Higher rotation rate (ω) causes a decrease in the diffusion layer thickness (δ) and from Equation 6-1 we should expect a rise in the limiting current density (j_L) of the oxygen reduction reaction. Thus, with the increase in j_L, mathematically we expect a positive shift in the value of corrosion potential (E_{corr}) from the equation of corrosion potential explained in Section 2-2

$$E_{corr} = E_0 + \frac{RT}{\alpha F} \left(\ln \left(\frac{j_L}{j_0} \right) \right).$$
(6-2)

6.1.2. Corrosion Potential vs Saccharin Concentration for different rotation rates

The corrosion potential (E_{corr}) of electrodeposited CoFe alloys as a function of the saccharin concentration in the electrodeposition bath determined form Figure 6-1 for different rotation rates is shown in Figure 6-2.



Figure 6-2. Corrosion potential of electrodeposited CoFe alloy as a function of saccharin concentrations in CoFe plating solution for different rotation rates. The testing solution is 0.05 M NaCl.

It is evident from Figure 6-2 that the corrosion potential shifts to 200 mV positive when rotation rate increases from 0 to 300 rpm, but there is not much variation in the corrosion potential change from 300 to 1000 rpm. As the rotation rate increases, the corrosion potential becomes almost independent of the rotation rate meaning that the oxygen reduction reaction becomes activation controlled.

The CoFe alloy electrodeposited without saccharin ($C_{sac}=0$ g/L) has the least negative corrosion potential of -325 mV vs SCE indicating that it is most resistant to corrosion. A small addition of saccharin of 0.06 g/L to the electrochemical deposition bath causes a negative shift of E_{corr} by 250 mV vs SCE indicating that it is saccharin incorporation which is responsible for the deterioration of corrosion properties. The most negative corrosion potential is observed for the alloy with saccharin concentration of $C_{sac}=0.12$ g/L and for concentrations of saccharin higher than that, the corrosion potential is not significantly affected. Thus, we do not see a very direct dependence of the corrosion potential on the saccharin concentration. Previous research [7] on the sulfur incorporation in CoFe alloys electrodeposited with varying concentrations of saccharin yielded a relation between the saccharin concentration in the plating bath (C_{sac}) and sulfur incorporation rate (R_s) as

$$R_{s} = R_{R} + K_{1} \cdot \frac{b \cdot C_{sac}}{\left(1 + b \cdot C_{sac}\right)^{2}} + K_{2} \cdot \frac{b \cdot C_{sac}}{1 + b \cdot C_{sac}},$$
(6-3)

where the term b is the saccharin adsorption constant (L/g), $K_1 \cdot \frac{b \cdot C_{sac}}{(1+b \cdot C_{sac})^2}$ indicates incorporation of sulfur due to saccharin molecule as a whole (R_M) and the term $K_2 \cdot \frac{b \cdot C_{sac}}{1+b \cdot C_{sac}}$ indicates incorporation of sulfur due to electroreduction mechanism (R_{ER})

i.e. reduction of saccharin to form sulfides namely CoS, FeS, CoFeS. Here, K_2 is the electroreduction rate constant defined as $K_2 = \chi k \Gamma_{ML}$ where χ is the efficiency factor that was introduced to take into account that not every sulfur atom belonging to the initially electroreduced saccharin molecule gets incorporated into the CoFe deposit, k is the reduction rate constant defined in per-second units and K_1 is the molecular incorporation

rate constant defined as $K_1 = \frac{\Gamma_{ML} \cdot \Delta v}{d_{sac}}$, where Γ_{ML} is the concentration of the full saccharin monolayer, d_{sac} is the diameter of the saccharin molecule, Δv is the difference in the growth rate of the free CoFe surface and the growth rate of the CoFe surface covered by the saccharin molecule. Hence, representing the corrosion potential of the

CoFe alloys electrodeposited with saccharin as a function of the sulfur incorporation

mechanisms gives a much clearer picture since the corrosion potential is seen to be a linearly decreasing function of the sulfur incorporation rate (R_s). Sulfides in metal deposits have been known to be detrimental for corrosion resistance [94]. Tabakovic et al earlier attempted to study the corrosion in electrodeposited CoFe alloys in terms of sulfur-assisted corrosion by investigating the structure of sulfur containing molecules included in the deposit [6]. This work explained the reduction of sulfur to metal sulfides via a 4 step reduction. The sulfide inclusions are likely to initiate localized corrosion on heterogeneous surface defects like step edges, dislocations and grain boundaries. Additionally, Frankel performed experiments on Permalloy films electroplated with saccharin and the presence of Sulfur along with Carbon and Nitrogen along pit walls indicate that the increased corrosion was due to sulfur from saccharin [8]. The reason is sulfur catalyzes anodic dissolution and hinders passivation due to the strong metal-sulfur bonds that weakens the metal-metal bonds and sulfur at surface blocks sites for OH⁻ adsorption which is necessary for passivation. This hypothesis was verified by means of STM analysis which demonstrated reconstruction of the Ni surface due to S to form chemisorptions sites [94]. This weakening of the metal-metal bonds results in lowering the activation energy for dissolution of surface metal atoms.



Figure 6-3. Sulfur induced weakening of surface metal-metal bonds and enhancement of anodic dissolution [95].

The expression for sulfur incorporation in terms of its incorporation mechanism from Equation 6-3 helps us to interpret corrosion potential (E_{corr}) as a function of sulfur incorporation rate (R_s) in the electrodeposition bath and the corresponding graphs are expressed in Figure 6-4.



Figure 6-4. Corrosion potential of electrodeposited CoFe alloys as a function of sulfur incorporation rate due to saccharin in the CoFe electrodeposition bath. Testing solution is 0.05 M NaCl. This relation is by considering b as 11L/g and K_1 as 5.3 and K_2 as 0.625 [7].

Figure 6-4 demonstrates corrosion potential as a function of the sulfur incorporation rate using the data from Figure 6-2 and equation 6-3. The value of the adsorption constant b is chosen to be as 11 L/g [87]. The figure indicates a direct linear dependence of the corrosion potential of electrodeposited CoFe alloy to the sulfur incorporation rate due to saccharin in the plating bath.

6.2. Determination of Corrosion Parameters for CoFe alloys electrodeposited with varying saccharin concentrations.

The exchange current density (j_0) , charge transfer resistance (R_{ct}) and electrooxidation potential (E_{ox}) are parameters that help in understanding the corrosion behavior of an alloy and its corrosion rate. These parameters are determined from the linear sweep voltametry measurements performed on electrodeposited CoFe alloys in 0.05 M NaCl testing solution. Figure 6-5 shows the LSV for CoFe alloys electrodeposited with varying concentrations of saccharin.



Figure 6-5. Linear sweep voltammetry (LSV) for CoFe alloy electrodeposited with different concentrations of saccharin with a scan rate of 5 mV/s. The testing solution is 0.05 M NaCl.

6.2.1. Determination of Charge Transfer Resistance

Figure 6-6 is the linear sweep voltametry for the CoFe alloy electrodeposited with 0.12 g/L of saccharin and Figure 6-5B represents the initial overpotential linear region selected from the linear sweep voltametry for the calculation of charge transfer resistance.



Figure 6-6. (A) Linear sweep voltametry for CoFe alloy electrodeposited with 0.12 g/L of saccharin and (B) Initial overpotential region of 20 mV used in calculation of R_{ct} .

From Figure 6-6A, we consider only the first 20mV linear overpotential region from the point where anodic dissolution starts and fit those points with the equation $j = \frac{1}{R_{ct}}\eta$. The reciprocal of the slope gives us the charge transfer resistance in Ohms.cm²

as shown in Figure 6-7.



Figure 6-7. (A) R_{ct} as a function of the saccharin concentration (C_{sac}) in the CoFe plating bath and (B) R_{ct} as a function of the sulfur incorporation via saccharin electroreduction mechanism considering b as 11 L/g.

From Figure 6-7, it is observed that the charge transfer resistance is maximum for CoFe alloy electrodeposited without saccharin with a value of about 5400 Ohms.cm² and for increasing concentrations of saccharin in the bath, there is no obvious linear dependence observed. However, when the charge transfer resistance is plotted against the term representing S incorporation via electroreduction mechanism $\frac{b \cdot C_{sac}}{1 + b \cdot C_{sac}}$ and considering b as 11 Lg⁻¹ [7]. We observe a linear regression function indicating that the incorporation of S into alloy as metal sulfides contributes majorly to the CoFe alloy corrosion phenomenon.

6.2.2. Determination of Exchange current density

The exchange current density (j_0) of the corrosion reaction is determined from the linear overpotential region of the linear sweep voltametry by the equation [64]

$$j_0 = \frac{R \cdot T}{F \cdot R_{ct}} \quad [\text{mA·cm}^{-2}].$$
(6-4)

Thus, the exchange current density is inversely proportional to the charge transfer resistance and is represented in Figure 6-8 as a function of the saccharin concentration (C_{sac}) in the CoFe electrodeposition bath. However, j_0 does not seem to have a clear linear dependence on the saccharin concentration. A better understanding of the effect of saccharin on j_0 is demonstrated if j_0 is plotted against the term representing sulfur incorporation via electroreduction mechanism. The higher the exchange current density, more negative is the corrosion potential and thus greater is the tendency of the alloy to corrode.



Figure 6-8. Exchange current density using $R_{ct} = \frac{RT}{F \cdot j_0}$ as a function of the saccharin concentration.

Using the data in Figure 6-8 and by considering the saccharin adsorption constant b as 11 L/g [7], we can obtain relation for j₀ as a function of term $\frac{b \cdot C_{sac}}{1 + b \cdot C_{sac}}$ representing the S incorporation via electroreduction mechanism to form metal sulfides and is as shown in Figure 6-9.



