Ultrahigh Density Magnetic Recording Media: Quantitative Kinetic Experiments and Models of the A1 to L1₀ Phase Transformation in FePt and Related Ternary Alloy Films

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ABSTRACT

L1₀ ordered FePt continues to be of interest for ultrahigh density magnetic recording media, in particular, heat assisted magnetic recording (HAMR) media. However, when deposited at room temperature, the alloy film forms in the chemically disordered A1 state, requiring a post-deposition anneal at high temperatures or for long times, or deposition onto heated substrates at temperature ≥ 400 °C to form the ordered L1₀ phase. It has been of interest to identify ternary alloying additions that can reduce the post deposition annealing or the elevated deposition temperatures, and to examine the impact of deposition at elevated temperatures on the transformation kinetics.

Binary and ternary alloy films were sputter deposited from elemental targets at nominally room temperature at two different thicknesses of 1 micron and 500 nm. The latter films were used for composition analysis using energy dispersive X-ray spectrometry (EDS). The transformation from the A1 phase to the L1₀ phase was studied by differential scanning calorimetry (DSC) using freestanding micron-thick films. The kinetic ordering temperature (KOT), defined as the peak temperature of the DSC trace at a heating rate of 40 °C/min, was used to evaluate the impact of alloy composition and alloying additions on the ordering transformation.

The nine ternary alloying elements and composition ranges are: 0.0 - 2.6 at.% Mg, 0.7 - 12.2 at.% V, 2.2 - 16.3 at.% Mn, 1.6 - 21.5 at.% Ni, 1.3 - 17.3 at.% Cu, 0.0 - 16.7 at.% Ag, 1.9 - 13.8 at.% Au, 1.2 - 12.9 at.% B and 1.4 at.% C. Compared with binary FePt, Cu additions have no impact on the (KOT), whereas all the other additions except C result in an increase of KOT. Additional experiments are necessary to better evaluate the

impact of C additions. Elevated temperature deposition experiments showed that higher deposition temperatures result in faster transformation only for binary films with > 46 at.% Pt.

The time-temperature-transformation (TTT) and isothermal transformation curves for binary FePt and ternary $Fe_{46.7}Cu_{2.4}Pt5_{0.9}$ films were calculated using the Michaelsen-Dahms (MD), $k_2(T)$, $k_2(T)N(T)$ and a new continuous nucleation model, $k_2(T)N(T,t)$. The model that most closely agrees with all available experimental data is the $k_2(T)$ model.

TABLE OF CONTENTS

ACKNOWLEDGMENT	·I
ABSTRACT	III
LIST OF TABLES	ΊΠ
LIST OF FIGURES	XI
LIST OF ACRONYMS / ABBREVIATIONS	ЛХ
1 - INTRODUCTION	• 1
2 - BACKGROUND AND MOTIVATION	· 3
2.1 - Motivation and Hypothesis	· 3
2.2 - Magnetic Recording	• 4
2.2.1 - Magnetic Recording Technology	- 4
2.2.2 - Signal to Noise Ratio	• 7
2.2.3 - Superparamagnetism	. 9
2.2.4 - Alloy Selection	10
2.2.5 - Heat Assisted Magnetic Recording (HAMR)	12
2.3 - The A1 to $L1_0$ Phase Transformation	14
2.3.1 - The Fe-Pt Binary System	14
2.3.2 - Thermodynamics of Phase Transformations	17
2.3.3 - Kinetics of Phase Transformations	20
2.3.4 - Nucleation Condition	24
2.3.5 - Transformation Models	25
2.3.6 – Au-Cu and Ti-Al Binary System	33
2.4 - Rationale for Selecting of Ternary Alloying Elements	37
2.5 - Techniques	40
2.5.1 - Sputtering	40
2.5.2 - Differential Scanning Calometry	41
2.5.3 - Energy Dispersive X-ray Spectrometry (EDS), Wavelength	
Dispersive X-ray Spectrometry (WDS) and Energy Dispersive	
X-ray Fluorescence (EDXRF)	43

3 - Experiment	45
3.1 - Fabrication of FePt Binary and Ternary Alloy Films	45
3.2 - Differential Scanning Calorimetry	46
3.3 - Composition Analysis	50
3.4 - Phase Identification	51
4 - Results and Discussion	53
4.1 - Film Composition	53
4.2 - Binary FePt Films	56
4.3 - Impact of Ternary Additions on the A1 to $L1_0$ Phase Transformation	63
4.3.1 - Impact of Mg to Additions on the A1 to $L1_0$ Phase Transformation	
	64
4.3.2 - Impact of V Additions on the A1 to $L1_0$ Phase Transformation	
	68
4.3.3 - Impact of Mn on Additions on the A1 to $L1_0$ Phase Transformation	
	72
4.3.4 - Impact of Ni and Cu Additions on the A1 to $L1_0$ Phase Transformation	1
	76
4.3.5 - Impact of Ag Additions on the A1 to $L1_0$ Phase Transformation	
	82
4.3.6 - Impact of Au Additions on the A1 to $L1_0$ Phase Transformation	
	86
4.3.7 - Impact of B Additions on the A1 to $L1_0$ Phase Transformation	
	90
4.3.8 – Impact of C Additions on the A1 to $L1_0$ Phase Transformation	10
-	94
4.4 - Elevated Temperature Deposition of FePt Films	97
	71
4.5 - The JMAK Models for the A1 to $L1_0$ Phase Transformation in FePt and	
Related Ternary System	102
4.6 - The A1 to $L1_0$ Transformation Mechanism in FePt System	123
5 - Summary and Conclusions	124
6 - Future Work	127

Appendix A: Binary FePt System and Ternary Alloying Fe-X-Pt Systems	128
Appendix B: X-ray Diffraction Calculation	150
Appendix C: XRD Calculation Validation and Sample Area Correction	156
Appendix D: Order Parameter of FePt System	170
Appendix E: Fitting of k2(T)N(T,t) model	174
Appendix F: X-ray Diffraction Patterns and DSC Traces	178
REFERENCE	276
VITA	287

LIST OF TABLES

Table 2.1: Magnetocrystalline anisotropy energy densities, K_u, for materials related to orof interest for ultra-high density magnetic recording media.[Klemmer 1995; Weller 2000;Shimatsu 2005]p. 11

Table 2.2: The crystal structure designation, namely the prototype, Strukturbericht designation, space group, Pearson's symbol and the ball model of the unit cell, for (γ Fe,Pt), Fe₃Pt, FePt and FePt₃. p. 16

Table 2.3: The numerical values and corresponding physical conditions for nucleationconditions, growth dimensionality and growth mechanism.p. 23

Table 2.4: JMAK parameters, the effective activation energy determined from the JMAKformulation, and the activation energy determined using the Kissinger method for eachnucleation condition.[Kissinger 1956; Berry 2007]p. 26

Table 2.5: Extended volume fraction for the non-isothermal JMAK equations.[Kissinger1956; Berry 2007]p. 26

Table 2.6: The expressions for fraction transformed and the DSC traces of isothermalconditions for constant nucleation rte, burst and site saturation conditions.p. 32

Table 4.1: Composition of binary films of [Berry 2007] re-measured with EDXRF, WDSEDS.p. 54

Table 4.2: Compositions of ternary FeNiPt Films of [Berry 2007] re-measured with EDS.p. 54

Table 4.3: Compositions of ternary FeCuPt Films of [Berry 2007] re-measured with EDS.p. 55

Table 4.4: Film composition, number of grains measured, and grain sizes of A1 and $L1_0$ phases for binary ambient deposited FePt films. The film grain size is determined fromTEM bright field image and XRD using Scherrer's equation.p. 58

Table 4.5: Calibration of nominal temperatures for elevated temperature deposition.

p. 97

Table 4.6: Comparison of the pre-exponential term for the growth velocity, k_2 , and the nucleation conditions in four transformation models, namely, MD, $k_2(T)$, $k_2(T)N(T)$ and $k_2(T)N(T,t)$ models. p. 102

Table 4.7: A serial of shape factor for heterogeneous nucleation (S) and interfacial energy between A1 and L1₀ phase (γ) in k₂(T)N(T,t) model. The decrease of S is compensated by the increase of γ , and S γ^3 is a constant.

Table 4.8: Film composition measured by EDS, equilibrium ordering temperature, Te, estimated from the phase diagrams, and transformation enthalpy, ΔH , fitted from MD model for the four alloys for which TTT diagrams are plotted using MD, k₂(T), k₂(T)N(T) and k₂(T)N(T,t) models. The experimentally determined ΔH is also provided. p. 107

Table 4.9: Film composition measured by EDS, the frequency factor, v, is the fitting parameters for the MD model. The density of nuclei, N, the A1-L1₀ interfacial energy, γ , the growth velocity, v, at 300 and 500 °C, respectively, and the critical nucleus volume, V^* , are calculated after the fitting. The values of γ from this table is used in the k₂(T) and k₂(T)N(T) models.

Table 4.10: Film composition measured by EDS, the growth (Q_G) and nucleation (Q_N) activation energies, growth dimensionality (*m*) and interfacial energy between A1 and L1₀ phase (γ) used for calculating isothermal and TTT curves by using the k₂(T)N(T,t) model. γ is a fitting parameter for this model. p. 108

Table 4.11: Film composition measured by EDS, the density of nuclei, N, and the growth velocity, v, at 300 and 500 °C, respectively, and critical nucleus volume, V^* , for the four alloys for which TTT diagrams are plotted using the $k_2(T)N(T,t)$ model. N,v and V^* are calculated after the fitting.

Table 4.12: The equilibrium temperature, T_e , the coherent stability temperature, T_k , and the coherent instability temperature, T_s for binary AuCu and FePt system. p. 123

LIST OF FIGURES

Figure 2.1: Areal storage density by year for both HDD products and laboratory demonstrations. Figure reproduced from [Coufal 2006]. p. 5

Figure 2.2: Schematic of longitudinal and perpendicular recording techniques. Figure reproduced from [Grochowski 2005]. p. 6

Figure 2.3: Simplified bit pattern on grain structure illustrating effect of grain size on SNR. In actual recording systems, bit transitions will follow the grain boundaries, and therefore have more jagged boundaries than shown here. Figure reproduced from [Berry 2007].

Figure 2.4: A schematic writing process of heat assisted magnetic recording. Figure reproduced from [Kryder 2008]. p. 13

Figure 2.5: Phase Diagram of Fe-Pt binary system. Figure reproduced from [Massalski 1990]. p. 15

Figure 2.6: Schematic of shape factor for heterogeneous nucleation. p. 19

Figure 2.7: Phase Diagram of Au-Cu binary system. Figure reproduced from [Massalski 1990]. p. 34

Figure 2.8: Phase Diagram of Ti-Al binary system. Figure reproduced from [Massalski 1990]. p. 36

Figure 2.9: Periodic Table used for choosing ternary elements to FePt binary system. Figure reproduced from [Lower 2005]. p. 37

Figure 2.10: Schematics of magnetron sputtering system. Figure reproduced from [VG Scienta 2007]. p. 40

XI

Figure 2.11: Schematics of differential scanning calometry (DSC). Figure reproduced from [The Evitherm Society 2010]. p. 42

Figure 2.12: The principle of WDS,EDS and EDXRF. p. 44

Figure 3.1: Schematic of the construction of the Pt envelope used as sample holders for free-standing films in DSC experiments. Figure reproduced from [Lucadamo 1999; Berry 2007]. p. 49

Figure 3.2: The schematic drawing of PANAlytical X'Pert x-ray diffractometer. Figurereproduced from [Berry 2007].p. 52

Figure 3.3: θ -2 θ XRD patterns for Fe_{44.2} Ag_{16.7}Pt_{39.0} samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peaks such as 001 and 110. The formation of A1 (fcc) Ag upon annealing is also clearly evident. The sample was annealed at 40 °C/min to 700 °C.

Figure 4.1: Kinetic ordering temperature is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 59

Figure 4.2: Activation energy is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 59

Figure 4.3: Transformation enthalpy is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 59

Figure 4.4: Curie temperature of $L1_0$ phase is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.5: Curie temperature as a function of composition for the A1 to $L1_0$ transformation in FePt. These values are compared with Curie temperatures reported in the literature, Lines are shown to guide the eyes. [Fallot 1938; Kußmann 1950; Wirths 1976; Gasnikova 1983; Klemmer 1995; Nose 2003] p. 60

Figure 4.6: The plan-view bright field TEM image for $Fe_{51.4}Pt_{48.7}$ film. (a) left: asdeposited and (b) right: annealed to 700 °C. p. 61

Figure 4.7: The cross-section bright field TEM images for as-deposited Fe_{51.4}Pt_{48.7} film at two magnifications. p. 61

Figure 4.8: The cross-section dark field TEM images for as-deposited Fe_{51.4}Pt_{48.7} film at two magnifications. p. 62

Figure 4.9: The cross-section TEM images for as-deposited Fe_{51.4}Pt_{48.6} film (a) left: bright filed and (b) right: dark field. p. 62

Figure 4.10: θ -2 θ XRD patterns for Fe_{52.1}Mg_{1.8}Pt_{46.1} samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 001 and 110. The sample was annealed at 40 °C/min to 700 °C. p. 65

Figure 4.11: Kinetic ordering temperature is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.12: Activation energy is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 66

Figure 4.13: Transformation enthalpy is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 66

Figure 4.14: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 66

Figure 4.15: Kinetic ordering temperature is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.16: Activation energy is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 67

Figure 4.17: Transformation enthalpy is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 67

Figure 4.18: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 67 Figure 4.19: θ -2 θ XRD patterns for Fe_{56.0}V_{0.7}Pt_{43.3} samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 001 and 110. The sample was annealed at 40 °C/min to 700 °C. p. 69

Figure 4.20: Kinetic ordering temperature is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 70

Figure 4.21: Activation energy is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 70

Figure 4.22: Transformation enthalpy is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 70

Figure 4.23: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 70

Figure 4.24: Kinetic ordering temperature is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 71

Figure 4.25: Activation energy is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 71

Figure 4.26: Transformation enthalpy is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 71

Figure 4.27: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 71

Figure 4.28: θ -2 θ XRD patterns for Fe_{45.7}Mn_{10.7}Pt_{43.6} samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 001 and 110. The sample was annealed at 40 °C/min to 700 °C. p. 73

Figure 4.29: Kinetic ordering temperature is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 74

Figure 4.30: Activation energy is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 74

Figure 4.31: Transformation enthalpy is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 74

Figure 4.32: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 74 Figure 4.33: Kinetic ordering temperature is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.34: Activation energy is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 75

Figure 4.35: Transformation enthalpy is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 75

Figure 4.36: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.37: Kinetic ordering temperature is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 78

Figure 4.38: Activation energy is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 78

Figure 4.39: Transformation enthalpy is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 78

Figure 4.40: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 78

Figure 4.41: Kinetic ordering temperature is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 79

Figure 4.42: Activation energy is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 79

Figure 4.43: Transformation enthalpy is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 79

Figure 4.44: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 79

Figure 4.45: Kinetic ordering temperature is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 80

Figure 4.46: Activation energy is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 80

Figure 4.47: Transformation enthalpy is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 80

Figure 4.48: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 80

Figure 4.49: Kinetic ordering temperature is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.50: Activation energy is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 81

Figure 4.51: Transformation enthalpy is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 81

Figure 4.52: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 81

Figure 4.53: θ -2 θ XRD patterns for Fe_{44.3}Ag_{16.7}Pt_{39.0} samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peaks such as 001 and 110. The formation of A1 (fcc) Ag upon annealing is also clearly evident. The sample was annealed at 40 °C/min to 700 °C.

Figure 4.54: Kinetic ordering temperature is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.55: Activation energy is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 84

Figure 4.56: Transformation enthalpy is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 84

Figure 4.57: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.58: Kinetic ordering temperature is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 85

Figure 4.59: Activation energy is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 85

Figure 4.60: Transformation enthalpy is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 85

Figure 4.61: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.62: θ -2 θ XRD patterns for Fe4_{5.2} Au_{13.8} Pt_{41.0} samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 110. The formation of A1 (fcc) Au upon annealing is also clearly evident. The sample was annealed at 40 °C/min to 700 °C. p. 87

Figure 4.63: Kinetic ordering temperature is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 88

Figure 4.64: Activation energy is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 88

Figure 4.65: Transformation enthalpy is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 88

Figure 4.66: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 88 Figure 4.67: Kinetic ordering temperature is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.68: Activation energy is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 89

Figure 4.69: Transformation enthalpy is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 89

Figure 4.70: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.71: θ -2 θ XRD patterns for Fe_{43.0} B_{11.8} Pt_{45.22}samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 001 and 110. The sample was annealed at 40 °C/min to 700 °C. p. 91

Figure 4.72: Kinetic ordering temperature is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 92

Figure 4.73: Activation energy is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 92

Figure 4.74: Transformation enthalpy is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines The solid black curve is drawn to guide the eye. p. 92

Figure 4.75: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 92

Figure 4.76: Kinetic ordering temperature is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 93

Figure 4.77: Activation energy is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 93

Figure 4.78: Transformation enthalpy is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 93

Figure 4.79: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 93

Figure 4.80: Kinetic ordering temperature is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 95

XXIII

Figure 4.81: Activation energy is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 95

Figure 4.82: Transformation enthalpy is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 95

Figure 4.83: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 95

Figure 4.84: Kinetic ordering temperature is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 96

Figure 4.85: Activation energy is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 96

Figure 4.86: Transformation enthalpy is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. p. 96

Figure 4.87: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye. p. 96 Figure 4.88: θ -2 θ XRD pattern for Fe_{50.5}Pt_{49.5} sample. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 001 and 110. p. 100

Figure 4.89: θ -2 θ XRD pattern for Fe_{56.4}Pt_{43.6} sample. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 001 and 110. p. 100

Figure 4.90: ETDPT is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as black dashed vertical lines. The solid black curve is drawn to guide the eye. The blue and red dashed vertical lines indicates the compositions for films deposited at 200 and 300 ° C, respectively.

Figure 4.91: Activation energy is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as black dashed vertical lines. The solid black curve is drawn to guide the eye. The data points with vertical grey dashed line samples without DSC peaks. p. 101

Figure 4.92: Transformation enthalpy is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as black dashed vertical lines. The data points with vertical grey dashed line are samples without DSC peaks.

Figure 4.93: Curie temperature of $L1_0$ phase is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as black dashed vertical lines. The data points with vertical grey dashed line are samples without DSC peaks.

Figure 4.94: The fitting of MD model with four non-isothermal DSC traces for the A1 to $L1_0$ transformation in Fe_{52.9}Pt_{47.1} at the heating rate of (a) 20°C/min, (b) 40°C/min, (c) 80°C/min and (d) 160°C/min. p. 109

Figure 4.95: Comparison of experimental and simulated DSC trace using $k_2(T)N(T,t)$ model for the A1 to L1₀ transformation in Fe_{52.9}Pt_{47.1} at the heating rate of (a) 20°C/min, (b) 40°C/min, (c) 80°C/min and (d) 160°C/min. p. 110

Figure 4.96: TTT diagrams for the A1 to L1₀ transformation in Fe_{46.7}Cu_{2.4}Pt_{50.9} calculated using the (a) MD, (b) $k_2(T)$, (c) $k_2(T)$ N(T) and $k_2(T)$ N(T,t) models. The compositions used for these four models are from EDS results. These TTT diagrams give the times and temperatures needed for an isothermally annealed film to achieve a desired fraction transformed. Here, the leftmost solid line represents a fraction transformed of 0.05, while the dashed line and the following solid line are 0.50 and 0.95, respectively. A1 is the quenched metastable phase, whereas L1₀ is the thermodynamically stable phase. T_e is the equilibrium order-disorder temperature for this alloy.

Figure 4.97: Fraction transformed vs time at multiple annealing temperatures for $Fe_{46.7}Cu_{2.4}Pt_{50.9}$. The lines are predicted curves using (a) MD, (b) $k_2(T)$, (c) $k_2(T)$ N(T) and $k_2(T)$ N(T,t) models, and the points are found experimentally. The agreement between the MD and $k_2(T)$ models and experiment is excellent, whereas that of the $k_2(T)$ N(T) model is not. For this latter model, all of the calculated curves are shifted to significantly longer times.

Figure 4.98: TTT diagrams comparing the transformation kinetics in $Fe_{44.5}Pt_{55.5}$, $Fe_{51.4}Pt_{48.6}$ and $Fe_{52.9}Pt_{47.1}^*$ using (a) MD, (b) $k_2(T)$, (c) $k_2(T)$ N(T) and (d) $k_2(T)$ N(T,t) models. The compositions used for these four models are from EDS results. These TTT diagrams give the times and temperatures needed for an isothermally annealed film to achieve a desired fraction transformed. Here, the leftmost solid line represents a fraction transformed of 0.05, while the dashed line and the following solid line are 0.50 and 0.95, respectively. A1 is the quenched metastable phase, whereas $L1_0$ is the thermodynamically p. 113

Figure 4.99: The experimental and the $k_2(T) N(T,t)$ calculated DSC traces for the A1 to $L1_0$ transformation in Fe_{44.5}Pt_{55.5}. The compositions used for these four models are from EDS results. T_e is taken as 675 °C from binary FePt phase diagram p. 114

Figure 4.100: (a) Phase diagram of Fe-Pt binary system.[Massalski 1990] (b) the schematic drawing for determining T_e for Fe_{44.5}Pt_{55.5} film from phase diagram. T_e is chosen as the temperature exactly midway between the boundary temperatures marked with open circles at the terminal of the vertical line. p. 115

Figure 4.101: Comparison of elevated deposition results of binary FePt films with around 49.0 at.% Pt with TTT diagrams of $Fe_{51.4}Pt_{48.6}$ calculated using (a) $k_2(T)$, (b) $k_2(T)$ N(T) and (c) $k_2(T)$ N(T,t) models. The deposition temperature and time for binary FePt films with around 49.0 at.% are presented in blue cycles. The states of fully and partially transformed to L1₀ phase after deposition are presented by closed and open cycles, respectively.

Figure 4.102: TTT diagrams comparing the transformation kinetics in 1 μ m and 10 nm thick Fe_{51.4}Pt_{48.6} film using (a) k₂(T), (b) k₂(T) N(T) and (c) k₂(T) N(T,t) models. The compositions used for these three models are from EDS results. These TTT diagrams give the times and temperatures needed for an isothermally annealed film to achieve a desired fraction transformed. Here, the leftmost solid line represents a fraction transformed of 0.05, while the dashed line and the following solid line are 0.50 and 0.95, respectively. A1 is the quenched metastable phase, whereas L1₀ is the thermodynamically stable phase.

