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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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by

Bincheng Wang

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ABSTRACT

$L_10$ 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 $\geq 400 \, ^\circ C$ to form the ordered $L1_0$ 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 $L1_0$ 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 $40 \, ^\circ C/\text{min}$, 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}Pt_{50.9} 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.
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## LIST OF ACRONYMS/ABBREVIATIONS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>Areal density</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive x-ray spectrometry</td>
</tr>
<tr>
<td>EDXRF</td>
<td>Energy dispersive x-ray fluorescence</td>
</tr>
<tr>
<td>GMR</td>
<td>Giant magnetoresistance</td>
</tr>
<tr>
<td>HAMR</td>
<td>Heat assisted magnetic recording</td>
</tr>
<tr>
<td>HDD</td>
<td>Hard drive disk</td>
</tr>
<tr>
<td>LMR</td>
<td>Longitudinal magnetic recording</td>
</tr>
<tr>
<td>MCA</td>
<td>Magnetocrystalline anisotropy energy</td>
</tr>
<tr>
<td>MR</td>
<td>Magnetoresistive</td>
</tr>
<tr>
<td>PMR</td>
<td>Perpendicular magnetic recording</td>
</tr>
<tr>
<td>RAMAC</td>
<td>Random access method of accounting and control</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal to noise ratio</td>
</tr>
<tr>
<td>SUL</td>
<td>Soft underlayer</td>
</tr>
<tr>
<td>TTT</td>
<td>Time-temperature-transformation</td>
</tr>
<tr>
<td>WDS</td>
<td>Wavelength dispersive x-ray spectrometry</td>
</tr>
<tr>
<td>Λ</td>
<td>Atomic jump distance</td>
</tr>
<tr>
<td>ϕ</td>
<td>DSC signal</td>
</tr>
<tr>
<td>Γ</td>
<td>Interface energy</td>
</tr>
<tr>
<td>τ</td>
<td>Nucleation time for L1₀ phase</td>
</tr>
<tr>
<td>Ω</td>
<td>Vibration frequency of the atoms</td>
</tr>
</tbody>
</table>
\( \Delta G^* \)  
Critical free energy

\( \Delta G_m \)  
Atomic migration free energy per atom.

\( \Delta G_{mol} \)  
Molar free energy

\( \Delta G_S \)  
Misfit strain free energy

\( \Delta G_V \)  
Volumetric free energy

\( \Delta H \)  
Latent heat

\( \Delta S_m \)  
Migration entropy

\( C_0 \)  
Number of potential nucleation sites per unit volume

\( C_1 \)  
Heterogeneous nucleation sites per unit volume

\( I \)  
Nucleation rate

\( I_0 \)  
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

\( M \)  
Growth dimensionality

\( N \)  
Avrami exponent

\( N \)  
Nucleation density

\( Q_{\text{eff}} \)  
Effective activation energy

\( Q_G \)  
Activation energy for growth

\( Q_{\text{kiss}} \)  
Kissinger activation energy

\( Q_N \)  
Activation energy for nucleation

\( r^* \)  
Critical radius for nucleus
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$S(\theta)$</td>
<td>Shape factor for heterogeneous nucleation</td>
</tr>
<tr>
<td>$T$</td>
<td>Growth time for L1$_0$ phase</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Curie temperature of L1$_0$ phase</td>
</tr>
<tr>
<td>$T_e$</td>
<td>Equilibrium ordering temperature</td>
</tr>
<tr>
<td>$v$</td>
<td>Growth velocity</td>
</tr>
<tr>
<td>$V^\alpha$</td>
<td>Real volume of parent phase</td>
</tr>
<tr>
<td>$V^\beta$</td>
<td>Real volume of product phase</td>
</tr>
<tr>
<td>$X_E$</td>
<td>Extended volume fraction transformed</td>
</tr>
<tr>
<td>$X_v$</td>
<td>Actual volume fraction transformed</td>
</tr>
<tr>
<td>$Z$</td>
<td>Zeldovich non equilibrium factor</td>
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</table>
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 L₁₀ 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, k₂(T) and k₂(T)N(T) have been re-investigated with updated film compositions; and a new continuous nucleation model, k₂(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 k₂(T) model. Elevated temperature deposition for films (with ~ 48.6 at.% Pt) and laser annealing of room temperature deposited films result in faster transformation kinetics than predicted by the k₂(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\textsubscript{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\textsubscript{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 L1₀ 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 L1₀ 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/in^2. It is envisioned that hard disk drives will reach 1 Tbits/in^2 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].](image)

