Oxygen Nanodistributions in Cobalt-Iron Electrodeposited Thin Films:

Some Effects on Magnetic Properties

High Resolution Analytical Electron Microscopy

by

Shereen Elhalawaty

A Dissertation Presented in Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

Approved April 2012 by the
Graduate Supervisory Committee:

Ray Carpenter, Chair
Ralph Chamberlin
Martha McCartney
Terry Alford

ARIZONA STATE UNIVERSITY
May 2012
ABSTRACT

Soft magnetic alloys play a significant role for magnetic recording applications and highly sensitivity magnetic field sensors. In order to sustain the magnetic areal density growth, development of new synthesis techniques and materials is necessary. In this work, the effect of oxygen incorporation during electrodeposition of CoFe alloys on magnetic properties, magnetoresistance and structural properties has been studied. Understanding the magnetic properties often required knowledge of oxygen distribution and structural properties of the grown films.

Transmission electron microscopy (TEM) was a powerful tool in this study to correlate the oxygen-distribution nanostructure to the magnetic properties of deposited films. Off-axis electron holography in TEM was used to measure magnetic domain wall width in the deposited films. Elemental depth profiles of Fe, Co, O were investigated by secondary ion mass spectroscopy (SIMS). Magnetic properties have been determined by superconducting quantum interference device (SQUID) measurements. Oxygen content in the CoFe deposited films was controlled by electrolyte composition. Films were deposited on Si 100 substrates and on other substrates such as Cu and Al. However, a good film quality was achieved on Si substrate. Electron energy loss and x-ray spectroscopies showed that the low oxygen films contained intragranular Fe\textsuperscript{2+} oxide (FeO) particles and that the high oxygen films contained intergranular Fe\textsuperscript{3+} (Fe\textsubscript{2}O\textsubscript{3}) along grain boundaries. The films with oxide present at the grain boundary had significantly increased coercivity, magnetoresistance and reduced...
saturation magnetization relative to the lower oxygen content films with intragranular oxide. The differences in magnetic properties between low oxygen and high oxygen concentration films were attributed to stronger mobile domain wall interactions with the grain boundary oxide layers.

The very high magnetoresistance values were achieved for magnetic devices with nanocontact dimension < 100 nm and oxide incorporation in this nanoconfined geometry. The content of oxide phase in nanocontact was controlled by concentration of the Fe$^{3+}$ ions in the electrodeposition solution. Magnetic device integrity was improved by varying amount of additive into plating solution. These results indicated that electrodeposited CoFe nanocontact is a novel class of materials with large application for magnetic field sensors.
Dedicated to my parents, brothers, loving husband and sweet daughter Sarah.
ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my advisor, Prof. Ray Carpenter for his support, guidance and advice throughout my doctoral study. His encouragement, discussion, patience have given me the confidence and success during my graduate career. I will always remember him as a great microscopist, knowledgeable advisor and dear friend.

I would like also to thank my committee members: Prof. Martha McCartney, Prof. Terry Alford and Prof. Ralph Chamberlin for serving on my committee and their helpful discussions and suggestions.

I am also grateful to Prof. Stanko Brankovic and his group (University of Houston, Texas) for the successful collaboration and productive discussions.

I would like to acknowledge Karl Weiss, Dr. A. John Mardinly, Gordon Tam, Dr. Zhenquan Liu, Timothy Karcher, Dr. Emmanuel Soignard, Kenneth Mossman and Dr. Lynda Williams for their guidance and assistance. I would like to thank my lab mates: Jaejin kim, Desai Zhang, Zhaofeng Gan, Dinghao Tang and Lu Ouyang for their discussion and friendship. I would like to acknowledge my former group mate Dr. Karalee Jarvis for her immense help during my initial training on TEM.

Finally, I would like to express my gratitude to my family, all my Professors and advisors at Cairo and Arizona State Universities and to every one who had contributed to this work.
TABLE OF CONTENTS

Page

LIST OF TABLES .............................................................................................................. x

LIST OF FIGURES .......................................................................................................... xi

CHAPTER

1 INTRODUCTION ............................................................................................................. 1

1.1 Magnetism (a brief history) ..................................................................................... 1

1.2 Basic Definition of Magnetism .............................................................................. 2

1.3 Classification of Magnetic Materials .................................................................... 3

1.4 Ferromagnetic Domains ....................................................................................... 7

1.5 Magnetic Data Storage Systems .......................................................................... 9

1.5.1 Hard-Disk Drives ............................................................................................ 9

1.5.2 Future Magnetic Areal Density ...................................................................... 10

1.5.3 How MR Sensor Works .................................................................................. 12

1.5.4 Types of MR Sensors ...................................................................................... 13

1.5.4.1 Anisotropic Magnetoresistance (AMR) ..................................................... 14

1.5.4.2 Giant Magnetoresistance (GMR) ............................................................... 15

1.5.4.3 Colossal Magnetoresistance (CMR) ......................................................... 17

1.5.4.4 Tunneling Magnetoresistance (TMR) ....................................................... 17

1.5.4.5 Ballistic Magnetoresistance (BMR) .......................................................... 18

1.6 Cobalt-Iron (CoFe) Alloys: alloys of choice for this research ......................... 19

1.7 Magnetic Materials Fabrications ....................................................................... 21

1.8 Outline of Thesis ..................................................................................................... 22
<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>CHARACTERIZATION TOOLS</td>
<td>24</td>
</tr>
<tr>
<td>2.1</td>
<td>Transmission Electron Microscopy (TEM)</td>
<td>24</td>
</tr>
<tr>
<td>2.1.1</td>
<td>Diffraction Contrast Imaging</td>
<td>26</td>
</tr>
<tr>
<td>2.1.2</td>
<td>Phase Contrast Imaging</td>
<td>28</td>
</tr>
<tr>
<td>2.2</td>
<td>Scanning Transmission Electron Microscopy (STEM)</td>
<td>30</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Z Contrast STEM Imaging</td>
<td>31</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Aberration Corrected STEM Imaging</td>
<td>33</td>
</tr>
<tr>
<td>2.3</td>
<td>Analytical Electron Microscopy (AEM)</td>
<td>41</td>
</tr>
<tr>
<td>2.4</td>
<td>Superconducting Quantum Interference Device (SQUID)</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>EXPERIMENTAL METHODS</td>
<td>48</td>
</tr>
<tr>
<td>3.1</td>
<td>Synthesis Process</td>
<td>48</td>
</tr>
<tr>
<td>3.2</td>
<td>TEM Sample preparation</td>
<td>50</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Conventional (Ion-Milling) Method</td>
<td>50</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Focused Ion Beam (FIB)</td>
<td>52</td>
</tr>
<tr>
<td>3.3</td>
<td>Transmission Electron Microscopy (TEM)</td>
<td>55</td>
</tr>
<tr>
<td>3.4</td>
<td>Superconducting Quantum Interference Device (SQUID)</td>
<td>60</td>
</tr>
<tr>
<td>3.5</td>
<td>Other Characterization Tools</td>
<td>61</td>
</tr>
<tr>
<td>3.5.1</td>
<td>Scanning Electron Microscopy (SEM)</td>
<td>61</td>
</tr>
<tr>
<td>3.5.2</td>
<td>Secondary Ion Mass Spectroscopy (SIMS)</td>
<td>61</td>
</tr>
<tr>
<td>3.5.3</td>
<td>X-ray Photoelectron Spectroscopy (XPS)</td>
<td>62</td>
</tr>
<tr>
<td>3.5.4</td>
<td>X-ray Diffraction (XRD)</td>
<td>62</td>
</tr>
<tr>
<td>CHAPTER</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>3.5.5 Atomic Force Microscopy (AFM)</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>4 CHARACTERIZATION OF COBALT-IRON FILMS ON Coppers AND ALUMINUM SUBSTRATES</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>4.1 Motivation</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>4.2 Experimental details</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>4.3 Results and discussions</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>4.4 Conclusions</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>5 CHARACTERIZATION OF COBALT-IRON FILMS ON SILICON SUBSTRATES</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>5.1 Motivation</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>5.2 Experimental details</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>5.3 Results and discussion</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>5.3.1 TEM analysis (non aberration, JEOL 2010F)</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>5.3.1.1 Diffraction and Phase Contrast</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>5.3.1.2 HREM Imaging</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>5.3.1.3 STEM/EDS</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>5.3.1.4 STEM/EELS</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>5.3.1.4.1 Effect of Deconvolution on White Line ratios and O-K Edge</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>5.3.1.4.2 Low loss EELS Spectra</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>5.3.2 Aberration-Corrected STEM (JEOL-ARM 200)</td>
<td>109</td>
<td></td>
</tr>
<tr>
<td>CHAPTER</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>5.3.3 Off-axis Electron Holography</td>
<td>117</td>
<td></td>
</tr>
<tr>
<td>5.3.4 X-ray diffraction (XRD)</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>5.3.5 X-ray Photoelectron Spectroscopy (XPS)</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>5.3.6 Secondary Ion Mass Spectroscopy (SIMS)</td>
<td>123</td>
<td></td>
</tr>
<tr>
<td>5.3.7 Atomic Force Microscopy (AFM)</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>5.3.8 Super-conducting Quantum Interference Device (SQUID)</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>5.4 Conclusions</td>
<td>134</td>
<td></td>
</tr>
</tbody>
</table>

6 CHARACTERIZATION OF ELECTRODEPOSITED COBAL-IRON NANOCONTACTS | 135 |
| 6.1 Motivation | 135 |
| 6.2 Experimental details | 136 |
| 6.3 Results and discussion | 138 |
| 6.3.1 TEM results | 138 |
| 6.3.1 Magentoresistance results | 142 |
| 6.4 Conclusions | 144 |

7 SUMMARY AND FUTURE WORK | 145 |
<p>| 7.1 Summary | 145 |
| 7.2 Future work | 146 |
| 7.2.1 TEM sample preparation | 146 |
| 7.2.2 Identification of crystallinity of oxide phases | 147 |
| 7.2.3 Continuity of grain boundary oxide | 147 |</p>
<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2.4 Type of second phase</td>
<td>147</td>
</tr>
<tr>
<td>7.2.5 Electrodeposition process</td>
<td>148</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>149</td>
</tr>
<tr>
<td>APPENDIX</td>
<td></td>
</tr>
<tr>
<td>A foil thickness and inelastic mean free path</td>
<td>156</td>
</tr>
<tr>
<td>B Volume fraction of oxide phase calculations</td>
<td>158</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Terminology for Eikonal Coefficients</td>
</tr>
<tr>
<td>3.1</td>
<td>Aqueous solution compositions and electodepositing parameters</td>
</tr>
<tr>
<td>3.2</td>
<td>Calculated ferromagnetic mass and volume for different TEM samples</td>
</tr>
<tr>
<td>5.1</td>
<td>Characteristics of onset O-Kedge of dark areas in S1 and S3</td>
</tr>
<tr>
<td>5.2</td>
<td>White line ratios of Fe L-edges, L_3/L_2</td>
</tr>
<tr>
<td>5.3</td>
<td>Ep and M_{2,3} of Fe, CoFe matrix and FeO</td>
</tr>
<tr>
<td>5.4</td>
<td>Magnetic properties and magnetoresistance of CoFe films</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>A typical hysteresis loop of ferromagnetic materials</td>
<td>5</td>
</tr>
<tr>
<td>1.2</td>
<td>Schematic representation of spins: (a) ferromagnetism, (b) antiferromagnetism and (c) ferrimagnetism</td>
<td>6</td>
</tr>
<tr>
<td>1.3</td>
<td>(a) One domain with all spins in a single direction. (b) Two domains with opposite spin directions. (c) Four domains with less magnetostatic energy relative to b. (d) closure domains with the lowest magnetostatic energy (no leakage)</td>
<td>7</td>
</tr>
<tr>
<td>1.4</td>
<td>Hard-disk drive components</td>
<td>10</td>
</tr>
<tr>
<td>1.5</td>
<td>Magnetic areal density vs. year of IBM product introduction</td>
<td>11</td>
</tr>
<tr>
<td>1.6</td>
<td>Basic scaling for magnetic recording</td>
<td>12</td>
</tr>
<tr>
<td>1.7</td>
<td>MR sensor element reading bits on a hard disk</td>
<td>13</td>
</tr>
<tr>
<td>1.8</td>
<td>The origin of AMR</td>
<td>15</td>
</tr>
<tr>
<td>1.9</td>
<td>GMR effect with high and low resistance configurations</td>
<td>16</td>
</tr>
<tr>
<td>1.10</td>
<td>Schematic diagram of TMR showing the availability of empty states of the same spin orientation when the two ferromagnetic layers are aligned parallel and the lack of available states when they are aligned antiparallel</td>
<td>18</td>
</tr>
<tr>
<td>1.11</td>
<td>Schematic configuration of nanocontact in BMR</td>
<td>19</td>
</tr>
<tr>
<td>1.12</td>
<td>Binary phase diagram of Fe-Co system</td>
<td>20</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematic diagram for a typical TEM column</td>
<td>25</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>Two basic operations of TEM imaging systems: (a) diffraction mode and (B) image mode.</td>
<td>26</td>
</tr>
<tr>
<td>2.3</td>
<td>Placing an objective aperture around (A) the direct beam forms BF image and (B) the diffracted beam forms DF image in TEM.</td>
<td>28</td>
</tr>
<tr>
<td>2.4</td>
<td>(A) Translational and (B) rotational Moiré fringes.</td>
<td>29</td>
</tr>
<tr>
<td>2.5</td>
<td>Schematic of different detectors used in STEM mode. Each detector is associated with a range of scattering angles.</td>
<td>31</td>
</tr>
<tr>
<td>2.6</td>
<td>Contrast transfer function for (a) coherent imaging conditions and (b) incoherent imaging conditions.</td>
<td>32</td>
</tr>
<tr>
<td>2.7</td>
<td>Schematic diagram of A STEM convergent beam diffraction (CBED) pattern, showing Z-contrast image where the total signals are detected on the annulus as a function of probe position on the specimen.</td>
<td>33</td>
</tr>
<tr>
<td>2.8</td>
<td>Spherical aberration effect in the lens.</td>
<td>35</td>
</tr>
<tr>
<td>2.9</td>
<td>Schematic drawing of the optical design of a hexapole STEM corrector.</td>
<td>37</td>
</tr>
<tr>
<td>2.10</td>
<td>Single hexapole element of STEM hexapole corrector.</td>
<td>38</td>
</tr>
<tr>
<td>2.11</td>
<td>Calculated Probe intensities before correction (left): Cs= 1.5 mm and after correction (right): Cs= -0.04.</td>
<td>40</td>
</tr>
<tr>
<td>2.12</td>
<td>Schematic showing STEM combined with AEM.</td>
<td>42</td>
</tr>
<tr>
<td>2.13</td>
<td>The ionization process.</td>
<td>42</td>
</tr>
<tr>
<td>2.14</td>
<td>Energy loss spectrum of YBCO.</td>
<td>43</td>
</tr>
<tr>
<td>2.15</td>
<td>Schematic diagram of parallel energy-loss spectrometer.</td>
<td>45</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>2.16</td>
<td>Schematic showing SQUID consisting of a superconductor with poorly conducting (weak link)……………………………47</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic shows specimen configurations for (a) thin film and (b) nanocontact. PR is photoresist……………………………49</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>Rod and tube method………………………………………………51</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Dimpling time of CoFe /Si specimen vs dimpling depth……………… 52</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>FIB LO procedure steps from (a) through (f)……………………… 53</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>Cross-sectional TEM specimen taken by (a) SEM and (b) TEM……… 54</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>Schematic showing the main components in TEM column and a photograph of the JEOL 2010F TEM/STEM……………………56</td>
<td></td>
</tr>
<tr>
<td>3.7</td>
<td>JEM-ARM200F located in Southwestern Center for Aberraion Corrected Electron Microscopy at ASU…………………………58</td>
<td></td>
</tr>
<tr>
<td>3.8</td>
<td>Schematic showing three essential components for off-axis electron holography in the CM200 FEG……………………………60</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>$B_s$ vs. $[Fe^{3+}]$ dependence for electrodeposited CoFe alloys………………65</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>SEM images of CoFe film in conjunction with EDS from (a) spot 6 (bright area) (b) spot 7 (dark area)………………………… 66</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>SEM image of cross-sectional FIB sample on Cu substrate………………67</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>TEM image of cross-sectional CoFe sample…………………………… 68</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>SEM image of CoFe film on Au/Al substrate showing pinholes………69</td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>BF TEM image showing columnar structure of CoFe film………………70</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>(a) BF and (b) DF images of the film in fig. 4.6………………… 70</td>
<td></td>
</tr>
</tbody>
</table>
Table of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8</td>
<td>Z contrast image of CoFe film on Au/Al substrate</td>
</tr>
<tr>
<td>4.9</td>
<td>Fig. 4.9. (a) BF, (b) Fe-L₂₃, (c) Co-L₂₃ and (d) O-k images of CoFe film with high oxygen content on Au/Al substrates. CM200</td>
</tr>
<tr>
<td>4.10</td>
<td>TEM image of CoFe /Au/NiP/Al substrate</td>
</tr>
<tr>
<td>5.1</td>
<td>SEM image of cross-sectional TEM sample prepared by FIB</td>
</tr>
<tr>
<td>5.2</td>
<td>(a) TEM image showing the specimen configuration with interface flatness (b) higher magnification of fig. 5.2 (a)</td>
</tr>
<tr>
<td>5.3</td>
<td>SAED pattern from CoFe film S3 showing a bcc crystal structure</td>
</tr>
<tr>
<td>5.4</td>
<td>Plan-view SAED pattern (inverted contrast) from S3 showing presence of amorphous oxide second phase (α-Fe₂O₃)</td>
</tr>
<tr>
<td>5.5</td>
<td>(a) BF and (b) DF for S3 showing the matrix grain size is 10 to 20 nm</td>
</tr>
<tr>
<td>5.6</td>
<td>Plan-view HREM image for low oxygen content S1. Arrowed areas show lack of periodicity relative to CoFe matrix</td>
</tr>
<tr>
<td>5.7</td>
<td>Cross-sectional HREM of low oxygen content specimen S1 showing Moiré fringes</td>
</tr>
<tr>
<td>5.8</td>
<td>FFT from areas shown in fig. 5.7</td>
</tr>
<tr>
<td>5.9</td>
<td>FFT from area B1 shown in fig. 5.7</td>
</tr>
<tr>
<td>5.10</td>
<td>Cross-sectional HREM image of ion-milled S3 showing the lattice spacing of CoFe alloy and some amorphous regions</td>
</tr>
<tr>
<td>5.11</td>
<td>Cross-sectional HREM image of FIB specimen (S3)</td>
</tr>
<tr>
<td>5.12</td>
<td>(a) Z contrast STEM image for S1 (JEOL 2010f)</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>5.12</td>
<td>NanoEDS spectrum collected from (b) bright area, (c) dark area shown in fig. 5.12(a).</td>
</tr>
<tr>
<td>5.13</td>
<td>Schematic diagram shows the foil thickness relative to particle size.</td>
</tr>
<tr>
<td>5.14(a)</td>
<td>Z contrast STEM image for S2 (JEOL 2010f).</td>
</tr>
<tr>
<td>5.14</td>
<td>NanoEDS spectrum collected from (b) particle (c) lamella regions shown in fig. 5.14(a).</td>
</tr>
<tr>
<td>5.15</td>
<td>O-K edge EELS spectra after background subtraction collected from areas shown in fig. 5.12(a). Spectra are displaced vertically for clarity.</td>
</tr>
<tr>
<td>5.16(a)</td>
<td>Z contrast image for S3, (b) same sample with higher magnification shows line over which EELS spectrum was collected. Inset: net O-K counts along the line shown in the image.</td>
</tr>
<tr>
<td>5.17</td>
<td>O, Fe and Co edges EELS spectra of S1 from bright and dark areas shown in fig. 12(a).</td>
</tr>
<tr>
<td>5.18</td>
<td>Fe L-edge EELS spectra after background subtraction, collected from bright and dark areas of S1 shown in fig. 5.12 (a).</td>
</tr>
<tr>
<td>5.19</td>
<td>Background subtracted O K-edge from EELS nanospectra from spherical and lamellar particles.</td>
</tr>
<tr>
<td>5.20(a)</td>
<td>O, Fe and Co edges of S1 before deconvolution, (b) after deconvolution.</td>
</tr>
<tr>
<td>5.21</td>
<td>O-K edge of S1 with and without deconvolution.</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>5.22</td>
<td>Low loss spectrum from (a) Fe, (b) CoFe matrix and (c) FeO dark area in S1.</td>
</tr>
<tr>
<td>5.23</td>
<td>Low loss spectrum of Fe$_2$O$_3$ from (a) Atlas and (b) from dark grain boundary area in S3.</td>
</tr>
<tr>
<td>5.24</td>
<td>STEM HAADF images shows oxygen rich phase distributed at grain boundaries with (a) low and (b) high magnification.</td>
</tr>
<tr>
<td>5.25</td>
<td>High-resolution STEM Z-contrast image of S3 shows dark regions displaying a lack of periodicity (arrowed) relative to CoFe matrix.</td>
</tr>
<tr>
<td>5.26</td>
<td>(a) HAADF region of interest for SI, (b) O-K image showing nearly continuous distribution. (c) Fe-L image. (d) Co-L image.</td>
</tr>
<tr>
<td>5.27</td>
<td>(a) ABF STEM image, (b) FFT of area A1, (c) FFT of area A2 and (d) HAADF STEM image of S3.</td>
</tr>
<tr>
<td>5.28</td>
<td>(a) Reconstructed holographic phase image. (b) Line profile from AB line in fig. 5.28(a). (c) Magnetic induction map and overlaid arrows indicated by color wheel shown in fig. 5.28(d).</td>
</tr>
<tr>
<td>5.29</td>
<td>Reconstructed phase image from CoFe film in S3. The arrows show 180° domain walls. The inset: line profile across phase changes as shown in fig. 5.29.</td>
</tr>
<tr>
<td>5.30</td>
<td>X-ray diffraction patterns obtained from S1 and S3.</td>
</tr>
<tr>
<td>5.31</td>
<td>(a) Co 2p$_{3/2}$ and (b) O 1s XPS peaks.</td>
</tr>
<tr>
<td>5.32</td>
<td>Fe 2p$_{3/2}$ XPS spectrum for S1.</td>
</tr>
</tbody>
</table>
Figure | Page
--- | ---
5.33 | (a) SIMS depth profile for S1 and (b) O/Fe ratio for S1 and S3 ……… 124
5.34 | AFM images of (a) S1, (b) S2 and (c) S3…………………………………… 127
5.35 | In-plane magnetization curves for S1 and S3…………………………… 128
5.36 | Resistance vs field of S3………………………………………………… 129
5.37 | Frequency vs ΔV (histogram) for (a) S1 and (b) S3………………….. 132
6.1 | A schematic of cross-sectional magnetic sensor……………………… 136
6.2 | FIB LO process…………………………………………………………………… 137
6.3 | TEM image of CoFe nanocontact………………………………………… 138
6.4 | High magnification TEM image of Fig. 6.3 showing the nanocontact width…………………………………………………………………… 139
6.5 | SAD of (a) CoFe nanocontact and (b) Co layer………………………… 140
6.6 | BF STEM image of nanocontact……………………………………………… 140
6.7 | (a) HAADF region of interest for SI. (b) O-K image showing nearly continuous distribution. (c) Fe-L image. (d) Co-L image……………… 141
6.8 | HAADF STEM image of nanocontact………………………………………. 142
6.9 | Resistance vs field showing MR value exceeds 1000%………………….. 143