Figure 4.103: Comparison of TTT diagrams for 10 nm thick $Fe_{51.4}Pt_{48.6}$ film using (a) $k_2(T)$, (b) $k_2(T)$ N(T) and (c) $k_2(T)$ N(T,t) models with laser and furnace annealed results. The compositions used for these three models are from EDS results. These TTT diagrams give the times and temperatures needed for an isothermally annealed film to achieve a desired fraction transformed. Here, the leftmost solid line represents a fraction transformed of 0.10., while the dashed line and the following solid line are 0.50 and 0.90, respectively. A1 is the quenched metastable phase, whereas $L1_0$ is the thermodynamically stable phase. The blue cycles on left are laser annealed 10 nm thick FePt film with order parameter of 0.1. The blue, olive and red open cycles present furnace annealed FePt sample with order parameter of 0.1, 0.5 and 0.9, respectively. The blue closed cycles are laser annealed room temperature deposited 10 nm Fe₅₀Pt₅₀ film with 10% ordering.[Inaba 2010] The open cycles in blue, olive and red are 60 seconds furnace annealed room temperature deposited 10 nm Fe₅₀Pt₅₀ film with 10%, 50% and 90% ordering, respectively.[Inaba 2010] p. 120-121

Figure 4.104: The calculated fraction transformed curve at 700 °C for $Fe_{51.4}$.Pt_{48.6} film using (a) $k_2(T)$, (b) $k_2(T)$ N(T) and (c) $k_2(T)$ N(T,t) models. The black solid and open cycles are laser and furnace annealed 10 nm thick FePt film, respectively. The red closed cycles are 700 °C laser annealed Fe_{50} Pt₅₀ films,[Inaba 2010] and the blue open cycles are 700 °C furnace annealed FePt films.[Ristau 1999] p. 122

LIST OF ACRONYMS/ABBREVIATIONS

AD	Areal density
DSC	Differential scanning calorimetry
EDS	Energy dispersive x-ray spectrometry
EDXRF	Energy dispersive x-ray fluorescence
GMR	Giant magnetoresistance
HAMR	Heat assisted magnetic recording
HDD	Hard drive disk
LMR	Longitudinal magnetic recording
MCA	Magnetocrystalline anisotropy energy
MR	Magnetoresistive
PMR	Pperpendicular magnetic recording
RAMAC	Random access method of accounting and control
SNR	Signal to noise ratio
SUL	Soft underlayer
TTT	Time-temperature-transformation
WDS	Wavelength dispersive x-ray spectrometry
А	Atomic jump distance
ϕ	DSC signal
Г	Interface energy
τ	Nucleation time for L1 ₀ phase
Ω	Vibration frequency of the atoms

ΔG^*	Critical free energy
ΔG_m	Atomic migration free energy per atom.
ΔG_{mol}	Molar free energy
ΔG_S	Misfit strain free energy
ΔG_V	Volumetric free energy
ΔH	Latent heat
ΔS_m	Migration entropy
C_0	Number of potential nucleation sites per unit volume
C_1	Heterogeneous nucleation sites per unit volume
I	Nucleation rate
Io	Pre-exponential factor in the expression for nucleation rate
K	Geometry factor
k ₂	Pre-exponent term for growth velocity
K _u	Magnetocrystalline anisotropy energy density
М	Growth dimensionality
Ν	Avrami exponent
Ν	Nucleation density
Q_{eff}	Effective activation energy
Q _G	Activation energy for growth
Q _{kiss}	Kissinger activation energy
Q _N	Activation energy for nucleation
r*	Critical radius for nucleus

S(θ)	Shape factor for heterogeneous nucleation
Т	Growth time for L1 ₀ phase
T _c	Curie temperature of L10 phase
Te	Equilibrium ordering temperature
v	Growth velocity
V^{α}	Real volume of parent phase
V ^β	Real volume of product phase
X_E	Extended volume fraction transformed
X _v	Actual volume fraction transformed
Z	Zeldovich non equilibrium factor

1 Introduction

The hard drive industry is facing the challenge of manufacturing drives with an areal density over 1 terabit per square inch. The main challenge is that the current Co based alloy is reaching its physical limit, namely superparamagnetism, wherein the thermal energy at room temperature is able to demagnetize small grains and result in loss of stored information.[Bandic 2008] Therefore, the solution is to adopt a material that has a higher magnetocrystalline anisotropy (MCA) constant. Ordered L1₀ FePt is the most promising candidate because of its higher MCA than current recording media and better corrosion resistance compared with rare-earth based alloys.[Klemmer 1995; Weller 1999] Ambient temperature sputtered films form in the chemically disordered A1 phase. Post deposition annealing at high temperature or at low temperature for long annealing times is necessary to form the chemically ordered L1₀ phase. The alternative way is to deposit FePt at an elevated temperature to form the L1₀ phase.

The impact of film composition on the A1 to $L1_0$ transformation has been studied and the lowest kinetic ordering temperature is ~ 359 °C.[Berry 2007] Further work on lowering the deposition temperature or shortening the transformation time by adding ternary alloying elements or by choosing alternative fabrication methods is expected to benefit the hard drive industry.

In this work, the impact of ternary additions as well as deposition temperature on the A1 to L1₀ transformation in FePt have been systematically evaluated. The ternary additions, Mg, V, Mn, Ni, Cu, Ag, Au, B and C, present a variety of chemical properties and cover seven groups in the periodic table.[Wang 2010] In addition, three transformation models, namely MD, $k_2(T)$ and $k_2(T)N(T)$ have been re-investigated with updated film compositions; and a new continuous nucleation model, $k_2(T)N(T,t)$, has been developed. The time-temperature-transformation (TTT) and isothermal transformation curves for several films have been calculated. The transformation model that best fits all available experimental data is the $k_2(T)$ model. Elevated temperature deposited films result in faster transformation kinetics than predicated by the $k_2(T)$ model.

2 Background and Motivation

2.1 Motivation and Hypothesis

In the past decade, the hard drive industry is striving for next generation hard drive with areal density in the Terabit range. The most promising candidate for the magnetic recording medium is ordered $L1_0$ FePt because of its high MCA and good corrosion resistance. However, ambient temperature sputtered films form the chemically disordered A1 phase. Post deposition annealing at high temperature or at low temperature with long annealing time is necessary to form the chemically ordered $L1_0$ phase. The alternative way is to deposit binary FePt at elevated temperatures.

The impact of composition on the transformation kinetics of ambient temperature deposited FePt films has been reported.[Berry 2007] The lowest kinetic ordering temperature, defined as the peak temperature of DSC trace at the heating rate of 40 C/min, is around 359 °C. Although hard drive companies are able to manufacture magnetic recording media above 400 °C, there is still interest in identifying ternary

additions that could reduce the kinetic ordering temperature or the elevated deposition temperature.

The hypotheses that this work aims to test is the following; that it is possible (i) to enhance the kinetic of $L1_0$ formation by the addition of a ternary element or (ii) by modification of the processing steps.

Developing transformation models combined with elevated temperature deposition experiments can assist in quantitatively describing the A1 to $L1_0$ phase transformation kinetics in binary FePt films.

2.2 Magnetic Recording

2.2.1 Magnetic Recording Technology

The idea of magnetic storage was introduced by Oberlin Smith back in 1888 in the journal Electrical World.[Daniel 1999] The first magnetic recording device, which only recorded a signal on a magnetic drum, was invented by Valdemar Poulsen in 1898. More than half a century later, in 1956 Rey Johnson at IBM utilized a particulate film to make the first hard drive disk (HDD), named RAMAC (Random Access Method of Accounting and Control), which stored 5 MB over 240 square feet of surface area.[Hoagland 2003] Since then, an eight order of magnitude increase in areal density (AD) was primarily achieved by scaling down the device dimensions along with the switch from iron oxide
particles to Co based thin film media. The introduction of the magnetoresistive (MR) sensor in the early 90's and the transition to giant magnetoresistance (GMR) sensor resulted in the sharp increase for the areal density since 1990s.[Speliotis 1999; McFadyen 2006] Recently, Toshiba has released MK7559GSXP hard drive with AD of 541 Gbit/in². It is envisioned that hard disk drives will reach 1 Tbits/in² in the foreseeable future. (Figure 2.1)



Figure 2.1: Areal storage density by year for both HDD products and laboratory demonstrations. Figure reproduced from [Coufal 2006].

Nowadays, two magnetic recording technologies, longitudinal magnetic recording (LMR) and perpendicular magnetic recording (PMR), coexist in the commercial market. The magnetization in a bit is directed circumferentially along the track direction for conventional LMR or perpendicular to the disk surface in current PMR as shown in Fig. 2.2).[Grochowski 2005] Longitudinal magnetic recording technology has dominated the hard disk drive industry since the invention of the first hard drive, whereas the first

commercially available hard drive with perpendicular magnetic recording technology manufactured by Toshiba was released to the consumer market in 2005. Due to the technical progress of the SUL (soft underlayer) and significant improvement of head design, PMR can deliver >3X of increase in the storage density because of the cylinder shape of the magnetic bits; and can provide comparable or even superior performance to LMR. [Piramanayagam 2007; Merritt 2010]



Figure 2.2: Schematic of longitudinal and perpendicular recording techniques. Figure reproduced from [Grochowski 2005].

2.2.2 Signal to Noise Ratio

The stored information on a hard dirsk drive is recorded by a series of zeros and ones that corresponds to the absence or presence of the change in magnetization direction, respectively. In order to read back the data on HDD, the magnetic head must be able to identify the difference between zeros and ones, ie., it must be able to sense the transition of the magnetization direction of each magnetic bit. Thus an acceptable signal to noise ratio (SNR) defined in Eq. 2.1, which is proportional to the channel density, D_{ch}, the bit size, B, and track width, W, and is inversely proportional to the grain size, D, is a must for magnetic recording.[Wang 1999]

$$SNR = \frac{D_{ch}B^2W}{2\pi D^3}$$
(2.1)

Figure 2.3 demonstrates the correlation between grain size and bit size, and the effect of grain size on SNR.[Berry 2007] Storage areal densities that are several orders of magnitude higher than for current media can be achieved by shrinking the bit size, which is comprised of a collection of uniformly magnetized smaller crystalline grains. However, with current technology, the magnetic read-head cannot distinguish the transition of magnetization direction for adjacent bits due to poor SNR that is caused by the decrease of bit size when the grain size is kept the same. To overcome this issue and maintain reliable SNR, it is necessary for recording media to have a small grain size.



Figure 2.3: Simplified bit pattern on grain structure illustrating effect of grain size on SNR. In actual recording systems, bit transitions will follow the grain boundaries, and therefore have more jagged boundaries than shown here Figure reproduced from [Berry 2007].

2.2.3 Superparamagnetism

Small grain size leads current Co-based ferromagnetic alloys to their physical limit named superparamagnetism, wherein thermal energy at ambient temperature is sufficient enough to rotate the magnetization direction of a single bit away from its structure's easy axis in a relatively short time period (less than 10 years).[Bandic 2008] The stability of data storage is determined by the so-called "stability criterion", where the ratio of magnetocrystalline anisotropy energy density (MCA), K_u , and grain volume, V, to thermal energy, k_BT should at least over 50. (Eq. 2.2) [Weller 1999; Weller 2000]

$$\frac{K_u V}{k_B T} \ge 50 - 70 \tag{2.2}$$

Future ultrahigh density recording media with <10 nm grain size must have higher MCA than current Co-based alloys in order not to reach the superparamagnetic limit.

2.2.4 Alloy Selection

The magnetocrystalline anisotropy energy densities of four categories of alloy systems, including pure elements, Co-alloys and the L1₀ and rare-earth based alloys are listed in Table 2.1.[Klemmer 1995; Weller 2000; Shimatsu 2005] The chemically-ordered, tetragonal L1₀ crystal structure of FePt alloy with K_u at 6.6×10⁷ erg/cm³ is much higher than current Co-alloy based media. The high MCA together with good corrosion resistance compared to the rare-earth based alloys make FePt the most attractive candidate for use as next generation ultrahigh recording media in hard disk drives.

Table 2.1: Magnetocrystalline anisotropy energy densities, K_u, for materials related to or of interest for ultra-high density magnetic recording media.[Klemmer 1995; Weller 2000; Shimatsu 2005]

Alloy System	Material	$\frac{K_u (10^6 \text{ J/m}^3)}{(10^7 \text{ erg/cm}^3)}$				
Duro Elemente	hcp-Co	0.45				
Fulle Elements	Fe	0.048				
Co Allows	CoPtCr	1.0				
Co-Alloys	Co ₃ Pt	2.0				
	FePd	1.8				
L 1. Ordered Structures	FePt	6.6-10				
L1 ₀ Ordered Structures	CoPt	4.9				
	MnAl	1.7				
	$Fe_{14}Nd_2B$	4.6				
Rare-Earth Transition Metal Compounds	SmCo ₅	11-20				
	NdCo ₅	15				

2.2.5 Heat Assisted Magnetic Recording (HAMR)

Achieving ultrahigh storage areal density by reduction of magnetic bit size requires the reduction of grain size to maintain SNR in the medium. Adopting materials with higher Ku can overcome the superparamagnetic limit of current Co-based medium, but require stronger writing fields to switch magnetization direction of a bit due to the increase in the anisotropy field of the material. Conventional magnetic writing technology cannot be directly implemented for future magnetic recording because of the limitation in writing field (FeCo has the maximum known saturation magnetization of 2.4 T). A solution for the "trilemma" situation of balancing writeability, thermal stability and medium SNR is heat assisted magnetic recording (HMAR) proposed by Saga in 1999. [Saga 1999; Richter 2006]

The coercivity of high anisotropy ferromagnetic materials drops to zero at the Curie temperature, above which ferromagnetic material becomes paramagnetic. Therefore, magnetic recording can be realized by heating up the medium with a laser to a temperature where the coercivity is below writing field; and then applying a magnetic field at the given temperature to align the magnetic bits. The bits are stabilized to high coercivity when the medium is cooled back to ambient temperature. (Figure 2.4) [Rottmayer 2006; Kryder 2008]



Figure 2.4: A schematic writing process of heat assisted magnetic recording. Figure reproduced from [Kryder 2008].

2.3 The A1 to L1₀ Phase Transformation

2.3.1 The Fe-Pt Binary System

The chemically-ordered $L1_0$ FePt phase is the preferred candidate for future recording media. The most cost and time effective way of manufacturing recording medium for the hard drive industry is room temperature sputtering. However, room temperature deposited FePt forms the chemically disordered A1 structure, which unfortunately has low MCA and cannot be used for the magnetic recording layer. A post anneal step is necessary to form the chemically ordered $L1_0$ phase. To better understand the relationship between the A1 and $L1_0$ structures for Fe-Pt binary system, it is useful to examine the phases presented in binary Fe-Pt phase diagram.

Figure 2.5 is the phase diagram for Fe-Pt system, wherein 7 phases, including three chemically ordered crystal structures Fe₃Pt, FePt, and FePt₃, one liquid, and three chemically disordered solid solution structures, (α -Fe), (δ -Fe) and (γ -Fe,Pt), are present in the system.[Massalski 1990] The crystal structure designation for each phase of interest, including the prototype, Strukturbericht designation, space group, Pearson's symbol and the ball model of the unit cell, is listed in Table 2.2.

The prototype of L1₀ unit cell is AuCu I, where Cu atoms occupy the $(0, \frac{1}{2}, \frac{1}{2})$ position and Au atoms occupy the (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, 0)$ positions. Therefore, for perfect L1₀ FePt with the equiatomic composition, Fe atoms take up one type of lattice sites while Pt atoms take up the other type of lattice sites.

The L1₂ phases of Au₃Cu and AuCu₃ with site positions at (0, 0, 0) and $(0, \frac{1}{2}, \frac{1}{2})$, are the prototypes of L1₂ Fe₃Pt and FePt₃, respectively. In both structures, Fe and Pt atoms substitute for Au and Cu, respectively. The ordered phases are either ferromagnetic with low anisotropy field or paramagnetic, thus L1₂ Fe₃Pt and FePt₃ are not the phases of interest for magnetic recording.[Gutfleisch 2005]

The chemically disordered A1 phase has a FCC structure with Fe and Pt atoms are randomly distributed on the lattice sites. FePt alloys with A1 phase are unsuitable for the magnetic recording medium because of low values of the MCA.



Figure 2.5: Phase Diagram of Fe-Pt binary system. Figure reproduced from [Massalski 1990].

Phase	Prototype	Strukturbericht Designation	Space Group	Pearson's Symbol	Unit Cell
(y Fe, Pt)	Cu	A1	Fm3m	cF4	
Fe ₃ Pt	AuCu ₃	L1 ₂	Pm∃m	cP4	
FePt	AuCu I	L1 ₀	$P\frac{4}{m}mm$	tP2	
FePt ₃	AuCu ₃	L1 ₂	Pm3m	cP4	

Table 2.2: The crystal structure designation, namely the prototype, Strukturbericht designation, space group, Pearson's symbol and the ball model of the unit cell, for (γ Fe,Pt), Fe₃Pt, FePt and FePt₃.

2.3.2 Thermodynamics of Phase Transformations

Room temperature sputtered FePt films with the chemically disordered A1 structure require a post-anneal step to form the chemically ordered L1₀ structure. The ordering transformation of FePt can be defined as heterogeneous, thermally activated, interface controlled, and a order-disorder transformation according to Christian's designation. [Christian 1975]

In general, the driving force, ΔG , for the phase transformation can be expressed as Eq. 2.3, where V is the volume of transformed phase, A is the interface area, γ is interface energy, ΔG_V and ΔG_S are the magnitude of the volumetric free energy change and misfit strain free energy, respectively.

$$\Delta G = -V\Delta G_V + A\gamma + V\Delta G_S \tag{2.3}$$

If we ignore the variation of γ with interface orientation and assume a spherical shape for nucleus with radius of r, then Eq. 2.3 becomes

$$\Delta G = -\frac{4}{3}\pi r^3 \left(\Delta G_V - \Delta G_S \right) + 4\pi r^2 \gamma \tag{2.4}$$

Differentiating Eq. 2.4 yield critical radius for nucleus and critical free energy.

$$r^* = \frac{2\gamma}{\left(\Delta G_V - \Delta G_S\right)} \tag{2.5}$$

$$\Delta G^* = \frac{16\pi r^3}{3\left(\Delta G_V - \Delta G_S\right)^2} \tag{2.6}$$

The rate for homogeneous nucleation is the form in Eq. 2.7

$$I = \dot{N}_{HOM} = Z\omega C_0 \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right)$$
(2.7)

where ω is the vibration frequency of the atoms, Z is the Zeldovich non equilibrium factor and C₀ is the number of potential nucleation sites per unit volume in the phase and ΔG_m is the atomic migration free energy per atom.

The activation energy barrier for heterogeneous nucleation is given by

$$\frac{\Delta G_{Het}^*}{\Delta G_{Hom}^*} = S(\theta)$$
(2.8)

where $S(\theta)$ is a shape factor given by

$$S(\theta) = \frac{1}{2} (2 + \cos \theta) (1 - \cos \theta)^2$$
(2.9)

where θ , shown in Fig. 2.6, is the contact angle for two phases. The rate for heterogeneous nucleation can be expressed in Eq. 2.10, where C₁ is the heterogeneous nucleation sites per unit volume. [Porter 1981]

$$\dot{N}_{Het} = \omega C_1 \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right)$$
 (2.10)



Figure 2.6: Schematic of shape factor for heterogeneous nucleation.

2.3.3 Kinetics of Phase Transformations

The transformation kinetics for FePt can be modeled by using Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory, which is widely used in the field of transformations because of its generality and simplicity. For the A1 to $L1_0$ phase transformation, the JMAK theory can be expressed as simple as Eq. 2.11, where X_v and X_E are the volume fraction transformed and extended volume fraction transformed, respectively.

$$X_{v} = 1 - \exp\left(-X_{E}\right) \tag{2.11}$$

The extended volume, which counts for the entire transformed volume without considering impingement of transformed domains, is a virtual concept. Thus the overlapped domains should be counted twice or even multiple-times in order to obtain the virtually defined extended volume.

Considering a transformation from parent α phase to product β phase in an infinitely large system, the total volume V is given

$$V = V^{\alpha} + V^{\beta} \tag{2.12}$$

where V^{α} and V^{β} are the real volume of parent and product phases, respectively. The extended volume, V_E^{β} , the total volume of extended β phase that accounts for both the impinged area for the growing region and phantom nucleation sites within already transformed regions, can be related to V_{β} by applying the correction (Eq. 2.13) with two

basic assumptions; first, nuclei and growth regions are spatially randomly distributed and second, the growth rate is constant.

$$dV^{\beta} = X^{\alpha} dV_{E}^{\beta} = \left(1 - \frac{V^{\beta}}{V}\right) dV_{E}^{\beta} = \left(1 - X^{\beta}\right) V_{E}^{\beta}$$
(2.13)

where X^{α} and X^{β} are fraction of α and β phases, respectively. The general JMAK expression can be acquired by rearranging the Eq. 2.13 and integrating the integrals.

$$\frac{dV^{\beta}}{\left(1-X^{\beta}\right)} = dV_{E}^{\beta} \tag{2.14}$$

$$-\ln\left(1-X^{\beta}\right) = X_{E}^{\beta} \tag{2.15}$$

$$1 - X_V^\beta = \exp\left(-X_E^\beta\right) \tag{2.16}$$

Developing and validating transformation models by implementing JMAK theory with several scenarios of nucleation and growth can facilitate the research on the A1 to $L1_0$ transformation. The mathematical modeling studies for transformation are focused on two experimental conditions, isothermal and constant heating rate.

The JMAK theory for isothermal experiments can be expressed as

$$X(t) = 1 - \exp(-(kt)^{n})$$
 (2.17)

where X(t) is the fraction transformed at time t, k is the pre-factor and n is the Avrami exponent (Eq. 2.18), which includes the contributions from nucleation mode, growth mechanism and dimensionality (Table 2.3). Rearranging Eq.2.17 yields Eq. 2.19. The slope of the line function equals to the Avrami exponent and the intercept is lnK^n .

Avrami exponent (n) = nucleation condition + growth dimensionality \times growth mechanism (2.18)

$$\ln\left(-\ln\left(1-X_{V}\right)\right) = \ln K^{n} + n\ln t \qquad (2.19)$$

Table 2.3 The numerical values and corresponding physical conditions for nucleation conditions, growth dimensionality and growth mechanism.

Nucleation condition	Growth dimensionality	Growth mechanism				
0: site-saturated nucleation	1: 1-D growth	½: diffusion controlled transformations				
1: constant nucleation rate	2: 2-D growth	1: interface controlled transformations				
	3: 3-D growth					

2.3.4 Nucleation Condition

In order to implement the JMAK theory and to develop mathematical models for the transformation kinetics, it is necessary to identify the transformation scenarios associated with nucleation and growth. Three possible nucleation conditions, namely, athermal site-saturated, burst and continuous (constant nucleation rate for isothermal anneals) nucleation conditions, are considered in this work.

The nucleation density for athermal site-saturated condition is independent of temperature, and the nucleation activation energy is zero. For burst nucleation, the nucleation density is function of temperature, therefore, the transformation activation energy is the combined result of nucleation and growth activation energies. For the continuous nucleation condition, the nucleation density is a function of both temperature and time.

2.3.5 Transformation Models

To understand the transformation kinetics in the FePt system, four variants of the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model, namely, MD, $k_2(T)$, $k_2(T)N(T)$ and $k_2(T)N(T,t)$ models, have been developed to evaluate the nucleation and growth of the L1₀ phase. Table 2.4 gives the JMAK parameters, Kⁿ (defined in Eq. 2.19), the effective activation energy determined from the JMAK formulation, and the average activation energy determined using the Kissinger method for the four variants models.[Berry 2007] In the Table 2.4, *k* and k_2 are the geometry factor and pre-exponent term for growth velocity, respectively. Q_N and Q_G are activation energy for nucleation and growth, respectively. I_0 is the pre-exponential factor in the expression for nucleation rate, and *N* is the nucleation density.