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 disk 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, i.e., 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, $k_B T$ should at least over 50. (Eq. 2.2) [Weller 1999; Weller 2000]

$$\frac{K_u V}{k_B T} \geq 50 - 70$$

(Eq. 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 L1_0 and rare-earth based alloys are listed in Table 2.1.[Klemmer 1995; Weller 2000; Shimatsu 2005] The chemically-ordered, tetragonal L1_0 crystal structure of FePt alloy with $K_u$ at $6.6 \times 10^7$ erg/cm$^3$ 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]

<table>
<thead>
<tr>
<th>Alloy System</th>
<th>Material</th>
<th>$K_u \ (10^6 \text{ J/m}^3)$</th>
<th>$K_u \ (10^7 \text{ erg/cm}^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Elements</td>
<td>hcp-Co</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>0.048</td>
<td></td>
</tr>
<tr>
<td>Co-Alloys</td>
<td>CoPtCr</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co3Pt</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>L10 Ordered Structures</td>
<td>FePd</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FePt</td>
<td>6.6-10</td>
<td></td>
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<tr>
<td></td>
<td>CoPt</td>
<td>4.9</td>
<td></td>
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<tr>
<td></td>
<td>MnAl</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Rare-Earth Transition Metal Compounds</td>
<td>Fe14Nd2B</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SmCo5</td>
<td>11-20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NdCo5</td>
<td>15</td>
<td></td>
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</table>
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 (HAMAR) 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 L1₀ 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 L1₀ phase. To better understand the relationship between the A1 and L1₀ 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, ½, ½) position and Au atoms occupy the (0, 0, 0) and (½, ½, 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 \( L_1^2 \) phases of \( Au_3Cu \) and \( AuCu_3 \) with site positions at \((0, 0, 0)\) and \((0, \frac{1}{2}, \frac{1}{2})\), are the prototypes of \( L_1^2 Fe_3Pt \) and \( FePt_3 \), 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 \( L_1^2 Fe_3Pt \) and \( FePt_3 \) 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.

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

<table>
<thead>
<tr>
<th>Phase</th>
<th>Prototype</th>
<th>Strukturbericht Designation</th>
<th>Space Group</th>
<th>Pearson’s Symbol</th>
<th>Unit Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>(γ Fe, Pt)</td>
<td>Cu</td>
<td>A1</td>
<td>Fm$\overline{3}$m</td>
<td>cF4</td>
<td></td>
</tr>
<tr>
<td>Fe₃Pt</td>
<td>AuCu₃</td>
<td>L₁₂</td>
<td>Pm$\overline{3}$m</td>
<td>cP₄</td>
<td></td>
</tr>
<tr>
<td>FePt</td>
<td>AuCu I</td>
<td>L₁₀</td>
<td>P$\frac{4}{m}$</td>
<td>tP₂</td>
<td></td>
</tr>
<tr>
<td>FePt₃</td>
<td>AuCu₃</td>
<td>L₁₂</td>
<td>Pm$\overline{3}$m</td>
<td>cP₄</td>
<td></td>
</tr>
</tbody>
</table>
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 L1\textsubscript{0} 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, $\Delta G$, for the phase transformation can be expressed as Eq. 2.3, where $V$ is the volume of transformed phase, $A$ is the interface area, $\gamma$ is interface energy, $\Delta G_v$ and $\Delta G_s$ are the magnitude of the volumetric free energy change and misfit strain free energy, respectively.

$$\Delta G = -V\Delta G_v + A\gamma + V\Delta G_s$$ (2.3)

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

$$\Delta G = -\frac{4}{3}\pi r^3 (\Delta G_v - \Delta G_s) + 4\pi r^2 \gamma$$ (2.4)

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

$$r^* = \frac{2\gamma}{(\Delta G_v - \Delta G_s)}$$ (2.5)
\[ \Delta G^* = \frac{16\pi r^3}{3\left(\Delta G_v - \Delta G_s\right)^2} \]  

(2.6)

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

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

(2.7)

where \( \omega \) is the vibration frequency of the atoms, \( Z \) is the Zeldovich non equilibrium factor and \( C_0 \) is the number of potential nucleation sites per unit volume in the phase and \( \Delta G_m \) is the atomic migration free energy per atom.