xvii
Chapter 1

INTRODUCTION

1.1 Magnetism (a brief history)

Magnetism is one of the oldest phenomena in the history of natural science. The magnetism was early noticed by a shepherd who observed the iron tip of his stick was attracted by a stone [1]. This stone was a mineral called magnetite (Fe₃O₄) and found in the magnesia district, in which now is modern Turkey [2]. It was also known to the Greeks that a small piece of iron would become magnetic if it were contacted with magnetite. The early scientific study of magnetism was done by Englishman William Gilbert (1540-1603), who published his book on magnetism in 1600 and translated in 1958 [3]. He showed that a compass needle orients itself in the earth’s magnetic field. No discoveries of any importance in magnetism were made till eighteenth century. The first electromagnet was made in 1819 by Hans Christian Oersted and published in 1820 [4], in which electric current produced a magnetic field. Then in 1820 Jean-Baptiste Biot and Felix Savart performed experiments to determine the force exerted on a compass by a current carrying wire (Biot-Savart Law). Detailed descriptions of electromagnetism were published by both Faraday and Maxwell in the mid of nineteenth century. Weiss introduced the concept of molecular field to model the magnetic interaction [5]. In 1928 Heisenberg [6] established the quantum mechanics of electron spins and exchange interactions. The domain structure, in which the local magnetization was uniform, was discussed by Bloch in 1932 [7] and further elaborated by Landau and Lifshitz in 1935 [8], who
predicted the domains are formed to minimize the total energy of the magnetic system.

1.2 Basic definition of Magnetism

The applied external magnetic field and the field inside the material can be defined as the magnetic field strength $H$ and magnetic flux density (magnetic induction) $B$, respectively. $H$ and $B$ are related by the following equation [9]:

$$ B = \mu H = \mu_r \mu_o H \quad (1.1) $$

where $\mu$ is the permeability of the material, $\mu_r$ is the relative permeability and $\mu_o$ is the permeability of free space.

Materials behave differently when they are exposed to an external magnetic field. The response to the magnetic field can be described by magnetization $M$, where it is defined as:

$$ M = \frac{\mu_m}{V} \quad (1.2) $$

where $\mu_m$ is the magnetic moment and $V$ is the volume of material. The magnetic susceptibility $\chi$ describes the response of the material to an externally applied field. It is defined as:

$$ \chi = \frac{M}{H} \quad (1.3) $$

The relationship between the susceptibility and the relative permeability is

$$ \mu_r = 1 + \chi \quad (1.4) $$

The relationship between these parameters is

$$ B = \mu_o (H + M) \quad (1.5) $$
1.3 Classification of Magnetic Materials

Based on different response to an external applied magnetic field, materials can be classified as:

(1) Diamagnetic materials:
Diamagnetism is associated with the tendency of electrical charges to shield the interior of a material from an external applied magnetic field. Most diamagnetic materials have weakly negative magnetic susceptibility \( \chi \sim -10^{-6} \) to \(-10^{-5}\). In a superconductor, the internal field \( B \) is zero. This means that the magnetization is equal and opposite to the external magnetic field strength, which is a perfect diamagnet. Susceptibility of superconductor is -1.0, which is larger than for a normal diamagnetic. Examples of diamagnetic materials are Ag, Au, and Pb [10].

(2) Paramagnetic materials:
Paramagnetic materials consist of stable atomic magnetic moments. They are disordered in the absence of a magnetic field, but they tend to align with the presence of magnetic field and give a positive susceptibility. There are two components to paramagnetism: electron spin and electron orbital moment. Some examples of paramagnetic elements are Al, Ca and Cr. The susceptibility \( \chi \) is temperature dependent and governed by the Curie-Weiss law:

\[
\chi = \frac{C}{T-\theta}
\]  

(1.6)

where \( C \) is the Curie constant, \( \theta \) is the temperature shift and \( T \) is the absolute temperature.
(3) Ferromagnetic materials:

Ferromagnetic materials are the specific interest in this dissertation. So we will discuss it in more detail than other materials. The ferromagnetic elements: iron, cobalt and nickel are characterized by unfilled d-band. Ferromagnetism has tendency for spontaneous electron spin alignment without applying an external magnetic field. The magnetic moments are typically ordered, giving arise to large positive susceptibility. In 1907, Pierre-Ernest Weiss proposed the mean-field magnetic theory [11]. He stated that the total magnetic field (Hₜ) acting on a magnetic moment is composed of two parts: the external field (Hₑ) and the molecular field (Hₘ). The Hₘ is produced by interaction of the individual magnetic moments and is responsible for parallel alignment of spins. From the quantum mechanics point of view, the molecular field is essentially the exchange force. The exchange integral was calculated by Slater and Bethe [2]. They solved appropriate Schrodinger equation for two atoms. The potential energy includes the exchange forces between the nuclei a and b, the forces between electron 1 and 2, and the interactions between the nuclei and their neighboring electrons. The exchange integral can be defined as:

\[
I_{ex} = \int \psi_a (1) \psi_b (2) \psi_a (2) \psi_b (1) \left[ \frac{1}{r_{ab}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{r_{12}} \right] d\tau \tag{1.7}
\]

A small distance between electrons and a large distance between nuclei and neighboring electrons r_a2 and r_b1 yield a positive I_{ex} value. This means that parallel spins are energetically more favorable than antiparallel spins, which produce ferromagnetism. The magnetic properties of ferromagnetic materials can
be characterized by their hysteresis loop. Figure 1.1 shows a typical of ferromagnetic hysteresis loop, which is a plot of external applied magnetic field H versus magnetization M. The figure displays important parameters obtained from a hysteresis loop as discussed below.

![Hysteresis Loop Diagram](image)

**Fig. 1.1.** A typical hysteresis loop of ferromagnetic materials

If H is increased the magnetization eventually reaches saturation at a value which is identified as $M_s$. When the external field is reduced to zero, the remaining magnetization is called the remnant magnetization $M_r$. The magnetization can be reduced to zero after being saturated by applying a reverse magnetic field of strength $H_c$, which is known as the coercivity. Ferromagnetic materials lose their magnetic ordering above critical temperature, called the Curie temperature. This is due to high thermal energy, and the materials become paramagnetic, with effectively randomly oriented ionic magnetic moments above $T_c$ [12].
(4) Antiferromagnetic materials:

Antiferromagnetic materials have positive small susceptibilities, on order of $10^{-3}$, but they increase with temperature up to a critical temperature, and then fall off again. The critical temperature is called the Neel Temperature, above this temperature an antiferromagnet becomes a paramagnet. Antiferromagnetic materials consist of two interpenetrating sublattices. The net magnetic moment for this classification of material is zero due to antiparallel alignments of the spins. Many compounds are antiferromagnetic such as MnO, FeO and NiO.

(5) Ferrimagnetic materials:

The general formula for ferrite is $M\text{O.}Fe_2\text{O}_3$, where $M$ is a bivalent metallic ion like Fe, Mn or Cu. They have two sublattices with different magnitude of magnetic moments, and they align opposite to each other, but do not cancel. Figure 1.2 shows a schematic representation of spins in ferromagnetism, antiferromagnetism and ferrimagnetism.

![Schematic representation of spins](image)

Fig. 1.2. Schematic representation of spins: (a) ferromagnetism, (b) antiferromagnetism and (c) ferrimagnetism
1.4 Ferromagnetic Domains:

Ferromagnetic domains and domain walls are important concepts for a better understanding of the magnetic properties of ferromagnetic and ferrimagnetic materials. Magnetized regions are separated by domain walls. The magnetization vectors of the domains are arranged in such a way that their vector sum is zero and no net magnetization. The presence of domains is a result of minimization of magnetostatic energy, which was discussed by Landau and Lifshitz [8]. The magnetostatic energy would be linked to the leakage of magnetic flux into the surrounding space. Fig 1.3 shows reduction of magnetostatic energy due to flux leakage by formation of magnetic domains.

![Diagrams](a) One domain with all spins in a single direction. (b) Two domains with opposite spin directions. (c) Four domains with less magnetostatic energy relative to b. (d) closure domains with the lowest magnetostatic energy (no leakage).
A wall is the space between neighboring domains in which the magnetic vectors pass smoothly from one domain to another. There are two main different walls present in magnetic films in order to reduce the magnetostatic energy. The first one is a Bloch wall in which the magnetization vectors rotate out of the plane of the wall. The second one is Neel wall, in which the magnetization vectors rotate in the plane of the wall, and this type of wall occurs in thin films less than 200 nm thick [10].

Based on domain structures and magnetic hysteresis shown in fig. 1.1, the magnetization process consists of (1) domain growth and domain wall displacement and (2) rotation of spins within a domain with respect to direction of applied field. The rate of changing magnetization is decreased in the latter. Ferromagnetic materials can be classified into two categories: soft and hard materials. These classifications are based on the coercivity. Soft (high permeability) magnetic materials have lower Hₙ, less than 1 A/m relative to hard (permanent) magnetic materials with greater than 2kA/m. Soft magnetic materials has been widely utilized in several applications, such as magnetic recording heads, magnetic bearings for high speed motors, transformers and magnetic sensors [13,14]. Whereas hard magnetic materials also have their distinctive applications, such as telephone industry particularly in loudspeakers and electric motors [10].
1.5 Magnetic Data Storage Systems

As computer technology advances, there is a necessity to store information and data for long periods. Magnetic methods have progressively advanced relative to mechanical, chemical, optical and electrical methods during recent years. Magnetic storage devices work quickly and reliably. They need no continuous energy feed and can be cleared and re-used as often as required. The applications of magnetic storage are increasing tremendously in our daily life. The magnetic systems for data storage include hard disks, flexible disks and tapes. Hard (rigid) disk is our main interest in this research. Binary digital signals are quite convenient for magnetic recording. They are written by reversal of a head field sufficient to saturate the recording medium. In order to minimize the errors, heads, media, and data channels are designed to write and read the data transitions with minimum shift in the timing of the reproduced pulses [15].

1.5.1 Hard-Disk Drives

Figure 1.5 shows schematically the main parts of a hard disk drive [16]. It contains a stack of disks coated with thin magnetic films. They are mounted on a spindle and rotate at high speed. The magnetic heads are writing and reading heads, each one is attached to an arm with spring suspension and moves across the disk surface by high-speed actuator.
Fig. 1.4. Hard-disk drive components [16].

Digital recording is used and the information is read back as string of encoded positive and negative voltage pulses that are detected in a recording channel. The head disk assembly runs the analog read signals and digital write current pulses. The actuator control system controls the position of actuator and the head-arm assembly over the disk surface [14].

1.5.2 Future Magnetic Areal Density

Similar to Moore’s law, Kryder’s law states that the areal density of magnetic recording has to be doubled every eighteen months. Figure 1.5 shows areal density trend since 1970 [17].
Fig. 1.5. Magnetic areal density vs. year of IBM product introduction [17].

In order to sustain the areal density growth beyond 1 Tbit/in$^2$ and fulfill the demands for new desktop computers and other consumer applications, heads have been reduced in size, and the materials and processes used have been improved to produce smaller gaps and narrower tracks [15,17]. Figure 1.6 shows the basic scaling for magnetic recording. As the reader can see from the figure, shrinkage of everything by factor of $s$ requires process improvement [18].
However, the most abrupt growth in areal density is the development of magnetoresistive (MR) sensors. They have greatly accelerated the increase in areal density since the early 1990s due to high signal-to-noise ratio, high sensitivity by reading smaller bits, high lateral resolution and high data reliability [17].

1.5.3 How MR Sensor Works

MR sensor is a sensitive detector of magnetic field and it is considered to be the heart of advanced recording head. Figure 1.7 shows schematically MR sensor element on a hard disk [19]. The data is written by an electromagnet that magnetizes a small part of the disk medium to create each information element called a bit (binary digit). The data is encoded as transitions, which are changes between two bits magnetized in opposite directions. The presence of a transition means a binary 1 and the absence of transition means a binary 0. During the reading process, the vertical magnetic
field at the transition changes the orientation at the sensor giving a change in resistance.

![Diagram of MR sensor element reading bits on a hard disk](image)

Fig. 1.7. MR sensor element reading bits on a hard disk [19].

Then changes in resistance are detected as voltage changes. These voltage fluctuations called signals are sent via wires to the disk-drive electronics for decoding the time sequence of pulses into binary ones and zeroes.