Table 2.5 lists the expression of extended volume fraction for the non-isothermal JMAK equations of three nucleation conditions.[Berry 2007] The time t' and τ are the growth time and nucleation time for L1₀ phase, respectively. β is the heating rate for the DSC experiment.

The approach of solving continuous nucleation rate case is to derive the expression for the fraction transformed, and then use a numerical calculation to obtain the DSC signal for the temperature range of interest. Attention should be paid to the nucleation term in the expression for the fraction transformed, because either the energy barrier for the formation of a critical nucleus, ΔG^* , or the activation energy barrier for nucleation, Q_N , could be used. For easy calculation of the critical radius and volume for nucleation, the ΔG^* term is adopted as the first step to tackle the issue.

Table 2.4: JMAK parameters, the effective activation energy determined from the JMAK formulation, and the activation energy determined using the Kissinger method for three nucleation condition.[Kissinger 1956; Berry 2007]

	Constant nucleation rate	Burst nucleation	Pre-existing nuclei				
Models	$k_2(T)N(T,t)$	$k_2(T)N(T)$	MD and $k_2(T)$				
K ⁿ	$\frac{k I_0 k_2^m}{m+1} exp\left(-\frac{Q_N + m Q_G}{k_B T}\right)$	$k I'_{0} k_{2}^{m} exp\left(-\frac{Q_{N} + mQ_{G}}{k_{B}T}\right)$	$k N k_2^m exp\left(-\frac{m Q_G}{k_B T}\right)$				
п	<i>m</i> +1	т	т				
$Q_{\it eff}$	$Q_N + mQ_G$	$Q_N + mQ_G$	mQ _G				
Q _{Kiss}	$\frac{Q_N + mQ_G}{n}$	$\frac{mQ_G}{n}$	$\frac{mQ_G}{n}$				

Table 2.5: Extended volume fraction for the non-isothermal JMAK equations.[Kissinger 1956;Berry 2007]

Models	Nucleation Conditions	X _E	Analytically Solvable
k ₂ (T)N(T,t)	Continuous Nucleation	$k I_0 \int_{\tau=0}^{\tau=t} \left[exp\left(-\frac{Q_N}{k_B T(\tau)}\right) \left(\int_{t'=\tau}^{t'=t} k_2 exp\left(-\frac{Q_G}{k_B T(t')}\right) dt'\right)^m d\tau \right]$	No
k ₂ (T)N(T)	Burst nucleation	$k I'_{0} \exp\left(-\frac{Q_{N}}{k_{B} T(\tau_{0})}\right) \left(\int_{t'=\tau_{0}}^{t'=t} k_{2} \exp\left(-\frac{Q_{G}}{k_{B} T(t')}\right) dt'\right)^{m}$	No
k ₂ (T) MD	Pre-existing nuclei	$k N \left(\frac{k_2}{\beta}\right)^m \left(\frac{k_B T^2}{Q_G}\right)^m exp\left(-\frac{m Q_G}{k_B T}\right)$	Yes

In isothermal experiments, the radius of a given nucleus that formed at time τ is given as the integral from τ to t.

$$r = \int_{t'=\tau}^{t'=t} v dt' = v(t-\tau)$$
(2.20)

The fraction of transformed can be written as Eq. 2.21, where k is the geometry factor and I is the nucleation rate

$$X_{V} = 1 - \exp\left(-\int_{\tau=0}^{\tau=t} k I v^{m} \left(t-\tau\right)^{m} d\tau\right)$$
(2.21)

The nucleation rate I is defined as

$$I = \omega \ C_0 Z \exp\left(-\frac{\Delta G_m}{k_B T}\right) \exp\left(-\frac{\Delta G^*}{k_B T}\right)$$
(2.22)

 C_0 is the number of all potential sites for nucleus per unit volume, and the Zeldovich nonequilibrium factor Z, which accounts for the probability that a nucleus reached the critical size will dissolve back into solution, is taken as 0.0375. [Zeldovich 1943; Kostorz 2001; Berry 2007] ΔG_m is the activation free energy for migration (Eq. 2.23). Where ΔH_m is the activation enthalpy for migration and ΔS_m is the activation entropy for migration. Below we will take $\Delta H_m = Q_g$, the activation energy for growth. The energy barrier for the formation of a critical nucleus, ΔG^* , can be expressed as Eq. 2.24.

$$\Delta G_m = \Delta H_m - T \Delta S_m \tag{2.23}$$

$$\Delta G^* = \frac{16\pi r^3}{3\Delta G_V} \tag{2.24}$$

where γ is the surface energy between A1 and L1₀ phase, and ΔG_V is the volumetric free energy converted from molar driving force, ΔG_{mol} .

The growth velocity is defined as [Christian 1975].

$$v = k_2 \exp\left(-\frac{Q_G}{k_B T}\right) = \alpha \,\omega\left(\frac{\Delta S_m}{k_B}\right) \left(1 - \exp\left[-\frac{\Delta G}{k_B T}\right]\right) \exp\left(-\frac{Q_G}{k_B T}\right) \quad (2.25)$$

 α , the atomic jump distance for FCC metal, is taken as the distance between nearest neighbor. The vibration frequency ω was defined by [Christian 1975].

$$\omega = \frac{k_B T}{h} \tag{2.26}$$

where h is the Planck's constant. This relationship for vibration frequency is valid below the Debye temperature. The entropy of migration ΔS_m is approximated as [Zener 1952]

$$\Delta S_m \approx \lambda \xi \frac{Q_m}{T_{melt}} \tag{2.27}$$

where λ and ξ , the coefficients that are related to the elastic modulus and the melting temperature, are taken as 0.55 and 0.35, respectively. [Shewmon 1963]

The driving force ΔG_{mol} is approximated by

$$\Delta G_{mol} = \frac{\Delta H \Delta T}{T_e} = \frac{\Delta H}{T_e} \left(T - T_e \right)$$
(2.28)

the ΔH and T_e are latent heat and equilibrium ordering temperature for the given alloy composition, respectively.[Massalski 1990]

Integrated Eq.2.21 yields

$$X_{v} = 1 - \exp\left(-\frac{k}{m+1}Iv^{m}t^{m+1}\right)$$
(2.29)

Substituting Eq. 2.22 - 2.28 into Eq. 2.29 gives

$$X_{V} = 1 - \exp\left(-\frac{k k_{2}^{m} \omega C_{0} Z}{m+1} \exp\left(-\frac{\Delta G_{m} + \Delta G^{*} + m Q_{G}}{k_{B} T}\right) t^{m+1}\right)$$
(2.30)

The expression for relating the fraction transformed to DSC signal, ϕ , is

$$\Phi = \Delta H \frac{dX_{V}}{dt}$$
(2.31)

Differentiating the volume fraction transformed with respect to time and substituting into Eq. 2.31 yields the DSC signal for isothermal transformation.

$$\Phi = \Delta H \, k \, k_2^m \, \omega \, C_0 \, Z \, \exp\left(-\frac{\Delta G_m + \Delta G^* + m Q_G}{k_B T}\right) t^m$$
$$\exp\left(-\frac{k k_2^m \omega C_0 Z}{m+1} \exp\left(-\frac{\Delta G_m + \Delta G^* + m Q_G}{k_B T}\right) t^{m+1}\right) \tag{2.32}$$

For the constant heating rate experiments, the nucleation rate I is a function of temperature and time, therefore, the total number of nucleation sites, N, should be written as

$$N = \int_{\tau=0}^{\tau=t} I \, d\tau = \int_{\tau=0}^{\tau=t} \omega \, C_0 \, Z \, \exp\left(-\frac{\Delta G_m}{k_B T}\right) \exp\left(-\frac{\Delta G^*}{k_B T}\right) d\tau \tag{2.33}$$

combined with the radius of growing ordered domain, the fraction transformed can be expressed

$$X_{V} = 1 - \exp\left(-k \int_{\tau=0}^{\tau=t} I\left[\int_{t'=0}^{t'=t} k_{2} \exp\left(-\frac{Q_{G}}{k_{B}T}\right) dt'\right]^{m} d\tau\right)$$

$$= 1 - k k_{2} \omega C_{0} Z$$

$$\exp\left(-\int_{\tau=0}^{\tau=t} \exp\left(-\frac{\Delta G_{m}}{k_{B}T}\right) \exp\left(-\frac{\Delta G^{*}}{k_{B}T}\right) \left[\int_{t'=0}^{t'=t} \exp\left(-\frac{Q_{G}}{k_{B}T}\right) dt'\right]^{m} d\tau\right)$$

(2.34)

The theoretical DSC traces for constant heating experiments cannot be analytically solved by Eq. 2.34, but can be numerically calculated using Eq. 2.35.

$$\Phi = \Delta H \beta \frac{dX_{\nu}}{dT} = \Delta H \beta \frac{X_{\nu 1} - X_{\nu 2}}{T_1 - T_2}$$
(2.35)

For isothermal and non-isothermal scenarios of the constant nucleation rate condition, the expressions for fraction transformed and DSC signals are given in Table 2.6.

Table 2.6: The expressions for fraction transformed and the DSC signals of isothermal and non-isothermal conditions for the constant nucleation rate condition.

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Isothermal
Case
$$X_{\nu} = 1 - \exp\left(-\frac{k k_{2}^{m} \omega C_{0} Z}{m+1} \exp\left(-\frac{\Delta G_{m} + \Delta G^{*} + mQ_{G}}{k_{B}T}\right) t^{m+1}\right)$$

$$\Phi = \Delta H k k_{2}^{m} \omega C_{0} Z \exp\left(-\frac{\Delta G_{m} + \Delta G^{*} + mQ_{G}}{k_{B}T}\right) t^{m}$$

$$\exp\left(-\frac{k k_{2}^{m} \omega C_{0} Z}{m+1} \exp\left(-\frac{\Delta G_{m} + \Delta G^{*} + mQ_{G}}{k_{B}T}\right) t^{m+1}\right)$$

$$X_{\nu} = 1 - k k_{2} \omega C_{0} Z \exp\left(-\frac{\Delta G_{m} + \Delta G^{*} + mQ_{G}}{k_{B}T}\right) \exp\left(-\frac{\Delta G^{*}}{k_{B}T}\right) d\tau$$

$$X_{\nu} = 1 - k k_{2} \omega C_{0} Z \exp\left(-\frac{m}{k_{B}T}\right) \exp\left(-\frac{\Delta G^{*}}{k_{B}T}\right) d\tau$$

$$\Phi = \Delta H \beta \frac{dX_{\nu}}{dT} = \Delta H \beta \frac{X_{\nu 1} - X_{\nu 2}}{T_{1} - T_{2}}$$

$$T_{1} \text{ and } T_{2} \text{ are adjacent temperature values in the calculation.}$$

$$\beta \text{ is the heating rate.}$$

$$X_{\nu_{1}} \text{ and } X_{\nu_{2}} \text{ is the fraction transformed at temperature } T_{1} \text{ and } T_{2}, \text{ respectively.}$$

2.3.6 Au-Cu and Ti-Al Binary System

Au-Cu system has been used as a classic example for studying the atomic ordering transformation. At equiatomic composition, AuCu forms chemically disordered A1 (FCC) and ordered AuCu I ($L1_0$) structure at high (>410 °C) and low temperature (<385 °C), respectively. The pseudo-orthorombic ordered AuCu II phase is present between the A1 and $L1_0$ structures. The phase diagram of Au-Cu system is presented in Fig. 2.7.[Massalski 1990]

The enthalpies for the transformation of AuCu I \rightarrow AuCu II and AuCu II \rightarrow disordered A1 are 2.5 and 9.4 J/g-atom, respectively; and the onset peak temperature at the heating rate of 0.5 °C/min are 397.5 and 422.1 °C, respectively.[Feutelais 1999] The reported overall transformation enthalpies for AuCu I \rightarrow disordered A1 in literature range from 10.7 to 29.8 J/g-atom.[Oriani 1958; Tissot 1978; Battezzati 2001]

For the studies of the A1 to $L1_0$ phase transformation, the A1 samples are usually quenched to room temperature and then annealed at the temperature of interest.[Chandra 1970; Van Tendeloo 1986; Hisatsune 1995] The governing transformation mechanism between T_e (equilibrium temperature of transformation) and T_k (coherent stability boundary) is heterogeneous nucleation. Between T_k and T_s (the coherent instability boundary), the transition is dominated by homogeneous nucleation. Spinodal ordering occurs below T_s.[Cook 1976]. The T_s, T_k and T_e temperatures are experimentally determined as 357, 375 and 410 °C, respectively.[Tanaka 1994] The transformation from A1 to L1₀ phase is faster than from A1 to AuCu II because the AuCu II structure requires a long incubation time.[Van Tendeloo 1986; Tanaka 1994]



Figure 2.7: Phase Diagram of Au-Cu binary system. Figure reproduced from [Massalski 1990].

The Ti-Al system, as shown in Fig 2.8, contains three intermetallic compounds, namely, TiAl₃, TiAl and Ti₃Al.[Massalski 1990] The phase relevant to the current study is the chemically ordered γ -TiAl (L1₀ structure). Unlike other L1₀ binary systems, the c/a ratio for L1₀ phase TiAl is greater than 1. The c/a ratio for TiAl is composition dependent with the lowest value reported at the equiatomic composition. [Vujic 1988; Whang 1988] L1₀ TiAl can be fabricated by rapid solidification, mechanical alloying, and magnetron sputtering.[Whang 1988; Valencia 1989; Cocco 1990; Yan 1990; Wang 2002]

Coelho et al. reported that sputtered TiAl films form a different structure depending on the composition. Alloying films with less than 50.5 at.% Al form the α -Ti (HCP) structure, whereas films with over 63.5 at.% Al form the A1 (FCC) phase. TiAl films with 58 – 59.5 at.% Al have a mixture of α -Ti and A1.[Coelho 2000] However, Abe et al found a amorphous structure for sputtered Ti₅₂Al₄₈ films.[Abe 1994] And Padmaprabu et al reported amorphous TiAl alloys if films have 35-55 at.% Al and the deposition temperature is below 300 °C.[Padmaprabu 2000] Limited surface diffusion could be the reason for forming the amorphous phase at low temperature. Post deposition annealing is necessary to form the ordered γ -TiAl for room temperature deposited alloy films. It is worth noting that ordered hexagonal α 2-Ti₃Al (DO₁₉) is observed during the transformation. [Abe 1994; Banerjee 1996; Wang 2002] The alternative way of fabricating L1₀ TiAl is to deposit alloy films at high temperature. TiAl films with 55.8 – 66.2 at.% Al form the L1₀ structure when deposited between 300 and 600 °C. [Padmaprabu 2000]



Figure 2.8: Phase Diagram of Ti-Al binary system. Figure reproduced from [Massalski 1990].

2.4 Rationale for Selecting of Ternary Alloying Elements

The motivation of adding ternary additions to FePt is to lower the kinetic ordering temperature. The elements chosen for the study are Mg from column 2, V from column 5, Mn from column 7, Ni from column 10, Cu, Ag and Au from column 11, B from column 13 and C from column 14. These elements present a varity of chemical properties and cover seven group in the periodic table (Fig. 2.9).[Lower 2005] The selection of ternary additions that have potential of lowering kinetic ordering temperature or deposition temperature are based on four criteria.

IA 1	6	alkali	metal	s									no	ble ga	ases		VIIA 18
H					utle e	1	pos	t-tran	sition	meta	lls	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	Не
Li	Be		aikai	ine ea tr	arths ansiti	j ion m	etals					В	С	Ν	0	F	Ne
Na	Mg	IIIB 3	IVB 4	VB 5	VIB 6	VIIB	VIII 8	VIII 9	VIII 10	IB 11	IIB 12	AI	Si	Ρ	S	СІ	Ar
к	Са	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Cs	Sr	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	Т	Xe
Rb	Ва	La	Hf	Та	w	Re	Os	Ir	Pt	Au	Hg	ті	Pb	Bi	Ро	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds			se	/ mime ⁻	tals			
(metalloids) halogens																	
Ce	Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu lanthanides																
Th	n Pa	a U	N	ο Ρι	u Ar	n Cr	n Bl	k C	f E	s Fr	n M	d N	o L	r ac	tinide	s k	

Figure 2.9: Periodic Table used for choosing ternary elements to FePt binary system. Figure reproduced from [Lower 2005].

i) Kinetics of Formation in the Ternary Fe-X-Pt System

The choice of Ag, Au, B and C is based on the kinetics of formation in the ternary system. In the literature, ternary additions of Ag, Au, B and C are claimed to enhance the transformation kinetics according to the observation that ternary alloy films show an increase of coercivity (H_c) at lower temperature than in binary FePt.[Platt 2002; Nishimura 2004; You 2006; Lee 2007; Chen 2009; Perumal 2009] Moreover, underand/or over- layers of Au and Ag are declared to promote transformation because of the coercivity increment.[Xu 2003; Zhao 2004; Chen 2006] It is well known that coercivity depends on microstructure and texture of the films, therefore, this property is not a direct kinetic measurement of transformation, thus any conclusions drawn based on the DSC results are more convincing.

ii) Kinetics of Formation in the Bianry X-Pt System

MnPt film is reported to have a kinetic ordering temperature ~ 340 °C and the activation energy for formation of the $L1_0$ phase is ~ 1.5 eV.[Ladwig 2003] Since the KOT and transformation activation energy for MnPt are slightly lower than FePt alloys, Mn additions to FePt may result in enhancing $L1_0$ FePt formation kinetics.

iii) Stability of the L1₀ X-Pt Phase

The choice of V and Mg as possible candidates is based on the facts that the calculated formation enthalpies of $L1_0$ phase VPt (-51.6 J/g-atom) and MgPt(-86.6 J/g-atom) are higher than $L1_0$ FePt (-25.7 (measured -27.2) J/g-atom).[Skriver 2004]

iv) Atomic Size and Magnetic Moment

The choice of Mg is based on the rationale of atomic size and magnetic moment. Previous studies showed that Ni additions result in an increase of KOT, whereas Cu additions have no impact on KOT regardless of Cu content.[Berry 2007] The additions of Co to FePt system also slow down the overall transformation. The additions of Mg are made to further examine the impact of a non-ferromagnetic element of small size on the transformation kinetics.

2.5 Techniques

2.5.1 Sputtering

The sputtering process, which includes DC (Direct Current) and RF (Radio Frequency) sputtering, is a common method of fabrication thin films in the hard drive industry. Figure 2.10 is a schematic drawing for magnetron sputtering technologies.[VG Scienta 2007]



Figure 2.10: Schematics of magnetron sputtering system. Figure reproduced from [VG Scienta 2007].

In a typical DC sputtering process, the sputtering target is connected to the negative terminal of a DC power supply as a cathode. After introducing a medium gas, usually Ar or He, into the vacuum chamber and applying a high voltage on the target, a discharge region that is made up of positive gas ions around the target materials is created. By striking the sputtering target, positive gas ions are able to knock off and transfer
momentum to the target atoms, resulting in depositing target atoms onto the substrates, which are directly facing the sputtering target. The sputtering process can be sustained by continuously introducing gas and applying DC power to the sputtering target. In addition, the substrate can be biased, heated or cooled with special purpose. Depositing non-conductive materials, which is almost impossible to conduct with DC sputtering, can be realized with RF sputtering at frequency of 13.56M Hz. For magnetron sputtering, the presence of magnetic field near the discharged region can dramatically improve the ionization efficiency by creating more ionizing collisions of gas ions with neutral gases near the target, and result in an increase of deposition rate.

2.5.2 Differential Scanning Calorimetry

Power compensation differential scanning calorimetry (DSC) is a technique to measure the heat involved with transformations or reactions during a temperature scan. Figure 2.11 is the schematic drawing of power compensation DSC.[The Evitherm Society 2010] The sample and reference measuring systems have their own heating element and temperature sensor; and are separately positioned inside a large furnace. During a temperature program, the sample and reference furnaces are supplied with same power until the sample is undergoing a transformation or reaction, the heating element for sample furnace will simultaneously adjust its output to compensate for the heat involved in order to maintain same temperatures for both furnaces. The advantage of power compensated DSC is that all the heat involved with phase transformation or reaction can be directly obtained from the dsc trace by integration the peak area over the interested temperature region.[Michaelsen 1997]

Calibrations for temperature, thermal lag, heat and baseline must be done for the DSC measurements. The temperature calibration is assigning true temperatures to measured temperatures of several calibration standards. The thermal lag calibration is to adjust the onset temperature shift for a standard substance due to various heating rates. Heat calibration, similar to temperature calibration, is to designate true enthalpies to measured enthalpies from known calibration standards. The purpose of baseline calibration is to obtain reliable and repeatable baseline for thermal analysis.



Figure 2.11: Schematics of differential scanning calometry (DSC). Figure reproduced from [The Evitherm Society 2010].

2.5.3 Energy Dispersive X-ray Spectrometry (EDS), Wavelength Dispersive X-ray Spectrometry (WDS) and Energy Dispersive X-ray Fluorescence (EDXRF)

To determine the compositions of a thin film, several techniques, namely energy dispersive X-ray spectrometry (EDS), wavelength dispersive X-Ray spectrometry (WDS) and energy dispersive X-ray fluorescence (EDXRF), can be utilized. In an EDS analysis, electrons at inner shell can be knocked out by a high energy electron beam. As the electrons at an out shell migrate to an inner shell to fill the newly created vacancy, the characteristic x-ray is emitted. In the EDS analysis, a voltage pulse received by Si energy dispersive spectrometer is proportional to the energy of the incoming x-ray photon. The composition of a sample is determined by analyzing the spectrum. In the WDS analysis, the emitted x-rays are diffracted from an analyzing crystal; and only those x-rays that meet the Bragg's condition are detected by a gas-filled proportional counter. The peak positions are converted to wavelengths through Bragg's law; and Moseley relationship is applied to determine elemental composition. In EDXRF technique, x-rays rather than electrons in the EDS are used to knock out the electrons at inner shell; and the emitted xrays fluoresce are used for composition analysis. Figure 2.12 is the principle for WDS, EDS and EDXRF. The external stimulation for WDS, EDS and EDXRF are electrons, electrons and x-ray, respectively. The radiation energy for these techniques is characteristic x-ray.

WDS has better resolution and detection limit, but longer experimental time and higher beam current than EDS and EDXRF. Although lacking high resolution, EDXRF is capable of analyzing large sample areas (cm range) in a fast pace.



Figure 2.12: The principle of WDS,EDS and EDXRF.