The activation energy barrier for heterogeneous nucleation is given by

\[ \frac{\Delta G_{\text{Het}}^*}{\Delta G_{\text{Hom}}^*} = S(\theta) \]  

(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 \( \theta \), 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 \( C_1 \) 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.

\[
X_v = 1 - \exp(-X_E)
\]  
(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 \(\alpha\) phase to product \(\beta\) phase in an infinitely
large system, the total volume \(V\) is given

\[
V = V^\alpha + V^\beta
\]  
(2.12)

where \(V^\alpha\) and \(V^\beta\) are the real volume of parent and product phases, respectively. The
extended volume, \(V_E^\beta\), the total volume of extended \(\beta\) phase that accounts for both the
impinged area for the growing region and phantom nucleation sites within already
transformed regions, can be related to \(V^\beta\) 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.

\[
dV^\beta = X^\alpha dV_E^\beta = \left(1 - \frac{V^\beta}{V}\right) dV_E^\beta = (1 - X^\beta)V_E^\beta
\]  

(2.13)

where \(X^\alpha\) and \(X^\beta\) are fraction of \(\alpha\) and \(\beta\) phases, respectively. The general JMAK expression can be acquired by rearranging the Eq. 2.13 and integrating the integrals.

\[
\frac{dV^\beta}{(1 - X^\beta)} = dV_E^\beta
\]  

(2.14)

\[
-\ln(1 - X^\beta) = X_E^\beta
\]  

(2.15)

\[
1 - X_E^\beta = \exp(-X_E^\beta)
\]  

(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\textsubscript{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

\[ X(t) = 1 - \exp\left(-\left(kt\right)^n\right) \quad (2.17) \]

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 \( \ln K^n \).

Avrami exponent \((n) = \text{nucleation condition} + \text{growth dimensionality} \times \text{growth mechanism} \quad (2.18)\)

\[
\ln\left(-\ln\left(1 - X_p\right)\right) = \ln K^n + n \ln t \quad (2.19)
\]
Table 2.3 The numerical values and corresponding physical conditions for nucleation conditions, growth dimensionality and growth mechanism.

<table>
<thead>
<tr>
<th>Nucleation condition</th>
<th>Growth dimensionality</th>
<th>Growth mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>0: site-saturated nucleation</td>
<td>1: 1-D growth</td>
<td>½: diffusion controlled transformations</td>
</tr>
<tr>
<td>1: constant nucleation rate</td>
<td>2: 2-D growth</td>
<td>1: interface controlled transformations</td>
</tr>
<tr>
<td></td>
<td>3: 3-D growth</td>
<td></td>
</tr>
</tbody>
</table>
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 L1_0 phase. Table 2.4 gives the JMAK parameters, $K^n$ (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 $\tau$ are the growth time and nucleation time for L1_0 phase, respectively. $\beta$ 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, $\Delta G^*$, or the activation energy barrier for nucleation, $Q_N$, could be used. For easy calculation of the critical radius and volume for nucleation, the $\Delta G^*$ 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 conditions.[Kissinger 1956; Berry 2007]