1.5.4 Types of MR Sensors

In order to keep S/N ratio acceptable, head sensitivity has increased by changes in the type of MR used over passed two decades. Before going into details of classification of MR, we need to identify MR and explain its origin in normal metals and ferromagnetic metals. Magnetoresistance is the change of resistivity upon applying magnetic field. MR can be described by the following
relationship:

\[
\text{MR}\% = \frac{R_{\text{max}} - R_{\text{min}}}{R_{\text{min}}} \\
\]

(1.8)

where \( R_{\text{max}} \) is the resistance when the magnetic moments in the ferromagnetic layers are antiparallel and \( R_{\text{min}} \) when they are parallel. We will explain this later in giant magnetoresistance type. The MR ratio indicates the maximum signal that can be obtained from the sensor to detect the stored data bit. The MR in metal (non ferromagnetic) has a very small effect and doesn’t have a technological application. Since the Lorentz force curls the electrons as they travel further and are scattered by imperfections such as phonons, impurities and dislocations, the resistance is large in the presence of magnetic field. Therefore, the MR in normal metal is positive. Whereas, the MR in ferromagnetic metals is of great interest in high technology applications such as magnetic sensors, magnetic read recording heads and magnetic memories [20]. Conduction electrons are scattered by magnetic impurities due to interactions between the magnetic moments of these scattering regions and the spins of the conduction electrons [21]. MR in ferromagnetic metals can be classified as follow:

1.5.4.1 Anisotropic magnetoresistance (AMR)

AMR, discovered in 1857 by William Thomson [22], occurs in ferromagnetic metals and their alloys with a typical MR ratio of 1-2%. It is termed anisotropic because it depends on the direction of magnetic field with respect to the current direction. The process is shown schematically in fig. 1.8
When the magnetization is perpendicular to the current direction, the scattering cross section is decreased, whereas when the magnetization is parallel to the current direction the scattering cross section increased. The s electrons are scattered by orbital angular momentum of 3d electrons.

Fig. 1.8. The origin of AMR [20].

1.5.4.2 Giant Magnetoresistance (GMR)

The GMR effect in thin film multilayers was discovered in 1988 by Baibich [23]. The term giant was created because the 10-15% change in resistance found in GMR, is very large compared to AMR. A GMR device consists of two or more layers of ferromagnetic metal separated by ultra thin non-magnetic metal spacer layer as schematically shown in fig. 1.9. To obtain the GMR effect, the spacer layer must be thin compared to the electron mean free path.
path so the electrons spin polarized in one layer can pass into other layer before their polarization is disturbed by scattering [21].

Fig. 1.9. GMR effect with high and low resistance configurations [21].

The spacer layers allow the magnetic direction of the layers to differ while still permitting the passage of electrons. A common term to describe the physics of GMR is spin dependent scattering (SDS). When the magnetic layers are aligned in opposing direction (antiferromagnetic configuration) a high resistance is obtained as shown in fig. 1.9 (a). This is due to spin-up electrons are scattered by spin-down electrons and vice versa. But, when the magnetic layers are aligned in the same direction under applied magnetic field, as shown in fig. 1.9 (b), low resistance is obtained. In this case, the external magnetic field is strong enough to overcome antiferromagnetic coupling and change the rotation of magnetization to ferromagnetic configuration. Thus, the electrons are able to pass relatively freely.
with minimal scattering. This effect is due to differences in conduction properties of spin-up and spin-down conduction electrons. In addition, ferromagnetic metals have a sizable mismatch in the density of states for up and down electrons at the Fermi energy [21]. This effect is schematically shown in fig. 1.10 as explained later in tunneling magnetoresistance. A modified version of GMR is a spin valve where the magnetization can be switched from antiparallel to parallel configuration at low applied field. The structure of a spin valve is similar to GMR configuration except it has antiferromagnetic layer (pinning layer) to hold the adjacent magnetic layer spin direction fixed (pinned layer) [20,21].

1.4.4.3 Colossal Magnetoresistance (CMR)

CMR was observed in the perovskite structure, La$_{0.67}$Ca$_{0.33}$MnO$_3$, in 1994 by Jin et al [24]. The name colossal was chosen because of the very large change in resistance from insulating to conducting state in the presence of the magnetic field. CMR materials don’t have practical applications in magnetic sensors or read heads because a very high-applied field is required to cause resistance change.

1.5.1.3 Tunneling Magnetoresistance (TMR)

Changes of resistance with magnetic field up to 70% have been observed in TMR structures [25]. TMR structures are similar to GMR except that they utilize an ultra thin insulating layer to separate two magnetic layers rather than a conductor. Electrons pass from one layer to the other through insulator by quantum mechanical tunneling. The tunneling process is dependent on the
available electron state in the ferromagnetic layers. The magnetic dependence of the process is similar to a GMR structure in a sense of electrical resistance with respect to magnetic orientation of ferromagnetic layers. The process is also known as spin-dependent tunneling (SPT) which is schematically shown in fig. 1.10 [16].

![Schematic diagram of TMR showing the availability of empty states of the same spin orientation when the two ferromagnetic layers are aligned parallel and the lack of available states when they are aligned antiparallel](image)

Fig. 1.10. Schematic diagram of TMR showing the availability of empty states of the same spin orientation when the two ferromagnetic layers are aligned parallel and the lack of available states when they are aligned antiparallel [16].

TMR technology is being developed for hard-disk read heads and advanced magnetoresistive random access memories (MRAM).

1.5.1.4 Ballistic Magnetoresistance (BMR)

BMR has been introduced to the scientific community in 1999 by Garcia et al [26,27]. In order to reach ultrahigh density storage systems in Tbit/in$^2$, the
magnetic readers have to scale down to the nanoscale bits. At this scale, higher sensitivity read heads are being investigated. BMR effect in ferromagnetic nanocontacts is a promising avenue in this regard which gives much larger MR ratio than GMR. Consequently, BMR has the potential to replace TMR and GMR in nonvolatile memory chips and hard disk read heads [28]. The most amenable model of BMR is based on the spin dependent scattering (SDS) from magnetic domain wall (MDW) existing in the confined geometry of the nanocontact [29,30]. Figure 1.11 shows schematically typical nanocontact configurations [31].

Fig. 1.11. Schematic configuration of nanocontact in BMR [31].

1.6 Cobalt-Iron (CoFe) Alloys: Alloys of choice for this research

Near equiatomic Fe-Co alloys have been extensively used in magnetic recording heads [32], and high temperature applications such as gas turbine engines and magnetic bearings for high-speed motors [33]. This is due to their soft ferromagnetic behavior, with high Curie temperature (~950°C), large saturation
magnetic flux density $B_S$ (2.4 T), high permeability associated with the very low magnetocrystalline anisotropy $K_1$ and low coercivity [34]. Given their high $B_S$, CoFe alloys become competitive for synthesis of magnetic recording heads among other soft magnetic alloys such as: Ni$_{81}$Fe$_{19}$ (Permalloy) with $B_S$ of 1.05 T, Ni$_{45}$Fe$_{30}$Co$_{25}$ (Perminvar) with $B_S$ of 1.55 T and Fe$_{97}$Si$_3$ with $B_S$ of 2.01 T [12]. Figure 1.12 shows a phase diagram of Fe-Co binary system [35].

![Binary phase diagram of Fe-Co system](image)

Fig. 1.12. Binary phase diagram of Fe-Co system [35].

As we can see from fig. 1.12, the high temperature f.c.c phase has been referred to as $\gamma$ (A1), the disordered b.c.c phase as $\alpha$ (A2) and its ordered state as $\alpha'$ (B2).
1.7 Magnetic Materials Fabrications

The increase in areal density of magnetic recording brought many of the processes involved in fabrication of magnetic heads to the level of nano-science for instance: vacuum evaporation [36], chemical vapor deposition [37], thermal decomposition (Pyrolysis) [38], spin casting [39], RF magnetron sputtering [40,41], and electrodeposition [42,43]. One of the most promising ones to be used for future magnetic recording heads is electrodeposition [44]. It has been demonstrated that electrodeposition is capable of delivering high quality CoFe nanostructures with critical dimensions of ~ 40 nm to meet the design requirements of future magnetic recording heads [45]. Furthermore, electrodeposition allows fabrication of alloys with soft magnetic properties with relatively low capital cost and energy consumption requirements [46]. The magnetic properties of the deposited film are affected by synthesis parameters such as: current density, surface structure of the cathode (substrate), electrolyte composition, pH, and bath temperature, which all affect the film nanostructure, composition, and magnetic properties [47].

The research in this dissertation is focused on electrodeposited CoFe films and nanocontacts because electrodeposition is the most economical method for mass production and highest technological interest. Early experiments showed that the oxygen incorporation during synthesis process increased the magnetoresistance among other element. TMR was a useful type of MR to describe the presence of oxide (inter/intragranular) in the matrix alloys. Whereas, BMR was a predominant mechanism to explain higher values of MR in
nanocontacts. We embarked in this study to determine nanostructure of oxides in CoFe films and to relate that to magnetoresistance and other magnetic properties.

1.8 Outline of Thesis

In order to develop sustainable magnetic devices, studying the structural properties and correlating them to magnetic properties is crucial. This dissertation explains the state of the art techniques of transmission electron microscopy and their applications to study the nanostructure ferromagnetic materials. It also presents a detailed study determining type, morphology and composition of nanodistributed oxide phases in the matrix CoFe alloys and their impact on magnetoresistance and other magnetic properties.

Chapter two introduces various techniques of characterization tools used in this dissertation and theoretical principles behind them. Transmission electron microscopy (TEM), including imaging and spectroscopy techniques, was the primary tool in this study. Aberration corrected electron microscopy has been utilized for this dissertation as well.

Chapter three provides the experimental details of the film synthesis process, sample preparation, and the processes of acquiring images and spectra in TEM. Chapter four describe some TEM characterization of CoFe films electrodeposited on different substrates such as Cu and Al.

Chapter five covers most of the experimental results, including a detailed study of type, structure and nanodistribution of oxide phases and magnetic properties characterizations of CoFe films electrodeposited on Si substrates.
Chapter six provides some TEM study on CoFe nanocontacts and their impact on magnetoresistance values.

Finally, chapter seven provides conclusions of our studies done on CoFe alloys for magnetic field sensors applications and scope for future work.
Chapter 2

CHARACTERIZATION TOOLS

2.1 Transmission Electron Microscopy (TEM)

The characterization of structure and electronic properties of materials at the atomic scale is essential for the nanotechnology and nano-science fields. The performance of any device relies on the relationship between structure and properties at the nano-scale level. In order to tailor the nanostructure of materials, transmission electron microscopy (TEM) is a powerful tool to correlate the processing parameters to properties of materials for achieving desired applications. TEM is sometimes called CTEM (Conventional Transmission Electron Microscopy) to distinguish it from STEM (Scanning Transmission Electron Microscopy), which is discussed below. Figure 2.1 shows schematically a TEM column with various lenses [50]. Basically, the instrument can be divided into three parts. First part: the illumination system includes the gun and condenser lenses to transfer electrons from source to the sample. Second part: objective lens/stage is the heart of TEM where the electron-sample interaction takes place and hence imaging and diffraction pattern (DP) can be obtained as shown in fig. 2.2 [51]. Third part: Imaging system utilizes intermediate and projector lenses to magnify the final image or DP to be displayed on the viewing screen or on a detector such as charge coupled device (CCD). In order to see a DP, imaging system lenses are adjusted so the back focal plane of objective lens acts as the object plane for the intermediate lens, as shown in fig. 2.2(a). To see an image, the intermediate lens is readjusted so the object plane is the image plane of the
objective lens as shown in fig. 2.2(b).

Fig. 2.1 Schematic diagram for a typical TEM column [50].
Fig. 2.2. Two basic operations of TEM imaging systems: (A) diffraction mode and (B) image mode [51].

2.1.1 Diffraction Contrast (Amplitude Contrast) Imaging

As electrons pass through the specimen, a nonuniform distribution of electrons emerges from the exit surface of the sample. This nonuniform distribution consists of angular distribution scattering (DP) and spatial distribution scattering (Image Contrast). Since the electron has wave-particle duality, imaging and DP deal with electron wave. As electron passes through the sample, it
changes both its amplitude and its phase, resulting in image contrast. The
amplitude contrast consists of two main types: (1) mass-thickness contrast and (2)
diffraction contrast. Mass thickness contrast is an incoherent imaging process
with contrast dependent on “absorption”, i.e. specimen thickness and atomic
weight. It is useful for amorphous and biological specimens. “Diffraction” or
“amplitude” contrast results from coherent scattering of Bloch waves traversing a
crystalline specimen; the image is formed by one such wave on the exit surface of
the foil, which is congruent with the objective lens image plane. This differs from
phase contrast imaging, which requires phase-wise reconstruction of several
diffracted beams at the image plane (see below). Figure 2.3 shows the principles
of performing these bright field (BF) and dark field (DF) images [2]. Strong
diffraction contrast can be obtained by tilting the crystal to two-beam conditions
(direct and diffracted beams).
Fig. 2.3. Placing an objective aperture around (A) the direct beam forms BF image and (B) around the diffracted beam forms DF image in TEM [51].

2.1.2 Phase Contrast Imaging

As mentioned earlier, phase contrast images occur due to difference in phases of the electron waves scattered by a sample and collected on the detector. The objective lens also induces phase changes in transmitted beams that contribute to phase contrast images. Phase contrast (high-resolution TEM) can be obtained by placing a large or no objective aperture in the back focal plane (BFP) to collect more than one beam at the image plane. However, this technique is difficult to interpret without aid of simulation due to various factors such as: focus and astigmatism of objective lens, thickness variations and orientation. Formation
of Moiré fringes can be seen in phase contrast images due to interference of beams for two sets of planes that have nearly common periodic arrangements.

Moiré fringes can occur from diffraction by single phase nanocrystalline or multiphase specimens. Moiré fringes are classified into three types:

1. Translational Moiré fringes which arise from two different g-vectors with different d-spacing as shown in fig. 2.4 (A). The fringe spacing is [51]:

\[ d_{tm} = \frac{d_2 - d_2}{1 - \frac{d_2}{d_1}} \]  

(2.1)

2. Rotational Moiré fringes have two identical g-vectors and rotated with certain angle as shown in fig. 2.4 (B). The fringe spacing is given by:

\[ d_{rm} = \frac{d}{2 \sin \frac{\beta}{2}} \]  

(2.2)

3. Mixed Moiré fringes lie between above-mentioned Moiré fringes.

\[ d_{mm} = \frac{d_1 d_2}{(d_1 - d_2)^2 + d_1 d_2 \beta^2}^{1/2} \]  

(2.3)

![Fig. 2.4. (A) Translational and (B) rotational Moiré fringes [51].](image-url)
2.2 Scanning Transmission Electron Microscopy (STEM)

STEM is a very straightforward technique where a fine probe is scanned across a specimen and the intensity of the transmitted electron signals are measured by one or more electron detectors in planes congruent with BFP of the objective lens, i.e, the diffraction plane. Different STEM images can be obtained by changing the collection angle of the detector by varying camera length L. Figure 2.5 shows schematically different detectors in STEM collecting a certain range of scattering angles [52]. The main differences between TEM and STEM are: (1) STEM images are created by digitally stepping a small (1 to 10 Å) probe on the surface of thin specimen and recording the scattered intensity in the back focal plane of the objective lens [53]. (2) TEM images are recorded in parallel, formed by a broad (large diameter) beam incident on the specimen, on the objective lens image plane using a CCD or film detector.

The primary advantage of STEM for materials research is the small high current probe. This probe creates some images that are chemically sensitive and spectroscopy signals for chemical analysis with high spatial resolution.

However, BF STEM image relates quantitatively to BF TEM image if the range of angular integration in the BF STEM detector plane is close to the angle of beam convergence in the TEM, and the STEM incident convergence is equal to the TEM detector collection angle. These two quantities are defined on the opposite sides of the specimen and the relation is referred to as “Theorem of Reciprocity” [54].
Fig. 2.5. Schematic of different detectors used in STEM mode. Each detector is associated with a range of scattering angles [51].

2.2.1 Z Contrast STEM Imaging

As mentioned earlier, coherent phase contrast images are difficult to interpret without simulation of images. The STEM Z contrast technique demonstrated a remarkable capability for imaging single heavy atoms on low z substrates [55]. In Z contrast images, single atoms elastically scatter incoherently (>50 mrad) and the image intensity is the sum of individual atomic scattering
contributions. Additionally, Incoherent images have no phase contrast and interpretable Scherzer resolution is higher than coherent images as shown in fig. 2.6 [56].

Fig. 2.6. Contrast transfer function for (a) coherent imaging conditions and (b) incoherent imaging conditions.

The incoherent imaging involves collection of high angle scattering of incident electrons by high angle annular detector as shown schematically in fig. 2.7 [57]. These scattered electron have undergone screened Rutherford nuclear scattering and their intensity is proportional to $Z^n$, where $Z$ is the atomic number of the scattering atom (or average atomic number of the scattering region) and $1.7<n<2$ depending on the chemical identity of the scattering atom. The intensity of the image is given by the convolution of the specimen object function with the probe intensity as follows [56]:

$$I(R) = (O(R)*A(R))^2$$  \hspace{1cm} (2.4)

where $O(R)$ is the object function and $A(R)$ is the probe complex amplitude.
Fig. 2.7. Schematic diagram of A STEM convergent beam diffraction (CBED) pattern, showing Z-contrast image where the total signals are detected on the annulus as a function of probe position on the specimen [57]. In Z contrast the camera length will be reduced so that the brag spots goes through the central hole of the detector.

2.2.2 Aberration Corrected STEM Imaging

The term aberration in electron microscope refers to imperfections of the lenses or in other words lens effects. There are ten types of lens defects ad described by Reimer [58]. The isotropic aberrations include: (1) spherical, (2) astigmatism, (3) field curvature, (4) distortion and (5) coma. The anisotropic
errors are: (6) anisotropic coma, (7) anisotropic astigmatism and (8) anisotropic distortion. If the electron beam is not monochromatic, resulting in (9) chromatic aberration. Departure of electron beam from rotational symmetry causes an (10) axial astigmatism. However, the most important ones are spherical aberration, chromatic aberration and astigmatism, which affect electron microscope image and probe significantly. Herein, we will focus on spherical aberration which determines the resolution of image. The resolution limit is given by the following equation [59]:

\[
d = AC_s^{1/4} \lambda^{3/4}
\]

(2.5)

where A is the constant depending on the imaging conditions, A is 0.43 for incoherent imaging [56], \(C_s\) is the spherical aberration coefficient and \(\lambda\) is the electron wavelength.