Figure 6-9. Exchange current density (j_0) as a function of sulfur due to saccharin electroduction term where b =11 L/g [7].

From Figure 6-9, we observe a linear dependence of the exchange current density for the sulfur incorporation due to electroreduction mechanism and can be represented as linear function of the form

$$j_{0(sac)} = j_0(no \ sac) + K \cdot \frac{b \cdot C_{sac}}{1 + b \cdot C_{sac}},$$
(6-5)

where K is the slope from Figure 6-9 and determined to be 2.18 and b is the saccharin adsorption constant expressed in L/g, $j_{0(no sac)}$ is the exchange current density for the CoFe alloy electrodeposited without any saccharin. Equation 6-5 is used to fit the data in Figure 6-10 and the equation can be represented as

$$j_{0(sac)} = X + \frac{Y \cdot C_{sac}}{1 + Z \cdot C_{sac}} \cdot$$
(6-6)

Here X, Y, Z are the fitting parameters. X is the term $j_{0(no sac)}$, Z is the saccharin adsorption constant and Y=K·b. The model fit to the data is as represented in Figure 6-10.



Figure 6-10. Model fit using Equation 6-6 to the data in Figure 6-10.

The fitting parameters obtained from the fit are the saccharin adsorption constant as 48 L/g which is close to the earlier calculated value of 11 L/g [7]. Also, the value of $j_{0(no \ sac)}$ obtained from the fit are $4.5*10^{-6}$ mA/cm² which is close to the experimental value which proves the validity of the model.

6.3. Determination of the Electro-oxidation potential

Electro-oxidation potential is the point in a linear sweep voltamtery curve where the process of oxidation just initiates, and current starts to increase with positive values. It can be considered as the reversible potential of an alloy and is determined from the Linear sweep voltametry measurement. Figure 6-11 A represents the linear sweep voltametry curve for CoFe alloy electrodeposited with 0.12 g/L saccharin and shows the point in the curve which is considered to the electro-oxidation potential.



Figure 6-11. (A) Linear sweep voltametry for CoFe alloy electrodeposited with 0.12 g/L of saccharin and (B) Electro-oxidation potential of electrodeposited CoFe alloy as a function of Saccharin concentration (Csac) in the plating bath. Testing solution is 0.05 M NaCl.

From Figure 6-11 B is the graph for E_{ox} as a function of saccharin concentration in the CoFe electrodeposition bath and we observe that the E_{ox} for CoFe alloy 135

electrodeposited with no saccharin, i.e. the CoFe alloy with least amount of sulfur content has the least negative electro-oxidation potential of about -190 mV and then the electrooxidation potential for CoFe alloys electrodeposited with varying saccharin concentration does not vary a lot. Hence, from Figure 6-10 B we can assume that the electro-oxidation potential for CoFe alloy electrodeposited with saccharin is constant ~ -600 mV. Thus, there is a clear distinction between the electro-oxidation potential for CoFe alloys electrodeposited with and without saccharin. During the modeling of the corrosion potential, we can consider the electro-oxidation potential as equivalent to the reversible potential of the CoFe alloy.

6.4 Analytical model for the Corrosion Potential

Using Mixed Potential theory [5,27], and from Section 2.2, the corrosion potential for an alloy is expressed as

$$E_{corr} = E_0 + \frac{RT}{\alpha F} \left[\ln \left(\frac{\frac{nFD_{O_2}}{\delta} C_{O_2}}{\frac{j_0}{\delta}} \right) \right],$$
(6-7)

where E_{corr} is the corrosion potential of an alloy, E_0 is the reversible potential and can be considered as the electro-oxidation potential, α is the charge transfer coefficient, n is the number of electrons involved in the oxygen reduction reaction (4), F is the Faraday's constant =96500 C/mol, C₀₂ is the bulk oxygen concentration and can be considered to be 2.6* 10⁻⁴ M at standard pressure [33], D_{o_2} is the diffusion constant of dissolved O₂ in solution and is dependent on temperature, δ is the diffusion layer thickness and is dependent on the agitation rate and i_0 is the exchange current density expressed in A/cm². As shown in Section 6.3 and Equation 6-5, $j_0 = j_{0(nosad)} + K \cdot \frac{b \cdot C_{sac}}{1 + b \cdot C_{sac}}$, the exchange

current density can be expressed as a linear function of the amount of S incorporated due to saccharin electroreduction to form metal sulfides and so we can express E_{corr} to be a function of saccharin concentration (C_{sac}) in the plating bath as

$$E_{corr} = E_0 + \frac{RT}{\alpha F} \left[\ln \left(\frac{j_L}{j_{0(nosac)} + K \frac{b \cdot C_{sac}}{1 + bC_{sac}}} \right) \right].$$
(6-5)

The data for corrosion potential as a function of saccharin concentration is fit by 2 methods.

Method 1.

In Method 1, we consider the model explained above and allow 6 fitting parameters and the corrosion potential is fit by the following function

$$E_{corr} = A + B \cdot \ln\left(\frac{C}{D + \left(\frac{E \cdot x}{1 + F \cdot x}\right)}\right),\tag{6-6}$$

where, A is the reversible potential of the CoFe alloy, B is the term $\frac{RT}{\alpha F}$, C is the

diffusion limited current density expressed as $j_L = \frac{nFD}{\delta} \cdot C_{O_2}$, D is the exchange current

density for CoFe alloy electrodeposited with no saccharin, E is the term K b where K is

the proportionality constant and b is the saccharin adsorption constant represented by F. We can test the validity of this fit to see if these parameters obtained from the analytical model fit have physical significance.

Method 2

The diffusion limited current density (j_L) depends on the rotation rate and can be calculated. Also, the term $\frac{RT}{\alpha F}$ can be calculated to be 0.05 by considering R=8.314 JK⁻¹mol⁻¹, T=300 K, F=96500 C/mol and $\alpha = 0.5$. Thus, there are 3 fitting parameters in this approach and the equation can be represented as

$$E_{corr} = A + 0.05 \ln \left(\frac{j_L}{D + \left(\frac{E \cdot x}{1 + 11 \cdot x} \right)} \right).$$
(6-7)

The next step is to test the validity of this analytical model for different rotation rates.

6.4.1. Analytical model fit to E_{corr} vs C_{sac} for rotation rate (ω =0 rpm)

The corrosion potential as a function of C_{sac} for $\omega=0$ rpm from Figure 6-2 A is fitted to Equation 6-4 and is as represented in Figure 6-12.



Figure 6-12. (A) Analytical model fit to corrosion potential (E_{corr}) for electrodeposited CoFe alloy as a function of saccharin concentration in the plating bath for rotation rate ω =0 rpm using Equation 6-6 (Method 1) and (B) E_{corr} vs C_{sac} dependence using Equation 6-7 (Method 2).

Figure 6-12A is the analytical model fit using Method 1 to the data in Figure 6-2 and the parameters extracted from the model fit from Figure 6-11A are $j_L=0.1$ A/cm² and $E_0=-0.57$ V, saccharin adsorption constant b=41.72 L/g, $\frac{RT}{\alpha F}=0.07$ and thus 36.95 C

$$j_0 = 0.014 + \frac{36.93 \cdot C_{sac}}{1 + 41.73 \cdot C_{sac}}$$

Calculation of j_L for $\omega = 0$ rpm.

We can consider the data from literature as δ =0.05 cm, C_{O_2} =2.6*10⁻⁴ M [33], the

diffusivity of oxygen in water is chosen to be $2*10^{-5} \text{ cm}^2/\text{s}$ [96]. Thus, $j_L = \frac{nFD}{\delta}C_{o_2} = 0.015 \text{ A/cm}^2$. Using this data, and b as 11 L/g [7] the corrosion potential is fitted using

Method2 and is as shown in Figure 6-12B. Thus, there are 3 fitting parameters as shown

in Equation 6-7. The parameters extracted from the fit are $A=E_{ox}=-0.450$ V vs SCE, and

$$j_0 = 0.017 + \frac{13.54 \cdot C_{sac}}{1 + 11 \cdot C_{sac}}$$
.

Table 6-1. Values for various parameters determined from the fit using Method 1, Method 2 and literature values for $\omega=0$ rpm.

	Value extracted from fit	Calculated value using data from literature
j l	0.1 A/cm^2	0.015A/cm ²
b	41.72 L/g	12 L/g
RT/aF	0.07	0.05
E ₀	-0.57 V(Method1)	-0.45 V(Method2)

6.4.2. Analytical model fit to E_{corr} vs C_{sac} for rotation rate (ω =300 rpm)



Figure 6-13. (A) Analytical model fit to corrosion potential (E_{corr}) for electrodeposited CoFe alloy as a function of saccharin concentration (C_{sac}) in the plating bath for rotation rate ω =300 rpm using (A) Method 1 with Equation 6-6 and (B) E_{corr} vs C_{sac} dependence using Equation 6-7 (Method 2).

Figure 6-13 A is the analytical model fit to the data for corrosion potential of electrodeposited CoFe alloys as a function of C_{sac} for rotation rate ω = 300 rpm using Equation 6-6. From Figure 6-12A, the parameters extracted from the fit are A=E₀=-0.58 V, B=RT/ α F=0.086, C=j_L=0.3356 A/cm², and F=b=22.2. The values for the reversible potential (E₀), $\frac{RT}{\alpha F}$, b are comparable to data from literature which proves the validity of the fit

the fit.