<table>
<thead>
<tr>
<th>Models</th>
<th>Constant nucleation rate</th>
<th>Burst nucleation</th>
<th>Pre-existing nuclei</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_2(T)N(T,t)$</td>
<td>$k_2(T)N(T)$</td>
<td>$MD$ and $k_2(T)$</td>
</tr>
<tr>
<td>$K^n$</td>
<td>$\frac{k I_0 k_2^m}{m + 1} \exp\left(-\frac{Q_N + m Q_G}{k_B T}\right)$</td>
<td>$k I'_0 k_2^m \exp\left(-\frac{Q_N + m Q_G}{k_B T}\right)$</td>
<td>$k N k_2^m \exp\left(-\frac{m Q_G}{k_B T}\right)$</td>
</tr>
<tr>
<td>$n$</td>
<td>$m + 1$</td>
<td>$m$</td>
<td>$m$</td>
</tr>
<tr>
<td>$Q_{eff}$</td>
<td>$Q_N + m Q_G$</td>
<td>$Q_N + m Q_G$</td>
<td>$m Q_G$</td>
</tr>
<tr>
<td>$Q_{Kiss}$</td>
<td>$\frac{Q_N + m Q_G}{n}$</td>
<td>$\frac{m Q_G}{n}$</td>
<td>$\frac{m Q_G}{n}$</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Models</th>
<th>Nucleation Conditions</th>
<th>$X_E$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Continuous Nucleation</td>
<td>$k I_0 \int_{\tau=0}^{\tau=t} \exp\left(-\frac{Q_N}{k_B T(\tau)}\right) \left(\int_{\tau'=\tau}^{\tau=t} k_2 \exp\left(-\frac{Q_G}{k_B T(t')}\right) dt'\right)^m d\tau$</td>
</tr>
<tr>
<td></td>
<td>Burst nucleation</td>
<td>$k I'<em>0 \exp\left(-\frac{Q_N}{k_B T(\tau_0)}\right) \left(\int</em>{\tau'=\tau_0}^{\tau=t} k_2 \exp\left(-\frac{Q_G}{k_B T(t')}\right) dt'\right)^m$</td>
</tr>
<tr>
<td></td>
<td>Pre-existing nuclei</td>
<td>$k N \left(\frac{K_2}{\beta} \right)^m \left(\frac{k_B T^2}{Q_G}\right)^m \exp\left(-\frac{m Q_G}{k_B T}\right)$</td>
</tr>
</tbody>
</table>

Analytically Solvable:
- No
- Yes
In isothermal experiments, the radius of a given nucleus that formed at time $\tau$ is given as the integral from $\tau$ to $t$.

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

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

$$X_v = 1 - \exp \left( - \int_{\tau=0}^{t} k I v^n (t - \tau)^m \, d\tau \right) \quad (2.21)$$

The nucleation rate $I$ is defined as

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

$C_0$ is the number of all potential sites for nucleus per unit volume, and the Zeldovich non-equilibrium 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] $\Delta G_m$ is the activation free energy for migration (Eq. 2.23). Where $\Delta H_m$ is the activation enthalpy for migration and $\Delta S_m$ 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, $\Delta G^*$, can be expressed as Eq. 2.24.
\[ \Delta G_m = \Delta H_m - T \Delta S_m \]  

(2.23)

\[ \Delta G^* = \frac{16 \pi r^3}{3 \Delta G_V} \]  

(2.24)

where \( \gamma \) is the surface energy between A1 and L1\textsubscript{0} phase, and \( \Delta G_V \) is the volumetric free energy converted from molar driving force, \( \Delta G_{mol} \).

The growth velocity is defined as [Christian 1975].

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

(2.25)

\( \alpha \), the atomic jump distance for FCC metal, is taken as the distance between nearest neighbor. The vibration frequency \( \omega \) was defined by [Christian 1975].

\[ \omega = \frac{k_B T}{h} \]  

(2.26)

where \( h \) is the Planck’s constant. This relationship for vibration frequency is valid below the Debye temperature. The entropy of migration \( \Delta S_m \) is approximated as [Zener 1952]

\[ \Delta S_m \approx \lambda \xi \frac{Q_m}{T_{melt}} \]  

(2.27)
where \( \lambda \) and \( \xi \), 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 \( \Delta G_{\text{mol}} \) is approximated by

\[
\Delta G_{\text{mol}} = \frac{\Delta H \Delta T}{T_e} = \frac{\Delta H}{T_e} (T - T_e)
\]  
(2.28)

the \( \Delta H \) and \( T_e \) are latent heat and equilibrium ordering temperature for the given alloy composition, respectively.[Massalski 1990]

Integrated Eq.2.21 yields

\[
X_v = 1 - \exp\left(-\frac{k}{m+1} I_v^m t^{m+1}\right)
\]  
(2.29)