The spherical aberration is caused by the lens field acting inhomogeneously on the off-axis rays. The further off-axis the electron is, the more strongly bent back towards the axis as shown schematically in fig. 2.8 [51].
Schrezer showed in 1936 that spherical and chromatic aberration were unavoidable for rotationally symmetric magnetic lenses [60]. In 1939, Schrezer described two strategies to deal with spherical aberration as the resolution-limiting factor by decreasing the wavelength of the electron or by shortening the focal lens [61,62]. However, both strategies have drawbacks. First. Decreasing the electron wavelength means increasing the accelerating voltage and consequently knock-on radiation damage would be critically increased for many materials. Second, smaller focal length implies narrower pole piece gap, which is limiting the tilt range of the specimen [62]. Therefore, in 1949 Schrezer proposed to
overcome this limitation by breaking one of his conditions [62,63].

Nowadays, TEM field is undergoing significant changes and breakthroughs in image resolution based on breaking the rotational symmetry of the system [64]. The way to do that is to correct high order aberration such as fifth-order axial aberration by two main classes of aberration correctors: quarapole-octupole corrected system and hexapole corrected systems. Figure 2.9 shows a schematic drawing of the optical design of a hexapole STEM corrector [65].
Fig. 2.9. Schematic drawing of the optical design of a hexapole STEM corrector with: two principal hexapole elements (HP1, HP2), five transfer lenses (TL11/TL12/TL21/TL22, ADL), eight x/y alignment deflectors (DP11/DP12/DP21/DP22, DPH2, BTlt, BSh), and two stigmators (QPol/Hpol) for twofold and threefold astigmatism [65].
These multipoles, like the alignment coils in TEM, are magnetic lenses. They are named for their rotational symmetry. The strong principal hexapole fields are generated by two multipole elements. A single hexapole element is shown in fig. 2.10 [65]. The hexapole element has six ferromagnetic pole pins with pole piece coils and yoke.

Fig. 2.10. Single hexapole element of STEM hexapole corrector [65].

Hexapole correctors, stemming from an idea by Beck [66], depend on imparting spherical aberration to a round beam in addition to the effect of threefold astigmatism.
The aberration function can be described by the following equation [62]:

\[
\chi(\theta) = \frac{1}{2} \theta^2 C_1 + \frac{1}{4} \theta^2 C_3 \tag{2.6}
\]

where \( C_1 \) is defocus and \( C_3 \) spherical aberration coefficient. Employing the notation of the complex angle \( \omega \) for the angle \( \theta \):

\[
\chi(\omega) = \Re \left( \frac{1}{2} \omega \bar{\omega} C_1 + \frac{1}{4} (\omega \bar{\omega})^2 C_3 \right) \tag{2.7}
\]

Considering all feasible axial aberrations up to seventh order (Eikonal function):

\[
\chi(\omega) = \Re \begin{pmatrix}
\frac{1}{2} \omega \bar{\omega} C_1 + \frac{1}{2} \omega \bar{\omega}^2 A_1 + \frac{1}{3} \omega \bar{\omega}^3 A_2 + \omega^2 \bar{\omega} B_2 \\
+ \frac{1}{4} (\omega \bar{\omega})^2 C_3 + \frac{1}{4} \omega \bar{\omega}^4 A_3 + \omega^3 \bar{\omega} S_3 + \frac{1}{3} \omega \bar{\omega}^5 A_4 \\
+ \omega^3 \bar{\omega}^2 B_4 + \omega^4 \bar{\omega} D_4 + \frac{1}{6} (\omega \bar{\omega})^3 C_5 + \frac{1}{6} \omega \bar{\omega}^6 A_5 \\
+ \omega^5 \bar{\omega} R_5 + \omega^4 \bar{\omega}^2 S_5 + \frac{1}{7} \omega \bar{\omega}^7 A_6 + \omega^4 \bar{\omega}^3 B_6 \\
+ \omega^5 \bar{\omega}^2 D_6 + \omega^6 \bar{\omega} F_6 + \frac{1}{8} (\omega \bar{\omega})^4 C_7 \\
+ \frac{1}{8} \omega \bar{\omega}^8 A_7 + \omega^7 \bar{\omega} G_7 + \omega^6 \bar{\omega}^2 R_7 + \omega^5 \bar{\omega}^3 S_7
\end{pmatrix} . \tag{2.8}
\]

The traditional terminology for the Eikonal coefficients for the axial aberration figure and subscripts for Seidel order is summarized in Table 1 [65].
Aberration correction has a significant effect on both the distribution and the spatial localization of the electron probe intensity. Figure 2.11 shows the calculated probe intensities before and after correction [67]. Aberration correction delivers smaller probe size and higher probe current, and hence provides higher spatial resolution and signal to noise ratio images.

![Calculated Probe Intensities](image)

Fig. 2.11. Calculated Probe intensities before correction (left): Cs= 1.5 mm and after correction (right): Cs= -0.04 [67].
2.3 Analytical Electron Microscopy (AEM)

Energy dispersive x-ray spectroscopy (EDX) and electron energy-loss spectroscopy (EELS) are the two most commonly used spectroscopies for elemental analysis techniques on the nanometer scale in TEM. More importantly, the combination of atomic resolution Z-contrast with EELS or EDS represents a powerful tool to link the atomic and electronic structure and composition of solids to their macroscopic properties, which allows nanoscale system to be probed in exceptional detail. Previously, we discussed several TEM techniques which use elastic scattering signals. AEM, on the other hand, utilizes inelastic scattering signals and deals with electron particle.

A schematic illustrating the main component of STEM with EDS and EELS is shown in fig. 2.12 [68]. The high angle elastic scattering signals are collected by annular dark field detector, whereas, inelastic scattering signals are collected by EELS or EDS as shown in fig. 2.12. AEM techniques cause atomic ionization process as schematically illustrated in fig. 2.13 [51]. When a high-energy beam electron interacts with the inner shell electron of an atom, the incident electron loses some energy (detected by EELS) and the inner shell electron escapes to a vacant state above the Fermi level and leaves a hole behind it (excitation process). Electron from outer shell (high energy state) fills the hole (low energy state) with emission of X-rays (decay process).
Fig. 2.12. Schematic showing STEM combined with AEM [68].

Fig. 2.13. The ionization process [51].
EDX is most widely used because it is relatively simple and easy to interpret. On the other hand, it is less sensitive for light element detection. EELS is more difficult technique to employ due to complication of the instrumentation and quantification procedures. However, it is superior to EDX in detecting light elements. The other important difference between EELS and EDS is energy resolution, resulting from instrumentation differences. Energy resolution for EELS is about 1 eV enabling both bonding and composition determinations. Energy resolution in EDS is about 159 eV, enabling composition determination only. EELS has been demonstrated various types of analytical applications such as determination of the bonding state, dielectric constant, composition, band structure and chemistry [69]. EELS can also be used to determine local specimen thickness. A schematic diagram of the energy-loss spectrum of yttrium barium copper oxide (YBCO) is shown in fig. 2.14 [69].

![Energy loss spectrum of YBCO](image)

Fig. 2.14. Energy loss spectrum of YBCO [69].
It is helpful to divide the spectrum into three regions as shown in fig. 2.14. (1) zero-loss peak where most of electrons don’t experience any inelastic scattering. (2) Low loss region (2-50 eV) arises from excitation of weakly bound outer-shell electrons and includes Plasmon excitations. (3) core-loss region (inner-shell excitation) shows characteristic signals corresponding to ionization potential of particular group of electrons being excited.

EELS instrument utilizes magnetic and electric field to disperse the electron into their different energy components by a magnetic prism. A magnetic prism bends, disperses and focuses an electron beam in a such way similar to the way a glass prism behaves for light. The instrument is very compact with good electron and optical characteristics and it easily fitted under the camera chamber. It has 2-D CCD array in the image plane of spectrometer to detect the spectrum. There are two types of spectrum collection: serial collection and parallel collection. A parallel collection system shown schematically in fig. 2.15 is more efficient because all channel are detected simultaneously [51].
Fig. 2.15. Schematic diagram of parallel energy-loss spectrometer [51].
2.4 Superconducting Quantum Interference Device (SQUID)

Magnetic properties can be measured with ultimate resolution by SQUID. The SQUID consists of a superconducting ring with small insulating layer (Josephson junction) or weak link as shown schematically in fig. 2.16 [70]. Josephson [71] predicted the possibility of electrons tunneling from superconducting region to another that had been separated by a resistive (insulating) barrier. When the magnetic flux passes through the ring, it is quantized once the ring undergoes superconducting state. The weak link allows the flux trapped in the ring to change by discrete amounts. With a weak link, magnetic flux can enter the ring and the super current in the weak link tries to oppose the entry of flux. The relation between the flux density in the ring and the flux density due to an applied field is given by [70]:

$$ \phi = \phi_a + LI_s $$

(2.9)

where $\phi$ is the flux density in the ring, $\phi_a$ is the flux due to the applied field, $L$ is the inductance of the ring and $I_s$ is the super current which produces a flux of $\phi_s = LI_s$. The SQUID is a very sensitive device can measure small changes in magnetic field.
Fig. 2.16. Schematic showing SQUID consisting of a superconductor with poorly conducting (weak link).
Chapter 3

EXPERIMENTAL METHODS

3.1 Synthesis Process

For this research, synthesis processing of CoFe thin films and nanocontacts was done by Prof. Brankovic’s group at the University of Houston, TX. A standard three electrode cell configuration with solution volume of 250 mL was used to electrodeposit Co$_{40-37}$Fe$_{60-63}$ films (1-2 μm thick), having different oxygen contents, on different substrates such as Cu, Al, and Si. The various substrates affected the integrity of the CoFe films in interesting way. However, (100) Si wafer substrates were mainly used in this research because they improved surface continuity and smoothness of the deposited films. The geometrical configuration of CoFe films is schematically shown in fig. 3.1(a). The electrodeposition was carried out under galvanostatic control. The stagnant aqueous solution compositions and electrodeposition parameters for CoFe samples are tabulated in Table 3.1. For the higher oxygen content specimens, the Fe$^{3+}$ was introduced into the electrolyte solution by adding of Ferric Sulfate Fe$_2$(SO$_4$)$_3$·4H2O to the electrolyte, to introduce the additional amount of the oxide phase in the deposited film [48,72]. The maximum amount of hydrated ferric sulfate added into solution was 0.5 g/L (0.0025M).
Table 3.1 Aqueous solution compositions and electrodepositing parameters

<table>
<thead>
<tr>
<th>Solution component</th>
<th>(g/L)</th>
<th>Process parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO$_4$,7H$_2$O</td>
<td>28</td>
<td>pH</td>
</tr>
<tr>
<td>CoSO$_4$,7H$_2$O</td>
<td>15</td>
<td>Current Density (mA/cm$^2$)</td>
</tr>
<tr>
<td>H$_3$BO$_3$</td>
<td>25</td>
<td>Current Efficiency</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>16</td>
<td>Deposition Rate (nm/min)</td>
</tr>
<tr>
<td>Saccharin</td>
<td>0.12</td>
<td>Deposition Time (min.)</td>
</tr>
</tbody>
</table>

For Nanocontact samples, potentiostatic electrodeposition was performed at -1.1V vs saturated calomel electrode (SCE). Figure 3.1 (a) and (b) schematically show specimen configurations for CoFe thin film and CoFe nanocontact, respectively.

Fig. 3.1. Schematic shows specimen configurations for (a) thin film and (b) nanocontact. PR is photoresist.
3.2 TEM Sample Preparation

3.2.1 Conventional (Ion Milling) Method

Cross-sectional and plan-view samples were earlier prepared using conventional procedure up to mechanical dimpling. For cross-sectional method, approximately 3 mm squares were cut by diamond saw from the sample and two pieces with film layers were glued by M-bond after cleaning the two surface with acetone followed by alcohol. Then the two pieces were pressed with a clamp to provide a good mechanical bonding and inserted in the oven at temperature 90 °C for 40 minutes. After the curing process, the samples were mechanically polished using 30, 15, 6, 3 and 0.1 μm diamond lapping films until they exhibited scratch-free surfaces. Then, the sample was turned over and polished down to 100 μm thickness. Mechanical dimplers were used with 6 μm and 1 μm diamond paste to grind a bowl shape down to 10-20 μm thick at bottom. The sample thickness was determined using an optical microscope, initially every 10 minutes and then every 3 minutes. Then the sample was glued to a Cu grid with M-bond and inserted in the oven for 30 minutes for curing. After that, the sample immersed in acetone in order to remove the wax from the Cu grid and the glass stub. Further thinning was done by the Gatan precision-ion-polishing-system (PIPS), using Ar plasma guns with beam energy of 4 keV, incident at 4°. It is worth mentioning that the method described above was not such a successful way to prepare CoFe films particularly on Cu or Al substrates, due to poor adhesion between the CoFe films and substrates as a result of surface roughness. Therefore, we tried another sample
preparation method, which is called rod and tube to add more mechanical support.

![Fig. 3.2. Rod and tube method](image)

This method is similar to the one discussed earlier and the only difference is the first step. The specimen was placed inside the steel rod and the Cu tube was then slid over the steel rod tightly and forcefully as shown schematically in fig. 3.2. Then the whole assembly was sliced by diamond saw. Then the trimming process on the slices was continued as before. This method didn’t give a satisfactory result for Cu or Al substrates, although the adhesion between CoFe films was enhanced. During the dimpling step, the milling rate of Cu and Al was higher relative to CoFe films. So it ended up with a thin area in the substrate, especially when CoFe film was thinner (~50 nm thick). For these particular substrates, we used focused ion beam technique, discussed below, to overcome these obstacles. However, previous methods were fairly successful for Si substrate specimens due to surface
quality and larger film thickness. Figure 3.3 shows the dimpling depth rate of CoFe films on Si substrate during dimpling process. The dimpling rate for CoFe films on Si substrate was quite consistent, and was 0.85 µm/min.

![Dimpling depth rate](image)

Fig. 3.3. Dimpling time of CoFe /Si specimen vs dimpling depth.

3.2.2 Focused Ion Beam (FIB)

Cross-sectional TEM samples for CoFe thin films and CoFe nanocontacts were prepared using the focused ion beam lift out (FIB LO) technique. This technique was used to minimize the mass of ferromagnetic specimen material in the microscope objective lens pole piece gap, and thus minimizing disturbances of images and spectra. FIB was also used for nanocontact features ~ 50 nm width. FIB LO has produced successful results for high quality TEM specimens from a number of materials [73]. The procedure is illustrated in fig. 3.4. Platinum was
deposited on area of interest (step a). Two wide trenches (25×8.7×5 μm) were milled at a current of 20 nA at 30 kV (step b). Further thinning of the specimens on either side of usual the Pt strip was carried out at a reduced Ga ion current of 7 nA at 30 kV (step c). Release cuts were made and the sample was “lifted-out” by welding it to a thin probe with deposited Pt (step d), and then affixing it to a Cu grid, also by Pt deposition (step e). The final thinning and cleaning up (removing amorphous surface layers) of both sides of the sample were achieved with ion beam currents of 0.5 nA at 30 kV and 1 nA at 5 kV, respectively (step f). An electron beam maintained at 5 kV and a current of 1.6 nA was used for SEM imaging in the FIB.

Fig. 3.4. FIB LO procedure steps from (a) through (f). See text for more details.
This new technique has been developed to obtain TEM samples with thickness less than the CoFe grain size (10-20 nm), to improve TEM images and spectroscopy data accuracy, especially for aberration electron microscopy. This technique (with assistance of Dr. John Mardinly and Gordon Tam at the LeRoy Eyring Center for Solid State Science) showed that the foil thickness was down to sub-20 nm level. Figure 3.5 shows the final cross-sectional TEM sample prepared by this technique.

Fig. 3.5. Cross-sectional TEM specimen taken by (a) SEM and (b) TEM

This technique is similar to the one mentioned earlier in the experimental section, except the milling stage was done at angle of 5° on each side of the sample from the top view. Then final thinning was carried out at 1° at of both sides of the sample with ion beam currents of 0.1 nA at 5 kV. However, this technique didn’t provide such a smooth flat surface. The surface had streaky features due to
grooving, because the sample cannot be rotated in FIB (see fig. 3.5 (b)).

Magnetic disturbances were compared and controlled by using three different specimen preparation methods: (1) ordinary ion milled plan view, (2) ion milled cross section, and (3) FIB lift out specimens. Calculated ferromagnetic specimen mass and volume for each method are given in Table 3.2. The FIB specimens were most useful, requiring little microscope adjustment, although surface amorphization was troublesome. Cross section specimens required more stigmator adjustment after insertion and after stage translation. Plan view specimens were not useful.

<table>
<thead>
<tr>
<th></th>
<th>FIB lift out</th>
<th>Cross section</th>
<th>Plan view</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (cm³)</td>
<td>0.7x10⁻¹²</td>
<td>2.4x10⁻⁸</td>
<td>4.4x10⁻⁵</td>
</tr>
<tr>
<td>Mass (gm)</td>
<td>5.7x10⁻¹²</td>
<td>2x10⁻⁷</td>
<td>4x10⁻⁴</td>
</tr>
</tbody>
</table>

All samples were cleaned for 20-30 minutes just before conducting TEM analysis, using an Ar plasma cleaner from South Bay Technology (SBT).

3.3 Transmission Electron Microscopy (TEM)

TEM was a primary characterization tool for nanostructure and chemical analysis of CoFe films and nanocontacts. Three TEM machines were used throughout this dissertation: JEOL 2010F, JEM ARM 200 (aberration corrected), and Philips-FEI CM200.
Structure and composition characterization of the grown films were analyzed using a 200 keV TEM/STEM-2010F (JEOL, without aberration correction), equipped with a thin-window light-element-sensitive X-ray spectrometer (EDS) and a Gatan Enfina energy-loss spectrometer (EELS). A picture of the JEOL 2010F is shown in fig 3.6. Nanostructure of the films were examined using STEM high angle annular dark field (HAADF) imaging, high-resolution phase contrast imaging (HREM), diffraction contrast imaging, and selected area electron diffraction (SAED). EELS were acquired in STEM mode with 15 mrad convergence half angle (α) and 22 mrad collection half angle (β). The beam current density and the spot size were 2.6 pA/cm² and 1 nm, respectively. The exposure time was 1 s for each spectrum. The dispersion for all the spectra shown in this study was 0.3 eV/channel to display the core loss K and L EELS edges of O, Fe and Co, respectively.