Calculation of j_L for ω =300 rpm.

$$j_L = \frac{nFD}{\delta} C_{O_2}$$

The ratio of diffusivity to diffusion layer thickness is calculated as

 $\frac{\delta}{D} = 1.61 D^{-0.67} \omega^{-0.5} \upsilon^{0.7}$ [64]. The diffusivity of oxygen in air is assumed to be 2*10⁻⁵ cm²/s [96] and thus the calculated value of $i_L=0.2$ A/cm². The value obtained for i_L from fit using Method1 ($i_L=0.33$ A/cm²) is close to the calculated value, which provides further validity to the proof. The calculated value of i_L and $\frac{RT}{\alpha F}$ is used to fit the data using Equation 6-7. Thus the data in Figure 6-4 is fit using the known value from literature or calculated values and Equation 6-7. This fit is represented in Figure 6-12B and the values extracted from the fit are $E_{ox} = -0.42$ V.

	Value extracted from fit	Calculated value using data from literature
jı	0.34 A/cm^2	0.2 A/cm^2
b	22.2 L/g	11 L/g
RT/aF	0.08	0.05
E ₀	-0.58 V	-0.42 V
	(Method1)	(Method2)

Table 6-2. Values for various parameters determined form the fit using Method1, Method2 and literature values for ω =300 rpm.

6.4.3. Model fit to E_{corr} vs C_{sac} for rotation rate (ω =1000 rpm)



Figure 6-14. (A) Analytical model fit to corrosion potential (E_{corr}) for electrodeposited CoFe alloy as a function of saccharin concentration(C_{sac}) in the plating bath for rotation rate ω =1000 rpm using (A) Method 1 with Equation 6-6 and (B) E_{corr} vs C_{sac} dependence using Equation 6-7 (Method 2).

Figure 6-14A is the analytical model fit to the data for corrosion potential of electrodeposited CoFe alloys for rotation rate ω =1000 rpm as a function of saccharin concentration (C_{sac}) using Equation 6-6. From Figure 6-14A, the parameters extracted from the fit are A=E₀=-0.5398 V vs SCE, B= $\frac{RT}{\alpha F}$ =0.084, C= j_L=0.503 A/cm², F=b (saccharin adsorption constant)=16.3 L/g. The values for the reversible potential and saccharin adsorption constant are close to the literature value which proves the validity of the fit.

Calculation of j_L for ω =1000 rpm.

Using the calculation similar in Section 6.4.2, for ω =1000 rpm, we obtain j_L as 0.37 A/cm². Thus the calculated value for diffusion limited current density is close to the value obtained from fit (Method1). The calculated value of j_L is then used in method2 and the fit is as shown in Figure 6-14B. The values obtained from fit using method 2 is E_{ox}=-0.54 V.

In conclusion, we can say that the analytical model developed by using mixed potential theory fits our experimental data well and the parameters obtained have physical significance. In order to confirm the validity of the model and experimental data, we tabulate the results for various parameters for the three rotation rates.

	Value extracted from fit	Calculated value using data from literature
jl	0.5 A/cm^2	0.37 A/cm^2
b	16.3 L/g	11 L/g
RT/αF	0.08	0.05
E ₀	-0.54 V	-0.5 V
	(Method1)	(Method2)

Table 6-3. Values for various parameters determined form the fit using Method1, Method2 and literature values for ω =1000 rpm.

6.5. Optimizing the saccharin concentration in electrodeposited CoFe alloys to obtain corrosion resistant alloys

The allowed corrosion between pole and head is about 3nm. Form Section 6.4, we can approximate the corrosion current density (j_{corr}) to be about 10^{-6} A/cm². Also considering the density of Co-Fe to be 8 g/cm3, Faraday's constant as 96500 C/mol and the total seconds in a year to be 31536000 sec/year, the total amount of mass disintegrated is about 10nm/year. This is more as compared to the accepted value and hence it is necessary to maintain an optimum. Thus, from Section 6-2, where we obtain a relation of exchange current density as a function of saccharin concentration in the plating bath, the optimum concentration can be chosen so that the corrosion rate is within acceptable limits. However, this would mean a compromise in the coercivity value.

One technique to obtain softer alloys and yet demonstrate high corrosion resistance is by incorporating little concentration of noble metals like Gold, Platinum of about 10^{-4} M in the electrodeposition bath. The graph of the OCP of the CoFe alloys with and without noble metal (Pt) is as shown in Figure 6-15.



Figure 6-15. OCP of CoFe alloys electrodeposited with and without Pt.

As observed in Figure 6-15, the OCP for the CoFe alloys electrodeposited with noble metals is about 300 mV positive as compared to the alloys fabricated without incorporation of noble metal.

6.5 In-situ stress Measurements in CoFe alloys

6.5.1. Saccharin Adsorption on CoFe Electrode Surface

Saccharin is a condensed organic molecule having the benzyl and heterocyclic rings in its structure. Previous reports suggest that saccharin adsorbs on the metal surface during electrodeposition process forming a certain type of condensed phase [97-99]. The

saccharin molecule has very small dipole moment and it is expected to adsorb on a metal surface in the region near the potential of zero charge (PZC) [30]. The density and the coverage of the adsorbed saccharin phase are dependent on the potential of the electrode surface and saccharin concentration in solution [30,31]. Our EIS measurements of double layer capacitance for electrodeposited CoFe films are shown in Figure 6-16.



Figure 6-16. (A) Double layer capacitance vs. CoFe electrode potential for two different saccharin concentration in solution, (B) Calculated saccharin coverage vs. electrode potential. Data in (B) calculated using Equation (6-8) and data in (A). The line indicates potential of CoFe surface during electrodeposition process.

The measurements are performed in 0.4 M H₃BO₃ (25 gL⁻¹) + 0.3 M NH₄Cl (16 gL⁻¹) solution with 0.12 gL⁻¹ and 1gL⁻¹ concentrations of saccharin. Considering the high concentration of electrolyte, one expects that double layer capacitance should not have significant dependence on electrode potential [100]. However, a pronounced capacitance well centered at the potential of \approx -1.33 V with minimum, $C_{DL}\approx5\times10^{-6}$ F, indicates that saccharin adsorbed phase is present on CoFe surface [99] [30]. The width of the capacitance well is \approx 0.1 V for solution with 0.12 gL⁻¹ of saccharin and increases to \approx 0.2 V in solution containing 1 gL⁻¹ saccharin concentration. From C_{DL} vs. *E* data, Figure 6-16A, the corresponding saccharin coverage of CoFe electrode, θ , can be calculated using *Frumkin* relation [31];

$$\theta(E) = \frac{C_{DL}^{\max} - C_{DL}(E)}{C_{DL}^{\max} - C_{DL}^{\min}} .$$
(6-8)

Here, C_{DL}^{max} and C_{DL}^{min} represent the maximum and minimum double layer capacitance of the CoFe surface for a given potential range and $C_{DL}(E)$ is the capacity of double layer at potential for which the saccharin coverage is calculated. From data in Figure 6-16A, the θ vs. *E* dependence is calculated using Equation (6-8) for these two solutions, Figure 6-16B.

During our *insitu* stress measurements, the CoFe films were deposited galvanostatically from solutions containing different saccharin concentrations. The electrode rest potential in those experiments was -1.1 ± 0.01 V. At this potential (Figure 6-16B) the apparent saccharin coverage of CoFe surface was found to be, θ = 80% (C_{sac} = 0.12 gL⁻¹) and θ =96% (C_{sac} = 1 gL⁻¹). Undoubtedly, the results in Figure 6-16A and 6-16B suggest that by choosing different concentration of saccharin in the plating solution,

one can effectively control the coverage of this additive during the CoFe electrodeposition process [30]. The control of saccharin coverage means a direct control of its action as an additive.





Figure 6-17. (A) At % of Co and Fe in CoFe films as function of saccharin concentration in plating solution, (B) The average grain size of CoFe films electrodeposited from solutions with different concentrations of saccharin. The data in (B) obtained from FWHM measurements of <110> peak from 20 XRD scan.

In Figure 6-17A, the compositions of electrodeposited CoFe films from solution containing different concentrations of saccharin are presented. These results suggest that the composition of the CoFe films does not change to an appreciable extent for a wide range of investigated saccharin concentrations. The Fe content in CoFe films was found \approx 71 at % and Co \approx 29 at%. The observed variation in Fe and Co atomic composition of individual CoFe films is within the error bar of the EDX measurements ($< \pm 2\%$), thus the CoFe film composition could be considered constant and independent of the saccharin concentration in the plating solution. The XRD measurements revealed that all CoFe films have a body-centered cubic (BCC) structure with predominant <110> texture. This is not surprising since the Fe is a BCC metal and its content in CoFe films is dominant (>50%). We have used full width of half maxima (FWHM) measurements of the <110>peak in 20 scans to calculate the average grain size of CoFe films[78] produced from solutions containing different saccharin concentration. The grain size was calculated by using the Debye Scherrer's law given as $d = \frac{0.9\lambda}{B\cos\theta}$. These data are shown in Figure 2B. The error bars in Figure 6-17B represent the standard deviations of Gaussian function fit to the <110> peaks in 2 θ scans from which the FWHM is determined. It is evident that different saccharin concentrations in the plating solution have no effect on the grain size of CoFe deposit. The estimated grain size from XRD measurements for all films is in (20 \pm 1) $\times 10^{-9}$ m range, Figure 6-17B. Considering the previous reports in the literature [92,93,97,101], this is a bit surprising result. However, the deposition (rest) potential for all CoFe surface during electrodeposition was the same for all samples (E=-1.1 ± 0.01 V, Table 1). The deposition current/flux was the same for all samples as well, (j= -4 mAcm⁻

 2 , Table 1). Therefore, the essential conditions for nucleation and growth were the same for all CoFe films. The growth of CoFe films was not affected by the different content of saccharin in the plating solution and consequently a different coverage of the saccharin phase adsorbed on the CoFe surface. In order to re-confirm this result, the transmission electron microscopy study was performed on several CoFe films produced from solutions with 0 gL⁻¹, 0.12 gL⁻¹ and 1.5 gL⁻¹ saccharin concentrations as shown in Figure 6-17C.