Substituting Eq. 2.22 - 2.28 into Eq. 2.29 gives

\[
X_v = 1 - \exp\left(-\frac{k k_2^m \omega C_0 Z}{m+1} \exp\left(-\frac{\Delta G_m + \Delta G^* + mQ_G}{k_B T}\right) t^{m+1}\right)
\]  
(2.30)

The expression for relating the fraction transformed to DSC signal, \( \phi \), 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.

\[
\Phi = \Delta H k k_2^m \omega \theta_0 Z \exp \left( -\frac{\Delta G_m + \Delta G^* + mQ_G}{k_B T} \right) t^m \\
\exp \left( -\frac{kk_2^m \omega \theta_0 Z}{m + 1} \exp \left( -\frac{\Delta G_m + \Delta G^* + mQ_G}{k_B T} \right) t^{m+1} \right) 
\]

(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

\[
N = \int_{t=0}^{t^a} I \, d\tau = \int_{t=0}^{t^a} \omega \theta_0 Z \exp \left( -\frac{\Delta G_m}{k_B T} \right) \exp \left( -\frac{\Delta G^*}{k_B T} \right) d\tau 
\]

(2.33)

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

\[
X_v = 1 - \exp \left( -k \int_{t=0}^{t^a} \int_{t'=0}^{t^a} k_2 \exp \left( -\frac{Q_G}{k_B T} \right) dt' \right) d\tau
\]

\[
= 1 - kk_2 \omega \theta_0 Z \exp \left( -\int_{t=0}^{t^a} \exp \left( -\frac{\Delta G_m}{k_B T} \right) \exp \left( -\frac{\Delta G^*}{k_B T} \right) \int_{t'=0}^{t^a} \exp \left( -\frac{Q_G}{k_B T} \right) dt' \right) d\tau
\]

(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.

\[ \Phi = \Delta H \beta \frac{dX_v}{dT} = \Delta H \beta \frac{X_{v1} - X_{v2}}{T_1 - T_2} \]  \hspace{1cm} (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.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal Case</td>
<td>$X_v = 1 - \exp \left( -\frac{k k_m^m \omega C_o Z}{m+1} \exp \left( -\frac{\Delta G_m + \Delta G^* + mQ_G}{k_BT} \right) t^{m+1} \right)$</td>
</tr>
<tr>
<td></td>
<td>$\Phi = \Delta H k k_m^m \omega C_o Z \exp \left( -\frac{\Delta G_m + \Delta G^* + mQ_G}{k_BT} \right) t^m$</td>
</tr>
<tr>
<td></td>
<td>$\exp \left( -\frac{k k_m^m \omega C_o Z}{m+1} \exp \left( -\frac{\Delta G_m + \Delta G^* + mQ_G}{k_BT} \right) t^{m+1} \right)$</td>
</tr>
<tr>
<td>Non-isothermal Case</td>
<td>$X_v = 1 - k k_2 \omega C_o Z \exp \left[ -\int_{\tau=t}^{\tau=d} \exp \left( -\frac{\Delta G_m}{k_BT} \right) \exp \left( -\frac{\Delta G^*}{k_BT} \right) d\tau \right]$</td>
</tr>
<tr>
<td></td>
<td>$\Phi = \Delta H \beta \frac{dX_v}{dT} = \Delta H \beta \frac{X_{v1} - X_{v2}}{T_1 - T_2}$</td>
</tr>
</tbody>
</table>

$T_1$ and $T_2$ are adjacent temperature values in the calculation.

$\beta$ is the heating rate.

$X_{v1}$ and $X_{v2}$ is the fraction transformed at temperature $T_1$ and $T_2$, 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 (L1₀) structure at high (>410 °C) and low temperature (<385 °C), respectively. The pseudo-orthorombic ordered AuCu II phase is present between the A1 and L1₀ structures. The phase diagram of Au-Cu system is presented in Fig. 2.7.[Massalski 1990]

The enthalpies for the transformation of AuCu I → AuCu II and AuCu II → 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 → 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 L1₀ 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 Al (FCC) phase. TiAl films with 58 – 59.5 at.% Al have a mixture of α-Ti and Al.[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 α₂-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 variety 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.