Fig. 3.6. Schematic showing the main components in TEM column and a photograph of the JEOL 2010F TEM/STEM.
High-resolution STEM images of CoFe films were obtained using JEM-ARM200F (spherical aberration corrected) with Schottky field emission gun, equipped with windowless light-element-sensitive X-ray spectrometer (EDS) and a Gatan super-Enfina energy-loss spectrometer (EELS). With super-Enfina EELS, dualEELS acquisition operates, which allows two parts of the EELS spectrum (core loss and low loss) to be acquired in a fast, sequential manner with independent energy ranges and exposure times. STEM is equipped with HAADF, MAADF, ABF and BF detectors. This microscope has capability to operate at 200, 120 and 80 KeV. Figure 3.7 shows a picture of this state-of-the-art aberration corrected electron microscope located in the Southwestern Center for Aberration Corrected Electron Microscopy. The new building is especially designed to provide a high stability environment for our two aberration corrected microscopes, the JEOL ARM and a NION UltraStem 100.
The ARM200F, incorporates a spherical aberration corrector for electron probe as standard, and the maximum level of electrical and mechanical stability, has achieved a scanning transmission image (STEM-HAADF) resolution of 0.08 nm, the highest in the world among the non-monochromated commercial transmission electron microscopes.

HR STEM images were acquired with spot size 9C (0.095 nm), condenser aperture of 40 µm, and camera length of 8 cm. The inner and outer collection half angles for HAADF were 68 mrad and 280 mrad, respectively. For BF with 1mm
aperture the collection half angle was 5.6 mrad. For MAABF the collection half angle was 8.2 mrad. EELS spectra were acquired with bigger spot size 7C (0.12 nm).

Domain wall width of the films was examined (with assistance of Prof. Molly McCartney) using off-axis electron holography in an FEI CM200 FEG TEM equipped with an electrostatic biprism, at 200 kV. The electrostatic biprism is located in the selected area aperture plane to facilitate electron holography technique. A Lorentz lens is located beneath the normal objective lens to provide field-free imaging for magnetic materials. Electron holography is a unique technique to determine the phase change of the electron wave due to magnetic or electric field. There are three essential components in order to acquire a hologram as shown in fig. 3.8: (1) field emission gun (FEG) to provide coherent incident illumination, (2) electrostatic biprism to overlap the reference (vacuum) wave with object wave and (3) Charge coupled device (CCD) for quantitative recording of hologram [74].
Fig. 3.8. Schematic showing three essential components for off-axis electron holography in the CM200 FEG [74].

3.4 Superconducting Quantum Interference Device (SQUID)

Magnetic properties of CoFe films such as coercivity and saturation magnetization were determined by SQUID at room temperature in the plane of the deposited films. All the samples were cut with dimension of 3mmx3mm. Most of CoFe samples saturated at field 2000-3000 Oe. Small field step size was taken around the coercive field to determine the coercivity of the film precisely. Magnetic Barkhausen emission signals were determined as a voltage produced by the dc field with time. The Barkhausen effect is the phenomenon of discontinuous
changes in the flux density within a ferromagnetic as the magnetic field is
changed continuously [70]. The Barkhausen effect was discovered in 1919 [75]
when a secondary coil was wound on a piece of iron and connected to amplifier
and speaker. As the field was increased a series of clicks were heard over the
loudspeaker due to small voltage pulses induced in the secondary coil.
Barkhausen emission is closely related to the microstructure of the magnetic
materials and considered to be a basis tool for material characterization [76].

3.5 Other Characterization Tools

3.5.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) used to images CoFe film surface
features and map elemental composition over the surface. SEM images combined
with EDS were obtained using a FEI XL30 ESEM-FEG.

3.5.1 Secondary Ion Mass Spectroscopy (SIMS)

Elemental depth profiles for Fe, Co, Cu and especially for H and O in the
CoFe films were carried out by secondary ion mass spectroscopy (SIMS) using a
Cameca IMS-6f instrument with a Cs\(^+\) primary ion beam incident at 10 keV and -
9000V sample voltage (impact energy of 19kV), a beam diameter of 50-75 µm,
and a beam current of 75 nA. The primary beam was rastered over 250 × 250 µm
area. This is the only characterization technique used that is sensitive to hydrogen
in the specimen.
3.5.2 X-ray Photoelectron Spectroscopy (XPS)

The O/Fe and Fe/Co ratios were determined by X-ray photoelectron spectroscopy (XPS) with a VG ESCALAB 220i-XL running Avantage software. The X-ray source was monochromatic 1486 eV photons, with a 500 micron spot size. The line width was 0.68 eV FWHM for the Ag$_{3d}$ peak (from an ion etched Ag surface). The take off angle between sample and analyzer was 90 degrees. The average sampling depth was 3-5 nm. Typical calibration used the C1s peak (284.6 eV) as the reference peak. The samples were sputter cleaned for 7 min. Chemical states were determined from XPS spectra using Computer Aided Surfaces Analysis for X-ray photoelectron spectroscopy (CASA XPS) software.

3.5.3 X-ray Diffraction (XRD)

The crystalline structure and phase of the CoFe films were also investigated using a PANalytical Xpert Pro X-ray diffractometer using fixed divergence slits of 1/2° and a X'Celerator detector. The data was collected with omega (x-ray incident angle on the sample) 1/2 of 2θ (diffraction angle). Data was collected over a 2θ range of 30-90°. Each pattern was collected for 10 minutes with a resolution of 0.05 deg 2θ. XRD results were consistant with our electron diffraction experiment.
3.5.4 Atomic Force Microscopy (AFM)

Surface roughness of CoFe films on Si substrates was studied using atomic force microscopy (AFM) in acoustic mode (tapping mode), using a Molecular Imaging Pico SPM system. AFM was utilized in this study to correlate CoFe film surface roughness to magnetic properties and growth conditions.
Chapter 4

CHARACTERIZATION OF COBALT-IRON FILMS ON COPPER AND ALUMINUM SUBSTRATES

Several different substrates were used for synthesis of CoFe films. This chapter describes some TEM characterizations of electrodeposited Co_{36-40}Fe_{64-60} films on Cu, Au/NiP/Al and Au/Al substrates. It also describes the morphology of grown films and investigation of a second phase present in CoFe films. In the next chapter we describe results for more successful Si substrates.

4.1 Motivation

As mentioned earlier in section 1.6, near equiatomic CoFe alloys have received a great interest due to superior soft magnetic properties that make them a good candidates for magnetic recording application and magnetic field sensors. Recently, the electrodeposited CoFe alloys with desired magnetic properties were obtained [44,77]. The effect of oxygen incorporation in electrodeposited CoFe films were described by (our collaborator) S. Brankovic et al [72]. Introducing Fe^{3+} into the deposition solution reduced the magnetic moment almost by twofold as shown in fig. 4.1[72]. As we can see from fig. 4.1, adding Fe^{3+} into solution up to 0.0015 mol/L decreased the saturation magnetic flux density B_s abruptly. However, further addition of Fe^{3+} above 0.002 mol/L didn’t contribute to further decrease of B_s. At this point, neither structural characterization nor magnetic properties had been investigated to elucidate this phenomenon.
Fig. 4.1. $B_s$ vs. $[\text{Fe}^{3+}]$ dependence for electrodeposited CoFe alloys [72].

4.2 Experimental details

CoFe films were deposited on Cu and Au/Al substrates by electrodeposition with addition of FeCl$_3$ into solution (0, 0.0015, 0.0025 M). The experimental method has been described in detail earlier in section 3.1 and 3.2. Cross-sectional TEM samples were prepared by FIB. All TEM samples were cleaned 20 minutes just before conducting TEM analysis, using a South Bay Technology (SBT) Ar plasma cleaner.
4.3 Result and discussion

4.3.1 CoFe/ Cu substrates

Surface features and chemical composition of CoFe films were examined by SEM and EDS. Figure 1 shows EDS spectra from different spots located at the surface of the sample. SEM images show that there are gray and bright areas. Spot # 1, 5, and 7 corresponding to gray areas have mainly Cu. However, spots # 2, 3, 4, and 6 corresponding to bright areas have Fe, Co, and Cu elements. This indicates that CoFe film is not uniformly distributed on the Cu substrate, i.e. thickness is not uniform. There are holes in the electrodeposit.

![SEM images and EDS spectra](image)

Fig. 4.2. SEM images of CoFe film in conjunction with EDS from (a) spot 6 (bright area) (b) spot 7 (dark area).
Fig. 4.3 shows high resolution SEM image. The dark line presents the CoFe layer. As we can see the Fe-Co layer is not uniform and has thickness variations along the FIB sample (50-200 nm).

Fig. 4.3. SEM image of cross-sectional FIB sample on Cu substrate.

Figure 4.4 shows a TEM image of CoFe sample. The surface roughness of Cu substrate is clearly observed in fig. 4.4 resulting in nonuniformity of grown film. No oxide phases were observed at these magnifications in CoFe films except Fe oxide on the top layer due to air oxidation. The same results were obtained for different Fe$^{3+}$ concentrations.
4.3.2 CoFe/Au/Al substrates

The electrodeposited CoFe films were not continuous on Au/Al substrate. SEM image shows the CoFe film had pinholes as illustrated in fig. 4.5.

Chemical analysis was performed with SEM to detect the chemical composition of different areas on the surface.

Fig. 4.4. TEM image of cross-sectional CoFe sample.
Fig. 4.5. SEM image of CoFe film on Au/Al substrate showing pinholes.

Figure 4.6 shows a BF image of CoFe/Au/Al specimen. The final chromium oxide layer was deposited on CoFe layer to avoid any iron oxidation on the surface. The CoFe films were polycrystalline and had columnar-like grain structures, which are noticeably seen, in a pair of BF and DF images in fig. 4.7. The lateral dimension of the columnar grain is approximately ~10-20 nm. The surface roughness of these grown films did not improve significantly relative to the previous case. However, electrodeposition on Au/Al brought to notice some issues, such as film delamination due to weak adhesion between Au and Al substrate. These issues probably related to lattice mismatch between these layers. As a consequence of a weak bonding between Au and Al, CoFe alloy diffused between these layers as illustrated in fig. 4.6.
Fig. 4.6. BF TEM image showing columnar structure of CoFe film.

Fig. 4.7. (a) BF and (b) DF images of the film in fig. 4.6.
Z contrast STEM image of the same sample is shown in fig. 4.8 below. It is clearly visible the deposited CoFe film was not flat and diffused between Au layer and Al substrate.

Fig. 4.8. Z contrast image of CoFe film on Au/Al substrate

EELS elemental mapping of O K, Fe L\textsubscript{23} and Co L\textsubscript{23} edges are shown in fig. 4.9.
Fig. 4.9. (a) BF, (b) Fe-L$_{23}$, (c) Co-L$_{23}$ and (d) O-k images of CoFe film with high oxygen content on Au/Al substrates. CM200.

The oxygen was only bonded to Cr (Cr$_2$O$_3$) in top layer and bonded to Al (Al$_2$O$_3$) in bottom layer. No oxide phase was detected in CoFe films. All CoFe specimens showed the same morphology and structure. No magnetic measurements because poor mechanical structure. It is important to mention that, prior to deposition
CoFe films on Au/Al substrates, nickel phosphate (NiP) layer was deposited between Au layer and Al substrates. These particular structure configurations were not successful due to strong delamination between NiP and Al substrate as shown below in fig. 4.10. This is due to lattice mismatch between NiP and Al substrate ~13%, which induced stress in these layers.

Fig. 4.10. TEM image of CoFe /Au/NiP/Al substrate.
4.4 Conclusion

The Cu and Al substrate sample specimens were made by focused ion beam (FIB). The FIB method produced the largest electron transparent areas, which was the objective. The standard cross section method was not successful because the specimens were not flat enough, resulting in a glue joint that was too thick to produce specimens with large thin areas. In addition, the milling rate was faster in the substrate than in CoFe films during dimpling process.

Choice of substrate quality substantially affected the morphology and mechanical quality of the deposited CoFe films. Neither Cu nor Al substrate provided desired magnetic properties. No oxide phases were detected in CoFe films to improve magnetoresistance of the films. However, structure and morphology of CoFe films/Al substrate was a little improved and more identified relative to Cu substrate.

Next chapter will describe new developed configuration specimens to improve mechanical structure of grown films. A detailed microscopy study will be also described.
Chapter 5

CHARACTERIZATION OF COBALT-IRON FILMS ON SILICON SUBSTRATES

This chapter describes the structural, morphology and magnetic properties of Co$_{36-40}$Fe$_{64-60}$ films on Si substrate. Si substrates produced the best quality electrodeposited films. This chapter also describes nanostructure and nanodistribution of oxide phases in CoFe matrix alloys. The main experimental methods were transmission electron microscopy (TEM), energy loss (EELS) and energy dispersive nanospectroscopies (EDS). Secondary ion mass spectroscopy (SIMS) for elemental depth profiling was utilized in this study. Some of these results have already been published [48,49].

5.1 Motivation

Synthesis process was well controlled in this study by choosing suitable substrates such as Si. The effect of oxide/hydroxide incorporation into electrodeposited Co$_{40-36}$Fe$_{60-64}$ alloys on their structural and magnetic properties have been investigated. The aim of this work was to gain more information about the state and quality of the oxide phase in electrodeposited Co$_{40-36}$Fe$_{60-64}$ alloys and to correlate its structure and origin to the composition of the electrolyte. In addition, the effort was made to establish relations between the observed magnetic properties of the Co$_{40-36}$Fe$_{60-64}$ films and the structure of the incorporated oxide/hydroxide phase (inclusions) and how they impacted the magnetoresistance.
of the deposited films. It has been suggested that presence of oxide phase will affect the magnetoresistance values [78,79] and the magnetic properties of Co-Fe alloy, through oxygen incorporation during synthesis. The oxygen rich samples were produced from the electrolytes containing Fe$^{3+}$ ions. In this case the main oxygen incorporation mechanism was through the precipitation of Fe(OH)$_3$ or Fe$_2$O$_3$·xH$_2$O at the electrochemical interface, and its subsequent incorporation into the deposit during the film growth [72]. The low oxygen content samples were produced from the bath that did not have a significance Fe$^{3+}$ presence; here the main oxygen incorporation mechanism was as a result of trapped anions (SO$_4$, BO$_3$) or from Fe(OH)$_2$ or FeO·xH$_2$O precipitates on the electrochemical interface during the film growth. Each oxygen source in the sample resulted in distinctively different structural and magnetic properties of CoFe films, which were studied in detail and are reported in this chapter.

5.2 Experimental details

CoFe films were deposited on Cu (seed layer thickness 200 nm)/Ti (adhesion layer thickness30 nm)/Si substrates. (100) Si wafer substrates were used to improve surface continuity and smoothness of the deposited films. The aqueous solution compositions and electrodeposition parameters for CoFe samples have been described in detail earlier in sections 3.1 and 3.2. Fe$^{3+}$ was introduced into the electrolyte solution by adding varying amount of ferric sulfate Fe$_2$(SO$_4$)$_3$·4H$_2$O (0, 0.2, and 0.5) g/L, denoted as S1, S2, and S3, respectively. For the highest oxygen content specimens, the Fe$^{3+}$ (0.0025M) was introduced into the
electrolyte solution by adding 0.5 g/L of Ferric Sulfate Fe_2(SO_4)_3·4H_2O, to introduce the additional amount of the oxide phase in the deposited film. For lowest oxygen content specimens, no ferric sulfate was introduced into the electrolyte solution. All solutions in this study were deaerated for two hours before deposition experiments and during deposition experiments, in order to minimize additional formation of Fe^{3+} in the electrolyte through the oxygen reduction process (4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O) [48,72].

Cross-sectional TEM specimens were prepared by FIB and conventional method. Conventional methods including cross-section and plan-view were successfully obtained due to strong bonding between layers and surface uniformity. The quality of grown films was drastically improved as illustrated by SEM image of FIB cross-sectional specimen shown in fig. 5.1.

Oxide nanodistributions in CoFe films have been characterized using an extensive range of TEM imaging and analytical techniques, including phase contrast, dffract contrast, Z contrast imaging, EELS and EDS.

The magnetic properties of the CoFe films were determined using SQUID at room temperature. The MR measurements were obtained by four-point probe measurement at a testing current of 10 µA, fields from ±700 Oe. The sweep was 20 Oe/sec.
5.3 Results and discussion

5.3.1 TEM analysis (without aberration correction, JEOL 2010F)

5.3.1.1 Diffraction and Phase Contrast

Cross-sectional TEM images of CoFe sample are shown in fig. 5.2 (a) and (b). It is clearly seen the quality of grown films on Cu/Ti/Si substrates were greatly improved compared to grown films on Cu or Al substrates discussed in chapter 4. It seemed all layers were strongly bonded to each other. All surfaces were entirely flat. CoFe films were ~1.8 - 2.1 µm thick, Cu layer were ~280 nm thick, and Ti layer were ~ 30 nm. Cu substrate exhibited columnar grain-like structures.
Fig. 5.2. (a) TEM image showing the specimen configuration with interface flatness (b) higher magnification of fig. 5.2 (a).
A selected area electron diffraction (SAED) pattern for a cross section specimen of S3, presented in fig. 5.3, showed that the crystal structure of CoFe was bcc with a weak <110> texture in the film plane. Figure 5.4 shows a plan view SAED with inverted contrast for the same sample. The texture in a plan view sample was not as well defined as in cross-section specimens. SAED patterns displayed single-phase spotty ring patterns with low background, indicating small grain size, and weak diffuse rings, which are clearly visible in fig. 5.4.

Fig. 5.3. SAED pattern from CoFe film S3 showing a bcc crystal structure.
The diffuse rings could be attributed to the presence of an amorphous second phase in S3. The rings are near the d-spacing positions of (012), (110) and (116) planes in $\alpha$-Fe$_2$O$_3$. S1 and S2 exhibited similar diffraction patterns with fewer and less intense diffuse rings than S3 due to less oxygen content present in S1 and S2.

Fig. 5.4. Plan-view SAED pattern (inverted contrast) from S3 showing presence of amorphous oxide second phase ($\alpha$-Fe$_2$O$_3$).

Figure 5.5 (a) and (b) show a pair of cross-sectional TEM bright field (BF)/dark field (DF) images from S3. They revealed that the grain size ranged from 10-20 nm. Diffraction contrast images of S1 and S2 were essentially the same as S3.
Similar grain size was obtained from plan-view TEM specimen confirming equiaxed grain-like structure of CoFe films.