Figure 6-17. (C) Representative TEM images of CoFe films electrodeposited from solution containing 0, 0.12 and 1.5 gL⁻¹ of saccharin.

The representative TEM images of the samples are shown in Figure 6-17C for illustration purpose. The careful analysis of TEM images revealed qualitatively the same result as the XRD data. The average grain sizes in these samples were the same ($d_G \approx 15$ -20 nm).

6.5.3. Insitu Stress Measurements and Analytical Model

In the literature there are scarce reports about the effect of additive concentration in solution on the level of growth stress in electrodeposited SHMM films. Most of the data are obtained for saccharin as an additive using ex-situ wafer curvature measurements

[92,101-103]. The observed stress sign is usually positive (tensile) with the decreasing trend for increasing concentration of saccharin in solution [101].



Figure 6-18. (A)Stress-Thickness curves during in-situ CoFe film stress measurements. (B)The maximum of average stress in CoFe films(circles) and average stress at 0.3microns thickness as function of saccharin concentration in plating bath [87].

In Figure 6-18A, the *insitu* average film stress is presented for electrodeposited CoFe films from solutions containing 9 different saccharin concentrations. The average

stress acting on the cross-section of CoFe films (σ_{AVRG}) during thickness evolution is tensile, except for very initial region ($t_f < 0.03 \times 10^{-6}$ m) where compressive stress is observed due to the CoFe films nucleation on Au seed [2]. As expected, the CoFe film electrodeposited from solution without saccharin shows largest tensile stress level. For all CoFe films, the shape of stress curves is very similar. The main difference among them is the value of the maximum tensile stress. The maximum stress vs. saccharin concentration dependence is presented in Figure 6-18B together with the stress data for 0.3×10^{-6} m film thickness. The difference for these two sets of data is very small. All CoFe films reach the maximum tensile stress at about the same thickness, ($t_f = 0.08 \pm 0.01 \text{ } \mu\text{m}$). After the maximum tensile stress is developed, little change in stress value is observed as the film thickness increases. This is evident on both Figure 6-18A and 6-18B. This type of stressthickness behavior is characteristic of low surface adatom mobility metals (type I) [34] and is not surprising for our alloy system. The electrodeposition is a room temperature growth process at which both Fe and Co have low surface diffusivity. Along with this argument it should be added that Fe^{2+} and Co^{2+} are reduced to the metallic state through the formation of intermediate hydroxides adsorbed on the growing CoFe surface [92]. For relatively large deposition rate in our experiments $((35\pm2) \times 10^{-9} \text{ m} \cdot \text{min}^{-1})$ it is likely that arriving Fe and Co adatoms on the surface immediately nucleate or attach to already existing nuclei rather than continue diffusing over the surface to incorporate in the grain boundaries.

For low surface mobility metals [34], the maximum tensile stress in the film is set during the grain coalescence stage as a result of the grain boundary formation or so called grain *zipping* process [3,35,40,104,105].



Figure 6-19. Schematics of grain zipping process for (A) clean CoFe surface and (B) Saccharin covered CoFe surface.

The value of the maximum tensile stress due to grain boundary formation of hemispherical shaped CoFe grains can be evaluated as[40];

$$\sigma_{AVRG,CoFe}^{\max} = 8 \frac{\Delta \gamma_{CoFe}}{d_G}.$$
(6-9)

The d_G represents the average diameter of the grains in the deposit while the term $\Delta \gamma_{CoFe}$ is the driving force for the grain zipping process. It represents the positive difference between the surface energy of impinging CoFe grains, γ^{S}_{CoFe} and $\frac{1}{2}$ of the energy of the

newly formed grain boundary, γ_{CoFe}^{GB} ($\Delta \gamma_{CoFe} = \gamma_{CoFe}^{S} - \frac{1}{2} \cdot \gamma_{CoFe}^{GB}$). For CoFe film

electrodeposited from solution without saccharin, the observed $\sigma_{AVRG,CoFe}^{max} = 450 \times 10^6$ Pa,

Figure 6-18B. Knowing that d_G is 20×10^{-9} m, Figure 6-18B, Equation 6-9 yields the value for $\Delta \gamma_{CoFe}$ to be 1.125 Jm⁻². The literature data (vacuum experiments) suggest that $\gamma_{Co}^{s} \approx \gamma_{Fe}^{s} = 2.48$ Jm⁻² [106]. Considering that our work refers to the CoFe surface in contact with the electrolyte we can take the value of 2.48 Jm⁻² to be an upper limit for surface energy of CoFe films in contact with electrolyte, γ_{CoFe}^{s} . The upper limit for $\frac{1}{2} \gamma_{CoFe}^{GB}$ of CoFe films electrodeposited without saccharin is calculated as 1.36 Jm⁻². It is evident that values, $\Delta \gamma_{CoFe}$ and $\frac{1}{2} \gamma_{CoFe}^{GB}$ calculated from our experimental data and theoretical framework of Equation 6-9 are realistic, and they fall within the physically meaningful range. This proves that our insitu stress measurements system is reliable and accurate and that all implemented approximations in cantilever curvature evaluation are physically correct.

The saccharin addition to the plating solution significantly lowers the maximum tensile stress in CoFe films, Figure 6-18A. The effect is proportional to the amount of saccharin in the plating solution. For example, the CoFe films electrodeposited from 0.03 gL⁻¹ and 1.5 gL⁻¹ saccharin solutions exhibit a 1.5 and 9 folds stress reduction as compared to the CoFe films electrodeposited from saccharin free solution. The very similar shape of σ_{AVRG} vs. t_f dependence for all films indicate that there is no fundamental change in the origin of tensile stress generation with introduction and increase of the saccharin concentration in the plating solution. The fact that d_G is the same for all CoFe films (20×10^{-9} m) suggests that saccharin's role in lowering stress in CoFe films is the reduction of the driving force for grain zipping process, Equation 6-9. This can be understood on the premise of saccharin adsorption phenomenon. The saccharin molecules which are adsorbed on the growing CoFe film surface modify the surface energy, and after grain zipping, the grain boundary energy of the CoFe films. Obviously, the extent of this effect is dependent on the coverage of adsorbed saccharin phase, θ . We can model
the surface energy of CoFe grains with adsorbed saccharin phase of arbitrary coverage, $\gamma(\theta)_{Sac/CoFe}^{s}$, as the linear combination between the surface energy of CoFe grains without adsorbed saccharin phase (γ_{CoFe}^{s}) and surface energy of CoFe grains with the maximum saccharin coverage, $\gamma_{Sac/CoFe}^{s}$ (θ =1), *viz*;

$$\gamma(\theta)_{Sac/CoFe}^{S} = \theta \cdot \gamma_{Sac/CoFe}^{S} + (1 - \theta) \cdot \gamma_{CoFe}^{S}.$$
(6-10)

Using the same analogy, the grain boundary energy of the grain boundaries formed after zipping process of grains having an arbitrary saccharin coverage $\gamma(\theta)_{Sac/CoFe}^{GB}$, can be expressed as;

$$\gamma(\theta)_{Sac/CoFe}^{GB} = \theta \cdot \gamma_{Sac/CoFe}^{GB} + (1 - \theta) \cdot \gamma_{CoFe}^{GB}.$$
(6-11)

Here, the term $\gamma_{Sac/CoFe}^{GB}$ represents the energy of the grain boundary formed by zipping of the two CoFe grains surface with the maximum saccharin coverage, (θ =1). Now, we can define the driving force for the zipping process of the CoFe grains (Figure 6-19B) with adsorbed saccharin phase having an arbitrary coverage θ as

$$\Delta \gamma(\theta) = \gamma(\theta)_{Sac/CoFe}^{S} - \frac{1}{2} \gamma(\theta)_{Sac/CoFe}^{GB} \cdot$$
(6-12)

Substituting Equations (6-10) and (6-11) into Equation (6-12) yields phenomenologically more transparent expression for $\Delta \gamma(\theta)$ as

$$\Delta \gamma(\theta) = \Delta \gamma_{CoFe} - \theta \cdot (\Delta \gamma_{CoFe} - \Delta \gamma_{Sac/CoFe}).$$
(6-13)

It is obvious that the driving force for zipping process of the grains with adsorbed saccharin phase is a strong function of saccharin coverage. Using the form of Equation(6-

9) we can now define the maximum tensile stress developed in electrodeposited CoFe films with an arbitrary coverage of adsorbed saccharin phase as:

$$\sigma_{AVRG}^{\max}(\theta) = 8 \frac{\Delta \gamma(\theta)}{d_G}.$$
(6-14)

Combining Equations (6-9)-(6-13) and (6-14) and defining the new term $\Delta \gamma^* = \Delta \gamma_{CoFe} - \Delta \gamma_{Sac/CoFe}$, the final form of the analytical model for maximum tensile stress in electrodeposited CoFe films as a function of the coverage of saccharin adsorbed phase is presented as

$$\sigma_{AVRG}^{\max}(\theta) = \sigma_{AVRG,CoFe}^{\max} - 8\frac{\Delta\gamma^*}{d_G} \cdot \theta.$$
(6-15)

The physical meaning of $\Delta \gamma^*$ term is the difference in driving force for zipping of CoFe grains with clean "saccharin free" surface and CoFe grains with maximum coverage of adsorbed saccharin phase, θ =1. The $\sigma_{AVRG,CoFe}^{max}$ is the maximum tensile stress in CoFe films electrodeposited from solution without saccharin. It is defined by Equation (6-9) and it can be measured experimentally, Figure 6-18. The second term on the right side of Equation (6-15) represents the reduction of the stress level due to presence of saccharin adsorbed phase on CoFe surface. It is a direct function of saccharin coverage, and it is directly dependent on the difference in the driving force for CoFe grain zipping with clean surface and CoFe grain zipping with surface having the maximum coverage of adsorbed saccharin.