![Figure 2.9: Periodic Table used for choosing ternary elements to FePt binary system. Figure reproduced from [Lower 2005].](image)
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, under- and/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 measure of the transformation kinetics. The KOT acquired from DSC scans is a direct kinetic measurement of transformation, thus any conclusions drawn based on the DSC results are more convincing.

ii) Kinetics of Formation in the Binary 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 $L1_0$ 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]

![Schematics of magnetron sputtering system. Figure reproduced from [VG Scienta 2007].](image)

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 x-rays 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% H\(_2\) gas at 20 SCCM. Alloy films with two different thicknesses of 0.5 and 1.0 \(\mu\)m 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 \(\mu\)m 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 \(\mu\)m 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
3.2 Differential Scanning Calorimetry

The transformation from the A1 phase to the L1₀ 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 isopropanol. 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 × 7 mm × 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 L10 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 L10 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 L10 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 L1₀ 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 L1₀ formation. The lower the kinetic ordering temperature and the lower the activation energy, the easier it is to form the L1₀ 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 µm-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 µm thick), fabricated by room temperature sputtering from elemental Fe and Pt targets, were used as standards for the EDXRF studies. The spectrum, acquired with voltage of 15 kV and current of 10 µA, was used for analyzing film composition. The working condition for WDS was set at 15 kV for voltage and 5 µA 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 µm 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 ºC/min to 700 ºC. 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 0-2θ 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 L1₀ phase. The lattice parameter can be calculated from the 2θ values obtained from x-ray diffraction pattern, while the integrated peak intensity can be used for calculating order parameter.
Figure 3.3: θ-2θ XRD patterns for Fe_{44.2}Ag_{16.7}Pt_{39.0} samples. The formation of the L1_0 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 3.2: The schematic drawing of PANalytical X’Pert x-ray diffractometer. Figure reproduced from [Berry 2007].
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 $\leq 1.4$ 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. Previous 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.
Table 4.1: Composition of binary films of [Berry 2007] re-measured with EDXRF, WDS and EDS.

<table>
<thead>
<tr>
<th>EDXRF (Foil Standard) [Berry 2007]</th>
<th>EDXRF (Thin Film Standard)</th>
<th>WDS</th>
<th>EDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe%</td>
<td>Pt%</td>
<td>Fe%</td>
<td>Pt%</td>
</tr>
<tr>
<td>59.2</td>
<td>40.8</td>
<td>53.5</td>
<td>46.5</td>
</tr>
<tr>
<td>54.4</td>
<td>45.6</td>
<td>50.2</td>
<td>49.8</td>
</tr>
<tr>
<td>52.8</td>
<td>47.2</td>
<td>48.9</td>
<td>51.1</td>
</tr>
<tr>
<td>49.3</td>
<td>50.7</td>
<td>45.4</td>
<td>54.6</td>
</tr>
<tr>
<td>44.7</td>
<td>55.3</td>
<td>40.8</td>
<td>59.2</td>
</tr>
</tbody>
</table>

The compositions are given in atomic percent.

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

<table>
<thead>
<tr>
<th>EDXRF (Foil standard) [Berry 2007]</th>
<th>EDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe%</td>
<td>Ni%</td>
</tr>
<tr>
<td>51.3</td>
<td>7.6</td>
</tr>
<tr>
<td>45.8</td>
<td>8.1</td>
</tr>
<tr>
<td>50.0</td>
<td>2.7</td>
</tr>
<tr>
<td>45.8</td>
<td>6.1</td>
</tr>
<tr>
<td>34.0</td>
<td>16.8</td>
</tr>
<tr>
<td>25.2</td>
<td>25.5</td>
</tr>
</tbody>
</table>

The compositions are given in atomic percent.
Table 4.3: Compositions of ternary FeCuPt Films of [Berry 2007] re-measured with EDS.