Fig. 5.5. (a) BF and (b) DF for S3 showing the matrix grain size is 10 to 20 nm.
5.3.1.2 HREM Imaging

Figure 5.6 shows a typical high-resolution electron microscopy (HREM) image of S1. Both lattice and Moiré fringes are present, the latter because the grains are generally smaller than the foil thickness. Some regions appeared amorphous (non periodic) are arrowed in fig. 5.6. These regions seemed to be round or spherical shapes with diffuse boundaries. The diameters of these areas were approximately 2-5 nm.

Fig. 5.6 Plan-view HREM image for low oxygen content S1. Arrowed areas show lack of periodicity relative to CoFe matrix.
Figure 5.7 shows a HREM for S1. We can see both lattice and Moiré fringes. Figure 5.8 shows Fast Fourier Transform (FFT) performed on some selected areas as shown in Fig. 5.7. Area A1 shows bcc crystal structure with [100] zone axis. However area A2 shows a second phase with larger d-spacing than the matrix. The second phase is corresponding to FeO (NaCl structure) with [110] zone axis. This is one of very few evidences for a crystalline oxide phase found in any of the CoFe film examined.

Fig. 5.7. Cross-sectional HREM of low oxygen content specimen S1 showing Moiré fringes.
Moiré fringes have been analyzed in the previous figure whether they are rotational or translational Moiré. Figure 5.9 shows FFT obtained from areas B1 shown in fig. 5.7. It is clearly seen that two g-vectors are identical and rotated through an angle $\beta$ as illustrated in fig. 2.4 (b).

Fig. 5.9. FFT from area B1 shown in fig. 5.7.
The fringe spacing was calculated by using equation 2.2. It was 1.1 nm. The calculated fringe spacing did agree well with Moiré fringe spacing in HREM in fig. 5.7, which was 1.14 nm. B2 is a more complicated example of crossed Moiré fringes.

The lattice spacing from both diffraction patterns and images agrees with those from Co_{40.36}Fe_{59.64} alloys of our compositions [35]. There was no strong experimental evidence for a crystalline second phase. Figure 5.10 shows cross-sectional HREM image of S3 with lattice spacing 0.202 nm and 0.143 nm for (110) and (200), respectively. The arrowed areas show some amorphous regions with lamellar rather than spherical distributions.

It is worthwhile to mention that the lattice spacings and atom arrangements were more clearly seen in 2010F from ion polished specimens relative to FIB specimens, especially with thickness greater than 80 nm. This is due to amorphous layers created by FIB. An example for HREM image of CoFe specimen (S3) prepared by FIB is illustrated in fig. 5.11.
Fig. 5.10. Cross-sectional HREM image of ion-milled S3 showing the lattice spacing of CoFe alloy and some amorphous regions.
From electrochemical deposition point of view, we expected two kinds of oxides/hydroxides formed in the deposit during the electrolytic deposition. The main incorporation mechanism of the oxide/hydroxide in both samples is through the Fe-hydroxide precipitation. The Fe is thought to form more insoluble hydroxide than Co and it is more likely to be incorporated in the film as a precipitate. In S1 sample, the form of Fe-hydroxide is Fe(OH)$_2$, while in S3 the
dominant source of incorporated hydroxide is Fe(OH)\textsubscript{3}. S2 has the combination of both hydroxides but mainly Fe(OH)\textsubscript{2}. To elaborate further on this point we discuss the necessary conditions for Fe-hydroxide precipitation and incorporation in the Co\textsubscript{40-36}Fe\textsubscript{60-64} films. These conditions are fulfilled when the pH level at the electrochemical interface (pH\textsubscript{i}) exceeds the limit set by the product of solubility for particular Fe-hydroxide, as given by equation (5.1) [44,45,72].

\[
\text{pH}_i > \text{pH}_{\text{limit}} = \frac{1}{n} \cdot \log \left( \frac{K_p}{[Fe^{n+}] \cdot (K_W)^n} \right)
\]  

(5.1)

In above expression, the K\textsubscript{p}, K\textsubscript{w} and n stand for the product of solubility of particular Fe-hydroxide, ionic product of water and oxidation state of the Fe ion. The [Fe\textsuperscript{n+}]\textsubscript{i} term represents the concentration of the Fe ions at the electrochemical interface that are being incorporated into the hydroxide. For each sample, electrodeposition does not occur at transport limiting conditions because that concentration of the Fe\textsuperscript{2+} ions at the interface is approximately equal to the bulk concentration. The same applies for Fe\textsuperscript{3+} ions since they do not participate directly in the electrodeposition process [72]. The value of the pH\textsubscript{i} is dependent on the parameters of the electrodeposition process such as pH of the solution, current density j, current efficiency g, and diffusion layer thickness d. The value of pH\textsubscript{i} can be calculated from [45,72]:

\[
pH_i = -\log \left( 10^{-pH} - \frac{j \cdot (1 - \gamma)}{F} \cdot \frac{\delta}{D_{H^+}} \right)
\]

(5.2)
Taking the values of $K_p$ for Fe(OH)$_2$ and Fe(OH)$_3$ as $4.87 \times 10^{-17}$ mol$^3$L$^{-3}$ and $2.79 \times 10^{-39}$ mol$^4$L$^{-4}$ [80], and the value of $\delta$ for stagnant electrolyte as $=0.05$ cm [81] and having $D_{H^+} = 9.28 \times 10^{-5}$ cm$^2$s$^{-1}$ [82], it is easily shown that the pH$_{\text{limit}}$ set by the right side of equation (5.1) is exceeded for both types of Fe-hydroxides during our deposition experiments (pH$_i=6.7$ vs. pH$_{\text{limit}} =6.3$ for Fe(OH)$_2$ and pH$_i=3.8$ vs. pH$_{\text{limit}} =2.02$ for Fe(OH)$_3$).

In CoFe specimens, oxygen in the film could also come from entrapment of {SO$_4^{2-}$} and {BO$_3^{3-}$} ions, to produce one form of oxide phase $A_xO_y$ with other elements trapped during electrodeposition process, such as S and B. Based on previous calculations, in S3, the predominant oxide phase was expected to be Fe$_2$O$_3$·xH$_2$O, which comes primarily from the introduction of maximum amount of ferric sulfate (Fe$_2$SO$_4$)$_3$ into the electrodeposition bath [72,83]. Accordingly, we expected S3 would have higher amount of oxide phase than S1 and S2 since the value of interfacial pH is significantly larger than the threshold required for precipitation of Fe(OH)$_3$ (equation 5.1).

5.3.1.3 STEM/EDS

Diffraction and phase contrast imaging did not reveal the presence of oxygen containing second phases in these rather complicated nanostructures except in rare instance as shown earlier, in diffraction patterns and HREM images. Therefore, we performed compositionally sensitive Z-contrast STEM imaging combined with EELS and EDS to investigate further. Figure 5.12(a) shows a Z contrast image for S1 and it is clearly seen that there are some dark particles/regions within the small gains, corresponding to regions of weaker
scattering, which could be regions of higher oxygen concentration (lower average
Z). This possibility was confirmed by nanospectroscopy.

Fig. 5.12 (a). Z contrast STEM image for S1 (JEOL 2010f).

Figure 12 (b) and (c) show corresponding EDS spectra collected with a 1 nm
probe positioned at bright region (matrix) and a dark regions of Fig. 10 (a). The
Fe/Co ratio was determined by the Cliff-Lorimer method [84].

\[
\frac{C_{Fe}}{C_{Co}} = k_{FeCo} \frac{I_{Fe}}{I_{Co}}
\]  
(5.3)
Fig. 5.12. NanoEDS spectrum collected from (b) bright area, (c) dark area shown in fig. 5.12(a).

In this case, the Cliff-Lorimer factor $k_{FeCo} = 1$ because the atomic weights, densities, cross sections and other parameters of Fe and Co are very nearly equal as described by the following equation [51]:

$$k_{FeCo} = \frac{1}{Z} \frac{(Qwa)_{Fe} A_{Co} \rho_{Fe}}{(Qwa)_{Co} A_{Fe} \rho_{Co}}$$  \hspace{1cm} (5.4)
where $Q$ is the ionization cross section, $w$ is the fluorescence yield for the characteristic X-ray, $a$ is the relative transition probability, $A$ is the self absorption factor and $\epsilon$ is the detector efficiency. The matrix Fe/Co atomic ratio in fig. 5.12(b) was $1.78 \pm 0.1$, which is consistent with the alloy composition Co$_{40.37}$Fe$_{60.63}$. However, the Fe/Co ratio from the spectrum of the dark area shown in fig. 5.12(c) was $3.4 \pm 0.5$. In these regions, where the oxygen was present in the film, the Fe content was enhanced relative to Co.

In this specimen geometry the incident electron beam passes through a column of Fe-Co matrix above and below the dark particle. Keeping in mind that TEM images are 2D projections from 3D objects, these spectra are from composite specimens composed of columns of matrix with small particles in them. Using the foil thickness relative to particle size, (typically 70 to 100 nm relative to 10 nm) at 200kV, as shown schematically in fig. 5.13, and the Fe/Co ratios from matrix and with the probe on a particle (1.78 to 3.4) we calculated that true metal composition of the oxide particles was about 97%Fe/3%Co, so the particles are nearly all iron oxide with little cobalt. This is consistent with the higher thermodynamic stability of iron relative to cobalt oxides [85]. More details about foil thickness and inelastic mean free path will be described in Appendix A.
Fig. 5.13. Schematic diagram shows the foil thickness relative to particle size.

Figure 5.14 (a) shows a Z-contrast image of S2. As we can see, the nanostructure of specimen S2 was relatively different than specimen S1. It has two different nanostructures: particles and few lamellar low contrast regions.

Fig. 5.14 (a). Z contrast STEM image for S2 (JEOL 2010f).
Figure 5.14 (b) and (c) show EDS spectra collected from dark particle and dark lamella, respectively, shown in fig. 5.14 (a).

![NanoEDS Spectrum](image)

**Fig. 5.14.** NanoEDS spectrum collected from (b) particle (c) lamella regions shown in fig. 5.14(a).

The Fe/Co ratios from the spectra shown in fig. 5.14 (b) and (c) were 3.1 and 2.7, respectively. The Fe/Co ratio from dark particle was essentially the same as in S1.
This observation confirming that the spherical particles in S1 and S2 belonged to the same type of Fe oxides. Whereas, the lamellar particles were associated to different Fe oxides. Investigation of different Fe valence states in oxides will be described in detail in the next section. Some traces of S and Cr were detected in fig. 5.14 (b) suggesting another type of oxide could be present in the grown films as discussed earlier, but these were minor amounts.

5.3.1.4 STEM/EELS

In order to investigate the oxidation states present in CoFe films, EELS was a robust technique especially in analyzing light elements such as oxygen. Figure 5.15 shows O K-edge EELS spectra collected from same areas shown in fig. 5.12 (a) for S1.

![O-K edge EELS spectra](image)

Fig. 5.15. O-K edge EELS spectra after background subtraction collected from areas shown in fig. 5.12(a). Spectra are displaced vertically for clarity.

96
The background has been subtracted by power law extrapolation as described in the following equation [69]:

\[ I = AE^{-r} \]  

(5.5)

where \( I \) is the intensity of energy loss \( E \), and \( A \) and \( r \) are constants. It is important to mention that the O K-edge, when bonded to Fe, is characterized by four distinctive peak positions which are labeled as a, b, c and d, according to Colliex et al. [86]. In this figure, the dark area has the largest O K-edge and the bright area has the smallest. This indicates that the darker the contrast the higher oxygen content. It is likely that the weak oxygen signal from the bright area is from a thin amorphous surface oxide, and not from oxygen incorporated during electrodeposition of the film. The O K-edge fine structure from the dark region is FeO oxide, according to the fingerprinting of Colliex et al.[86].

Figure 5.16 (a) shows a Z contrast image for specimen S3. Figure 5.16 (b) shows a Z contrast image for same sample but with higher magnification. The inset shows EELS oxygen concentration from a series of spectra along the line shown in fig 5.16(b), and the oxygen distribution shows a strong maximum at the grain boundary.
Fig. 5.16. (a) Z contrast image for S3, (b) same sample with higher magnification shows line over which EELS spectrum was collected. Inset: net O-K counts along the line shown in the image. The intensity is proportional to oxygen concentration along line scan.
The grain size in these Z-contrast images was consistent with the TEM image in fig. 5.5. Thus, the oxygen rich regions, which have a dark contrast compared to the CoFe matrix, were predominately distributed along the grain boundaries in S3, rather than intragranularly as in S1. The small grain size and corresponding large grain boundary area imply that the oxygen/oxide content of S3 is larger than S1. It is worth mentioning that EDS spectra collected from matrix and across grain boundaries were similar to those collected from bright and lamellar dark areas in S2. So, there are oxygen rich regions in all CoFe samples which are bonded preferentially to Fe, as mentioned earlier, forming a separate phase in CoFe films.

Figure 5.17 shows Fe-L edge and Co L-edge nanoEELS spectra collected from dark and bright areas of S1 shown in fig. 5.12 (a). It is obviously seen that the Fe L_{2,3}-edge and O-K edge were prominent compared to Co L_{2,3} edge in the dark area, whereas only a very weak O-K edge were detected in bright area. Co-L_{2,3} is stronger relative to Fe-L_{2,3} in the bright area. Same results were obtained from specimens S2 and S3.
Fig. 5.17. O, Fe and Co edges EELS spectra of S1 from bright and dark areas shown in fig. 12(a).

Figure 5.18 shows Fe L-edge EELS spectra, after background subtraction, collected from bright and dark areas of S1. The Fe L-edge displays two prominent peaks labeled \( L_3 \) and \( L_2 \). They are referred to as white lines, due to transitions from the \( 2p_{3/2} \) and \( 2p_{1/2} \) levels to the unoccupied \( 3d \) states [87]. They can be used to give information on charge and spin state of the excited atom. The two white lines components arise because of spin-orbit coupling. The spin quantum number \( (s = \pm 1/2) \) can couple in two ways with angular momentum \( l \) to give a total quantum number \( (j = l \pm 1/2) \). In the case of \( 2p \) excitation, \( j = 3/2 \) (lower binding energy, denoted as \( L_3 \)) or \( 1/2 \) (higher binding energy, denoted as \( L_2 \)). The \( l_2 \) peak is sitting on the background due to transition from \( j = 3/2 \) subshell to continuum states. The
separation between the peaks is the spin orbit coupling [88]. The change in the intensity of the L$_3$/L$_2$ ratio is correlated to a change in oxidation state of iron. The net integrated intensity ratio for the Fe L$_3$/L$_2$ edges increased from 1.4 in the bright matrix area to 1.8 in the dark oxygen-containing area. The ratio in bright matrix was consistent with the ratio in pure Fe standard sample. It is worthwhile to mention that bright and dark regions of S2 and S3 displayed the same EELS data trend as S1 shown in fig. 5.18. The white line ratio values of CoFe matrix, spherical and lamellar particles will be listed in table 5.2.

![Fe L-edge EELS spectra after background subtraction](image)

**Fig. 5.18.** Fe L-edge EELS spectra after background subtraction, collected from bright and dark areas of S1 shown in fig. 5.12 (a).
In order to investigate the type of Fe oxide phase in CoFe films, the near edge fine structure (NEFS) of the O-K edges is useful. It is of great interest in practical applications of EELS. This is due to the fact that it is relatively easy to observe, as the oscillations are large, and it gives bonding information. Different oxidation states of Fe give different O-K NEFS. Figure 5.19 shows O-K edge NEFS from dark spherical particles and lamellar particles of S1 and S3, respectively.

Fig. 5.19. Background subtracted O K-edge from EELS nanospectra. The spherical particle spectrum is from S1. The lamellar particle spectrum is from a dark matrix grain boundary region of S3. Curves displaced vertically for clarity.
The difference in the O-K edge onset peak between these samples, suggests strongly that the dark lamellar regions along the grain boundaries in S3 are a form of α-Fe₂O₃ whereas in S1 the dark particles are FeO [86]. It important to note that the spherical particle and lamellar particle in S2 gave the same results as S1 and S3, respectively. The characteristics onset O-K edge parameters of dark regions in S1 and S3 samples are listed in table 5.1. The values are in a good agreement with Colliex et al. [86].

Table 5.1. Characteristics of onset O-K edge of dark areas in S1 and S3

<table>
<thead>
<tr>
<th></th>
<th>ΔE (b-a)* eV</th>
<th>Width of (a)* peak (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 (FeO)</td>
<td>9</td>
<td>2.4</td>
</tr>
<tr>
<td>S3 (α-Fe₂O₃)</td>
<td>11</td>
<td>2.1</td>
</tr>
</tbody>
</table>

*a and b are defined in fig. 5.13

5.3.1.4.1 Effect of Deconvolution on White Line Ratios and O-K Edge

When the sample is thick (> 20 nm or I_p/I₀ > 0.1), plural scattering can change the observed shape of inner shell ionization edges. Good interpretation of NEFS or white line ratios should be done after removal of plural scattering by Fourier-Log deconvolution. In this method a single input is required: a continuous spectrum extending from zero loss through the edges of interest and having neither gaps nor regions of detector saturation. The continuous spectrum was obtained by using the splice function in Digital Micrograph software. In this technique each one of the zero loss plus single, double and triple scatterings is
convoluted with the resolution function (instrument response function). The
Fourier transform of the whole spectrum (F) is described by [51]:

\[
F = F(0) \exp \left( \frac{F(1)}{I_0} \right)
\]

(5.6)

where \( F(0) \) is the transform of the elastic contribution, \( F(1) \) is the single scattering
transform, and \( I_0 \) is the zero loss intensity. Figure 5.20 (a) shows O, Fe, and Co
edges of S1 without deconvolution. Figure 5.20 (b) shows the spectrum after
deconvolution. It is clearly seen that the deconvolution improved the jump ratio
\( (S+B)/B \), where S is the signal and B is the background. For accurate quantitative
EELS analysis, deconvolution should be carried out for thick samples.

![Graph](image)

Fig. 5.20 (a) O, Fe and Co edges of S1 before deconvolution, (b) after
deconvolution.