For practical purpose, it is convenient to express the saccharin coverage on the CoFe surface in terms of its concentration in the solution. This would provide a facile way to use our analytical model, Equation (6-15), to analyze the experimental stress vs. saccharin concentration data. The earlier work [7,15]has shown that saccharin adsorption on CoFe surface can be represented well by *Langmuir* adsorption formalism

$$\theta = \frac{b \cdot C_{saac}}{(1 + b \cdot C_{sac})} \cdot \tag{6-16}$$

In above expression the term B is equilibrium adsorption constant while C_{sac} is the concentration of saccharin in solution. Substituting eq.(6-16) into eq.(6-15) a more useful expression of the model is obtained given as

$$\sigma_{AVRG}^{\max}(C_{Sac}) = \sigma_{AVRG,CoFe}^{\max} - 8\frac{\Delta\gamma^*}{d_G} \cdot \frac{b \cdot C_{Sac}}{1 + b \cdot C_{Sac}} \cdot$$
(6-17)

The values of d_G and σ_{AVRG}^{max} are known (see previous discussion) while the parameters b and $\Delta\gamma^*$ are determined from the model fit to the $\sigma_{AVRG}^{max} vs.C_{sac}$ experimental data, Figure 6-16B. From the fit we determined the values of b=20.5±0.5 Lg⁻¹, and $\Delta\gamma^*=1.0\pm0.1$ Jm⁻². It is apparent that analytical model formulated by Equation (6-17) succeeds to represent well $\sigma_{AVRG}^{max} vs.C_{sac}$ experimental results. The extracted value of term b could be used to verify validity of the *Langmuir* adsorption formalism (Equation (6-16)) for our modeling consideration. For C_{sac} = 1 gL⁻¹ and b=20.5±0.5 Lg⁻¹we calculate that expected saccharin coverage of CoFe surface during CoFe thin film growth is θ =0.95±0.01. Previously, discussing our EIS measurements of C_{DL} in Figure 6-16B, we have determined that saccharin coverage of CoFe surface at electrode rest potential during electrodeposition of CoFe films is θ =0.96. The remarkably good agreement between these two measurements and calculations of θ is additional proof that *Langmuir* adsorption formalism provides realistic interpretation of the saccharin adsorption process during the growth of CoFe surface.

The extracted value of $\Delta \gamma^*$ from the model fit to experimental data is positive and smaller than the value of $\Delta \gamma_{\text{CoFe}}$ (1.125 Jm⁻²). This directly implies that $\Delta \gamma_{\text{Sac/CoFe}} < \Delta \gamma_{\text{CoFe}}$ $(\Delta \gamma_{\text{Sac/CoFe}}=0.125\pm0.1 \text{ Jm}^{-2})$. The obtained $\Delta \gamma_{\text{Sac/CoFe}} < \Delta \gamma_{\text{CoFe}}$ inequality proves the correctness of our initial assumptions and physical picture on which we based our modeling approach. The adsorbed saccharin additive lowers the driving force for grain zipping process during electrodeposition of CoFe films. In fact, it is clear that stress reduction in electrodeposited CoFe films is due to saccharin adsorption on the CoFe surface. The physical origin of this effect can be understood on a following way: The completely covered CoFe surface with adsorbed saccharin molecules is likely to have surface bonds saturated by adsorption process which means that saccharin adsorption effectively reduces the CoFe surface energy. At the same time, the grain boundaries that are formed by zipping of the CoFe grains/surfaces covered with adsorbed saccharin phase are likely to have more defects; less atom-atom coordination and atom packing density. These grain boundaries have higher grain boundary energy as compared to the grain boundaries formed during zipping process of "clean" CoFe surfaces. Therefore we can say that saccharin effect on stress reduction in electrodeposited CoFe films is, indeed, thermodynamic in nature.

6.5.4. Stress vs. Coercivity of CoFe Films

The CoFe alloys have relatively large value of magnetostriction [107] and because of that the high levels of intrinsic stress which develops during CoFe thin film growth can seriously alter their magnetic anisotropy. The CoFe films with high stress levels very often do not exhibit soft magnetic properties and low coercivity which limits their application for magnetic device fabrication [14]. In order to assess the effect of growth stress in CoFe films on their coercivity, the stress measurements were performed on 9 electrodeposited CoFe films. The films were electrodeposited from solution containing different saccharin concentrations so that different levels of growth stress ($t_f=0.3 \times 10^{-6}$ m) and their M-H loops were obtained by VSM to determine their coercivity. The results are presented in Figure 6-20.



Figure 6-20. Coercivity dependence on growth stress for 0.3 micron thick CoFe films.

As expected, the largest coercivity value was measured for the sample with highest level of stress. This sample was electrodeposited without saccharin in the solution, and it served as a starting point to which the other samples were compared $(\sigma_{AVRG} = 420 \times 10^6$ Pa, $H_c = 110$ Oe). As the saccharin concentration in the solution is increased from 0.0 gL⁻¹ towards 0.12 gL⁻¹ via several samples and saccharin concentrations, the σ_{AVRG} of CoFe films have further gradually decreased to 130 $\times 10^6\, Pa$ followed by decrease in H_c from 110 to 46 Oe. The Hc vs. σ_{AVRG} relation in this range of the data represents an almost a linear trend (red line, Figure 6-20). The observed trend is not surprising. The reducing stress levels in CoFe films result in smaller contribution of magnetoelastic anisotropy energy to the overall anisotropy energy of CoFe films and thus the measured coercivity of CoFe films was decreasing as well. However, for CoFe films with stress level $\sigma_{AVRG} < 130 \times 10^6$ Pa a sudden increase in H_c values was observed. This is bit surprising, and it cannot be attributed to the stress related magnetic anisotropy change of CoFe films. The trend is real and opposite from the one expected and at this point it is not well understood. All investigated CoFe films had the same grain structure and composition, and the increase in H_c with further decrease of σ_{AVRG} below 130×10⁶ Pa range does not follow any obvious trend. More work is necessary to elucidate this phenomenon. Perhaps, this unexpected H_c vs. σ_{AVRG} dependence can be explained by more detailed consideration of the additive incorporation phenomenon [7,15] and magnetic decoupling of the grains due to the additive related inclusion precipitation on the grain boundaries [97] since this phenomenon is observed for CoFe alloys having C_{sac} in plating bath $> 0.12 \text{ gL}^{-1}$. As saccharin concentration in the plating bath increases, the saccharin molecules are adsorbed on the surface and the grain boundaries. This causes the CoFe magnetic domains to be segregated by a distance which is larger than the exchange correlation length and leads to magnetic hardening. Thus sulfur gets incorporated on the grain boundaries, causing magnetic decoupling. Thus, increased quantities of saccharin (sulfur) in the plating bath leads to a non-magnetic layer in the grain boundaries represented by circles in Figure 6-21 which interrupts exchange interaction between the CoFe grains and this leads to increased coercivity. A sketch of this phenomenon is as shown in Figure 6-21.



Figure 6-21. Magnetic decoupling due to incorporation of Co, Fe sulfide molecules at grain boundaries.

6.6. Oxide Incorporation during Electrodeposition of CoFe alloys

6.6.1. Source of Oxygen and oxide/hydroxide Incorporation

During ferromagnetic metal and alloy electrodeposition, the hydrogen codeposition also occurs as a side reaction, due to which the current efficiency (γ) <1. This causes the depletion of hydrogen (H⁺) ions at the solution electrode interface, leading to formation of insoluble metal hydroxide species and is the main reason for the incorporation of oxygen in SHMM alloys [32]. Oxygen incorporation has deleterious

effects on the magnetic flux density and coercivity of the alloys [32,108-110] and hence a study of the various oxide phase formed in the electrodeposited alloy due to the Fe^{3+} incorporation along with the oxygen incorporation rate is essential.

During electrodeposition of CoFe alloys, the oxygen from air oxidizes Fe^{2+} to form Fe^{3+} by the reaction

$$O_2 + 4Fe^{2+} + 4H^+ \to 4Fe^{3+} + 2H_2O.$$
 (6-18)

If the concentration of Fe^{3+} and OH^- at the solution/electrode interface are such that the product of solubility for $\text{Fe}(\text{OH})_3$, (K_p) is exceeded, hydroxide precipitation and incorporation occurs in the growing CoFe deposit [32].

In order to determine the oxide phase in CoFe films electrodeposited with varying Fe^{3+} concentrations, CoFe alloys with different O content obtained by incorporating various Fe^{3+} concentrations in the CoFe plating bath was analyzed.

6.6.2. Oxygen Incorporation-Experimental Data and Analytical Model

CoFe alloys were electrodeposited with varying concentrations of Fe^{3+} and WDS measurements were performed to determine the oxygen content in electrodeposited CoFe films. The amount of Fe^{3+} was varied from 0 to 0.2 g/L FeSO₄.4H₂O. The results for the Oxygen content in electrodeposited CoFe alloy as a function of the Fe^{3+} concentration used in the plating bath is as shown in Figure 6-22.



Figure 6-22. Oxygen content in electrodeposited CoFe alloy as a function of Fe^{3+} concentration.