3 Experiment

3.1 Fabrication of FePt Binary and Ternary Alloy Films

Binary and ternary films were prepared by direct current (DC) or radio frequency (RF) magnetron sputtering from elemental, namely Fe, Pt, Ag, Au, B, C, Mg, Mn and V, targets at nominally room temperature. The base pressure for the sputtering chamber was $\leq 4 \times 10^{-8}$ Torr and the sputtering pressure was maintained at 3 mTorr by flowing Ar-4% H₂ gas at 20 SCCM. Alloy films with two different thicknesses of 0.5 and 1.0 µm were deposited onto 3" oxidized (100 nm) Si (100) wafers. For the elevated temperature (100, 150, 200, 250 and 300 °C) deposition studies, the substrates were placed on the stage for 0.5 hour at the given temperature before depositing any binary films. The 0.5 µm thick films, used for composition analysis and TEM, were deposited directly onto the oxidized silicon wafers with 9 nm-thick adhesion Ta layer. The 1.0 µm thick films were deposited onto a 200 nm soluble Cu layer previously deposited onto oxidized silicon wafers in order to obtain free-standing films used in DSC analysis. The diffusion distance of Cu to binary FePt and its ternary system is expected to be extremely short. Assuming the

diffusivity of Cu in FePt is comparable to Fe in FePt, the calculated diffusion distances at room temperature and 300 °C are around 10⁻³ and 10⁻¹⁰ nm, respectively.[Rennhofer 2006] A copper oxide layer, which forms on top of Cu layers when the deposited Cu wafer is exposed to air, makes the diffusion of Cu into FePt layer more difficult. Therefore, the soluble Cu layer should have no effect on the binary and ternary films studied in this work.

The desired film compositions, which are calibrated by using energy dispersive x-ray spectrometry (EDS), are achieved by maintaining the Fe deposition rate at 1.2 Å/s while adjusting the deposition rates for Pt and the ternary alloying elements. The deposition rates of all the elements are controlled by adjusting the sputtering power, and calibration using the crystal monitor. The deposition time can be calculated by dividing film thickness calibration using the profilometer by calibrated deposition rate.

3.2 Differential Scanning Calorimetry

The transformation from the A1 phase to the $L1_0$ phase was studied by differential scanning calorimetry (DSC) using the 1.0 µm thick films in freestanding form. To obtain the freestanding films, the 1.0 µm thick sample films were first broken into 9 pieces, The Cu layer was then dissolved in a diluted HNO₃ solution (volume ratio of HNO₃ : H₂O = 9 : 1). After about 2 hours lift-off, films were soaked with DI water for 10 minutes before rinsed with acetone and isoproponal. The films were dried for 48 hours before any DSC characterization.

The free standing films were wrapped into clean Pt envelopes, which is about 7 mm \times 7 mm \times 0.025 mm with 99.99 % purity. The Pt envelop not only provides better thermal conduction, but also prevents cross contamination between sample and DSC furnaces. The method of wrapping DSC samples into Pt foil is adopted from Lucadamo and Berry's DSC work.[Lucadamo 1999; Berry 2007] The Pt foil pieces were folded into an envelope shape by folding three of the corners into the center and slightly opening the folds into a small pouch (see schematic in Fig. 3.1). Depending on the composition of the films and experimental condition, approximately 5 to 15 mg of film was placed into the envelope before folding the last corner into center and flattening the envelope. The four corners were then folded into the center and flattened again. The sample weight was calculated by subtracting the weight of Pt envelope from the total weight of the envelope and sample.[Lucadamo 1999; Berry 2007]

The films were heated twice from 25 °C to 700 °C at four heating rates of 20, 40, 80 and 160 °C/min. The DSC trace for the A1 to $L1_0$ phase transformation at each heating rate is obtained by subtracting the second trace from the first trace.

The reason that the second DSC data run can be used as a baseline is because $L1_0$ phase FePt alloy films are stable during the cooling down and second heating period.

The transformation enthalpy can be directly obtained from the peak area under the DSC traces for the four heating rates. The transformation enthalpy was calculated per mole of atoms for the given alloy composition using the average enthalpy per gram from the areas under the DSC traces for the four given heating rates. In addition, the Curie temperature of A1 and $L1_0$ phases can be determined from the change in the slope of the DSC traces. This change in slope represents the change in heat capacity of the ordered

phase as it becomes paramagnetic.

The kinetic ordering temperature was taken as the DSC peak temperature at a heating rate of 40 °C/min. The use of the terminology "kinetic ordering temperature" is made to distinguish it from the equilibrium order-disorder temperature, which for binary equiatomic FePt is 1300 °C.

The activation energy for the transformation was calculated from the shift in peak temperatures with heating rate using the Kissinger method.[Kissinger 1956] For the transformation kinetics, the activation energy for the formation of the $L1_0$ phase and the kinetic ordering temperature provide simple, yet quantitative means for comparing the various alloy systems and alloy compositions in terms of the ease of $L1_0$ formation. The lower the kinetic ordering temperature and the lower the activation energy, the easier it is to form the $L1_0$ phase.



Figure 3.1: Schematic of the construction of the Pt envelope used as sample holders for free-standing films in DSC experiments. Figure reproduced from [Lucadamo 1999; Berry 2007].

3.3 Composition Analysis

Film compositions were measured by energy dispersive x-ray spectrometry (EDS) in the FEI XL-30 field emission gun scanning electron microscope using the 0.5 μ m-thick films. The EDS spectrum was obtained with beam voltage of 20 kV, magnification of 65 and the acquisition time was set at 30 second. The film composition was calculated by normalizing the percentages of each alloying element, which was acquired by taking the ratio of the integrated peak intensity for a given element to that of the respective pure elemental standard. All the correction factors for atomic number, absorption and fluorescence have been automatically taken into account by the software INCA for calculating film compositions.

In order to confirm the compositions of alloy films used for previous work, a series of FePt films were re-measured using three techniques: EDS, wavelength dispersive x-ray spectrometry (WDS) and energy dispersive x-ray fluorescence (EDXRF). Instead of using pure elemental foil standards (nominally 0.1 mm thick), the thin film standards (nominally 0.5 μ m thick), fabricated by room temperature sputtering from elemental Fe and Pt targets, were used as a standards for the EDXRF studies. The spectrum, acquired with voltage of 15 kV and current of 10 μ A, was used for analyzing film composition. The working condition for WDS was set at 15 kV for voltage and 5 μ A for current. The EDS technique is chosen for composition measurement because of the combination of availability, accuracy and time allowance.

3.4 Phase Identification

X-ray diffraction (XRD) was used for phase identification, determination of lattice parameter, and calculating the order parameter. The equipment used for XRD was PANalytical X'Pert diffractometer equipped Cu Kα radiation operating at 45 kV and 40 mA with graphite monochromator. The schematic setup for the PANalytical X'Pert is shown in figure 3.2. [Berry 2007]

Two sets of 0.5 μ m thick film samples were used for these studies: the as-deposited films and films annealed in the DSC furnace at a heating rate of 40 °C/min to 700 °C. Due to the size limitation of DSC chamber, the maximum sample size was 5 mm x 5 mm. The beam size for the XRD experiment of θ -2 θ scans was chosen as 5 mm (width) and 4 mm (height), in order to obtain enough peak intensities and complete the experiments in an acceptable time range. Examples of XRD scans of as-deposited and post-annealed for the Fe_{44.2} Ag_{16.7}Pt_{39.0} films were illustrated in figure 3.3.

The presence of peak 111 and 200 evidence the A1 structure for the as-deposit film, whereas the supperlattice peak 001 and 110 evidence the presence of $L1_0$ phase. The lattice parameter can be calculated from the 2 θ values obtained from x-ray diffraction pattern, while the integrated peak intensity can be used for calculating order parameter.



Figure 3.2: The schematic drawing of PANAlytical X'Pert x-ray diffractometer. Figure reproduced from [Berry 2007].



Figure 3.3: θ -2 θ XRD patterns for Fe_{44.2}Ag_{16.7}Pt_{39.0} samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peaks such as 001 and 110. The formation of A1 (fcc) Ag upon annealing is also clearly evident. The sample was annealed at 40 °C/min to 700 °C.

4 Results and Discussion

4.1 Film Compositions

The composition of a set of FePt films reported in [Berry 2007] were re-measured with EDXRF using thin film standards, along with two other techniques, EDS and WDS. The average composition differences of ≤ 1.4 at.% are within the limits noted for these techniques.[Goldstein 1992] Based on the new composition measurements for the subset of previously reported films, the compositions of the remaining films were adjusted using the average value of the shift in composition. In all the figures hereafter, the compositions are those measured by EDS or computed using the EDS results of Table 4.1. Pervious ternary FeNiPt and FeCuPt alloy films were re-measured with EDS and the composition results are listed in Table 4.2 and Table 4.3, respectively. The compositions are given such that the percentages add up to 100, whether the film is binary or ternary.

EDXRF (Foil Standard) [Berry 2007]		EDXRF (Thin Film Standard)		WDS		EDS	
Fe%	Pt%	Fe%	Pt%	Fe%	Pt%	Fe%	Pt%
59.2	40.8	53.5	46.5	56.7	43.3	56.0	44.0
54.4	45.6	50.2	49.8	51.3	48.7	50.5	49.5
52.8	47.2	48.9	51.1	49.6	50.4	50.0	50.0
49.3	50.7	45.4	54.6	46.0	54.0	45.0	55.0
44.7	55.3	40.8	59.2	42.0	58.0	42.0	58.0

Table 4.1 Composition of binary films of [Berry 2007] re-measured with EDXRF, WDS and EDS.

The compositions are given in atomic percent.

EDXF	RF (Foil star [Berry 2007]	ndard)	EDS			
Fe%	Ni%	Pt%	Fe%	Ni%	Pt%	
51.3	7.6	41.1	47.7	6.1	46.2	
45.8	8.1	46.1	42.3	6.7	51.0	
50.0	2.7	47.3	45.5	2.0	52.5	
45.8	6.1	48.1	41.8	5.0	53.2	
34.0	16.8	49.2	32.1	13.7	54.2	
25.2	25.5	49.3	23.6	21.5	54.9	

Table 4.2: Compositions of ternary FeNiPt Films of [Berry 2007] re-measured with EDS.

The compositions are given in atomic percent.

EDXRF (Foil standard) [Berry 2007]				EDS			
	Fe%	Cu%	Pt%	Fe%	Cu%	Pt%	
	50.5	4.7	44.8	46.2	4.4	49.3	
	35.3	19.4	45.3	32.1	17.3	50.7	
	40.6	13.4	46.0	37.2	12.0	50.8	
	50.3	2.7	47.0	46.7	2.4	50.9	
	49.7	1.0	49.3	45.9	1.3	52.8	
	47.2	2.9	49.9	42.8	3.2	54.1	
	44.8	5.2	50.0	40.8	4.9	54.4	
	47.7	1.3	51.0	42.1	3.2	54.7	
	39.2	10.6	50.2	35.7	9.2	55.0	
	34.7	14.5	50.8	31.7	12.9	55.4	

Table 4.3: Compositions of ternary FeCuPt Films of [Berry 2007] re-measured with EDS.

The compositions are given in atomic percent.

4.2 Binary FePt Films

The kinetic and thermodynamic study on the A1 to L1₀ phase transformation of FePt binary alloying films had been discussed in Berry's thesis.[Berry 2007] In the most recent study, the impact of composition on the kinetic ordering temperature, transformation activation energy, transformation enthalpy and the Curie temperature of L1₀ phase, illustrated in Figs. 4.1 - 4.4, respectively, were re-evaluated using EDS compositions. In addition, recent ambient temperature deposited binary FePt films were fabricated and measured in the DSC for comparison with published results. The data points for binary FePt labeled as "published" and "new" are taken from previous and recent work, respectively.[Barmak 2004; Barmak 2005; Berry 2005; Berry 2006; Berry 2007; Berry 2007; Wang 2010; Wang 2011]

The most recent experiments agree with those published results. The kinetic ordering temperatures and activation energy for binary FePt alloys have a minimum region around 48.6 at.% Pt. A similar trend is also observed in bulk ball-milled FePt samples.[Lyubina 2006] The nominally $Fe_{50}Pt_{50}$ ball-milled sample has the lowest peak temperature and transformation activation energy at 372 °C and 1.45 eV, respectively.[Lyubina 2006] The real composition for the nominal $Fe_{50}Pt_{50}$ sample is believed to be more Fe rich, because the only measured composition for nominal $Fe_{45}Pt_{55}$ sample contains 48 at.% Fe. Moreover, the study on post-annealed 50 nm thick FePt films shows $Fe_{52}Pt_{48}$ sample has the fastest transformation kinetics based on the stress and coercivity analysis.[Wierman 2003] The results for 50 nm and 1 µm thick films and ball-milled samples strongly indicate that the fastest A1 to L1₀ transformation occurs in alloys that are Fe-rich, but

near equiatomic composition.

The Curie temperature of the L1₀ phase shows a relatively flat region between 46 and 50 at.% Pt, and the transformation enthalpies are in the range of 6 to 14 kJ/g-atom. The comparison of the L1₀ phase Curie temperature is illustrated in Fig. 4.5. The behavior of Curie temperature for thin films is similar to those reported for bulk alloys.[Fallot 1938; Kußmann 1950; Nose 2003] The thin film results show a reasonable agreement with bulk values reported by Kußmann and Rittbergy and Fallot; but higher than those measured by Nosé et al.. For Fe₅₀Pt₅₀ sample, the bulk values acquired by Wirths et al and Gasnikova et al. are slightly lower than the thin film value.[Wirths 1976; Gasnikova 1983] Klemmer and Wu find similar behavior of Curie temperature for their thin film samples, but the values are shifted to lower Pt content.[Klemmer 1995]

The XRD patterns for the as-deposited and annealed binary FePt samples show that room temperature deposited films are strongly 111 textured. This observation agrees with Berry's and Wierman's studies of room temperature deposited 1 µm and 50 nm-thick films, respectively.[Wierman 2003; Berry 2007]

The grain sizes for as-deposited and annealed films are acquired from plan-view bright field TEM images and XRD using Scherrer's equation. Table 4.4 gives the film composition, number of grains used for counting grain size, and grain sizes obtained from TEM and XRD for films in the as-deposited and annealed states. The discrepancy of measured grain sizes between TEM and XRD reveals the inadequacy of Scherrer's method for determining grain size. Fig. 4.6 is plan-view bright field TEM images for as-deposited and annealed Fe_{52.4}Pt_{47.6} sample. The cross-section bright field and dark filed TEM images for as-deposited Fe_{52.4}Pt_{47.6} film in Fig. 4.7 and 4.8, respectively, shows that

the grains are columnar type II.[Thornton 1977] This observation agrees with Berry's result shown in Fig. 4.9. It is worth noticing that the grain size obtained from TEM image is in the film plane, whereas the calculated value from Scherrer's formula is in the through thickness direction.

Table 4.4: Film composition, number of grains measured, and grain sizes of A1 and $L1_0$ phases for binary ambient deposited FePt films. The film grain size is determined from TEM bright field image and XRD using Scherrer's equation.

Composition		TEM (Plan-view)				XRD	
Fe (at.%)	Pt (at.%)	# of A1 grains	A1 grain size (nm)	# of L1 ₀ grains	L1 ₀ grain size (nm)	A1 grain size (nm)	L1 ₀ grain size (nm)
54.3	45.7	100	23	73	120	18	17
52.4	47.6	126	21	70	136	15	18
47.7	52.3	109	21	30	108	20	17



Figure 4.1: Kinetic ordering temperature is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.3: Transformation enthalpy is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.2: Activation energy is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.4: Curie temperature of $L1_0$ phase is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.5: Curie temperature as a function of composition for the A1 to $L1_0$ transformation in FePt. These values are compared with Curie temperatures reported in the literature, Lines are shown to guide the eyes. [Fallot 1938; Kußmann 1950; Wirths 1976; Gasnikova 1983; Klemmer 1995; Nose 2003]



Figure 4.6: The plan-view bright field TEM image for $Fe_{51.4}Pt_{48.7}$ film. (a) left: as-deposited and (b) right: annealed to 700 °C.



Figure 4.7: The cross-section bright field TEM images for as-deposited $Fe_{51.4}Pt_{48.7}$ film at two magnifications.



Figure 4.8: The cross-section dark field TEM images for as-deposited Fe_{51.4}Pt_{48.7} film at two magnifications.



Figure 4.9: The cross-section TEM images for as-deposited $Fe_{51.4}Pt_{48.6}$ film (a) left: bright filed and (b) right: dark field.

4.3 Impact of Ternary Additions on the A1 to L1₀ Phase Transformation

The impact of 9 ternary elements on the A1 to $L1_0$ transformation were studied. These 9 chosen elements, which are Mg from IIA, V from VB, Mn from VIIB, Ni from VIII, Cu, Ag and Au from IB, B from IIIA and C from IVA, present a variety of chemical properties and cover seven groups in the periodic table (Fig. 2.6).[Lower 2005]

The study on the A1 to L1₀ phase transformation of ternary films is focused on four parameters, namely the kinetic ordering temperature, the activation energy, the Curie temperature of L1₀ phase, and the transformation enthalpy. Since we are not able to determine atom positions, the four parameters are plotted (i) as a function of Pt content and (ii) as a function of normalized Pt content. The Pt content refers to the atomic percent of Pt where the at.% of all three elements adds up to 100% (Fe% + X% + Pt% = 100%), while the normalized Pt content means the total atomic percents of Fe and Pt are 100 (Fe% + Pt% = 100%). These complementary results give a preliminary idea of the ternary effect on the disorder-order transformation for FePt. An in-depth investigation can be performed if the atomic position can be determined. For all the ternary systems studied, the ternary content is labeled adjacent to the data point. Although no L1₀ Curie temperatures are reported for several films, it is not possible to say whether the absence of the slope change is due to the fact that the change in heat capacity is too small to be observed in the DSC, or the L1₀ phase is not ferromagnetic.

4.3.1 Impact of Mg Additions on the A1 to L1₀ Phase

Transformation

Examples of x-ray diffraction patterns for FeMgPt with 1.8 at.% Mg in the asdeposited state and after annealing to 700 °C are shown in Fig. 4.10. The as-deposited film has the A1 structure with strong 111 texture. The superlattice peaks 001 and 110 in the annealed film evidence the presence of $L1_0$ phase.

Figs. 4.11 to 4.18 are the plot of kinetic ordering temperature, activation energy, transformation enthalpy and the Curie temperature of $L1_0$ phase as a function of Pt and normalized Pt content.

The Mg content that is labeled 0.0 at.% means that the amount of addition is below the detection limit of EDS. Figures 4.11 and 4.14 show that even small amount addition of Mg (2.6 at.%) to FePt results in a measurable increase of the kinetic ordering temperature when compared with binary FePt films at same Pt content. The same amount of Mg also causes the decrease of the Curie temperature for the L1₀ phase, as shown in Figs. 4.15 and 4.18. For a lower amounts of Mg (0.7 at.%), no measurable differences are observed for the kinetic ordering temperature and the Curie temperature of the L1₀ phase.



Figure 4.10: θ -2 θ XRD patterns for Fe_{52.1}Mg_{1.8}Pt_{46.1} samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 001 and 110. The sample was annealed at 40 °C/min to 700 °C.



Figure 4.11: Kinetic ordering temperature is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.13: Transformation enthalpy is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.12: Activation energy is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.14: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.15: Kinetic ordering temperature is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.17: Transformation enthalpy is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.16: Activation energy is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.18: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeMgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

4.3.2 Impact of V Additions on the A1 to L1₀ Phase Transformation

The as-deposited and annealed FeVPt samples with V additions from 0.7 to 12.7 at.% form chemically disordered A1 and ordered L1₀ phase, respectively. The crystal structures are evidenced by FCC 111 and superlattice 001 and 110 peaks in the x-ray diffraction scans, respectively. The XRD scans for the as-deposit and annealed to 700 °C $Fe_{56.0}V_{0.7}Pt_{43.3}$ film are shown in Fig. 4.19.

Increasing the amount of V additions to FePt results in an increase of kinetic ordering temperature. The sample with 12.7 at.% of V shows a significant increase of kinetic ordering temperature when compared to binary FePt with the same Pt content (Figs. 4.20 and 4.24). For ternary alloying films with over 3.1 at.% V, a slight increase of activation energy is observed (Figs. 4.21 and 4.25). However, V additions do not cause any noticeable change for transformation enthalpy due to the scatter of the data (Figs. 4.22 and 4.26). Same for the Curie temperature of the L1₀ phase, no measurable impact is obtained for V content up to 5.8 at.% (Figs. 4.23 and 4.27).



Figure 4.19: θ -2 θ XRD patterns for Fe_{56.0}V_{0.7}Pt_{43.3} samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 001 and 110. The sample was annealed at 40 °C/min to 700 °C.



Figure 4.20: Kinetic ordering temperature is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.22: Transformation enthalpy is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.21: Activation energy is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.23: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.24: Kinetic ordering temperature is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.26: Transformation enthalpy is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.25: Activation energy is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.27: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeVPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

4.3.3 Impact of Mn Additions on the A1 to L1₀ Phase Transformation

Ambient temperature deposited FeMnPt films with Mn contents ranging from 2.2 to 16.3 at.% have a strong 111 texture, and the annealed films transform to the $L1_0$ phase, as evidenced by superlattice peaks of 001 and 110. Figure 4.28 is examples of the x-ray diffraction patterns for FeMnPt with 10.7 at.% of Mn in the as-deposited state and after annealing to 700 °C.

Figures 4.29, 4.30, 4.33 and 4.34 show that Mn additions (less than 10.7 at.%) result in an increase of the kinetic ordering temperature and activation energy when compared to binary films with same Pt content. For same amount of Mn additions (below 10.7 at.%), no noticeable impact is observed for the transformation enthalpy, as shown in Figs. 4.31 and 4.35. Additions of Mn (2.2 and 6.0 at.%) to FePt lower the Curie temperature of L1₀ phase, while no values are obtained for other Mn contents (Figs. 4.32 and 4.36). The decrease of L1₀ Curie temperature for thin films are consistent with bulk FeMnPt alloys.[Menshikov 1987] The L1₀ Curie temperature for thin film Fe_{47.2}Mn_{6.0}Pt_{46.8} and bulk Fe₄₄Mn₆Pt₅₀ are 381 °C and 393 °C, respectively. These values are reasonably close considering that binary FePt films with reduced Pt content have a lower L1₀ Curie temperature when compared to film with equiatomic composition.

The film with 16.3 at.% Mn shows an increase in kinetic ordering temperature and activation energy when compared with FePt films with same Pt content. However, if plotted as normalized Pt content, the film is in the range of $L1_2$, which are not of the interest for the current research.



Figure 4.28: θ -2 θ XRD patterns for Fe_{45.7}Mn_{10.7}Pt_{43.6} samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 001 and 110. The sample was annealed at 40 °C/min to 700 °C.



Figure 4.29: Kinetic ordering temperature is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.31: Transformation enthalpy is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.30: Activation energy is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.32: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.33: Kinetic ordering temperature is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.35: Transformation enthalpy is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.34: Activation energy is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.36: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

4.3.4 Impact of Ni and Cu Additions on the A1 to L1₀ Phase Transformation

The compositions of ternary FeCuPt and FeNiPt films published by Berry [Berry 2007] have been re-measured by EDS. The new compositions of two serials of FeCuPt and FeNiPt are given in Table 4.5 and Table 4.6, respectively. The new compositions of the remaining films were adjusted using the average value of the shift in composition. In all the figures below, the compositions are those measured by EDS or computed using the EDS results of Table 4.5 and 4.6.