The white line ratios of Fe in CoFe matrix, in dark region of S1, in dark region of
S3 are listed in table 5.2.
In order to calculate the white line ratio, a background window of 30 eV was extrapolated over a signal window then subtracted to give the edge intensity. Then $I(L_3)$ and $I(L_2)$ were integrated over an energy window of 2 eV. We noticed from table 5.2, as the valence state of Fe increased, the white line ratio increased. The white line ratio of pure Fe sample was similar to CoFe matrix. Figure 5.21 shows O-K edge of S1 before and after deconvolution. The NEFS (a,b,c,and d peaks) remained the same after deconvolution. However, the plural scattering plasmon contribution to the post-edge structure intensity was removed.

Fig. 5.21. O-K edge of S1 with and without deconvolution.
5.3.1.4.2 Low loss EELS Spectra

Since low loss EELS spectra carries some useful information about outer shell loss, it is worthwhile to study low loss from different areas. In this section, we compared low loss spectra of Fe, CoFe matrix and dark area in S1 (FeO) and S3 (Fe₂O₅) as shown in fig 5.22 (a), (b) and (c) and fig. 5.23 (a) and (b).

![Low loss spectrum from (a) Fe, (b) CoFe matrix and (c) FeO dark area in S1.](image)

Fig. 5.22. Low loss spectrum from (a) Fe, (b) CoFe matrix and (c) FeO dark area in S1.
The low loss energy of Plasmon peaks (Ep) and M$_{2,3}$ edges of Fe, CoFe matrix and FeO in S1 are listed in table 5.3.

Table 5.3 Ep and M$_{2,3}$ of Fe, CoFe matrix and FeO.

<table>
<thead>
<tr>
<th></th>
<th>Ep</th>
<th>M$_{2,3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>23.5</td>
<td>57.8</td>
</tr>
<tr>
<td>CoFe matrix</td>
<td>23.5</td>
<td>57.8</td>
</tr>
<tr>
<td>(FeO)</td>
<td>24</td>
<td>58.8</td>
</tr>
</tbody>
</table>

We observed from fig. 5.20 that, Fe and CoFe matrix have the same Plasmon peak and M$_{2,3}$ edge low loss energy. However, there was an energy shift by 1 eV in M$_{2,3}$ edge of FeO in S1.

Figure 5.23 (a) shows low loss spectrum of Fe$_2$O$_3$ taken from atlas [89] and fig. 5.23 (b) shows EELS spectrum from Fe$_2$O$_3$ from S3 at a grain boundary. Low loss spectrum in fig 5.23(b) shows a small peak present at 7 eV which is matching the fingerprinting of fig. 5.23(a). The low count of this peak in S3 could be related to the following reasons: (1) bigger probe size (1 nm) compared to grain boundary width, (2) Foil thickness ~ 6-7 overlapped grains. We concluded that the grain boundary oxide phase is always Fe$^{3+}$ oxide and the intragranular oxides is Fe$^{2+}$ oxide. Both oxides contain very little Co relative to the matrix.
So far, we have presented some results obtained using a non-aberration corrected microscope (JEOL 2010F). The objective was determination of oxygen distribution, valence state and crystallinity, which affect the film’s magnetic properties. Resolution of the images, particularly in grain boundary regions, was limited by spherical aberration, which was difficult to correct due to the specimen field. Recently, we acquired STEM images of the same specimens using a STEM-corrected JEOL ARM at 200 keV, with appreciably better results, although the results were strongly dependent on sample configuration.

In the next section, some results taken from aberration-corrected microscope (JEOL-ARM 200) will be described.
5.3.2 Aberration-Corrected STEM (JEOL-ARM 200)

The effective correction of spherical aberration is a breakthrough for the whole field of electron microscopy. The application of corrected STEM microscopes to ferromagnetic specimens is a so far unexplored topic. The corrector enabled formation of relatively higher-current subatomic diameter probes, and thus STEM images with atomic resolution and higher contrast than for the uncorrected case. Whether the oxide was amorphous or crystalline, and continuous, or not, in nanocrystal grain boundaries were important questions. Figure 5.24 (a) and (b) shows a Z-contrast image of S3 with Fe$^{3+}$ oxide distributed at grain boundaries with low and high magnification. Note the achievable resolution and contrast in this image compared to Fig. 5.16.
Fig. 5.24. STEM HAADF images shows oxygen rich phase distributed at grain boundaries with (a) low and (b) high magnification.
A high-resolution STEM Z-contrast of the same specimen S3 is shown in fig. 5.25. Note the lattice resolution achieved for the ferromagnetic specimen with lattice constant of 0.286 nm, which is remarkable. Two dark regions (Fe oxides) that appear to have non-periodic atom arrays are arrowed. This is the strongest image evidence that we have for amorphous, or at least poorly ordered, oxide. It corroborates our earlier preliminary diffraction observation.

Fig. 5.25. High-resolution STEM Z-contrast image of S3 shows dark regions displaying a lack of periodicity (arrowed) relative to CoFe matrix. FIB LO specimen.

It was a quite troublesome to acquire a reliable spectrum image (mapping) from JEOL 2010F due to some factors such as specimen drifting and contamination and
other factors such as low beam current. However, aberration corrected high-current small STEM probes facilitated these SI experiments. The spectrum image in Fig. 5.26 shows that the oxide is nearly continuous in the nanocrystal grain boundaries. Other EELS measurements showed the oxide to be nearly Fe₂O₃, containing little Co. The Fe concentration in the oxide is less than in the matrix, which is the reason for the dark boundary contrast in Fig. 5.26(c). The low boundary contrast in Fig. 5.26(d) confirms the low oxide Co content.

Fig. 5.26 (a) HAADF region of interest for SI, (b) O-K image showing nearly continuous distribution. (c) Fe-L image. (d) Co-L image.
It is important to note that ADF contrast is based on scattering amplitude and known as atomic number Z contrast, whose sensitivity depends on the scattering power of the relevant atoms. However, Annular bright field (ABF) phase contrast imaging is a robust technique for detection of light atoms with extremely weak scattering, which is based on wave interference. It requires the atoms to alter the phase of a wave [90,91]. Figure 5.27 (a) shows ABF STEM image of S3. FFT was taken from selected areas in fig. 5.27(a) as shown in fig. 5.27 (b) and (c). Figure 5.25(d) shows HAADF STEM image of the same area of fig. 5.25(a). As we can see the lattice resolution is clearly visible in ABF relative to HAADF image. The Fe oxide at grain boundary is obviously non periodic. By indexing both FFT patterns, areas A1 and A2 are corresponding to zone axis <120> and <111>, respectively. The angular misorientation between two grains can be calculated by the following relation:

$$\cos \Phi = \frac{[h_1k_1l_1][h_2k_2l_2]}{\sqrt{(h_1^2+k_1^2+l_1^2)(h_2^2+k_2^2+l_2^2)}}$$

(5.7)

The calculated angular misorientation across the boundary was ~39°, confirming that grain boundary is a high angle grain boundary which is greater than 10-15° [92]. High-angle boundaries contain large areas of poor fit and have a relatively open structure.
The molar volume $V_m$ can be calculated by the following relation:

$$V_m = \frac{\text{at.wt}}{\rho}$$  

(5.8)

where, at.wt is the atomic weight and $\rho$ is the density. Taking the values of $\rho_{\text{CoFe}} = 8.2 \text{ g/cm}^3$ [10], $\rho_{\text{FeO}} = 5.9 \text{ g/cm}^3$ [24], and $\rho_{\text{Fe}_2\text{O}_3} = 5.26 \text{ g/cm}^3$ [93], The $V_m$ of
CoFe, FeO and Fe$_2$O$_3$ were 13.9, 12.17 and 30.36 cm$^3$/mole, respectively. The $V_m$ of both CoFe and FeO are closely matched, so the favorable place for nucleation of FeO particles within the grain (intragranular) without introducing any stain in the lattice. Whereas, $V_m$ of Fe$_2$O$_3$ is comparably larger than the matrix so it is favorable to nucleate at high misfit location such as high-angle grain boundary areas (intergranular) without introducing a significant strain in the lattice structure.
5.3.3 Off-axis Electron Holography

Domain wall width of low oxygen content specimen (S1) and high oxygen content specimen (S3) were estimated by off-axis electron holography technique. The reconstructed phase image of S1 is shown in fig. 5.28(a).

![Reconstructed holographic phase image](image1)

Fig. 5.28 (a) Reconstructed holographic phase image. (b) Line profile from AB line in fig. 5.28(a). (c) Magnetic induction map and overlaid arrows indicated by color wheel shown in fig. 5.28(d).

The domain wall thickness was estimated by measuring the distance over which the slope of phase abruptly changes [74]. Figure 5.28(b) shows the line profile
across the phase changes in fig. 5.28(a). The domain wall width $\delta$ was approximately $15 \pm 1.2$ nm thick. The magnetic flux was completely closed (vortex shape with counter clockwise chirality), which depends on size and shape of ferromagnetic specimen [94]. Figure 5.29 (a) shows the reconstructed holographic phase image of CoFe film in S3.

![Figure 5.29](image)

Fig. 5.29 Reconstructed phase image from CoFe film in S3. The arrows show $180^\circ$ domain walls. The inset: line profile across phase changes as shown in fig. 5.29.

The arrows show the magnetic induction is oriented roughly at $180^\circ$. The domain wall width $\delta$ was approximately $15 \pm 1.6$ nm thick. The $\delta$ of all CoFe films were falling within the same range.
5.3.4 X-ray diffraction (XRD)

The crystalline structure of the CoFe films was studied by XRD. Figure 5.30 shows X-ray diffraction patterns obtained from S1 and S3. The first two peaks: (002) and (111) are corresponding to Ti and Cu, respectively. The XRD results indicate that both CoFe films are polycrystalline and have strong (110) preferred orientation. The other CoFe peaks: (200) and (211) are broader and weaker than (110) peak. S3 demonstrated higher (110) peak intensity than S1. Also, the CoFe film in S3 shows a very weak (130) peak corresponding to Fe$_2$O$_3$ and is not present in S1.

The grain size $D$ of the CoFe films was calculated using the Debye-Scherrer equation as follows:

$$ D = \frac{0.9 \lambda}{\beta \cos \theta} $$

(5.7)

where, $\beta = B - b$, where B is the measured broadening of the diffraction line peak at an angle of $2\theta$, at half its maximum intensity (FWHM) and $b$ is the FWHM contribution of the instrument (which is 0.01) in radians, and $\lambda = 0.154$ nm. The FWHM of the major peak (110) is used to calculate D. The calculated grain size was ~17-20 nm. This result is consistent with TEM analysis.
Fig. 5.30. X-ray diffraction patterns obtained from S1 and S3.

5.3.5 X-ray Photoelectron Spectroscopy (XPS)

In order to compare the amount of oxygen incorporation during the electrodeposition process for both samples, the O/Fe ratios were determined by XPS. The O/Fe ratio for S1 was 0.24, compared to 0.49 for S3. This means S3 had two times higher oxygen content than S1, which is consistent with our expectation stated earlier. To investigate type of oxide/hydroxide phase in CoFe films, the chemical states of Fe 2p\textsubscript{3/2}, Co 2p\textsubscript{3/2} and O 1s were examined. Chemical states of Co 2p\textsubscript{3/2} and O 1s didn’t show any significant difference between S1 and S3. Figure 5.31 (a) and (b) show XPS of Co 2p\textsubscript{3/2} and O 1s spectra of S3, respectively.
Fig. 5.31. (a) Co 2p$_{3/2}$ and (b) O 1s XPS peaks.

The Co 2p$_{3/2}$ peak in fig. 19(a) was fitted with three curve peaks: a Co peak corresponding to a binding energy of 778.5 eV, a CoO corresponding to a binding energy of 780 eV, and a satellite peak corresponding to a binding energy of 783 eV.
eV [95]. As we can see from fig. 5.31(a), the predominant phase was Co metal rather than CoO. The O 1s peak in fig. 5.31(b) was fitted with three curve peaks: an oxide peak corresponding to a binding energy of 530 eV, a hydroxide or hydrated peak corresponding to a binding energy of 531.5 eV, and water corresponding to a binding energy of 532.5 eV [96,97]. The predominant peak in O 1s XPS spectrum was oxide rather than hydroxide.

The Fe 2p\(_{3/2}\) peak was fitted by multiplet peaks due its broadness and multiplet structure of Fe oxide [96,98]. Fig. 5.32 shows Fe 2p\(_{3/2}\) XPS spectra of S1.

![Fe 2p\(_{3/2}\) XPS spectrum for S1.](image)

The Fe 2p\(_{3/2}\) peak in S1 was fitted with three major different curves: an Fe peak corresponding to a binding energy of 706.8 eV, FeO multiplet peaks corresponding to a binding energies of 708, 709.4, and 710.6 eV, which are in a good agreement with ref [95], and a satellite peak corresponding to a binding energy of 783 eV. This leads to the predominant oxide phase in S1 is FeO which
agrees with EELS findings. Fe 2p\textsubscript{3/2} peak in S2 was similar to S1. XPS results was quite consistent with STEM/EELS and SIMS analysis (below). However, it was not a definitive tool to differentiate between different oxides present in CoFe films. Keep in mind that XPS analysis is performed at micro-scale level, however, STEM/EELS is performed at nano-scale level with high spatial resolution.

5.3.6 Secondary Ion Mass Spectroscopy (SIMS)

The elemental depth profiles of H, O, Co, and Fe for S1 are shown in Figure 5.33(a). The profiles are nearly constant throughout the film until the Cu intermediate layer below the CoFe layer is reached. The O\textsuperscript{18}/Fe\textsuperscript{56} ratio for S1 was \(~0.13\) compared to \(~0.29\) for S3 as shown in fig. 5.33(b), indicating that S3 had oxygen content of about \(~2\) times higher than S1, which is consistent with our XPS results. The larger Co count rate in fig.5.33(a) results from its larger ionization efficiency compared to Fe, and does not indicate a film composition difference from the value determined by EDS. The presence of some hydrogen was expected since aqueous electrodeposition media was used. It could have been present as hydroxide as shown previously by XPS peak fitting of the O 1s spectrum, which is less dominant than oxide phase. However we did not detect diffraction evidence for any crystalline hydrides or hydroxides. Hydrogen was detected during our SIMS analysis of both S1 and S2 films. This result is consistent with theoretical electrochemistry of the deposition process discussed above, and implies the oxygen-containing nanoregions we identified were iron hydroxides or hydrated oxides and anhydrous oxides. The SIMS spatial resolution
was insufficient to show that hydrogen was localized in the oxygen-containing second phases.

Fig. 5.33. (a) SIMS depth profile for S1 and (b) O/Fe ratio for S1 and S3.
The corresponding SIMS curve for S3 was smeared out because the surface roughness of S3 was much larger than S1, which prevented accurate depth profiling, but the same elements were present.

The EELS 1s peak for hydrogen occurs at about 13 eV loss and is obscured by the zero-loss peak tail and other low-loss peaks from the matrix, and therefore not detectable in our experiment. Most transition metal hydroxides and hydrated oxides undergo irradiation effect under 200 keV electron beam that result in structural disorder and loss of hydrogen and oxygen; these effects are dose dependent and visible in EELS spectra. Garvie [99] has shown that a transient peak, close to 530 eV loss (such as the threshold onset peak for S3 shown in our fig. 5.19) appears early in the damage process and then disappears at larger electron doses. It is due to O$_2$ nanobubbles that form during irradiation. The peak disappears as O$_2$ from OH or H$_2$O leaves the specimen with increasing dose. However, in the case of anhydrous Fe$_2$O$_3$ (hematite) this peak is stable due to the oxide itself: For our work this peak was stable, so our electron microscopy results do not provide any direct evidence to determine whether our oxygen containing regions also containing hydrogen as implied by electrochemistry described above. Indirect evidence, such as the lack of crystallinity observed for our oxygen-containing particles, implies that radiation effects occurred, as one would expected for hydrogen and perhaps oxygen-containing particles. It is also possible that some of the hydrogen detected by SIMS was in the CoFe matrix itself, absorbed during the electrodeposition process or acquired by migration from the oxygen containing particles. Hydrogen is highly mobile in bcc Fe and its alloys
even near room temperature ($D_{li} \approx 10^{-4}$ cm$^2$ s$^{-1}$) and segregated to lattice defects (such as grain boundaries, interfaces and dislocations) increasing its apparent solubility [100,101].

5.3.7 Atomic Force Microscopy (AFM)

The surface roughness of CoFe films was evaluated by AFM as shown in fig. 5.34. It is noticeable from fig. 5.34 that the surface roughness increased with addition of Fe$^{3+}$ into electrodeposited solution. The root mean square (rms) of S1, S2 and S3 are 11.56 nm, 12.31 and 19.49 nm, respectively. This is most likely due to the presence of Fe$_2$O$_3$ on grain boundaries causing irregularities in the CoFe nanocrystal nucleated during film growth.
Fig. 5.34. AFM images of (a) S1, (b) S2 and (c) S3.
5.3.8 Superconducting Quantum Interference Device (SQUID)

Figure 5.35 shows the magnetization loops for low oxygen specimen S1 and high oxygen specimen S3 in the plane of the alloy films. Specimen S2, not showing in fig. 5.35, displayed similar trend as in S1. S1 showed highest saturation magnetization and lowest coercivity.

Fig. 5.35 In-plane magnetization curves for S1 and S3.

The measured magnetic properties and magnetoresistance (MR) of S1, S2 and S2 are listed in table 5.4. Figure 5.36 shows the magnetoresistance loop for S3.
Table 5.4. Magnetic properties and magnetoresistance of CoFe films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$H_C$ (Oe)</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r/M_S$</th>
<th>MR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>14</td>
<td>77</td>
<td>0.28</td>
<td>6</td>
</tr>
<tr>
<td>S2</td>
<td>18</td>
<td>69</td>
<td>0.26</td>
<td>7.1</td>
</tr>
<tr>
<td>S3</td>
<td>48</td>
<td>40</td>
<td>0.13</td>
<td>13.3</td>
</tr>
</tbody>
</table>

Fig. 5.36 Resistance vs field of S3.