The oxygen atomic % for the CoFe alloy electrodeposited without any addition of Fe^{3+} is about 3 at%. The oxygen atomic % increases with the addition of Fe^{3+} and shows about 6 at% for 0.1 g/L of Fe^{3+} concentration. Further addition of Fe^{3+} does not cause any drastic effect in the oxygen content and remains almost constant. The Fe^{3+} concentration at which precipitation occurs at the solution/electrode interface is given by

$$C_{i,Fe^{3+}}^{*} = \frac{K_{p}}{(K_{w})^{3}} \cdot \left(10^{-pH} - \frac{j(1-\gamma)}{F} \cdot \frac{\delta}{D_{H^{+}}}\right).$$
 The value for $\frac{\delta}{D_{H^{+}}}$ for a rotating disk

electrode was estimated by the formula $\frac{\delta}{D_{H^+}} = 1.61 D^{-0.67} \omega^{-0.5} \upsilon^{0.17}$ and is 66.4 for a

rotation speed of 300 rpm. The hydrogen diffusivity at room temperature is considered to be $D_{H^+} = 9.3 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ [64] and was calculated to be 0.018 g/L. Also, the concentration at which Iron hydroxide precipitation occurs in the bulk solution

is given by $C^*_{\infty,Fe^{3+}} = \frac{K_p}{(K_w)^3} \times 10^{-3pH}$ and calculated to be around 0.12 g/L. Thus, from these

calculations and Figure 6-1, we observe that the oxygen atomic % shows a rapid increase for Fe^{3+} concentration when the equilibrium concentration for Fe-hydroxide at the interface is achieved and then remains constant for Fe^{3+} concentrations higher than the equilibrium Fe^{3+} concentration for which precipitation occurs at the bulk solution.

The R_{Fe(OH)3} is expressed as [32]

$$R_{Fe(OH)_{3}} = \frac{n_{molec}}{N_{A}} \cdot \Xi \exp\left(-\frac{16\pi\sigma_{hyd}^{3}\Omega^{2}}{3K^{3}T^{3}\cdot\left(\ln\left(pC_{\infty,Fe^{3+}}/(Kp/Kw)^{3}\cdot\left(10^{-pH}-(1-\gamma)j/F\cdot\left(\delta/D^{H^{+}}\right)\right)^{3}\right)\right)^{2}}\cdot\Phi\right)$$
(6-21)

Where,

n_{molec}= average number of molecules in stable nuclei

NA is the Avogadro's number

 Ξ is the nucleation rate constant in cm⁻²s⁻¹.

 $C_{\infty,Fe^{3+}}$ is the Fe³⁺ concentration in the bulk solution

 σ_{hyd} represents the Fe(OH)₃ crystal/solution interfacial free energy (J·cm⁻²)

 Ω is the volume of the Fe(OH)₃ molecule.

Also, $R_{Fe(OH)3}$ in terms of O at % is expressed as

$$O \ at\% = R_R + \frac{R_{Fe(OH)_3}}{R_{CoFe} + R_{Fe(OH)_3}} \times 100 \cdot$$
(6-22)

Here, R_R is the residual oxygen content, which comes from anions in the plating bath and sources other than Iron hydroxide. Combining Equation 6-21 and 6-22, we obtain an expression for the Oxygen atomic % in terms of the bulk Fe³⁺ concentration as

$$O \ at\% = E + \frac{A \times \exp\left(\frac{B}{\ln\left(\frac{C_{Fe^{3+}}^{\infty}}{C}\right)^{2}}\right)}{D + A \times \exp\left(\frac{B}{\ln\left(\frac{C_{Fe^{3+}}^{\infty}}{C}\right)^{2}}\right)},$$
(6-23)

where
$$A = \frac{n_{molec}}{N_A} \cdot \Xi$$
, $B = \frac{-16\pi\sigma^3_{hyd}\Omega^2}{3k^3T^3}$, $C = \left(\left(\frac{K_p}{(K_w)^3} \right) \left(10^{-pH} - (1-\gamma)\frac{j}{F} \cdot \frac{\delta}{D_{H^+}} \right)^3 \right)^2$ and

D=R_{CoFe}.

Equation 6-23 is used to fit the data for Oxygen atomic % obtained from WDS measurements as a function of Fe^{3+} concentration in the bulk solution and the model fit to the data is as shown in Figure 6-23.

The CoFe alloys electrodeposited with varying Fe^{3+} concentrations are used as the contact material for sensor fabrication. It has been reported that the large

magnetoresistance in electrodeposited nanocontacts is possible due to the presence of the oxide layer in the nanocontact. Thus, using this study, we were able to understand the type of oxide phase present in the nanocontact material and the analytical model developed also helps in understanding the oxygen content in the alloy.



Figure 6-23. Analytical model fit using Equation 6-23 to the experimental data from Figure 6-19.

The parameters obtained from the fit are the Fe(OH)₃ incorporation rate $R_{Fe(OH)3}$ and the CoFe incorporation rate R_{CoFe} . The fit results in a CoFe incorporation rate as $8.4*10^{-4}$ mol·cm⁻²s⁻¹. The other parameters extracted are the oxygen content in the alloy when no Fe³⁺ was added (R_R) which was found to be 3 atomic% and A=0.2648, B=5.895, C=0.1829, which implies $n_{molec} \cdot \Xi = 1.58*10^{23}$ cm⁻².s⁻¹, also the calculated value of C using literature values is 2.43 which is closer to the fit value, proving the validity of the fit. Thus the oxygen content in a solution with given Fe³⁺ concentration can be calculated.

6.6.2. Magnetic Characterization of CoFe films

Coercivity was measured for these CoFe films electrodeposited with varying concentrations of Fe^{3+} and is as shown in Figure 6-24.



Figure 6-24. Coercivity of the electrodeposited CoFe alloys as a function of Fe^{3+} concentration in the CoFe electrodeposition bath.

It is observed that the coercivity increases with increase in the Fe³⁺ concentration. The coercivity increases rapidly as soon as the equilibrium concentration at which precipitation of Fe³⁺ at the solution/electrode interfaces occurs. Thereafter, the coercivity increases but slightly and for an Fe³⁺ concentration of 0.085 g/L , we obtain a coercivity of 51 Oe. The oxygen content in the CoFe alloy electrodeposited with each of the Fe³⁺ concentrations was determined and is represented in Figure 6-22. Also, the relation of the oxygen atomic % in terms of the Fe³⁺ concentration using the experimental data helps us in determining the corresponding O at % in each of the CoFe alloy. Accordingly, Figure 6-25 represents the coercivity for the CoFe alloy as a function of Oxygen atomic %.



Figure 6-25. Coercivity as a function of the oxygen atomic %.

It has been known that presence of oxygen causes an increase in the coercivity [109-111] of the alloy. Hammer et al demonstrated increase in coercivity with increasing oxygen content for RF sputtered NiFe films [110]. It is observed that the coercivity for the CoFe alloy electrodeposited without any saccharin is about 30 Oe. The grain size for the CoFe alloys electrodeposited with varying concentrations of Fe^{3+} did not show an appreciable variation and hence the increase of coercivity due to grain size given by the Hertzer's rule, $H_c = c \cdot t^{-n}$ is not valid. The coercivity of ferromagnetic material is

expressed as [112] $H_c = \frac{p \cdot K_{eff}}{\mu_0 M_s}$, where p is a dimensionless factor that depends on the magnetization process, K_{eff} is the effective anisotropy energy and $\mu_0 M_s$ is the saturation magnetization. Previous research has shown that the amount of hydroxide increases the non-magnetic phase which is one of the reason for decrease in magnetic moment as the precipitation of Fe-hydroxide occurs [32]. Thus as μ_0 ·Ms decreases, H_c increases. Also,

as the oxygen content increases, the motion of domain walls is impeded strongly by the intergranular oxide phase as compared to that for the film with no additional Fe^{3+} added which contains intragranular oxide particles [108]. The higher coercivity is attributed to the variation in exchange coupling energy between the grains depending on the magnetic nature of the intergranular region. This increase in coercivity can also be explained by the inclusion theory where regions of second phase, which is the oxide/ hydroxide in this case act as magnetic inclusions [108].

6.7. Ferromagnetic Metal-Metal oxide/hydroxide electrodeposited nanocontact sensors

6.7.1. Electrodeposited Nanocontact Sensor-Principle and Material

The ferromagnetic sensors fabricated by electrodeposited nanocontacts is based on the phenomenon of Ballistic Magnetoresistance (BMR) which states that the huge magnetoresistance change arises due to the nonadiabatic spin scattering across narrow magnetic domain walls trapped at nanoconstrictions [9,10]. As shown in Figure 6-26, if the mean free path length (λ) > magnetic domain wall width (DWW), then the spin is conserved, resulting in a high reflection between spin up and spin down states and ballistic conduction results. On the other hand, if the mean free path length (λ) < DWW, then the electron spin accommodates itself adiabatically from one side of the domain wall to the other resulting in small MR [60], causing diffusive transport.



Figure 6-26. Diffusive (A) and ballistic (B) transport of conduction electrons through a nanocontact [113].

This is the assumption for the electrodeposited nanocontact that was fabricated with a nanocontact diameter ~ 70 nm. The concept that was developed for synthesis of Ferromagnetic Metal-Metal Oxide/Hydroxide Material is based on precipitation of insoluble hydroxide phase at the electrode surface during the electrodeposition of CoFe alloys as is explained in Section 6.6 and the fabrication procedure for the magnetic sensors is explained in great detail in Chapter 5. Figure 6-27 shows the TEM for various layers in the sensor material.



Figure 6-27. TEM of the actual nanocontact device cross-section indicating most important layers/materials [114].