To re-evaluate the impacts of Cu and Ni additions on the A1 to $L1_0$ phase transformation, figures of kinetic ordering temperature, activation energy and transformation enthalpy, and Curie temperature of $L1_0$ phase were re-plotted with EDS compositions (Figs. 4.37 to 4.52). However, contradictory conclusions on the impacts of Ni and Cu can be drawn based on the results shown in figs. 4.41 to 4.44 and 4.49 to 4.52. No phase other than $L1_0$ phase are observed in these films, therefore, it is a reasonable assumption that Cu and Ni substitute for Fe atoms.[Berry 2007]

Based on the plots using Pt content, several conclusions can be acquired. Cu additions have no measurable impact on the kinetic ordering temperature, activation energy and transformation enthalpy for a given Pt content. However, introducing Cu into FePt system lowers the $L1_0$ phase Curie temperature for FeCuPt samples when compared with same Pt content. For Ni additions, increasing the amount of Ni increases the kinetic ordering temperature, but lowers the $L1_0$ phase Cuire temperature for FeNiPt alloying films for a given Pt content. The increase of activation energy is caused by Ni additions,
but is not dependent on the Ni content. Additions of Ni in the $L1_0$ solid solution do not have a measurable effect on the transformation enthalpy.



Figure 4.37: Kinetic ordering temperature is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.39: Transformation enthalpy is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.38: Activation energy is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.40: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.41: Kinetic ordering temperature is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.43: Transformation enthalpy is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.42: Activation energy is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.44: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeNiPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.45: Kinetic ordering temperature is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.47: Transformation enthalpy is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.46: Activation energy is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.48: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.49: Kinetic ordering temperature is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.51: Transformation enthalpy is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.50: Activation energy is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.52: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeCuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

4.3.5 Impact of Ag Additions on the A1 to L1₀ Phase Transformation

X-ray diffraction results for FeAgPt films showed the formation of A1 (fcc) Ag in addition to the L1₀ phase upon annealing of films with \geq 6.9 at.% Ag. As an example, the XRD patterns for the FeAgPt with 16.7 at.% Ag in the as-deposited state and after annealing to 700 °C are shown in Fig. 4.53. The XRD results for the as-deposited films are in agreement with Platt et al.'s work showing that up to 40 at.% of Ag is soluble in A1 phase.[Platt 2002] In the annealed films, superlattice peaks such as 001 and 110 evidence the presence of L1₀. However, in addition to the L1₀ peaks, 111 and 200 peaks are seen for Ag contents of 6.9 at.% or more. Thus, Ag is not fully soluble in L1₀ FePt.

The 0.0 at.% of Ag in Fig. 4.54 and 4.58 means the Ag content inside the ternary film is below the detection limit of EDS. The additions of Ag result in an increase of kinetic ordering temperature. The impact on the activation energy is more difficult to determine, given the larger scatter in the data (Figs. 4.55 and 4.59). However, it is fair to say that Ag additions have no notable impact on the effective activation energy for ordering for the range of alloy compositions studied. Figures 4.56 and 4.60 show the enthalpy for decomposition of FeAgPt into L1₀ FePt and Ag is not measurably different than that for transformation of the A1 phase to the L1₀ phase in binary FePt. Figures 4.57 and 4.61 show that Ag additions have no impact on the Curie temperature of the L1₀ phase. This observation is consistent with the decomposition of the ternary alloy.



Figure 4.53: θ -2 θ XRD patterns for Fe_{44,3}Ag_{16.7}Pt_{39.0} samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peaks such as 001 and 110. The formation of A1 (fcc) Ag upon annealing is also clearly evident. The sample was annealed at 40 °C/min to 700 °C.



Figure 4.54: Kinetic ordering temperature is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.56: Transformation enthalpy is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.55: Activation energy is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.57: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.58: Kinetic ordering temperature is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.60: Transformation enthalpy is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.59: Activation energy is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.61: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeAgPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

4.3.6 Impact of Au Additions on the A1 to L1₀ Phase Transformation

X-ray diffraction results for FeAuPt films showed the formation of A1 (fcc) Au in addition to the L1₀ phase upon annealing of films with \geq 7.2 at.% Au. As an example, the XRD patterns for FeAuPt films with 13.8 at.% Au in the as-deposited state and after annealing to 700 °C are shown in Fig. 4.62. The absence of fcc Au peaks in the asdeposited films is in agreement with the work of Platt et al.[Platt 2002]. In the annealed films, superlattice peaks such as the 110 peak evidence the formation of the L1₀ phase. However, in addition to the L1₀ peaks, a strong 111 peak and a weak 200 peak are seen for fcc Au for gold contents of 7.2 at.% and higher. Thus, like Ag, Au is not fully soluble in L1₀ FePt. This observation is similar to that FeAuPt films studied previously.[Barmak 2004]

Au additions to the FePt system increase the kinetic ordering temperature for all the ternary films studied as shown in Fig. 4.63 and 4.67. Same as Ag, increasing the amount of Au additions increases the kinetic ordering temperature. However, Figs. 4.64 and 4.68 have shown that Au additions cause an increase of effective activation energies, but only notably higher for large additions of Au. Similar to Ag, Au additions have no measurable impact on the transformation enthalpy or the Curie temperature of the $L1_0$ phase as shown in Figs. 4.65, 4.66, 4.69 and 4.70. Chang also claimed that up to 40 at.% of Au additions have no impact on the $L1_0$ Curie temperature for melt span FePt ribbon.[Chang 2007]

The effects of Ag and Au on the transformation are similar except for the activation

energy. Further work on the transformation mechanism needs to be carried out to understand the difference in behavior of these two elements.



Figure 4.62: θ -2 θ XRD patterns for Fe4_{5.2} Au_{13.8} Pt_{41.0} samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 110. The formation of A1 (fcc) Au upon annealing is also clearly evident. The sample was annealed at 40 °C/min to 700 °C.



Figure 4.63: Kinetic ordering temperature is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.65: Transformation enthalpy is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.64: Activation energy is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.66: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.67: Kinetic ordering temperature is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.69: Transformation enthalpy is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.68: Activation energy is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.70: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeAuPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

4.3.7 Impact of B Additions on the A1 to L1₀ Phase Transformation

The x-ray diffraction is not capable of detecting B, therefore, only the crystal structures of FePt can be identified for all the ternary films studied. An example of x-ray diffraction patterns for FeBPt films with 11.8 at.% B in the as-deposited state and after annealing to 700 °C are shown in Fig. 4.71. The as-deposited films form the A1 (fcc) structure, and the annealed films are transformed to the $L1_0$ phase, evidenced by the superlattice peaks 001 and 110.

Due to the difficulty of acquiring actual compositions of B, the boron contents labeled in the figures below are nominal values. Figs. 4.72, 4.73, 4.76 and 4.77 show that ternary samples with ≥ 11.8 at.% B show notable higher values of kinetic ordering temperature and activation energy. For ternary films with Pt content near equiatomic range, no measurable effect is apprant for B contents less than 4.8 at.%. However, for Pt rich ternary films that have ≤ 4.8 at. % B, the additions of B result in an increase of kinetic ordering temperature and activation energy if compared with same Pt content, while the same amounts of B do not show noticeable impact when compared to normalized Pt content. B additions to FePt show no measureable impact on the transformation enthalpy and the Curie temperature of L1₀ phase, as shown in Figs. 4.74, 4.75, 4.78 and 4.79.



Figure 4.71: θ -2 θ XRD patterns for Fe_{43.0} B_{11.8} Pt_{45.22}samples. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 001 and 110. The sample was annealed at 40 °C/min to 700 °C.



Figure 4.72: Kinetic ordering temperature is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.74: Transformation enthalpy is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines The solid black curve is drawn to guide the eye.



Figure 4.73: Activation energy is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.75: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.76: Kinetic ordering temperature is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.78: Transformation enthalpy is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.77: Activation energy is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.79: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeBPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

4.3.8 Impact of C Additions on the A1 to $L1_0$ Phase Transformation

The carbon content labeled in figs. 4.80 and 4.84 is nominal value because of the challenge of acquiring actual C content in the ternary system. Because the carbon content (1.4 at.% C) is low, therefore, the kinetic ordering temperature, the activation energy, the transformation enthalpy and $L1_0$ phase Curie temperature are not effected (Figs. 4.80 to 4.87). To further assess the impact of carbon, experiments on more ternary films with higher carbon contents should be carried out in the future.



Figure 4.80: Kinetic ordering temperature is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.82: Transformation enthalpy is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.81: Activation energy is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.83: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.84: Kinetic ordering temperature is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.86: Transformation enthalpy is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines.



Figure 4.85: Activation energy is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.



Figure 4.87: Curie temperature of $L1_0$ phase is plotted as a function of composition for FeCPt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

4.4 Elevated Temperature Deposition of FePt Films

Binary FePt alloy films directly form the $L1_0$ phase when deposited onto heated substrates over 400 °C, but the questions of what is the lowest in-situ temperature to form $L1_0$ FePt and how long will it take are still not answered. In addition to understanding the impact of deposition temperature on the transformation behavior of FePt, the elevated deposition study combined with transformation models could better help understand the A1 to $L1_0$ transformation. Three compositions (around 43.5, 48.0 and 54.0 Pt at.%) and five nominal deposition temperatures, which are 100, 150, 200, 250 and 300 °C, are chosen for the elevated temperature deposition study. The calibration of nominal temperatures is presented in Table 4.5.

Nominal Temperature (°C)	100	150	200	250	300
Actual Temperature (°C)	99.7	150.3	199.5	249.8	300.9

Table 4.5: Calibration of nominal temperatures for elevated temperature deposition.

Binary films that are deposited between 100 and 200 $^{\circ}$ C form both A1 and L1₀ phases, whereas films deposited at 250 and 300 $^{\circ}$ C form only the L1₀ phase. Two examples of x-ray diffraction scans of Fe_{50.5}Pt_{49.5} deposited at 200 $^{\circ}$ C and Fe_{56.4}Pt_{43.6} deposited at 300 $^{\circ}$ C in the as-deposited form are presented in Fig. 4.88 and 4.89,

respectively. The as-deposited films show strong 111 texture, and the $L1_0$ structure is evidenced by the presence of superlattice 001 and 110 peaks.

Figs. 4.90 to 4.93 are the plots of elevated temperature deposition peak temperature at heating rate of 40 °C/min (ETDPT), activation energy, Curie temperature of $L1_0$ phase and transformation enthalpy as a function of composition. To indicate the compositions of films without ETDPT, colored dash lines were vertically drawn at the film compositions. The same treatment is also applied to the other two figures, the compositional dependence of transformation activation energy and transformation enthalpy.

Three alloying films (43.6, 48.5 and 53.6 at.% Pt) deposited at 300 $^{\circ}$ C and a binary film (48.2 at.% Pt) deposited at 250 $^{\circ}$ C directly form L1₀ phase during deposition. The evidence is from the presence of superlattice peaks in x-ray diffraction scans and absence of transformation peak in DSC traces.

Two transformation mechanisms for binary films deposited between 100 to 200 °C are observed. One set of binary films containing 46.9 - 54.0 at.% Pt have identical transformation behavior as films deposited at room temperature. Therefore, the peak temperature for heating rate at of 40 °C/min, activation energy and Curie temperature of $L1_0$ phase are same as those ambient deposited binary samples. As expected, the transformation enthalpies of this set of samples are less than those of room temperature deposited films. Another set of alloying samples with 42.4 to 45.6 at.% Pt have shown different transformation behavior. Increasing the deposition temperature of FePt results in an increase of ETDPT, but no measurable effect on activation energy. As expected, the Curie temperature of the $L1_0$ phase is not influenced by the temperature increase; and the

transformation enthalpy is less than these for films deposited at room temperature.

The mobility of Fe and Pt atoms at elevated temperature are higher than that at ambient temperature, therefore, it is reasonable that the films have partially or fully transformed to $L1_0$ phase depending on deposition temperature.



Figure 4.88: θ -2 θ XRD pattern for Fe_{50.5}Pt_{49.5} sample. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 001 and 110.



Figure 4.89: θ -2 θ XRD pattern for Fe_{56.4}Pt_{43.6} sample. The formation of the L1₀ phase is evidenced by the appearance of the superlattice peak such as 001 and 110.



Figure 4.90: ETDPT is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as black dashed vertical lines. The solid black curve is drawn to guide the eye. The blue and red dashed vertical lines indicates the compositions for films deposited at 200 and 300 ° C, respectively.



Figure 4.92: Transformation enthalpy is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as black dashed vertical lines. The blue and red dashed vertical lines indicates the compositions for films deposited at 200 and 300 ° C, respectively.



Figure 4.91: Activation energy is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as black dashed vertical lines. The solid black curve is drawn to guide the eye. The blue and red dashed vertical lines indicates the compositions for films deposited at 200 and 300 ° C, respectively.



Figure 4.93: Curie temperature of $L1_0$ phase is plotted as a function of composition for FePt films. The phase stability limits for the $L1_0$ phase from the binary FePt phase diagram are given as black dashed vertical lines.

4.5 The JMAK Models for the A1 to L1₀ Phase Transformation in FePt and Related Ternary System

To understand the transformation behavior, four transformation models that account for three nucleation conditions, namely, athermal, burst and continuous nucleation, have been examined. The fraction transformed curves and the time-temperature-transformation (TTT) diagrams for three models, namely MD, $k_2(T)$ and $k_2(T)N(T)$ models that cover athermal and burst conditions, have been recalculated using EDS compositions. The fourth $k_2(T)N(T,t)$ model has been newly developed to account for the constant nucleation condition. Summary of these four model variants are given in Table 4.6. The MD model simulates the athermal nucleation condition with the pre-exponential term for growth velocity, k_2 , constant. In $k_2(T)$ model, k_2 is temperature and thus driving force dependent. The k_2 and nucleation density are both temperature dependent in $k_2(T)N(T,t)$ model, whereas the nucleation density is temperature and time dependent in $k_2(T)N(T,t)$

	Atherma	al Nucleation	Burst Nucleation	Continuous Nucleation	
	MD		$k_2(T)N(T)$	$k_2(T)N(T,t)$	
\mathbf{k}_2	Constant Temperature Dependent		Temperature Dependent	Temperature Dependent	
Nucleation Density	Constant		Temperature Dependent	Temperature and Time Dependent	

Table 4.6 Comparison of the pre-exponential term for the growth velocity, k_2 , and the nucleation conditions in four transformation models, namely, MD, $k_2(T)$, $k_2(T)N(T)$ and $k_2(T)N(T,t)$ models.

For the MD model, the growth activation energy equals the effective activation energy determined from the four non-isothermal DSC traces by using the Kissinger method, and other parameters, namely, the Avrami exponent (n), the transformation enthalpy (Δ H), and the frequency factor, *v*, are acquired by fitting each non-isothermal DSC trace to the MD model. Fig. 4.94 illustrates the fitting of MD model to the DSC traces for Fe_{52.9}Pt_{47,1} film. Expressing the pre-exponential term for growth velocity, k₂, as a function of temperature and keeping the remaining parameters, namely, activation energy, Avrami exponent and transformation enthalpy, the same as in the MD model yield the k₂(T) model. Further incorporating a temperature term into nucleation density results in k₂(T)N(T) model. The isothermal transformation curves at given temperatures are calculated by implementing these acquired parameters. The temperature-timetransformation (TTT) diagrams are constructed by calculating the fraction transformed at the temperature range of interested.[Berry 2007]

With a set of input parameters, namely the growth activation energy (Q_G) , interfacial energy between A1 and L1₀ phase (γ), and growth dimensionality (m), the simulated DSC traces can be calculated using the k₂(T)N(T,t) model. An example of the comparisons is presented Fig. 4.95. The impact of fitting parameters, namely Q_G , m and γ , on the simulated DSC traces can be found in the appendix E. The nucleation activation energy can be calculated from the growth activation energy and the overall effective activation energy, the latter determined from the DSC experiments using the Kissinger method.[Kissinger 1956]

Figure 4.96 is the TTT diagram for $Fe_{46.7}Cu_{2.4}Pt_{50.9}$ that is calculated by using these four models. The TTT diagrams that acquired by MD, $k_2(T)$ and $k_2(T)N(T)$ models are

calculated by implementing EDS composition, and corresponding T_e temperatures and equilibrium temperatures. It is worth noting that the interfacial energy (γ) in k₂(T)N(T,t) model is a fitting parameter regardless of transformation mechanism. Therefore, the introduction of the shape factor (S<1), expressed in Eq. 4.1, for heterogeneous nucleation in the model is compensated by an increase of γ , because the term for nucleation must remain the same in order for the simulations to match the experimental peak positions at the four heating rates.

A series of S values with corresponding γ values is given in Table 4.7. The TTT curves calculated using k₂(T)N(T,t) as well as isothermal transformation curves remain the same no matter which set of S and γ is chosen. As S goes to zero, the continuous nucleation model reaches its limit, where no energy barrier exists for nucleation. The k₂(T) model is one implementation of this limit, for which the nucleation activation energy is zero.

$$\frac{\Delta G_{H_{et}}^*}{\Delta G_{H_{om}}^*} = S(\theta) \tag{4.1}$$

Table 4.7 A serial of shape factor for heterogeneous nucleation (S) and interfacial energy between A1 and L1₀ phase (γ) in k₂(T)N(T,t) model. The decrease of S is compensated by the increase of γ , and S γ^3 is a constant.

S	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.05
γ (mJ/m ²)	136	141	147	153	161	171	185	203	233	293	369
$\frac{S\gamma^3}{(mJ/m^2)}$		$Constant = 2.52 \times 10^{6}$									

Figure 4.97 is the isothermal transformation curves at four annealing temperatures for the $Fe_{46.7}Cu_{2.4}Pt_{50.9}$ sample. According to the isothermal experimental results taken form Berry's work, $k_2(T)$ appears to be the best fit among all these four models (Fig. 4.97).

Figure 4.98 shows the TTT diagrams comparing the transformation kinetics in Fe_{44.5}Pt_{55.5}, Fe_{51.4}Pt_{48.6} and Fe_{52.9}Pt_{47.1} using (a) MD, (b) $k_2(T)$, (c) $k_2(T)$ N(T) and (d) $k_2(T)$ N(T,t) models. However, the parameters needed to calculate the TTT diagram of Fe_{44.5}Pt_{55.5} by using the $k_2(T)$ N(T,t) model can not be obtained because no simulation can fit the experimental DSC traces. Figure 4.99 shows the simulation and experimental DSC traces at the heating rate of 40 °C/min for the Fe_{44.5}Pt_{55.5} film. The second peak in the simulation is caused by T₀ = T_e (675 °C), which is the average of two boundary temperatures for an alloy composition of 55.5 at.% Pt obtained from extension of the two equilibrium boundaries, as shown in Fig. 4.100. A proper values of T_e should be provided in order for the model to work for this composition.

Table 4.8 lists the film composition measured by EDS and the equilibrium ordering temperature, T_e , used for calculating the four kinetic models. Table 4.9 reports parameters that are either acquired by fitting or calculated for constructing TTT and isothermal fraction curves for MD, $k_2(T)$ and $k_2(T)N(T,t)$ models. Table 4.10 lists the effective (Q_{eff}), growth (Q_G) and nucleation (Q_N) activation energy, growth dimensionality (*m*) and interfacial energy between A1 and L1₀ phase (γ) used for calculated nucleation density and growth velocity at 300 and 500 °C, respectively, using the $k_2(T)N(T,t)$ model.

The MD model is not thermodynamically correct because the growth velocity does not drop to zero at the equilibrium temperature, therefore, this model is excluded from further comparisons. Figure 4.101 shows that the TTT curve for $k_2(T)$ model shows reasonably good agreement with the results for films deposited at elevated temperatures while the transformation kinetics for $k_2(T)N(T)$ and $k_2(T)N(T,t)$ models appear to be faster for films deposited at elevated temperatures.

Table 4.8: Film composition measured by EDS, equilibrium ordering temperature, Te, estimated from the phase diagrams, and transformation enthalpy, ΔH , fitted from MD model for the four alloys for which TTT diagrams are plotted using MD, $k_2(T)$, $k_2(T)N(T)$ and $k_2(T)N(T,t)$ models. The experimentally determined ΔH is also provided.

С	omposition (ED	S)	T _e	ΔH (kJ/g-atom)		
Fe (at.%)	Cu (at.%)	Pt (at.%)	(°C)	MD fitting	Experiment	
52.9	0	47.1	1287	5.8 ± 0.8	7.7 ± 1.1	
51.4	0	48.6	1295	7.2 ± 0.4	8.8 ± 1.6	
46.7	2.4	50.9	1287	8.1 ± 0.8	10.9 ± 2.7	
44.5	0	55.5	685	6.6 ± 0.5	8.5 ± 1.7	

Table 4.9: Film composition measured by EDS, the frequency factor, v, is the fitting parameters for the MD model. The density of nuclei, N, the A1-L1₀ interfacial energy, γ , the growth velocity, v, at 300 and 500 °C, respectively, and the critical nucleus volume, V^* , are calculated after the fitting. The values of γ from this table are used in the k₂(T) and k₂(T)N(T) models.

Composition (EDS)			N	v at (r	ım/s)		V*	
Fe (at.%)	Cu (at.%)	Pt (at.%)	(s^{-1})	(m ⁻³)	300 °C	500 °C	γ (mJ m ⁻²)	(unit cell)
52.9	0	47.1	1.34×10^{10}	6.89×10^{17}	1.34	1595.42	144	18.5
51.4	0	48.6	4.24×10^{10}	1.23×10^{19}	0.51	1080.40	142	15.0
46.7	2.4	50.9	2.57×10^{11}	1.53×10^{21}	0.08	292.93	134	10.0
44.5	0	55.5	1.97×10^{12}	1.66×10^{24}	7.8× 10 ⁻⁵	1.02	65	12.1

Table 4.10: Film composition measured by EDS, the growth (Q_G) and nucleation (Q_N) activation energies, growth dimensionality (*m*) and interfacial energy between A1 and L1₀ phase (γ) used for calculating isothermal and TTT curves by using the k₂(T)N(T,t) model. γ is a fitting parameter for this model.

Film Composition (EDS)			Q_G	Q_N	γ	m	
Fe (at.%)	Cu (at.%)	Pt (at.%)	(eV)	(eV)	(mJ/m^2)	111	
52.9	0.0	47.1	1.6	1.4	103	0.7	
51.4	0.0	48.6	1.6	1.6	112	0.7	
46.7	2.4	50.9	1.5	1.7	136	0.865	

Table 4.11: Film composition measured by EDS, the density of nuclei, N, and the growth velocity, v, at 300 and 500 °C, respectively, and critical nucleus volume, V^* , for the four alloys for which TTT diagrams are plotted using the k₂(T)N(T,t) model. N,v and V^{*} are calculated after the fitting.