$H_C$ and $M_s$ of both S1 and S2 films are larger and smaller, respectively than the values of these parameters for oxygen-free CoFe alloys of similar composition [10,102]. Obviously, the presence of Fe oxides in the films diluted the magnetic moment of the CoFe alloy film matrix. The simple argument based on volume partitioning of the electrodeposited films on the high value $M_s$
magnetic phase ($\text{Co}_{40.36}\text{Fe}_{60.64}$) and weakly magnetic/antiferromagnetic or nonmagnetic inclusions ($\text{FeO} \cdot x\text{H}_2\text{O}$ or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) is sufficient to explain this observation [2]. The oxide volume fractions were estimated (see Appendix 2) from Z-contrast STEM images of S1 (fig. 5.12(a)), S2 (fig. 5.14(a)) and S3 (fig.5.16(b)). The estimated oxide volume fraction of S1, S2 and S3 were 0.015, 0.04 and 0.24, respectively. Since all films have similar 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 S3, the motion of domain walls was impeded more strongly by intergranular oxide phase than in S1, which contained intragranular oxide particles. Higher applied magnetic field was required to saturate S3. This is due to a difference in the exchange coupling energy between the grains depending upon the magnetic nature of the intergranular region [103].

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 S1 are likely supported by the Kersten model [102] where $H_C \alpha f^{2/3}$, where $f$ is volume fraction of second phase (0.015). However, the second phase in S3 can be considered as lamellar regions, with $H_C \alpha f$, where $f = 0.24$, based on the Goodenough model [104]. Whereas, S2 has a combination of spherical regions (~80%) and lamellar regions (~20%), suggesting
the predominant second phase is a spherical regions. Consequently, the observed coercivity in S2 was slightly larger than S1 but not significant. Another contribution to the observed magnetic properties is domain wall motion interaction with the different oxide phases (pinning sites) in the matrix alloy. This contribution was supported by electron holography results showing all CoFe films have $\delta \sim 13-17$ nm within the same range of intergranular second phase distributed at grain boundaries of S3. However, the size of FeO intragranular particles in S1 was $\sim 2-4$ nm and the same for S2 with fewer percent of lamellar region. Thus, we expect that the grain boundary oxide-domain wall interaction led to increased coercivity [105].

For further investigation of domain wall motion interaction with second phases in CoFe alloy matrix, particularly S1 and S3, the Barkhausen effect was measured by SQUID. Voltage was obtained as a function of time at the coercive field of each sample, and then the data were analyzed in histograms. Figure 5.37 (a) and (b) show histograms for low oxygen content specimen S1 and high oxygen content specimen S3. The histograms of both samples were taken within same range of time period. Comparing the two histograms showing in fig. 5.37, S1 displays smaller jumps (smaller amplitude) than S3. In other words, the changes in voltages in S1 were relatively smoother than S3. This means domain wall in S3 interacted with many obstacles acting as pinning sites. Once the wall has broken away from a pinning site it will undergo rapid and irreversible motion, leading to discontinuity in the rate of change of magnetization with time [76]. This is the primary cause of Barkhausen emissions.
Fig. 5. 37. Frequency vs $\Delta V$ (histogram) for (a) S1 and (b) S3.
This result substantiates our discussion earlier in magnetic properties observation. It was revealed that the surface roughness induced domain wall pinning and thus increased the coercivity of the grown films [105,106]. Based on our AFM results, surface roughness increased with coercivity of the films which in a good agreement with above mentioned references. From electron holography and AFM, \( \delta \) was less than surface roughness of S3. This finding led to strong domain wall pinning and consequently enhanced coercivity of the film as shown by Swerts et al. This result was supported earlier in TEM nanostructure analysis and Barkhausen effect.

We observed a similar trend on the magnetoresistance (MR) in CoFe films. This change is attributed to surface roughness [107] and spin-dependent electron scattering at matrix/oxide interfaces [108]. Since S3 has larger intergranular interfacial area than intragranular interfacial area in S1 and S2, MR enhanced considerably in S3 relative to S1 and S2. In this particular case, we can consider the MR here produced from tunneling magnetoresistance (TMR) between ferromagnetic regions separated by insulating barrier (second phase). Specimen S3 gave arise to Inter-grain tunneling substantiated by Venkatesan et al.[109] and Chen et al. [110]. Whereas, specimen S1 gave a rise to intra-grain tunneling supported by Sarma et al [111]. Intra-grain tunneling was the predominant mechanism in S2.
5.4 Conclusions

In summary, the effect of oxygen incorporated in electrodeposited CoFe films has been studied. Each oxygen source in the sample resulted in characteristically different structural and magnetic properties of the deposited films. Z contrast STEM imaging combined with EELS and EDS confirmed the presence of oxygen rich regions in S1 (low oxygen), S2 and S3 (high oxygen) specimens. EELS indicated the predominant oxide formed in S1 and S2 was FeO, whereas in S3 was mainly Fe$_2$O$_3$. Introducing Fe$_2$(SO$_4$)$_3$ into the electrodeposition process enhanced formation of Fe$^{3+}$ oxide at the grain boundary areas in S3, resulting in the most effective domain wall pinning. As oxygen content increased in CoFe film, the surface roughness increased, the saturation magnetization decreased, the coercivity increased and magnetoresistance increased.
Chapter 6

CHARACTERIZATION OF ELECTRODEPOSITED COBAL-IRON NANOCONTACTS

This chapter describes some TEM characterization of electrodeposited CoFe nanocontact. Higher MR measurements were obtained from these nanoconfined contacts. The growth of nanocontact specimens and the MR measurement were performed by Prof. Brankovic’s group at the University of Houston.

6.1 Motivation

In order to reach beyond 1 Tbit/in\(^2\) areal density of magnetic storage, magnetic readers have to scale down in their critical dimension to nano-scale level. At this scale, the sensitivity and signal to noise of the magnetic field sensors based on GMR or TMR will not be sustainable. Note GMR and TMR were defined earlier in section 1.5.4. High values of MR in nanoconfined geometry of ferromagnetic nanocontact have been displayed in the last two decades [26,27,112,113]. This phenomenon called BMR as described earlier in section (1.5.4.5). Larger MR is obtained as a result of two factors: nanoconfined geometry of electrodeposited and oxide presence in nanocontact. It was shown that if there is no oxide in nanocontact, no significant MR was obtained [114].
6.2 Experimental details

CoFe nanocontact were electrodeposited on Cu (100 nm thick)/Co (200 nm thick)/Si substrates after patterning by photolithography technique. The aqueous solution compositions and electrodeposition parameters for CoFe samples have been described in detail earlier in section (3.1, 3.2 and 5.2). The sample geometry was shown earlier in fig. 3.1(b). The only difference is amount of saccharin that added into solution. It was varied from 0 - 1.5 g/L to optimize the magnetic device integrity. Four point probe measurements are performed on the final sensor device to determine the MR curves. Two contacts (I and V) at the top layer and two at the bottom were used. A Labview program was designed to record the measurements where the user was able to vary the maximum magnetic field, the input current or number of loops. The magnetic field in this case was varied between -700Oe to +700Oe. 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 schematic of the sensor cross section is shown in fig. 6.1.

![Diagram of cross-sectional magnetic sensor](image)

**Fig. 6.1** A schematic of cross-sectional magnetic sensor.
TEM specimens were prepared by FIB-LO technique as discussed previously in section (3.2.2). Figure 6.2 shows the process sequences of FIB LO.

Fig. 6.2 FIB LO process (a) Two trenches were milled after platinum deposit. Note: each mushroom represents a nanocontact. (b) The sample was lifted out by welding to a probe. (c) The sample was attached to grid and thinned. (d) Final thinning. The arrow shows the noncontact area.
6.3 Results and discussion

6.3.1 TEM results

Figure 6.3 shows a TEM image of the nanocontact specimen. As we can see from TEM image, there are some voids in nanocontact sample. Further development is still to be carried out to improve the nanocontact quality.

Fig. 6.3. TEM image of CoFe nanocontact.

Figure 6.4 is a high magnification TEM image of fig. 6.3 showing the nanocontact width. The nanocontact width was estimated from fig. 6.4 to be ~200 nm.
Fig. 6.4. High magnification TEM image of Fig. 6.3 showing the nanocontact width.

SAD patterns taken from CoFe nanocontact and Co layer are shown in fig. 6.5 (a) and (b), respectively. The CoFe nanocontact displayed a polycrystalline bcc structure similar to CoFe thin films in fig. 5.3. The Co layer is a single crystal structure with [0001] zone axis.
Varying amount of saccharin added into electrodeposition solution reduced the voids and improved the quality of nanocontact as shown in fig. 6.6. The nanocontact width was ~80 nm.
It is important to note that the final thinning during FIB was quite challenging in order to prepare nanocontact TEM specimens. It was difficult to stop thinning exactly at the center of nanocontact. As you can see from fig. 6.6 the nancontact is off center. Figure 6.7 shows spectrum imaging of O-K, Fe-L and Co-L edges.

Fig. 6.7 (a) HAADF region of interest for SI. (b) O-K image showing nearly continuous distribution. (c) Fe-L image. (d) Co-L image.
There are some oxide phases bonded with Fe rather than Co in the nanocotact region. This specimen is similar to S1 (no Fe$_2$(SO$_4$)$_3$ was added into solution).

The oxide is FeO type with intragranular particles as shown in fig. 6.8.

Fig. 6.8 HAADF STEM image of nanocontact. Note: poor resolution due to sample thickness ~120 nm.

6.3.2 Magentoresistance results

Preliminarily MR measurements show a promising avenue for ferromagnetic nanocontact for future magnetic field sensors. The very large values of MR at room temperature (>1000%) shown in fig. 6.9 with nanocontact dimension <100
nm and oxygen content 6-8 at% relative to 250% in S1.

Fig. 6.9. Resistance vs field showing MR value exceeds 1000%.

The MR in nanoconfined geometry of ferromagnetic nanocontacts is governed by two mechanism: TMR and BMR. In comparison with ferromagnetic thin films, the predominant mechanism in nanocontact is BMR. The BMR effect arises from nonadiabatic spin scattering across very narrow domain wall trapped at nanosized constrictions [115,116].
6.4 Conclusions

The very high MR values were achieved for magnetic devices with nanocontact dimension < 100 nm and oxide incorporation in this nanoconfined geometry. The content of oxide phase in nanocontact was controlled by concentration of the Fe$^{3+}$ ions in the electrodeposition solution. Magnetic device integrity was improved by varying amount of saccharin into plating solution. These results indicated that electrodeposited CoFe nanocontact is a novel class of materials with large application for magnetic field sensors.
Chapter 7

SUMMARY AND FUTURE WORK

7.1 Summary

The research of this dissertation has involved utilize of high-resolution analytical electron microscopy to characterize electrodeposited CoFe films on different substrates such as Cu, Al and Si. Additionally, this work has established a clear and well-defined correlation between the material structure of the ferromagnetic thin films and their magnetoresistance and magnetic properties for improved magnetic device efficiency in magnetic recording applications.

The electrodeposited CoFe films on Cu and Au/Al substrates were investigated by TEM imaging techniques in conjunction with EDS and EELS. These kinds of substrates didn’t provide a desirable mechanical structure of magnetic devices as a result of a weak bonding between the layers and surface roughness of substrates.

The electrodeposited CoFe films on Cu/Ti/Si substrates were significantly more successful to improve the grown film quality and magnetic device integrity. A detailed microscopy study has been performed in these grown films to investigate the presence of oxide nanodistributions in the alloy matrix and correlate them to magnetic properties. Each oxygen source in the sample resulted in characteristically different structural and magnetic properties of the deposited films. Z contrast STEM imaging combined with EELS and EDS was a successful technique to confirm the presence of oxygen rich regions. EELS indicated the
predominant oxide formed in S1 was FeO, whereas in S3 was mainly Fe₂O₃. Introducing Fe₂(SO₄)₃ into the electrodeposition process enhanced formation of Fe III oxide at the grain boundary areas in S3, resulting in the most effective domain wall pinning. As oxygen content increased in CoFe film, the saturation magnetization decreased, the coercivity increased and magnetoresistance increased.

The electrodeposited CoFe nanocontacts were demonstrated to have a very large value of magneto-resistance (>1000%). TEM showed the nanocontact dimensions were 100-200 nm. The nanocontact quality improved by adjusting the amount of saccharine added into electrodeposition solution, resulting in less voids in the nanocontact area. Smaller nanocontact dimension and higher oxygen content incorporation in nanocontacts yielded to larger MR values.

7.2 Future work
7.2.1 TEM sample preparation

New techniques need to be developed to obtain very thin TEM specimens less than the grain size, 10 nm thick. It would be very interesting to use a Nanomill TEM specimen preparation system. This system has a capability to operate at ultra low energy ion source, 50 eV, to obtain very thin specimens with less amorphous surface layer. It is would be also useful for post-FIB processing, especially with nanocontact samples.
7.2.2 Identification of crystallinity of oxide phases

Most of oxide phases observed in this research were nearly amorphous. All TEM study was carried out at operating voltage of 200 KeV. Further investigation of the crystallinity of these oxide phases needed to be carried out at 120 and 80 KeV using JEOL ARM 200. Most transition metal hydroxides and hydrated oxides undergo irradiation effect under 200 keV electron beam that result in structural disorder and loss of hydrogen and oxygen; these effects are dose dependent and should be visible in EELS spectra. Therefore, radiation damage experiment would be useful for these evaluations in this class of engineering materials.

7.2.3 Continuity of grain boundary oxide

Further high-resolution aberration corrected STEM with spectrum images need to be carried out to investigate the continuity/discontinuity of Fe oxide at grain boundaries. Further investigation of grain boundary width both structural and chemical width, would be vital to evaluate any diffusion of grain boundary species to the matrix grains.

7.2.4 Type of second phase

Hydrogen cannot be detected in CoFe films using electron probes because it is quite mobile under electron radiation, but oxygen is less so. So we are reporting the second phase as oxide. However, from electrochemical deposition point of view, SIMS and XPS results the second phase probably also contained
some hydrogen, either as water of hydration or hydroxyl ions. In order to investigate this type of second phase at high spatial resolution, Neon UltraStem 100 would be essential. This new microscope has 5th order corrected Enfiniem spectrometer which enables large collection angle without resolution degradation for fast high S/N collection. The whole spectrum collection is enabled by DualEELS. It is also has a monochromator with < 30 meV resolution, down to 30 keV. With this state-of-art microscope hydrogen will be detected.

7.2.5 Electrodeposition process

Electrodeposition is the choice for growing our CoFe films and nanocontacts in this research due to low capital cost and high yield. Furthermore, electrodeposition complemented with photolithography technique is capable of delivering high quality CoFe nanostructures with critical dimensions at nano-scale level. One key issue of optimizing the magnetic field sensors is to enhance the process conditions in terms of solution components and electrodeposition parameters. Further improvement in deposition technique will be needed to achieve better quality of CoFe nanocontact and to obtain smaller nanocontact dimension <20 nm. These factors will significantly increase the MR values of CoFe nanocontacts and hence will enhance the sensitivity of magnetic field sensors. The success of changes in electrodepositon parameters requires high-resolution analytical electron microscopy for evaluation.
REFERENCES


APPENDIX A

FOIL THICKNESS AND INELASTIC MEAN FREE PATH
The foil thickness was calculated by using the following relationship [69]:

$$t/\lambda = \ln \left( \frac{I_t}{I_0} \right)$$  \hspace{1cm} (1)

where, $t$ is the foil thickness, $\lambda$ is total mean free path for all inelastic scattering, $I_t$ is the total intensity of low loss spectrum, $I_0$ is the intensity of zero loss peak. $\lambda$ can be calculated by the following equations [69]:

$$\lambda = \frac{106F(E_0 / E_m)}{\ln(2\beta E_0 / E_m)}$$  \hspace{1cm} (2)

$$F = \frac{1 + E_0 / 1022}{(1 + E_0 / 511)^2}$$  \hspace{1cm} (3)

Substitute $E_0 = 200$ keV in equ. (2)

Thus, $F = 0.618$

$$E_m = 7.6 Z_{\text{eff}}^{0.36}$$  \hspace{1cm} (4)

$$Z_{\text{eff}} = \sum_i f_i Z_i^{1.3}$$  \hspace{1cm} (5)

From equ. (5), $Z_{\text{eff}}$ for Fe$_{60}$Co$_{40} = 13.4$

Substitute $Z_{\text{eff}}$ value in equ. 4, giving $E_m = 19.3$ eV

where $E_0$ is the accelerating voltage of the electron microscope, $\beta$ is the collection half angle in mrad and Z is the atomic number.

By substituting $E_m$ in equ. (2), the calculated $\lambda$ for Co$_{40}$Fe$_{60}$ alloy is $\sim 90$ nm.
APPENDIX B

VOLUME FRACTION OF OXIDE PHASE CALCULATIONS
The estimated oxide volume fraction was estimated from Z-contrast STEM images of S1 (fig. 5.10(a)), S2 (fig. 5.12(a)) and S3 (fig. 5.14(b)). The schematic figure below shows the oxide distributions in each sample.

The calculated volume fraction of S1 was estimated as follow:

The total area = \( L^2 = 493.3 \text{ nm}^2 \), where \( L \) is the length of square shown in above figure.

The total volume = \( L^2 \times t = 493.3 \times 90 = 44397 \text{ nm}^3 \), where \( t \) is the foil thickness calculated by EELS.

Total volume of particles = \( \frac{4}{3} \times 3.14 \times (r_1^3 + r_2^3 + r_3^3) = 669.9 \text{ nm}^3 \)

Total volume fraction = \( \frac{669.9}{44397} \approx 0.015 \)

Similarly, the volume fraction of S2 was calculated like in S1 except we assumed the lamellar particle as a thin plate with dimension of \( L = 25 \text{ nm} \) and width \( w = 1 \text{ nm} \).
In S3, the oxide is distributed continuously at grain boundaries. For simplicity, we assumed the grain has a cube configuration with length L= 20 nm and the grain boundary width is ~1nm.

Thus, the oxide volume per grain can be calculated as follow (see the above fig for S3):

\[ V = L^3 - (L-1)^3 = 20^3 - 18^3 = 2168 \text{ nm}^3 \]

Assuming there are 4 grains in the total area. The foil thickness from EELS= 90 nm, which contained ~4 grains.

Hence, the total oxide volume= \(2168 \times 4 \times 4 = 34688 \text{ nm}^3\)

Total volume= \(144000 \text{ nm}^3\)

Thus, the oxide volume fraction in S3 = \(34688/144000= 0.24\)