The nanocontact material for the magnetic sensors were made up of CoFe electrodeposited with varying concentrations of saccharin and Fe³⁺. In order to determine the oxide phase in CoFe films electrodeposited with varying Fe³⁺ concentrations, CoFe alloys with two different O content, named S1 and S2 obtained by various Fe³⁺ concentrations in the CoFe plating bath was analyzed. S1 is the CoFe alloy electrodeposited without any addition of Fe³⁺ while S2 is the CoFe alloy electrodeposited with 0.0025 M Fe³⁺. In these films, we expect formation of two different types of oxide/ hydroxide. Fe leads to more insoluble hydroxide as compared to Co and forms in the deposit as a precipitate [108]. In S1, the dominant source of oxide phase is Fe(OH)₂ while in S2, the dominant source is Fe(OH)₃. The necessary condition for Fe-hydroxide precipitation occurs when pH at the solution-electrode interface (pH_i) exceeds the limit set by the product of solubility for a particular Fe-hydroxide given as

$$pH_i > pH_{\lim it} = \frac{1}{n} \cdot \log\left(\frac{K_p}{\left[Fe^{n+1}\right]_i \cdot \left(K_w\right)^n}\right).$$
(6-23)

Here K_p , K_w and *n* stand for the product of solubility, ionic product of water and the oxidation state of Fe ion respectively. [Feⁿ⁺] represents the concentration of Fe ions at the electrochemical interface that is a constituent of the hydroxide incorporated in the deposit. The value of the pH at the interface, pH_i is dependent on parameters like pH of the solution, current density *j*, current efficiency γ and diffusion layer thickness δ and is expressed as

$$pH_{i} = -\log\left\{10^{-pH} - \frac{j \cdot (1-\gamma)}{F} \cdot \frac{\delta}{D_{H^{+}}}\right\}.$$
(6-24)

The pH_i and pH_{limit} for the two phase $Fe(OH)_2$ and $Fe(OH)_3$ is calculated using Equation 6-19 and 6-20. For Fe(OH)₂, pH_i=6.7 vs pH_{limit}=5.3, while for Fe(OH)₃, pH_i=3.8 vs pH_{limit}=2.02. Thus the pH_{limit} is exceeded for both types of hydroxides and as a result, Fe-hydroxide precipitation occurs [108]. The difference in the Oxygen-K edge onset peak in the NEFS (Near edge fine structure) spectra for samples S1 and S2 indicate that the dark regions along the grain boundaries in S2 are a form of α -Fe₂O₃ whereas in S1 the dark particles are FeO [115]. Thus S2 has higher amount of oxide as compared to S1 [108]. The more detailed analysis of the precipitated Fe_2O_3 at the grain boundaries of the CoFe sample deposited from solution containing Fe³⁺ ions is provided combining Annular Bright Field (ABF) and EELS methods to reveal the lighter (oxygen) atoms. In Figure 6-28 there is a pair of High Angle Annular Dark Field (HAADF) and ABF images of Fe₂O₃ segregated at the grain boundary of CoFe matrix. The darker region (oxygen rich region) in HAADF image appears as the brighter region in ABF image. The ABF image indicates that oxide phase is not periodic i.e. almost amorphous with a lot of defects. The thickness of the oxide/ Fe₂O₃ phase at the grain boundary appears to be around ~ 1 - 2 nm [115].



Figure 6-28. HRTEM image using HAADF (A) and ABF (B) imaging methods. The zoom outs (C and D) of the ABF image are showing selected fields A1 and A2 with the amorphous structure of the oxide at the grain boundary [114].

6.7.2. Magnetic Characterization and In-situ stress measurement for the nanocontact material

Magnetic characterization of the CoFe films containing different oxide type (FeO vs. Fe_2O_3) has shown higher saturation magnetization and lower coercivity for CoFe films containing only FeO oxide phase. All samples containing FeO or FeO + Fe_2O_3 phase have lower magnetic moment that expected for CoFe alloy of the same composition without any oxygen content (M_s =2.4 T). Obviously, the oxide/hydroxide incorporation dilutes the magnetic moment of electrodeposited films. The simple argument based on volume partitioning of the electrodeposited films on the high value M_s magnetic phase ($Co_{40-36}Fe_{60-64}$) and weakly magnetic / antiferromagnetic or nonmagnetic inclusions (FeO·xH₂O or Fe₂O₃·xH₂O) is sufficient to explain this observation [116]. Coercivity of both oxygen containing films was larger than oxygen-free $Co_{40.36}Fe_{60.64}$ alloy of the same composition. Since all CoFe films investigated have same grain size, the difference in coercivity cannot be attributed to a difference in grain size. The difference in magnetic properties is governed by the presence of oxide phase in terms of its content, type and distribution. In the higher oxygen content specimen containing Fe_2O_3 as the main oxide burring phase, the motion of domain walls was impeded more strongly than in the case of CoFe films which contained intragranular oxide particles [117]. This is due to a difference in the exchange coupling energy between the grains depending upon the magnetic nature of the intergranular region [112]. In general, one can invoke the inclusion theory to explain our magnetic properties observations, in which the separated regions of second phase with magnetic properties different from those of matrix act as magnetic inclusions. The magnetic inclusions (spherical regions) in films burring

FeO only are likely supported by the Kersten model [116] where coercivity is proportional to $H_c \propto f^{2/3}$, where f is volume percent of second phase. In the CoFe films burring Fe₂O₃ as the main oxide phase, the oxide at the grain boundaries can be considered as lamellar, having $H_c \propto f$ [117]. Thus, higher oxygen contents promote more pinning sites and a linear increase of coercivity with second phase present in the film.

In-situ stress measurement of CoFe alloys electrodeposited with 0.01M Fe³⁺ and varying concentration of saccharin were performed to measure the level of stress on these nanocontact materials. The in-situ data for Stress as a function of film thickness during deposition is shown in Figure 6-29A while the trend in stress of CoFe electrodeposited with 0.01 M Fe³⁺ as a function the saccharin concentration in the plating bath is shown in Figure 6-29B.





Figure 6-29. (A) In-situ stress curve of CoFe alloy electrodeposited with 0.01 M Fe³⁺ and 0.12 g/L saccharin and (B) Stress of CoFe alloy electrodeposited with 0.01 M Fe³⁺ as a function of saccharin content in the plating bath for a thickness of 0.6 μ m film.

It is observed that the in-situ stress decreases with increasing saccharin concentration in the plating bath from a tensile stress of 50 MPa for CoFe alloy electrodeposited with 0.01 M Fe³⁺ and 0 g/L saccharin to a compressive stress of -80 MPa for CoFe alloy electrodeposited with 0.01 M Fe³⁺ and 2 g/L saccharin.

6.7.3. Magnetoresistance curves for the electrodeposited nanocontacts

The electrodeposited nanocontacts were tested using a 4 point probe measurement to obtain MR curves as explained in Chapter 5. Figure 6-30 lists some of the typical transfer curves for various prototype devices.



Figure 6-30. Representative magnetic field sensor MR curves. (A) MR curve for nominal ~70 nm contact device, $\Delta R/R = 1000\%$. (B) MR curve for nominal 100-200 nm contact device, $\Delta R/R=50\%$. (C) MR curve for nominal 70 nm nanocontact device, $\Delta R/R=300\%$, (D) MR curve for nominal 70-100 nm nanocontact device, $\Delta R/R=300\%$, All nanocontacts are CoFe + (FeO + Fe₂O₃)·H₂O material with expected stress values of ~ 50-(-80) MPa within the nanocontact material. Testing current 0.1 mA, field sweep 20 Oe/sec.

The value of MR is calculated as
$$MR = \frac{R(H) - R(0)}{R(H)} * 100\%$$
, where R(H) and

R(0) are the resistances under field H and 0 respectively. The contact resistance R_c

determines the diameter d given by $d = \sqrt{\frac{1000}{R_c}}$, in nm of the nanocontact.(this is by

assuming that a quantum resistance of 13 k Ω is associated with one single atom

occupying an area of 0.1 nm^2). From Figure 6-30A, the contact diameter for a resistance of 25 Ω is about 7 nm as opposed to the physical dimension of 70 nm. This difference could be because there are several conductance channels that contribute to the MR phenomenon and hence we can assume each conductance channel to be about 7 nm.

We observe both positive (6-30 A and B) and inverse (6-30 C and D) MR curves. Let us consider Figure 6-30 A, Starting from 0 field, since the two ferromagnetic electrodes need different coercive fields to saturate, i.e. the top layer is a soft magnetic material (Permalloy) and the bottom is a hard magnetic material (Co), the electrodes are in an antiferromagentically aligned state or a high resistance state. As the field is sweeped, the magnetic domains align along each other and a state of parallel alignment is obtained resulting in a low resistance state. Each of the nanocontact devices were cycled to about 4times and still show similar MR values demonstrating good reproducibility and durability of the sensors. The MH loop for one of the devices is as shown in Figure 6-31 which shows that the magnetic saturation is obtained at about 500 Oe.



Figure 6-31. MH loop for one of the prototype devices with a coercivity of 58 Oe.

Both positive and negative magnetoresistance is observed in Figure 6-30 which is in agreement with results observed earlier for atomic nanocontacts and tunneling nanojunctions. The negative magnetoresistance could be explained by a phenomenon called as the resonant tunneling suggested by Tsymbal and previously observed in ferromagnetic nanojunctions with significant presence of oxide [66]. The total conductance is the sum of direct electron tunneling and tunneling via impurities in the barrier and on resonance, even single impurity could cause inversion of magnetoresistance [118]. It is intriguing because the positive and negative magnetoresistance has been observed for nanocontacts that are made of the same material. The possibility of tunneling granular magnetoresistance in the nanocontact geometry cannot be excluded as well considering the fact that the grain boundaries of the CoFe phase are coated with 1-2 nm thick amorphous layer of Fe₂O₃.

MR values as high as about 3000% are obtained and such high values cannot be explained by the phenomenon of domain wall scattering alone even if the spin is conserved because the density of states for spin up and spin down cannot provide such high values. The presence of the dead magnetic layer or the oxide layer at the nanocontact could be one of the reasons [10].

6.7.4. Scaling of the Devices

More than 250 devices were tested and a graph of the magnetoresistance ratio ($\Delta R/R$) as a function of the minimum conductance $G_{\min} = 1/R_{\min}$ for about 50 devices is as shown in Figure 6-32. The cumulative result for magnetoresistance as a function G displays a scaling behavior with exponent -1.2. This scaling phenomenon is a characteristic of the ballistic transport of electrons due to domain wall scattering and could be responsible for the huge MR values.