Composition (EDS)		N (m ⁻³)		v at (V*		
Fe (at.%)	Cu (at.%)	Pt (at.%)	300 °C	500 °C	300 °C	500 °C	(unit cell)
52.9	0	47.1	3.54×10^{25}	1.56×10^{32}	0.22	414.16	3.5
51.4	0	48.6	2.09×10^{20}	3.22×10^{26}	0.22	401.62	5.0
46.7	2.4	50.9	3.03×10^{18}	2.44×10^{22}	1.40	1617.65	6.2



Figure 4.94: The fitting of MD model with four non-isothermal DSC traces for the A1 to $L1_0$ transformation in Fe_{52.9}Pt_{47.1} at the heating rate of (a) 20°C/min (b) 40°C/min (c) 80°C/min and (d) 160°C/min.



Figure 4.95: Comparison of experimental and simulated DSC trace using $k_2(T)N(T,t)$ model for the A1 to $L1_0$ transformation in Fe_{52.9}Pt_{47.1} at the heating rate of (a) 20°C/min (b) 40°C/min (c) 80°C/min and (d) 160°C/min.



Figure 4.96: TTT diagrams for the A1 to $L1_0$ transformation in Fe_{46.7}Cu_{2.4}Pt_{50.9} calculated using the (a) MD, (b) $k_2(T)$, (c) $k_2(T)$ N(T) and $k_2(T)$ N(T,t) models. The compositions used for these four models are from EDS results. These TTT diagrams give the times and temperatures needed for an isothermally annealed film to achieve a desired fraction transformed. Here, the leftmost solid line represents a fraction transformed of 0.05, while the dashed line and the following solid line are 0.50 and 0.95, respectively. A1 is the quenched metastable phase, whereas $L1_0$ is the thermodynamically stable phase. T_e is the equilibrium order-disorder temperature for this alloy.



Figure 4.97: Fraction transformed vs time at multiple annealing temperatures for $Fe_{46.7}Cu_{2.4}Pt_{50.9}$. The lines are predicted curves using (a) MD, (b) $k_2(T)$, (c) $k_2(T)$ N(T) and $k_2(T)$ N(T,t) models, and the points are found experimentally. The agreement between the MD and $k_2(T)$ models and experiment is excellent, whereas that of the $k_2(T)$ N(T) model is not. For this latter model, all of the calculated curves are shifted to significantly longer times.


Figure 4.98: TTT diagrams comparing the transformation kinetics in $Fe_{44.5}Pt_{55.5}$, $Fe_{51.4}Pt_{48.6}$ and $Fe_{52.9}Pt_{47.1}^*$ using (a) MD, (b) $k_2(T)$, (c) $k_2(T)$ N(T) and (d) $k_2(T)$ N(T,t) models. The compositions used for these four models are from EDS results. These TTT diagrams give the times and temperatures needed for an isothermally annealed film to achieve a desired fraction transformed. Here, the leftmost solid line represents a fraction transformed of 0.05, while the dashed line and the following solid line are 0.50 and 0.95, respectively. A1 is the quenched metastable phase, whereas $L1_0$ is the thermodynamically stable phase.

*: the k₂(T) N(T,t) model does not apply to the film Fe_{44.5}Pt_{55.5}. See Figs. 4.99 and 4.100 and text for more detail.



Figure 4.99: The experimental and the $k_2(T) N(T,t)$ calculated DSC traces for the A1 to L1₀ transformation in Fe_{44.5}Pt_{55.5}. The compositions used for these four models are from EDS results. T_a is taken as 675 °C from binary FePt phase diagram.



Figure 4.100: (a) Phase diagram of Fe-Pt binary system.[Massalski 1990] (b) the schematic drawing for determining T_e for Fe_{44.5}Pt_{55.5} film from phase diagram. T_e is chosen as the temperature exactly midway between the boundary temperatures marked with open circles at the terminal of the vertical line.

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For thin films such as recording media (~ 10 nm), the fraction transformed can be calculated by implementing a geometry correction term ψ , yielding

$$X_V = l - exp(-X_E)\psi \tag{4.2}$$

$$\psi = \frac{1}{\sqrt[3]{Nd_{film}}} \left[\int_{0}^{\sqrt[3]{Nd_{film}}} exp\left(X_E f\left(\frac{z}{\sqrt[3]{Nr}}\right) \right) exp\left(X_E f\left(\frac{\sqrt[3]{Nd_{film}} - z}{\sqrt[3]{Nr}}\right) \right) \right] dz$$
(4.3)

$$f(s) = \frac{1}{4} (2 - 3s + s^3) \Theta(l - s)$$
(4.4)

where d_{film} is the film thickness, r is the effective radius of growth domain, and N is the number of nucleation sites. f(s) is the function that define the volume of a spherical cap and $\Theta(1-s)$ is the Heaviside step function, which accounts the nuclei inside a thin film.[Berry 2007]

The TTT diagrams for 10 nm binary $Fe_{51.4}Pt_{48.6}$ films are given in Fig. 4.102. The results show that 10 nm thick films transform slower than 1 µm thick films. The comparison of experimental data, both laser and furnace annealed 10 nm continuous films, with theoretical calculations using three models is presented in Fig. 4.103. In addition, the 700 °C fraction transformation curve is presented in Fig 4.104 as well as data points acquired from laser and furnace annealed samples. The model that most closely agrees with the experimental results is the k₂(T) model.

In summary, the transformation model that shows the best agreement with all available experiments, namely ternary $Fe_{46.4}Cu_{2.4}Pt_{51.2}$ isothermal, binary FePt elevated

temperature deposition, and laser and furnace annealed experiments, is the $k_2(T)$ model. Elevated temperature deposition and laser anneals are possible methods that can achieve ordered $L1_0$ phase FePt faster than the predication of $k_2(T)$ model.



Figure 4.101: Comparison of elevated deposition results of binary FePt films with around 49.0 at.% Pt with TTT diagrams of $Fe_{51.4}Pt_{48.6}$ calculated using (a) $k_2(T)$, (b) $k_2(T)$ N(T) and (c) $k_2(T)$ N(T,t) models. The deposition temperature and time for binary FePt films with around 49.0 at.% are presented in blue cycles. The states of fully and partially transformed to L1₀ phase after deposition are presented by closed and open cycles, respectively. *: the $k_2(T)$ N(T,t) model does not apply to the film Fe_{44.5}Pt_{55.5}.



Figure 4.102: TTT diagrams comparing the transformation kinetics in 1 μ m and 10 nm thick Fe_{51.4}Pt_{48.6} film using (a) k₂(T), (b) k₂(T) N(T) and (c) k₂(T) N(T,t) models. The compositions used for these three models are from EDS results. These TTT diagrams give the times and temperatures needed for an isothermally annealed film to achieve a desired fraction transformed. Here, the leftmost solid line represents a fraction transformed of 0.05, while the dashed line and the following solid line are 0.50 and 0.95, respectively. A1 is the quenched metastable phase, whereas L1₀ is the thermodynamically stable phase.





time (s)

Figure 4.103: Comparison of TTT diagrams for 10 nm thick $Fe_{51.4}Pt_{48.6}$ film using (a) $k_2(T)$, (b) $k_2(T)$ N(T) and (c) $k_2(T)$ N(T,t) models with laser and furnace annealed results. The compositions used for these three models are from EDS results. These TTT diagrams give the times and temperatures needed for an isothermally annealed film to achieve a desired fraction transformed. Here, the leftmost solid line represents a fraction transformed of 0.10., while the dashed line and the following solid line are 0.50 and 0.90, respectively. A1 is the quenched metastable phase, whereas $L1_0$ is the thermodynamically stable phase. The blue cycles on left are laser annealed 10 nm thick FePt film with order parameter of 0.1. The blue, olive and red open cycles present furnace annealed FePt sample with order parameter of 0.1, 0.5 and 0.9, respectively. The blue closed cycles are laser annealed room temperature deposited 10 nm $Fe_{50}Pt_{50}$ film with 10% ordering.[Inaba 2010] The open cycles in blue, olive and red are 60 seconds furnace annealed room temperature deposited 10 nm $Fe_{50}Pt_{50}$ film with 10% ordering.[Inaba 2010] The open cycles in blue, olive and 90% ordering, respectively.[Inaba 2010]



Figure 4.104: The calculated fraction transformed curve at 700 °C for $Fe_{51.4}$.Pt_{48.6} film using (a) $k_2(T)$, (b) $k_2(T)$ N(T) and (c) $k_2(T)$ N(T,t) models. The black solid and open cycles are laser and furnace annealed 10 nm thick FePt film, respectively. The red closed cycles are 700 °C laser annealed Fe₅₀Pt₅₀ films,[Inaba 2010] and the blue open cycles are 700 °C furnace annealed FePt films.[Ristau 1999]

4.6 The A1 to L1₀ Transformation Mechanism in FePt System

The equilibrium temperature, T_e , for binary FePt at the equiatomic composition is 1300 °C. Based on the relationship of T_e , T_k (coherent stability boundary) and T_s (the coherent instability boundary) for the Au-Cu system, the T_k and T_s for Fe₅₀Pt₅₀ can be estimated as 1219 and 1178 °C, respectively. The T_e , T_k and T_s for FePt and AuCu are given in Table 4.12. The governing mechanism for the A1 to L1₀ transformation below T_k could be either homogeneous nucleation or spinodal ordering if FePt behave similarly to the AuCu system. The presence of ordered L1₀ phase in a matrix of disordered A1 for samples annealed at 700 °C ($<T_s$) rules out the possibility of spinodal ordering for the A1 to L1₀ transformation.[Ristau 1998] The chemically disordered A1 structure is the kinetically stabilized phase at room temperature, and the L1₀ nuclei form during the deposition process. As described by the k₂(T) model, the only energy barrier for the transformation is the activation energy for growth.

	Equilibrium temperature, Te°CK410683		Coherent tempera	stability ture, T _k	Coherent instability temperature, T _s	
			°C	K	°C	K
AuCu			375	648	357	630
FePt	1300	1573	1219	1492	1178	1451

Table 4.12: The equilibrium temperature, T_e , the coherent stability temperature, T_k , and the coherent instability temperature, T_s for binary AuCu and FePt system.

5 Summary and Conclusions

Ternary Alloys

The impact of composition of the binary FePt films on the A1 to $L1_0$ phase transformation was evaluated using new compositions measured by EDS. The plot of kinetic ordering temperature (KOT) for these films indicated that the fastest disorder-order transformation with a KOT of ~ 357 °C was achieved at 48.6 at.% Pt.

For four ternary FeXPt alloy systems, where X = Mg, V, Mn and B, the formation of no phase other than the L1₀ phase was observed upon annealing. Small additions of the four ternary alloying elements Mg, V, Mn and B had little or no impact on the KOT, with the limit of what can be considered a small addition depending on the element and on the Pt content. The behavior of the activation energy for the A1 to L1₀ transformation mimicked that for the KOT, except for Mg additions, which showed no measurable impact for the compositions studied. The transformation enthalpies for the ternary alloys were found to be similar to those reported for binary FePt films. With regard to the Curie temperature, the additions of 2.6 at.% Mg, and 2.2 at% and 6.0 at.% Mn, and 4.8 at.% B lowered T_c when compared to binary FePt films with the same Pt content. All other alloy films, for which a Curie transition could be observed in the DSC, had T_c values that were similar to the binary films.

When room-temperature co-deposited ternary FeAgPt and FeAuPt films ware annealed, in addition to XRD peaks for the L1₀ phases, fcc Ag and Au peaks were seen for Ag \geq 6.9 at.% and Au \geq 7.2 at.%. For the full range of Ag and Au additions studied (1.5-16.7 at.% Ag, 1.9-13.8 at.% Au), the KOT was higher than that of the corresponding binary FePt film. However, the impact of the additions on the activation energy for ordering was more complex. The enthalpy for transformation/decomposition of the ternary alloys into the two phase mixture of L1₀ FePt and Ag or Au was not measurably different than that for transformation of the A1 phase to the L1₀ phase in binary FePt.

When ternary FeNiPt and FeCuPt alloys are compared with binary FePt alloys with the same Pt content, it is seen that additions of Ni slow the transformation kinetics, whereas additions of Cu have no measurable impact on the kinetics. The Curie temperature of the $L1_0$ phase was lowered by additions of Ni or Cu. The transformation enthalpy was lowered by large additions of Ni, but was unaffected by additions of Cu.

Only one FeCPt films was examined, therefore, additional experiments are necessary to better evaluate the impact of C additions.

Elevated Temperature Deposition

For binary FePt films deposited at elevated temperatures, two transformation behaviors were discovered with the boundary ~ 46 at.% Pt. For elevated temperature deposited binary FePt films with > 46 at.% Pt, no measurable impact on the peak temperature at the heating rate of 40 °C/min, activation energy and the Curie temperature

of $L1_0$ phase were observed when compared to films deposited at room temperature. For the other set of FePt samples with < 46 at.% Pt, the peak temperature at the heating rate of 40 °C/min increased as the deposition temperature increased, whereas the activation energy and the Curie temperature remained the same compared to room temperature sputtered films.

Kinetic Models

The kinetic model of continuous nucleation has been developed and used for calculating the time-temperature-transformation (TTT) diagram and isothermal transformation curves. Elevated temperature deposition and isothermal experimental results were used for evaluation of the kinetic models, namely MD, $k_2(T)$, $k_2(T)N(T)$ and $k_2(T)N(T,t)$ models. The $k_2(T)$ model was found to provide the best agreement with experimental results available to date.

In summary, ternary additions to FePt system did not achieve the goal of reducing the KOT. However, it may still be possible to identify ternary elements that can increase the nucleation density of $L1_0$ phase or speedup the growth rate of the $L1_0$ region. The elevated deposition experiment and comparison with simulation results provided extremely useful information for the hard drive industry to engineer the processing route for FePt magnetic recording layers.

6 Future Work

The studies of ternary additions have covered 7 groups in the periodic table, but no additions studied were able to reduce the KOT. Thus, future work should be focus on searching for other elements, which can increase the nucleation density or increase the growth rate of the $L1_0$ phase.

The elevated deposition experiments combined with the results from isothermal runs provide preliminary information for validation of kinetic models. Additional elevated deposition experiments, for instance, FePt samples sputtered in the temperature range of 200 to 300°C, will better define the boundary between the partially and fully-transformed state.

All binary and ternary films studied, both 0.5 and 1.0 micron thick samples, are considered too thick when compared with real recording media (usually in nanometer range). Although kinetic models can be developed to quantitatively describe the transformation behavior of very thin films, the best way would be to deposit nanometer-thick films at room and elevated temperatures; and quantify the transformed fraction, nucleation density and other kinetic parameters using transmission electron microscopy.

Appendix A:

Binary FePt System and Ternary Alloying Fe-X-Pt Systems

Table A-1 to 11 are the film composition, the kinetic ordering temperature (KOT), the activation enrgy (Q), the transformation enthalpy (Δ H) for the A1 to L1₀ transformation, and AA-1 to 11 are the lattice parameters and grain size for the A1 and L1₀ phases in FePt, FeMgPt, FeVPt, FeMnPt, FeNiPt, FeCuPt, FeAgPt, FeAuPt, FeBPt and FeCPt, respectively. For those films, of which the Curie temperature of L1₀ phase can be obtained, T_c is also given in the Table. The deposition temperatures for binary FePt films fabricated at elevated temperatures are also provide in Table I. For binary films that deposited at 250 and 300 °C, no values for the peak temperature at the heating rate of 40 °C/min (ETDPT), the transformation activation energy and the transformation enthalpy are provided due to the absence of peak in the DSC traces. The compositions of the ternary alloy films are listed in the order of increasing Pt content. The errors on the KOT and activation energy are estimated at ±2 °C and ±0.1 eV, respectively.

Table A-1: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (Δ H) for the A1 to L1₀ transformation in ambient temperature deposited binary FePt films. The Curie temperature of the L1₀ phase (T_c) is also given. The compositions of the binary alloy films are listed in the order of increasing temperature. The errors on the KOT and activation energy are estimated at ±2 °C and ± 0.1 eV, respectively.

	Composit	ion (EDS)	КОТ	T_c	Q	ΔH
Run ID	Fe (at.%)	Pt (at.%)	(°C)	(°C)	(eV)	(kJ / g - atom)
900 901	57.0	43.0	372	452±1	1.5	8.3±1.7
902 903	54.3	45.7	379	453±2	1.7	8.9±1.8
876 877	52.4	47.6	364	451±2	1.5	10.2±1.7
852 853	47.7	52.3	388	-	1.6	8.4±1.6
874 875	43.9	56.1	486	-	2.2	6.5±1.5

Lattice parameters(Å) Composition (EDS) Grain Size (nm) Run ID $L1_0$ A1 $L1_0$ A1 Pt (at.%) Fe (at.%) XRD TEM XRD TEM (a) (a) (c) 900 57.0 43.0 -------901 902 54.3 45.7 17 3.83 3.85 3.69 18 23 120 903 876 47.6 3.84 3.70 15 21 18 52.4 3.81 136 877 852 47.7 52.3 3.83 3.87 3.71 20 21 17 108 853 874 43.9 56.1 -------875

Table AA-1: Film composition measured by EDS, the lattice parameters of A1 (a) and $L1_0$ (a and c) phases, and grain sizes of as-deposited and annealed in ambient temperature deposited binary FePt films.

Table A-2: Deposition Temperature (T_D), film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (Δ H) for the A1 to L1₀ transformation in binary FePt films deposited at elevated temperature. The Curie temperature of the L1₀ phase (T_c) is also given. The compositions of the binary alloy films are listed in the order of increasing temperature. The errors on the KOT and activation energy are estimated at ± 2 °C and ± 0.1 eV, respectively.

	T _D Co		Composition (EDS)		T _C	Q	ΔH
Run ID	(°C)	Fe (at.%)	Pt (at.%)	(°C)	(°C)	(eV)	(kJ / g - atom)
1078 1079	100	56.2	43.8	398	426 ± 2	1.9	5.5 ± 0.7
1046 1047	100	54.4	45.6	413	442 ± 4	1.9	6.7 ± 1.3
1030 1031	100	51.2	48.8	370	457 ± 3	1.5	11.2 ± 1.0
1044 1045	100	46.5	53.5	415	419	1.6	6.9 ± 1.0
1066 1067	150	57.6	42.4	441	418 ± 1	1.5	5.4 ± 0.2
1052 1053	150	52.3	47.7	372	454 ± 2	1.5	9.7 ± 2.9
1068 1069	200	57.6	42.4	480	410	1.5	4.5 ± 0.6
1076 1077	200	56.4	43.6	440	418	1.6	3.9 ± 1.2
1036 1037	200	53.1	46.9	375	449 ± 1	1.5	4.1 ± 0.4
1032 1033	200	50.5	49.5	363	458 ± 1	1.5	6.4 ± 0.9
1038 1039	200	46.0	54.0	408	-	1.7	7.2 ± 1.7
1054 1055	250	51.8	48.2	-	451	-	-
1080 1081	300	56.4	43.6	-	-	-	-
1034 1035	300	51.5	48.5	-	-	-	-
1042 1043	300	46.4	53.6	-	-	-	-

Table AA-2: Deposition Temperature (T_D) , film composition measured by EDS, the lattice parameters of A1 (a) and L1₀ (a and c) phases, and the as-deposited and annealed grain sizes calculated using Scherrer's equation in binary FePt films deposited at elevated temperature.

	T _D	Composition (EDS)		Latti	ce paramete	rs(Á)	Grain Size (nm)	
Run ID	(°C)	Fe (at %)	Pt (at %)	A1	L	10	Al	Llo
	(0)	1 C (ut.70)	1 t (ut.70)	(a)	(a)	(c)		210
1078 1079	100	56.2	43.8	3.80	-	-	18	-
1046 1047	100	54.4	45.6	3.80	-	-	13	-
1030 1031	100	51.2	48.8	3.81	-	-	20	-
1044 1045	100	46.5	53.5	3.82	-	-	23	-
1066 1067	150	57.6	42.4	3.80	-	-	17	-
1052 1053	150	52.3	47.7	3.81	-	-	19	-
1068 1069	200	57.6	42.4	-	-	-	-	-
1076 1077	200	56.4	43.6	3.79	-	-	16	-
1036 1037	200	53.1	46.9	3.80	3.83	3.73	18	-
1032 1033	200	50.5	49.5	3.81	3.84	3.74	16	-
1038 1039	200	46.0	54.0	3.82	3.84	3.72	17	-
1054 1055	250	51.8	48.2	-	3.85	3.70	-	-
1080 1081	300	56.4	43.6	-	3.82	3.71	-	19
1034 1035	300	51.5	48.5	-	3.83	3.73	-	22
1042 1043	300	46.4	53.6	-	3.86	3.72	-	21

Table A-3: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (Δ H) for the A1 to L1₀ transformation in FeMgPt films. The Curie temperature of the L1₀ phase (T_c) is also given. The compositions of the ternary alloy films are listed in the order of increasing Pt content. The errors on the KOT and activation energy are estimated at ±2 °C and ± 0.1 eV, respectively.

	Co	mposition (EI	DS)	КОТ	T _C	Q	ΔH
Run ID	Fe (at.%)	Pt (at.%)	Mg (at.%)	(°C)	(°C)	(eV)	(kJ / g - atom)
898 899	57.2	42.1	0.7	384	448 ± 2	1.4	8.7 ± 2.1
938 939	52.1	46.2	1.8	413	435 ± 2	1.7	10.5 ± 1.6
886 887	53.8	46.3	0.0	373	449 ± 2	1.5	9.6 ± 0.9
896 897	53.3	46.4	0.3	382	447 ± 3	1.5	7.9 ± 1.7
940 941	48.8	48.6	2.6	436	419 ± 2	1.6	10.2 ± 1.1

Table AA-3:. Film composition measured by EDS, the lattice parameters of A1 (a) and $L1_0$ (a and c) phases, and the as-deposited and annealed grain sizes calculated using Scherrer's equation in FeMgPt films.

Run ID	Cor	Composition (EDS)			ce paramete	Grain Size (nm)		
	Fe (at.%)	Pt (at.%)	Mg (at.%	A1 (a)	(a)	1 ₀ (c)	A1	L1 ₀
898 899	57.2	42.1	0.7	3.79	3.83	3.69	13	17
938 939	52.1	46.2	1.8	3.82	3.87	3.68	15	18
886 887	53.8	46.3	0.0	3.81	3.84	3.69	21	19
896 897	53.3	46.4	0.3	3.81	3.85	3.69	16	18
940 941	48.8	48.6	2.6	3.84	3.88	3.73	15	15

Table A-4: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (Δ H) for the A1 to L1₀ transformation in FeVPt films. The Curie temperature of the L1₀ phase (T_c) is also given. The compositions of the ternary alloy films are listed in the order of increasing Pt content. The errors on the KOT and activation energy are estimated at ±2 °C and ± 0.1 eV, respectively.

Run ID	Co	mposition (EI	DS)	КОТ	T _C	Q	ΔH
	Fe (at.%)	Pt (at.%)	V (at.%)	(°C)	(°C)	(eV)	(kJ / g - atom)
1016 1017	43.0	44.8	12.2	502	-	1.9	8.1 ± 1.6
906 907	53.6	45.7	0.7	382	461 ± 1	1.6	9.7 ± 0.6
1014 1015	47.7	46.5	5.8	413	451 ± 1	1.9	10.6 ± 3.6
1012 1013	48.3	48.6	3.1	386	462 ± 1	1.9	10.5 ± 0.5

Table AA-4: Film composition measured by EDS, the lattice parameters of A1 (a) and $L1_0$ (a and c) phases, and the as-deposited and annealed grain sizes calculated using Scherrer's equation in FeVPt films.

	Cor	nposition (E	DS)	Latti	ce paramete	Grain Size (nm)		
Run ID	Fe (at.%)	Pt (at.%)	V (at.%)	A1 (a)	(a)	1 ₀ (c)	A1	L1 ₀
1016 1017	43.0	44.8	12.2	3.82	3.90	3.69	21	20
906 907	53.6	45.7	0.7	3.82	3.85	3.67	20	15
1014 1015	47.7	46.5	5.8	3.81	3.83	3.72	22	19
1012 1013	48.3	48.6	3.1	-	3.83	3.72	-	20

Table A-5: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (Δ H) for the A1 to L1₀ transformation in FeMnPt films. The Curie temperature of the L1₀ phase (T_c) is also given. The compositions of the ternary alloy films are listed in the order of increasing Pt content. The errors on the KOT and activation energy are estimated at ±2 °C and ± 0.1 eV, respectively.

	Co	mposition (EI	DS)	КОТ	T _C	Q	ΔH
Run ID	Fe (at.%)	Pt (at.%)	Mn (at.%)	(°C)	(°C)	(eV)	(kJ / g - atom)
1020 1021	45.7	43.6	10.7	525	-	2.3	10.0 ± 0.3
1022 1023	47.2	46.8	6.0	442	381 ± 2	2.0	10.7 ± 2.0
1024 1025	49.1	48.6	2.2	388	425 ± 2	1.8	9.0 ± 2.0
854 855	42.6	53.1	4.3	443	-	1.9	10.5 ± 3.4
856 857	28.3	55.4	16.3	555	-	3.2	8.1 ± 1.5

Table AA-5:Film composition measured by EDS, the lattice parameters of A1 (a) and $L1_0$ (a and c) phases,and the as-deposited and annealed grain sizes calculated using Scherrer's equation in FeMnPt films.

	Co	mposition (E	EDS)	Latt	ice paramete	Grain Size (nm)		
Run ID	Fe (at.%)	Pt (at.%)	Mn (at.%)	A1 (a)	(a)	1 ₀ (c)	A1	L1 ₀
1020 1021	45.7	43.6	10.7	3.81	3.88	3.66	19	17
1022 1023	47.2	46.8	6.0	-	-	-	-	-
1024 1025	49.1	48.6	2.2	-	-	-	-	-
854 855	42.6	53.1	4.3	-	-	-	-	-
856 857	28.3	55.4	16.3	3.87	3.92	3.68	22	21

Table A-6: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (Δ H) for the A1 to L1₀ transformation in FeNiPt films. The Curie temperature of the L1₀ phase (T_c) is also given. The compositions of the ternary alloy films are listed in the order of increasing Pt content. The errors on the KOT and activation energy are estimated at ±2 °C and ± 0.1 eV, respectively.

	Co	mposition (EI	DS)	КОТ	T _C	Q	ΔH
Run ID	Fe (at.%)	Pt (at.%)	Ni (at.%)	(°C)	(°C)	(eV)	(kJ / g - atom)
588 589	47.7	46.2	6.1	421	441 ± 2	1.7	7.5 ± 0.7
763	44.9	48.7	6.4	417	401 ± 4	1.8	8.9 ± 0.9
756 757	39.2	49.1	11.7	445	320 ± 2	1.8	6.1 ± 1.2
765 766	42.2	51.0	6.7	427	356 ± 4	1.8	9.1 ± 1.5
759 760	38.6	51.1	10.3	446	305 ± 5	1.8	6.2 ± 1.1
769	33.3	51.6	15.1	470	235	1.8	6.1 ± 1.0
592	45.5	52.5	2.0	396	420 ± 2	1.8	9.4 ± 2.7
597 612	45.4	53.0	1.6	401	416 ± 3	1.8	9.6 ± 1
594 595	41.8	53.3	5.0	430	359 ± 1	1.9	8.1 ± 1.1
604 605	32.1	54.2	13.7	503	208	2.0	6.2 ± 0.6
607 608	23.6	54.9	21.5	526	-	1.7	7.8 ± 2.8

	Cor	nposition (E	DS)	Latti	ce paramete	rs(Á)	Grain Size (nm)	
Run ID	Fe (at.%)	Pt (at.%)	Ni (at.%)	A1 (a)	(a)	1 ₀ (c)	A1	L1 ₀
588 589	47.7	46.2	6.1	3.82	3.83	3.69	-	-
763	44.9	48.7	6.4	3.82	3.85	3.70	-	-
756 757	39.2	49.1	11.7	3.82	3.85	3.70	-	-
765 766	42.2	51.0	6.7	3.83	3.86	3.70	-	-
759 760	38.6	51.1	10.3	3.83	3.86	3.69	-	-
769	33.3	51.6	15.1	3.83	3.85	3.67	-	-
592	45.5	52.5	2.0	3.84	3.85	.371	-	-
597 612	45.4	53.0	1.6	3.83	3.84	3.73	-	-
594 595	41.8	53.3	5.0	3.85	3.85	3.68	-	-
604 605	32.1	54.2	13.7	3.83	3.85	3.65	-	-
607 608	23.6	54.9	21.5	3.80	3.81	3.66	-	-

Table AA-6:. Film composition measured by EDS, the lattice parameters of A1 (a) and $L1_0$ (a and c) phases, and the as-deposited and annealed grain sizes calculated using Scherrer's equation in FeNiPt films.

Table A-7: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (Δ H) for the A1 to L1₀ transformation in FeCuPt films. The Curie temperature of the L1₀ phase (T_c) is also given. The compositions of the ternary alloy films are listed in the order of increasing Pt content. The errors on the KOT and activation energy are estimated at ±2 °C and ± 0.1 eV, respectively.

	Co	mposition (El	DS)	КОТ	T _C	Q	ΔH
Run ID	Fe (at.%)	Pt (at.%)	Cu (at.%)	(°C)	(°C)	(eV)	(kJ / g - atom)
SG3	52.8	45.1	2.1	416	398 ± 2	1.6	14.0 ± 6.2
SG2	48.3	47.4	4.3	368	397 ± 3	1.6	9.0 ± 1.8
779	43.2	48.8	8.0	362	335 ± 3	1.6	7.3 ± 1.4
471 470	46.2	49.3	4.4	366	386 ± 2	1.6	9.5 ± 1.2
786 787	32.1	50.7	17.3	367	-	1.6	8.9 ± 2.0
780 781	37.2	50.8	12.0	370	236	1.7	7.7 ± 0.9
462 463	46.7	50.9	2.4	363	407 ± 1	1.6	10.4 ± 2.6
453 455	45.9	52.8	1.3	384	409 ± 2	1.7	10.4 ± 3.7
381 391	42.8	54.1	3.2	402	362	1.8	7.6 ± 0.4
396 401	40.8	54.4	4.9	410	304	1.9	6.7 ± 1.2
SG1	39.9	54.6	5.5	429	-	1.8	8.1 ± 2.4
380 378	42.1	54.7	3.2	420	371 ± 1	1.8	8.0 ± 2.3
782 783	35.7	55.0	9.2	423	202	1.9	6.6 ± 0.8
784 785	31.7	55.4	12.9	436	-	2.0	7.3 ± 1.4

	Composition (EDS)				ce paramete	Grain Size (nm)		
Run ID	Fe (at.%)	Pt (at.%)	Cu (at.%)	A1 (a)	(a)	(c)	A1	L1 ₀
SG3	52.8	45.1	2.1	3.80	3.87	3.64	-	-
SG2	48.3	47.4	4.3	3.80	3.87	3.64	-	-
779	43.2	48.8	8.0	3.82	3.84	3.65	-	-
471 470	46.2	49.3	4.4	3.81	3.89	3.61	-	-
786 787	32.1	50.7	17.3	3.81	3.87	3.59	-	-
780 781	37.2	50.8	12.0	3.82	3.87	3.62	-	-
462 463	46.7	50.9	2.4	3.82	3.89	3.64	-	-
453 455	45.9	52.8	1.3	3.83	3.88	3.64	-	-
381 391	42.8	54.1	3.2	3.84	3.88	3.68	-	-
396 401	40.8	54.4	4.9	3.84	3.89	3.66	-	-
SG1	39.9	54.6	5.5	-	-	-	-	-
380 378	42.1	54.7	3.2	3.84	3.88	3.68	-	-
782 783	35.7	55.0	9.2	3.84	3.87	3.65	-	-
784 785	31.7	55.4	12.9	3.83	3.87	3.64	-	-

Table AA-7: Film composition measured by EDS, the lattice parameters of A1 (a) and $L1_0$ (a and c) phases, and the as-deposited and annealed grain sizes calculated using Scherrer's equation in FeCuPt films.

Table A-8: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (Δ H) for the A1 to L1₀ transformation in FeAgPt films. The Curie temperature of the L1₀ phase (T_c) is also given. The compositions of the ternary alloy films are listed in the order of increasing Pt content. The errors on the KOT and activation energy are estimated at ±2 °C and ± 0.1 eV, respectively.

Run ID	Со	mposition (El	DS)	КОТ	T _C	Q	ΔH
	Fe (at.%)	Pt (at.%)	Ag (at.%)	(°C)	(°C)	(eV)	(kJ / g - atom)
996 997	44.2	39.1	16.7*	460	448 ± 3	1.4	8.0 ± 2.9
994 995	50.0	43.1	6.9*	441	446 ± 3	1.4	-
946 947	49.1	47.5	3.4	410	454 ± 1	1.6	14.2 ± 2.0
988 989	50.5	49.5	0.0	369	457 ± 2	1.8	12.7 ± 1.3
944 945	48.7	49.8	1.5	406	440 ± 2	1.6	11.4 ± 0.7

*: films decompose into L10 FePt and Ag upon annealing.

Table AA-8: Film composition measured by EDS, the lattice parameters of A1 (a) and $L1_0$ (a and c) phases, and the as-deposited and annealed grain sizes calculated using Scherrer's equation in FeAgPt films.

Run ID	Со	mposition (E	EDS)	Latt	ice paramete	Grain Size (nm)		
	Fe (at.%)	Pt (at.%)	Ag (at.%)	A1	(a)	1_0 (c)	A1	L1 ₀
996 997	44.2	39.1	16.7*	3.86	3.85	3.69	15	17
994 995	50.0	43.1	6.9*	3.83	3.85	3.69	18	18
946 947	49.1	47.5	3.4	3.83	3.86	3.69	19	19
988 989	50.5	49.5	0.0	-	-	-	-	-
944 945	48.7	49.8	1.5	3.83	3.87	3.70	20	19

*: films decompose into L1₀ FePt and Ag upon annealing.

Table A-9: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (Δ H) for the A1 to L1₀ transformation in FeAuPt films. The Curie temperature of the L1₀ phase (T_c) is also given. The compositions of the ternary alloy films are listed in the order of increasing Pt content. The errors on the KOT and activation energy are estimated at ±2 °C and ± 0.1 eV, respectively.

Run ID	Co	mposition (El	DS)	КОТ	T _C	Q	ΔH
	Fe (at.%)	Pt (at.%)	Au (at.%)	(°C)	(°C)	(eV)	(kJ / g - atom)
1002 1003	45.2	41.0	13.8*	444	467 ± 2	2.0	9.4 ± 1.4
1000 1001	50.9	45.0	4.1	408	463 ± 1	1.9	8.9 ± 0.6
950 951	47.2	45.6	7.2*	430	465 ± 3	1.7	10.7 ± 1.7
998 999	52.2	45.9	1.9	386	455 ± 2	1.5	9.3 ± 0.9
952 953	38.6	54.2	7.2	480	-	-	-

*: films decompose into L1₀ FePt and Au upon annealing.

Table AA-9: Film composition measured by EDS, the lattice parameters of A1 (a) and $L1_0$ (a and c) phases, and the as-deposited and annealed grain sizes calculated using Scherrer's equation in FeAuPt films.

Run ID	Co	mposition (E	DS)	Latt	ice paramete	Grain Size (nm)		
	Fe (at.%)	Pt (at.%)	Au (at.%)	A1	L1 ₀		Al	$L1_0$
				(a)	(a)	(c)		
1002 1003	45.2	41.0	13.8	3.85	3.86	3.70	20	18
1000 1001	50.9	45.0	4.1	3.82	3.86	3.69	21	20
950 951	47.2	45.6	7.2	3.85	3.87	3.71	23	20
998 999	52.2	45.9	1.9	3.81	3.85	3.70	20	20
952 953	38.6	54.2	7.2	3.84	3.86	3.70	22	19

*: films decompose into L10 FePt and Au upon annealing.

Table A-10: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (Δ H) for the A1 to L1₀ transformation in FeBPt films. The Curie temperature of the L1₀ phase (T_c) is also given. The compositions of the ternary alloy films are listed in the order of increasing Pt content. The errors on the KOT and activation energy are estimated at ±2 °C and ± 0.1 eV, respectively.

	Co	mposition (EI	DS)	КОТ	T _C	Q	ΔH
Run ID	Fe (at.%)	Pt (at.%)	B (at.%)	(°C)	(°C)	(eV)	(kJ / g - atom)
928 929	46.3	40.8	12.9	497	452 ± 3	2.4	11.3 ± 2.2
932 933	45.1	42.7	12.3	484	456 ± 1	2.4	8.4 ± 0.9
934 935	43.0	45.2	11.8	466	442 ± 1	2.3	9.2 ± 0.6
872 873	49.9	45.3	4.8	368	454 ± 3	1.5	8.8 ± 0.8
878 879	50.9	46.5	2.6	364	452 ± 2	1.5	9.6 ± 0.2
866 867	44.1	51.2	4.8	442	391 ± 4	1.9	7.0 ± 1.8
868 869	44.5	53.1	2.4	438	-	1.9	13.9 ± 1.1
870 871	44.3	54.5	1.2	454	386	2.0	7.5 ± 0.7

	Co	mposition (E	EDS)	Latt	ice paramete	Grain Size (nm)		
Run ID	Fe (at %)	Pt (at %)	A_{11} (at $9/$)	A1	L	10	Δ 1	T 1
	1 C (dt. 70)	1 t (at. 70)	Au (al. 70)	(a)	(a)	(c)		L10
928 929	46.3	40.8	12.9	-	-	-	-	-
932 933	45.1	42.7	12.3	3.82	3.86	3.69	13	19
934 935	43.0	45.2	11.8	3.83	3.86	3.69	12	19
872 873	49.9	45.3	4.8	3.81	3.85	3.77	23	14
878 879	50.9	46.5	2.6	3.81	3.85	3.77	23	17
866 867	44.1	51.2	4.8	3.84	3.86	3.70	23	20
868 869	44.5	53.1	2.4	-	-	-	-	-
870 871	44.3	54.5	1.2	3.84	3.86	3.73	23	19

Table AA-10: Film composition measured by EDS, the lattice parameters of A1 (a) and $L1_0$ (a and c) phases, and the as-deposited and annealed grain sizes calculated using Scherrer's equation in FeBPt films.
Table A-11: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (Δ H) for the A1 to L1₀ transformation in FeCPt films. The Curie temperature of the L1₀ phase (T_c) is also given. The compositions of the ternary alloy films are listed in the order of increasing Pt content. The errors on the KOT and activation energy are estimated at ±2 °C and ± 0.1 eV, respectively.

Run ID	Composition (EDS)			КОТ	T _C	Q	ΔH
	Fe (at.%)	Pt (at.%)	C (at.%)	(°C)	(°C)	(eV)	(kJ / g - atom)
986 987	49.8	48.8	1.4	390	459 ± 3	1.5	11.0 ± 3.0

Appendix B:

X-ray Diffraction Calculation

X-ray diffraction (XRD) is a non-destructive technique that can be used for phase identification of as-deposited and annealed films; for determination of the long-range order parameter of the $L1_0$ FePt phase.

JCPDS (Joint Committee on Powder Diffraction Standards) and ICSD (Inorganic Crystal Structure Database) provide XRD patterns for variety of materials and chemicals. However, the XRD patterns of some materials, such as $L1_0$ FePt films at different compositions cannot be obtained from both sources.

The peak intensity for XRD patterns can be calculated by using Eq. B-1.[Warren 1990]

$$I = \frac{I_0}{16\pi R} \left(\frac{e^4}{m^2 c^4}\right) \frac{\lambda^2 M_{hkl} F_{hkl}^2}{2\,\mu \, v_a^2} \left(\frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin \theta \sin 2\theta}\right) Exp(-2M) \qquad B-1$$

Where I_0 is the incoming beam intensity, R is the radius of the diffractometer, e is the electron charge, m is the electron mass, c is the speed of light, λ is the wavelength of X-ray radiation, M_{hkl} is the multiplicity, v_a is the unit volume of the unit cell. The term $\frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin \theta \sin 2\theta}$ is the combined Lorentz and Polarization correction factors for the PANalytical X'Pert diffractometer. The $\cos^2 (2\theta_m)$ term accounts for the graphite monochromator that is placed before the detector; and the $2\theta_m$ angle for the monichromatorr is 26.57°.

For Si sample, μ is the averaged mass absorption coefficient; and is a constant for Si sample. F_{hkl}, the structure factor, can be expressed as equation B-2.

$$F_{hkl} = \sum_{j=1}^{\# of \ atoms \ in \ unit \ cell} f_j \exp\left(-2\pi i \left(hx_j + ky_j + lz_j\right)\right)$$
B-2

Where hkl are miller indices for the given reflection, x_j , y_j and z_j are fractional coordinates for atom j and f_j .

The atomic scattering factor, which can be expressed as equation B-3, includes the atomic scattering factor without correction (f₀) that can be obtained from equation B-4.[Wilson 1992] $\nabla f'$ and $\nabla f''$, which are the dispersion corrections for the real and imaginary parts, respectively, The term a, b, and c for the atomic scattering factor without correction are calculated parameters for the condition where 2.0 Å⁻¹ < sin θ / λ <6.0 Å⁻¹.[Wilson 1992]

$$f_j^2 = (f_0 + \nabla f')^2 + (f_0 + \nabla f'')^2$$
 B-3

$$f_0\left(\frac{\sin\theta}{\lambda}\right) = \left(\sum_{i=1}^4 a_i \exp\left(\frac{b_i \sin^2\theta}{\lambda}\right) + c_i\right)$$
B-4

The term M in the temperature factor for randomly oriented Si sample can be expressed as $M = B \frac{\sin \theta}{\lambda}$, where B can be obtained from values given in Sears' and Peng's.[Sears 1991; Peng 1996] λ is the wavelength of X-ray radiation and θ is the angle of x-ray incoming beam.

For FePt system, the absorption coefficient, μ , can be express as equation B-5.[Schulz 1949]

$$\mu = \left[\left(\frac{\mu}{\rho} \right)_{Fe} wt.\% Fe + \left(\frac{\mu}{\rho} \right)_{Pt} wt.\% Pt \right] \times \left[X_{Fe} \rho_{Fe} + X_{Pt} \rho_{Pt} \right]$$
B-5

 X_{Fe} and X_{Pt} are the atomic percentage of Fe and Pt in the sample, respectively. The values of μ/ρ can be find for Fe and Pt in Warren's book.[Warren 1990] ρ is the density of each element.

The temperature term M is given as

$$M = \frac{(Q\sigma)^2}{2}$$
B-6

Where σ is the root-mean-square displacement amplitude of atoms caused by dynamic and static displacement.[Cullity 1956; Berry 2007] *Q* is expressed as

$$Q = \frac{4\pi\sin\theta}{\lambda}$$
B-7

The structure factor, F for both the fundamental and superlattice peaks in $L1_0$ FePt alloys are expressed by [Cebollada 2002]

$$F_{fund} = 4 \left(X_{Fe} f_{Fe} + X_{Pt} f_{Pt} \right)$$
B-8

$$F_{\rm sup} = 2S(f_{Fe} - f_{Pt})$$
B-9

Where X_{Fe} and X_{Pt} are atomic percent of Fe and Pt in the system, respectively. f_{Fe} and f_{Pt} are atomic scattering factors for Fe and Pt, respectively. The term *S* is order parameter for L1₀ FePt sample.

Table B-1 is the calculation of 20 angles and corresponding peak intensities for randomly oriented Si and L1₀ FePt. The lattice parameters of a, b and c for Si are 5.4309 Å, and the lattice parameters of a, b and c for L1₀ FePt are 3.845, 3.845 and 3.701 Å, respectively. Figure B-1 and B-2 are calculated X-ray diffraction patterns for randomly oriented Si and L1₀ FePt, respectively.

Table B-1. The calculation of 2 θ angles and corresponding peak intensities for randomly-oriented Si and 0.5 µm thick L1₀ FePt. The lattice parameters of a, b and c for Si are 5.4309 Å, and the lattice parameters of a, b and c for L10 FePt are 3.845, 3.845 and 3.701 Å, respectively.

	Si		L1 ₀ FePt			
h k l	2θ (Degree)	Normalized Intensities (%)	h k l	2θ (Degree)	Normalized Intensities (%)	
111	28.44	100.00	001	24.06	50.21	
220	47.31	66.70	110	32.96	36.21	
311	56.13	39.50	111	41.22	100.00	
400	69.13	10.46	200	47.31	28.91	
3 3 1	76.38	15.67	0 0 2	49.26	12.25	
422	88.03	21.80	201	53.76	12.42	
5 1 1 3 3 3	94.96	12.47	112	60.55	7.77	
440	106.71	8.02	220	69.14	5.71	
531	114.10	15.50	202	70.69	10.35	
620	127.55	16.28	221	74.38	3.41	
533	136.90	9.12	003	0 0 3 77.39		
			310	78.74	2.73	



Figure B-1: Calculated X-ray diffraction patterns for randomly oriented Si.



Figure B-2: Calculated X-ray diffraction patterns for randomly oriented Si.

Appendix C:

XRD Calculation Validation and Sample Area Correction

The purpose of the experiments is to validate the method for calculating X-ray diffraction (XRD) peak intensities and to also determine the intensity relationship between large-thick and small (5mm x 5mm) - thick samples. The intensity relationship can be used as area factor for correcting the intensity of small (5mm x 5mm) $L1_0$ FePt sample.

Experiment

Three randomly-oriented Si powder samples, were used for the experiments. One sample was supplied by Seagate Technology and other two samples, which are large-thick and small (5mm x 5mm) - thick samples, were prepared at Carnegie Mellon University by mixing Si powder supplied from NIST (National Institute of Standards and Technology) with collodion. The sample is large compared to the beam size and thick compared with the absorption length for Si. Note that the Carnegie Mellon large-thick and small-thick samples were prepared separately. The small Seagate Si sample was obtained by covering the larger sample with Al foil and exposing only a 5mm x 4mm

region of the sample. All the XRD experiments were performed on a Philips X'Pert Xray Diffractometer using capillary optics and a beam size of 5 mm (height) x 4 mm (width). In addition, the larger-thick sample were also performed on a Rigaku X-ray Diffractometer to double check the validation of the calculation.