Figure 6-32. (A) The line in Figure 6-32B represents the power law function with exponent a = -1.2 (Equation (6-21)). Testing current 0.1 mA, field sweep 20 Oe/sec. (B) Comparison with the scaling principle proposed by Garcia [60] and (C) Comparison with scaling principle proposed by Coey for Fe₃O₄ point contacts [113].

The cumulative result from all testing devices is shown in Figure 6-32A. There is a huge variation in the MR ratio from 2000% to about 11% depending on the type of nanocontact material and the size of nanocontact. The typical testing was done with testing current of 0.1 mA making the average current density through the nanocontact of 10^{6} Acm⁻². The observed values of $\Delta R/R_{min}$ were between 50 and > 1000% making these prototype magnetic sensor devices the best ever reported. We observe a scaling trend associated with domain wall scattering associated with the BMR phenomenon observed previously by researchers like Garcia [60,119] and Coey for half-metallic point contacts [113]. Most of the devices $\Delta R/R_{min}$ values are grouped along the line representing the power function as

$$\frac{\Delta R}{R_{\min}} \sim (G)^a \tag{6-21}$$

with power exponent a = -1.2. This indicates that possible mechanism for the observed magnetoresistance is the spin polarized electron scattering from the magnetic domain wall constricted within the nanocontact boundaries or conducting channels with in the body of the nanocontact [60]. This scaling principle does not seem to apply to devices with MR ratio higher than 300 % and hence it is some other factors such as the presence of interface layer (dead magnetic layer) that is highly spin polarized and acts as filter for the spin of electrons could be responsible for the huge magnetoresistance value.

6.7.5. Low temperatures Resistivity Measurements

Conducting ballistic and tunneling magnetoresistances are obtained by matching the wave functions on both sides of the contact (BMR) and of the tunnel barrier (TMR). The only difference between these two mechanisms is that transmissivity values are of order unity for conducting ballistic electrons while for tunneling , the transmissivities decay exponentially with barrier width (*l*) [61]. At room temperature, the electrical resistivity is dominated by collision of conduction electrons with phonons , however at low temperatures the resistance due to collisions with impurities and mechanical imperfections in the lattice become dominant [69]. Thus, determining the I-V curves of the devices at low temperatures is one of the way of understanding the transport mechanism of the devices. Resistivity measurements using PPMS (Physical Property Measurement System) were performed at temperatures ranging from 300 K to 20 K. A graph of the I-V characteristics (Figure 6-33A) and the corresponding R-I curve (Figure 6-33B) for an electrodeposited nanocontact with 0.05 M Fe³⁺ and 0.12 gL⁻¹ saccharin is shown.





Figure 6-33. (A) IV curves and (B) R vs I curve for sensor with nanocontact material of CoFe electrodeposited with 0.05 M Fe^{3+} and 0.12 gL⁻¹ saccharin.

It is observed that the I-V curves are linear for temperatures down to 200 K and then the non-linearity increases with lower temperatures. This phenomenon is in accordance with the Glazman-Matveev model for grain boundary systems of ferromagnetic oxides and suggests that there could be an inelastic tunneling process between ferromagnetic grains via chains of local states in the GBs [120]. The Glazmann Matveev model for the inelastic tunneling process is as shown

$$G = g_s^V V^s \quad eV >> k_B T \tag{6-22}$$

$$G = g_s^T T^s, \ eV \ll k_B T \tag{6-23}$$

Here, $s = \frac{N-2}{N+1}$, $N \ge 2$, and N is the number of localized states composing the chain.

Thus the nonlinearity in I-V curves can be interpreted in terms of inter-grain tunneling [121] or inelastic hopping through tunneling barrier [122]. The presence of the localized states also causes the elastic tunneling via a single impurity in the barrier called as

resonant tunneling as explained earlier in Section 6.7.2 that is responsible for inverse magnetoresistance [66,120,123]. A similar trend is seen in Figure 6-29B (R vs I) where the resistance remains constant for all input currents at room temperature to about 200 K. For temperatures lower than 200 K, we observe a huge rise in resistance for smaller input current which could be due to the coulomb blockade effect.

Using the data in Figure 6-33, we can obtain a relation of R as a function of T for input current i=0.1 mA and is as shown in Figure 6-34.



Figure 6-34. Electrical resistance of the electrodeposited nanocontact device as a function of temperature for i=0.1mA.

In Figure 6-34, we observe that the resistance increases significantly at low temperatures. The R vs T follows the exponential law, $\rho = \rho_0 \exp\left[2(C/k_BT)^{1/2}\right]$, which is characteristic of thermally assisted tunneling conductance in granular cermets [124].Here, ρ_0 is the resistivity at infinite temperature, C is the effective activation energy defined by $C = 2\chi s E_c$, where $\chi = \left(2m^* \Phi h^2\right)^{1/2}$, $\Phi = U - E_F$ is the effective barrier height, m* is the effective mass of electrons, s is the mean separation of iron particles , E_c is the energy

necessary to generate a pair of neighboring charged grains during tunneling process, and k_B is the Boltzmann's constant. Another characteristic of insulating granular cermets is the dramatic increase of TMR at low T and these could not be fully observed because of the voltage limit. This anomalous increase of the resistance at temperature at 20 K could be attributed to the coulomb blockade effect and has been reported previously in granular tunnel films [56][71]. The anomalous temperature dependence is associated with the tunneling and thermal generation process for electrical conductance in insulating granular system. However, we observe a kink in the R-T dependence at around 200 K which is the Neel or transition temperature for FeO [116]. Another phenomenon called Verwey transition which is common in iron oxides is around 120 K [125] below which it becomes more insulating. This could be one of the reasons for the non-linearity or dominant tunneling behavior seen in I-V curves for temperatures below 120 K [126]. There is an almost exponential resistance decrease with increasing temperature and this behavior is common in insulating granular MR and tunneling MR in oxide tunnel junctions. This could be attributed to the increasing disorder of weakly coupled surface spins [127]. Thus from the above curves, we believe that the phenomenon more dominant among these electrodeposited nanocontacts is ferromagnetic intergrain tunneling. I-V measurement on more samples would be needed to fully understand the transport mechanism of these devices.

CHAPTER 7

CONCLUSION AND FUTURE WORK

This chapter gives a conclusion about the entire dissertation work and lists some of the possible future work that can help in understanding the concepts better.

7.1. Conclusion

1. The effect of saccharin incorporation on the corrosion potential of CoFe alloys was determined. The various parameters that help in determining the corrosion rate are discussed in terms of the S incorporation mechanisms and it was found that the S incorporation due to saccharin electroreduction had a dominant effect on the corrosion potential. An analytical model was developed based on mixed potential theory to understand the phenomenon of corrosion and the parameters extracted are close to the literature value.

2. The effect of saccharin as stress reducing additive in electrodeposition process of CoFe alloys was found to be thermodynamic in its nature. The saccharin adsorption on the growing CoFe surface during electrodeposition effectively changes the thermodynamic driving force for CoFe grain zipping process and consequently it changes the maximum level of stress in CoFe films. The control of the CoFe stress levels is achieved by effective control of saccharin coverage of CoFe surface during electrodeposition process. This can be achieved either by control of the deposition/adsorption potential for saccharin additive, or through the change of saccharin concentration in the solution i.e. the formulation of the plating solution. The latter approach is explored in detail, and phenomenological description of the maximum stress level in CoFe films as a function of

saccharin concentration in the plating solution is offered in a form of analytical model, to analyze the experimental data.

3. The amount of oxygen incorporation in CoFe alloys electrodeposited with varying Fe^{3+} concentrations was studied and the data correlated well with the analytical model developed to determine the variation in O content with the change in Fe^{3+} concentration in the electrodeposition bath. Z contrast STEM imaging combined with nanoEDS and nanoEELS confirmed the presence of predominant oxide formed in S1 is FeO.xH₂O while in S2 it was mainly Fe₂O3.xH₂O. The increasing oxygen content in the CoFe alloys also caused an increase in the coercivity of CoFe alloys.

4. The electrodeposited nanocontacts demonstrated high values of MR upto 3000%. Both positive and inverse magnetoresistance are obtained. The observance of inverse magnetoresistance was thought to be due to the resonant tunneling phenomenon. Also, the magnetoresistance values of electrodeposited nanocontacts demonstrates the universal scaling behavior which is a characteristic feature of ballistic transport observed in metals, semi-metals and insulators explained by researchers like Garcia and Coey. The huge values of MR were also attributed to the spin filtering through the dead magnetic layer or an oxide layer. Low temperature I-V measurements demonstrate an increasing resistance at lower temperatures and it was suggested that this could be due to the phenomenon called as the tunneling granular magnetoresistance, which happens due to tunneling among the grain boundaries in a ferromagnetic matrix.

7.2. Future Work

- More work is necessary on the analytical modeling of the corrosion phenomenon. The analytical model developed does not provide a good fit with the experimental data for the reversible potential which is assumed to be the electro-oxidation potential of CoFe electrodeposited with varying concentrations of saccharin.
- 2. STM analysis could be done on CoFe alloys electrodeposited with different concentrations of saccharin to observe if there is a reconstruction of the CoFe surface due to S to from chemisorptions sites. This study could be useful for the better understanding of the effects of S on CoFe alloys.
- The analytical model developed for stress in CoFe films could be applied to other SHMM alloys as well.
- 4. It is demonstrated that high temperatures annealing treatments modify the intergrain barriers in case of tunneling granular magnetoresistance devices. Hence, annealing measurements could be done on the sensors and the magnetoresistance ratio can be determined
- 5. Angle measurements could be performed on these devices to understand the angle dependence on the magnetoresistance value.
- 6. I-V measurements need to be performed on more sensors to fully understand the transport mechanism of these sensors.

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