To validate the method for the calculation of X-ray peak intensities, $\theta/2\theta$ scan was performed on the large-thick Si samples from CMU and Seagate. In order to determine the area correction needed in intensity calculations for small samples, $\theta/2\theta$ scan was also carried out on the small-thick CMU and Seagate Si samples. The X-ray diffraction pattern of the partially covered sample was checked to make sure that the Al peaks did not overlap with Si.

The intensity ratio of large (3" diameter wafer / small (5mm x 5mm) $L1_0$ FePt sample with 46.9 at.% Pt was acquired to verify the area factor obtained from Si results. The small sample was prepared by dicing a 3" diameter FePt sample that was annealed at 700 °C for 30 minutes.

Additional experiments of Psi scans on both small-thick and larger-thick samples are performed to acquire the tilting information. The randomness of all these Si samples were checked using Phi scans while fixing 20 at 28.47° (111) and 47.32° (220), respectively.

Result and Discussion

Figures C-1 and C-2 are XRD patterns for large-thick and small-thick samples, respectively. The XRD pattern for Al was shown in Fig. C-3. To validate the XRD calculation method, the intensities of large-thick sample was normalized by taking the intensity of (111) peak to be 100% and all the other peak intensities were divided by the intensity of (111) peak to obtain the relative intensities. Table C-1 is the comparison of experimental intensities from Seagate and CMU with the theoretical calculation. The experiments and theoretical calculation show reasonably good agreement. The difference may caused by lack of perfect randomness and sample roughness. By examining the ratio of theory/experiment, the CMU sample shows better result in terms of the standard deviation.



Figure C-1: XRD patterns of large-thick samples for (a) Seagate and (b) CMU.



Figure C-2: XRD patterns of small-thick samples for (a) Seagate and (b) CMU.



Figure C-3: XRD patterns of Al foil that is used for acquire small-thick Seagate sample.

Table C-1:	The peak intensity comparison between the theoretical calculations and randomly orientated large-thick Si
samples that	are provided by Seagate and fabricated at CMU

Experimental (Seagate)		Theoretical		Experimer	ntal (CMU)	Ratio of Theoretical / Experimental		
20 (Degree)	Normalized Intensities	20 (Degree)	Normalized Intensities	20 (Degree)	Normalized Intensities	Seagate	CMU	
28.44	100.00	28.44	100.00	28.43	100.00	1.00	1.00	
47.30	64.34	47.31	66.70	47.29	47.29 61.28		1.09	
56.13	32.31	56.13	39.50	56.11 33.58		1.22	1.18	
69.15	8.50	69.13	10.46	69.15	69.15 8.14		1.29	
76.36	12.38	76.38	15.67	76.38	14.01	1.27	1.12	
88.04	20.54	88.03	21.80	88.04	19.83	1.06	1.10	
94.97	9.81	94.96	12.47	94.96 10.89		1.27	1.14	
106.73	7.04	106.71	8.02	106.72 6.94		1.14	1.16	
114.19	12.59	114.10	15.50	114.10 13.31		1.23	1.16	
127.98	14.61	127.55	16.28	127.93	14.07	1.11	1.16	
137.35	8.48	136.90	9.12	137.41	8.35	1.08	1.09	
				Average of Ratio		1.15	1.13	
				STD of Ratio		0.10	0.07	

The XRD calculation was also validated with the result acquired from Rigaku X-ray diffractometer with parallel beam source. Figure C-4 is the XRD pattern of large-thick sample; and the average ratio of theoretical / experimental yield and standard deviation of ratio are 1.11 and 0.09, respectively. This results from parallel beam source also confirmed the methodology used for calculating the XRD patterns.



Figure C-4: XRD patterns of large-thick CMU sample by using Rigaku X-ray diffractometer with parallel beam source.

To determine the relationship between peak intensities of large-thick and small-thick samples, the intensities of the small sample were also normalized by taking the (111) peak intensity to be 100%. The intensity contribution from the Al foil was subtracted where necessary. For example, the Al foil has a small hump at 20 equals 46.85 (caused by alloying elements or impurities in the Al foil), which overlaps with the Si (220) peak (47.30), therefore, the intensity of this peak was subtracted from Si (220) peak. Table C-2 is the comparison of intensities for the small Si sample and theoretical calculation.

Theor	retical	Experimental (Seagate)	Experimental (CMU)	Ratio of Theoretical / Experimental		
20 (Degree)	Normalized Intensities	Normalized Intensities	Normalized Intensities	Seagate	CMU	
28.44	100.00	100.00	100.00	1.00	1.00	
47.31	66.70	137.19	101.15	0.49	0.66	
56.13	39.50	95.75	67.70	0.41	0.58	
69.13	10.46	25.05	19.68	0.42	0.53	
76.38	15.67	47.34	33.48	0.33	0.47	
88.03	21.80	76.51	48.78	0.28	0.45	
94.96	12.47	39.03	27.39	0.32	0.46	
106.71	8.02	21.76	17.98	0.37	0.45	
114.10	15.50	57.27	34.98	0.27	0.44	
127.55	16.28	60.20	37.12	0.27	0.44	
136.90 9.12		31.49	20.86	0.29	0.44	

Table C-2: The comparison of peak intensites between the theoretical calculations and randomly

 orientated small-thick Si samples that are provided by Seagate and fabricated at CMU

The relationship between intensities of large and small Si samples can be determined by plotting the intensity ratio of theoretical calculation / experimental as a function of 2θ , shown in Fig. C-5.



Figure C-5: The intensity ratio of theoretical calculation / experiment decrease as 20 increase.

As we can see, the trend is the same, but the Seagate result is below the CMU result. The possible reason is the low intensity of the (111) peak resulting from the blocking of incoming beam by the Al foil (shown in Figure C-6). Therefore, the intensity correction equation for small sample area (which is the case for measurements done on FePt films deposited on oxidized Si for order parameter measurements) should be calculated based on the CMU result, which is the equation C-1.

Theortical Value =
$$2.24 \times \exp\left(-\frac{Intensity\ from\ small\ sample}{20.78}\right) + 0.43$$
 C-1



Figure C-6: Demonstration of blocking incoming beam by Al foil onto small-thick Seagate sample.

The intensity ratios of (001) / (002) and (110) / (220) for lager FePt sample were compared with those for small FePt sample after implementing the area correction acquired from Si result (Eq. C-2). A scale factor of 1.11 with standard deviation of 4% was obtained to account for the difference between the large and small samples. Therefore the proper intensity ratio for superlattice / fundamental peaks for L1₀ FePt should be expressed as

Intensity ratio (superlattice / fundamental) for large sample = 1.11× Intensity ratio (superlattice / fundamental) for small sample

C-2

The defocusing curve and Gaussian fitting of large and small samples are given in figure C-7 and C-8. A 3D intensity correction map for randomly oriented small sample is plotted in Fig. C-9.

In addition, the randomness of Si sample for both large and small samples were checked by Phi scan while fixing 2θ at 28.47 and 47.32, respectively (Fig. C-10 and C-11).

Summary

The XRD calculation method has been validate by the Si result both sample from Seagate and prepared at CMU. The area correction should base on the result from CMU sample. The scale factor of 1.11 that acquired from FePt film should be implemented into calculation of order parameter for FePt system. In addition, a 3D intensity correction map has been provided.



Figure C-7: Defocusing curve and Gaussian fitting of large- thick sample for (a) (111) peak, (b) (220) peak, (c) (311) peak, (d) (400) peak, (e) (331) peak and (f) (422).



Figure C-8: Defocusing curve and Gaussian fitting of small- thick sample for (a) (111) peak, (b) (220) peak, (c) (311) peak, (d) (400) peak, (e) (331) peak and (f) (422).



Figure C-9: 3D Intensity correction map for randomly oriented small sample.



Figure C-10: Psi scan of randomly oriented large Si samples at 20 equal (a) 28.47 and (b) 47.32.



Figure C-11: Psi scan of randomly oriented small Si samples at 20 equal (a) 28.47 and (b) 47.32.

Appendix D:

Order Parameter of FePt System

The long rang order parameter on the magnetic properties of FePt system can be expressed as

$$S = \frac{r_a - X_A}{y_B}$$
D-1

where r_{α} is the fraction of α sites occupied by the correct atoms, X_A is the fraction of A atoms and y_{β} is the fraction of β sites. The order parameter can be determined from the intensity ratio of superlattice / fundamental peaks from XRD patterns (Eq. D-2).[Cullity 1956]

$$\frac{I_{\text{sup}}}{I_{\text{fund}}} = \frac{AF_{\text{sup}}^2 LP \exp(-2M)}{AF_{\text{fund}}^2 LP \exp(-2M)}$$
D-2

Where I_{sup} and I_{fund} are intensities for superlattice and fundamental peaks, respectively. And F_{sup} and F_{fund} are structure factors for superlattice and fundamental peaks, respectively. [Cebollada 2002] LP is the combined Lorentz and Polarization correction factors, and exp(-2M) is the temperature factor. A is absorption factor that can be expressed as D-5.

$$F_{fund} = 4 \left(X_{Fe} f_{Fe} + X_{Pt} f_{Pt} \right)$$
D-3

$$F_{\rm sup} = 2S(f_{Fe} - f_{Pt})$$
 D-4

$$A = 1 - \exp\left(\frac{-2\,\mu t}{\sin(\theta)\cos(\psi)}\right) \qquad D-5$$

where ψ is the tilt angle and *t* is the film thickness.[Schulz 1949]

The order parameter can be determined by comparing the intensity ratio of theoretical calculation and the experimental results, which has implemented the area correction and scale factor for FePt small samples. (Appendix B) Table D-1 is the order parameter for binary FePt system with EDS composition, area correction, scale factor and updated peak intensity. Figure D-1 and D-2 are the plot of order parameter and order fraction, respectively, as a function of Pt content in binary FePt system, The maximum values for order parameter and fraction are 0.78 and 0.81, respectively, at 48.6 at.% Pt. The deviation of order parameter could come from the integrated peak intensities acquired from x-ray diffraction scans.

Table D-1. Film composition, 2 θ angle and intensities for {001}, {002}, {110} and {220} peaks, and order parameter. The tilt angle, 36.5° or 53.7° were chosen to bring the {110} and {001} into Bragg condition for these <111> textured film. The value σ is fitted to be 0.16 for the purpose of minimum the standard deviation of S values obtained form {001}/{002} and {110}/{220}.

Run ID	Composition		Ψ	Peak Intensity				S	Sava / Smar			
Fe (at.%)		Pt (at.%)	(degree)	(001)	(002)	(110)	(220)	Dave	Dave / Dmax			
632 57.7	42.30	36.50	6626.30	6772.60	15652.10	12659.60	0.61±0.02	0.72				
		53.70	11549.10	19496.90	4215.40	2789.50		0.72				
728 56.2	56.2	43.80	36.50	5156.60	4427.50	58003.90	60204.70	0.54+0.02	0.61			
	50.2 45.0	15.00	53.70	41436.90	95020.80	3249.90	1586.60	0.54±0.05	0.01			
720	52.9	47.10	36.50	15717.20	10680.90	3598.90	2799.30	0.68±0.00	0.72			
,20	02.9	17.10	53.70	2914.30	4139.50	2471.90	1219.30		0.72			
441	51.4	48 60	36.50	9657.60	7531.20	15413.10	8596.30	0.84+0.02	0.86			
	01.1	10.00	53.70	13320.90	12373.10	5591.30	3215.80	0.84±0.03	0.00			
SG02	51.4	51.4 48.60	36.50	18416.30	20106.50	18975.00	13362.10	0.74±0.02	0.76			
5302	01.1	10.00	53.70	9857.40	11824.20	8638.70	6274.80					
638	51.4	48.60	36.50	11844.70	7468.30	7571.20	4666.10	0.77+0.00	0.80			
050 51.4	40.00	53.70	5783.40	6667.40	2898.50	1389.70	0.77±0.00	0.00				
479 50.3	50.3	49 70	36.50	10125.90	9517.40	10933.30	7716.60	0.76±0.03	0.76			
	19.70	53.70	8792.80	10239.50	5341.00	3629.90	0.70±0.03					
731	49.8	50.20	36.50	12477.00	7675.00	1599.00	1083.00	0.78±0.04	0.79			
, 51	17.0		53.70	1540.80	1652.60	1795.20	889.40					
353	47.2	47.2 52.80	36.50	15998.00	10689.50	12777.20	14273.00	0.61±0.01	0.65			
555	17.2		53.70	9312.60	18559.80	815.60	371.30					
492	47.2	52.80	36.50	2320.80	2441.60	20687.30	14683.90	0.82+0.00	0.87			
172	17.2	17.2 02.00	53.70	20167.00	19355.80	2051.80	1533.60	0.83±0.09	0.07			
641	46 3	46.3 53.70	36.50	6485.20	4317.10	28179.60	24935.00	0.001	0.71			
041					5	53.70	24330.60	47133.50	1269.40	631.60	0.66±0.04	0.71
635	44.6	55 40	36.50	6715.60	4558.60	39415.10	42493.70	0.58+0.07	0.65			
	11.0				53.70	32459.10	94955.90	1095.50	591.40	0.38±0.07	0.00	
	44.5		36.50	2714.50	2780.40	19446.50	14494.30	0.75±0.02				
496		55.50	53.70	17813.30	27167.70	2059.70	1607.80		0.84			
				53.70	5480.00	6654.20	2815.00	1293.20]			



Figure D-1: Long range order parameter (S) plotted as a function of Pt content for binary FePt films. Films with same or close compositions (≤ 0.1 at.%), the average values of S are calculated and presented.



Figure D-2: Order fraction (S/S_{max}) plotted as a function of Pt content for binary FePt films. Films with same or close compositions (≤ 0.1 at.%), the average values of (S/S_{max}) are calculated and presented.

Appendix E:

Fitting of k₂(T)N(T,t) model

To simulate the non-isothermal DSC traces at four heating rate, three parameters, namely Q_g , *m* and γ , were used in k₂(T)N(T,t) model. The fitting quality was determined from root mean square (RMS). Examples of the impact of Q_g , *m* and γ are given in Figs. E-1 to E-4 as well as the RMS values. Figs. E-1 and E-2 shows the correction between m and γ for same activation energy Q_g , whereas Figs. E-1 and E-3 illustrates the interaction of Q_g and γ for same m. These examples are served for demonstrating the impact of fitting parameters on the RMS.



RMS = 3.7

Figure E-1: Comparison of experimental and simulated DSC trace using $k_2(T)N(T,t)$ model for the A1 to L1₀ transformation in Fe_{52.9}Pt_{47.1} at the heating rate of (a) 20°C/min (b) 40°C/min (c) 80°C/min and (d) 160°C/min.



RMS = 4.7

Figure E-2: Comparison of experimental and simulated DSC trace using $k_2(T)N(T,t)$ model for the A1 to L1₀ transformation in Fe_{52.9}Pt_{47.1} at the heating rate of (a) 20°C/min (b) 40°C/min (c) 80°C/min and (d) 160°C/min.



RMS = 7.9

Figure E-3: Comparison of experimental and simulated DSC trace using $k_2(T)N(T,t)$ model for the A1 to L1₀ transformation in Fe_{52.9}Pt_{47.1} at the heating rate of (a) 20°C/min (b) 40°C/min (c) 80°C/min and (d) 160°C/min.

Appendix F:

X-ray Diffraction Patterns and DSC Traces

The appendix contains DSC traces and X-ray diffraction patterns for the binary FePt system and 7 ternary systems, namely, FeMgPt, FeVPt, FeMnPt, FeAgPt, FeAuPt, FeBPt and FeCPt.

For binary FePt films that were used for the elevated temperature study, the figures are given in the following format.

Sample Composition DSC traces XRD for as-deposited film at 0° tilt XRD for as-deposited film at 36.5° tilt XRD for as-deposited film at 53.7° tilt

The purpose of tilting as-deposited samples with 35.5° and 53.7° is to bring {110} and {001} planes into Bragg condition for the <111> textured films.

For room temperature deposited binary FePt films and ternary films studied, which include FeMgPt, FeVPt, FeMnPt, FeAgPt, FeAuPt, FeBPt and FeCPt, the figures are given in the following format.

Sample Composition DSC traces XRD for as-deposited film XRD for anneal film at 0° tilt XRD for anneal film at 36.5° tilt XRD for anneal film at 53.7° tilt

The purpose of tilting annealed sample with 35.5° and 53.7° is to bring {110} and {001} planes into Bragg condition for the <111> textured films.







Fig. F-1: (a) the DSC traces for $Fe_{56.2}Pt_{43.8}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.







Fig. F-2: (a) the DSC traces for $Fe_{54.4}Pt_{45.6}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.




Fig. F-3: (a) the DSC traces for $Fe_{51.2}Pt_{48.8}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.





Fig. F-4: (a) the DSC traces for $Fe_{46.5}Pt_{53.5}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.







Fig. F-5: (a) the DSC traces for $Fe_{57.6}Pt_{42.4}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.





Fig. F-6: (a) the DSC traces for $Fe_{52.3}Pt_{47.7}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.





Fig. F-7: (a) the DSC traces for $Fe_{57.6}Pt_{42.4}$ film







Fig. F-8: (a) the DSC traces for $Fe_{56.4}Pt_{43.6}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.







Fig. F-9: (a) the DSC traces for $Fe_{53.1}Pt_{46.9}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.







Fig. F-10: (a) the DSC traces for $Fe_{50.5}Pt_{49.5}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.







Fig. F-11: (a) the DSC traces for $Fe_{46.0}Pt_{54.0}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.





Fig. F-12: (a) the DSC traces for $Fe_{51.8}Pt_{48.2}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.







Fig. F-13: (a) the DSC traces for $Fe_{56.4}Pt_{43.6}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.





Fig. F-14: (a) the DSC traces for $Fe_{51.5}Pt_{48.5}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.





Fig. F-15: (a) the DSC traces for $Fe_{46.4}Pt_{53.6}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the as-deposited film at 36.5° tilt and (d) the XRD pattern for the as-deposited film at 53.7° tilt.





Fig. F-16: (a) the DSC traces for $Fe_{57.0}Pt_{43.0}$ film





Fig. F-17: (a) the DSC traces for $Fe_{54,3}Pt_{45,7}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.







Fig. F-18: (a) the DSC traces for $Fe_{52.4}Pt_{47.6}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.







Fig. F-19: (a) the DSC traces for $Fe_{47.7}Pt_{52.3}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.





Fig. F-20: (a) the DSC traces for $Fe_{43.9}Pt_{56.1}$ film.





Fig. F-21: (a) the DSC traces for $Fe_{57,2}Mg_{0,7}Pt_{42,1}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.







Fig. F-22: (a) the DSC traces for $Fe_{52.1}Mg_{1.8}Pt_{46.2}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.


Fe_{53.8}Mg_{0.0}Pt_{46.3}



Fig. F-23: (a) the DSC traces for $Fe_{53.8}Mg_{0.0}Pt_{46.3}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.





Fig. F-24: (a) the DSC traces for $Fe_{53.3}Mg_{0.3}Pt_{46.4}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.







Fig. F-25: (a) the DSC traces for $Fe_{48.8}Mg_{2.6}Pt_{48.6}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.







Fig. F-26: (a) the DSC traces for $Fe_{43.0}V_{12.2}Pt_{44.8}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.





Fig. F-27: (a) the DSC traces for $Fe_{53.6}V_{0.7}Pt_{45.7}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.







Fig. F-28: (a) the DSC traces for $Fe_{47.7}V_{5.8}Pt_{46.5}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.

 $Fe_{48.3}V_{3.1}Pt_{48.6}$





Fig. F-29: (a) the DSC traces for $Fe_{48.3}V_{3.1}Pt_{48.6}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.







Fig. F-30: (a) the DSC traces for $Fe_{45.7}Mn_{10.7}Pt_{43.6}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.



Fig. F-31: (a) the DSC traces for $Fe_{47.2}Mn_{6.0}Pt_{46.8}$ film.



Fig. F-32: (a) the DSC traces for $Fe_{49.1}Mn_{2.2}Pt_{48.6}$ film.



Fig. F-33: (a) the DSC traces for $Fe_{42.6}Mn_{4.3}Pt_{53.1}$ film.



Fe_{28.3}Mn_{16.3}Pt_{55.4}



Fig. F-34: (a) the DSC traces for $Fe_{28.3}Mn_{16.3}Pt_{55.4}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.







Fig. F-35: (a) the DSC traces for $Fe_{44,2}Ag_{16,7}Pt_{39,1}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.

Fe_{50.0}Ag_{6.9}Pt_{43.1}





Fig. F-36: (a) the DSC traces for $Fe_{50.0}Ag_{6.9}Pt_{43.1}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.

Fe_{49.1}Ag_{3.4}Pt_{47.5}





Fig. F-37: (a) the DSC traces for $Fe_{49,1}Ag_{3,4}Pt_{47.5}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.



Fig. F-38: (a) the DSC traces for $Fe_{50.5}Ag_{0.0}Pt_{49.5}$ film.

Fe_{48.7}Ag_{1.5}Pt_{49.8}





Fig. F-39: (a) the DSC traces for $Fe_{48.7}Ag_{1.5}Pt_{49.8}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.

Fe_{45.2}Au_{13.8}Pt_{41.0}





Fig. F-40: (a) the DSC traces for $Fe_{45.2}Au_{13.8}Pt_{41.0}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.

Fe_{50.9}Au_{4.1}Pt_{45.0}





Fig. F-41: (a) the DSC traces for $Fe_{50.9}Au_{4.1}Pt_{45.0}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.







Fig. F-42: (a) the DSC traces for $Fe_{47,2}Au_{7,2}Pt_{45.6}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.




Fig. F-43: (a) the DSC traces for $Fe_{52.2}Au_{1.9}Pt_{45.9}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.



Fe_{38.6}Au_{7.2}Pt_{54.2}



Fig. F-44: (a) the DSC traces for $Fe_{38.6}Au_{7.2}Pt_{54.2}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.



Fig. F-45: (a) the DSC traces for $Fe_{46.3}Au_{12.9}Pt_{40.8}$ film.





Fig. F-46: (a) the DSC traces for $Fe_{45.1}B_{12.3}Pt_{42.7}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.



 $Fe_{43.0}B_{11.8}Pt_{45.2}$



Fig. F-47: (a) the DSC traces for $Fe_{43.0}B_{11.8}Pt_{45.2}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.







Fig. F-48: (a) the DSC traces for $Fe_{49.9}B_{4.8}Pt_{45.3}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.







Fig. F-49: (a) the DSC traces for $Fe_{50.9}B_{2.6}Pt_{46.5}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.







Fig. F-50: (a) the DSC traces for $Fe_{44.1}B_{4.8}Pt_{51.2}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.





Fig. F-51: (a) the DSC traces for $Fe_{44.5}B_{2.4}Pt_{53.1}$ film.





Fig. F-52: (a) the DSC traces for $Fe_{44.3}B_{1.2}Pt_{54.5}$ film (b) the XRD pattern for the as-deposited film (c) the XRD pattern for the annealed film at 0° tilt (d) the XRD pattern for the annealed at film 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.





Fig. F-53: (a) the DSC traces for $Fe_{49.8}C_{1.4}Pt_{48.8}$ film.

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