<table>
<thead>
<tr>
<th>EDXRF (Foil standard) [Berry 2007]</th>
<th>EDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe%</td>
<td>Cu%</td>
</tr>
<tr>
<td>50.5</td>
<td>4.7</td>
</tr>
<tr>
<td>35.3</td>
<td>19.4</td>
</tr>
<tr>
<td>40.6</td>
<td>13.4</td>
</tr>
<tr>
<td>50.3</td>
<td>2.7</td>
</tr>
<tr>
<td>49.7</td>
<td>1.0</td>
</tr>
<tr>
<td>47.2</td>
<td>2.9</td>
</tr>
<tr>
<td>44.8</td>
<td>5.2</td>
</tr>
<tr>
<td>47.7</td>
<td>1.3</td>
</tr>
<tr>
<td>39.2</td>
<td>10.6</td>
</tr>
<tr>
<td>34.7</td>
<td>14.5</td>
</tr>
</tbody>
</table>

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; 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 Fe₅₀Pt₅₀ 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 Fe₅₀Pt₅₀ sample is believed to be more Fe rich, because the only measured composition for nominal Fe₄₅Pt₅₅ sample contains 48 at.% Fe. Moreover, the study on post-annealed 50 nm thick FePt films shows Fe₅₂Pt₄₈ 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 Rittberg 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 Fe₅₂.₄Pt₄₇.₆ sample. The cross-section bright field and dark filed TEM images for as-deposited Fe₅₂.₄Pt₄₇.₆ 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 L10 phases for binary ambient deposited FePt films. The film grain size is determined from TEM bright field image and XRD using Scherrer’s equation.

<table>
<thead>
<tr>
<th>Composition</th>
<th>TEM (Plan-view)</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (at.%)</td>
<td>Pt (at.%)</td>
<td># of A1</td>
</tr>
<tr>
<td>54.3</td>
<td>45.7</td>
<td>100</td>
</tr>
<tr>
<td>52.4</td>
<td>47.6</td>
<td>126</td>
</tr>
<tr>
<td>47.7</td>
<td>52.3</td>
<td>109</td>
</tr>
</tbody>
</table>
Figure 4.1: Kinetic ordering temperature is plotted as a function of composition for FePt films. The phase stability limits for the L10 phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.2: Activation energy is plotted as a function of composition for FePt films. The phase stability limits for the L10 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 L10 phase from the binary FePt phase diagram are given as dashed vertical lines.

Figure 4.4: Curie temperature of L10 phase is plotted as a function of composition for FePt films. The phase stability limits for the L10 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 L1₀ 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 L1₀ 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 as-deposited 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 L1₀ phase.

Figs. 4.11 to 4.18 are the plot of kinetic ordering temperature, activation energy, transformation enthalpy and the Curie temperature of L1₀ 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-2θ 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 4.12: 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 4.13: 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 4.14: 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 L10 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 L10 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 L10 phase from the binary FePt phase diagram are given as dashed vertical lines.

Figure 4.18: Curie temperature of L10 phase is plotted as a function of composition for FeMgPt films. The phase stability limits for the L10 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 Fe56.0V0.7Pt43.3 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: 0-2θ XRD patterns for Fe<sub>56.0</sub>V<sub>0.7</sub>Pt<sub>43.3</sub> samples. The formation of the L<sub>10</sub> 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 L1₀ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.21: Activation energy is plotted as a function of composition for FeVPt films. The phase stability limits for the L1₀ 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 L1₀ phase from the binary FePt phase diagram are given as dashed vertical lines.

Figure 4.23: Curie temperature of L1₀ phase is plotted as a function of composition for FeVPt films. The phase stability limits for the L1₀ 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 L10 phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

**Figure 4.25:** Activation energy is plotted as a function of composition for FeVPt films. The phase stability limits for the L10 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 L10 phase from the binary FePt phase diagram are given as dashed vertical lines.

**Figure 4.27:** Curie temperature of L10 phase is plotted as a function of composition for FeVPt films. The phase stability limits for the L10 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 L1₀ 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 Fe₄₇.₂Mn₆.₀Pt₄₆.₈ 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 L1₂, which are not of the interest for the current research.
Figure 4.28: 0-2θ XRD patterns for Fe$_{45.7}$Mn$_{10.3}$Pt$_{43.6}$ samples. The formation of the L1$_0$ 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\textsubscript{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 4.30: Activation energy is plotted as a function of composition for FeMnPt films. The phase stability limits for the L1\textsubscript{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\textsubscript{0} phase from the binary FePt phase diagram are given as dashed vertical lines.

Figure 4.32: Curie temperature of L1\textsubscript{0} phase is plotted as a function of composition for FeMnPt films. The phase stability limits for the L1\textsubscript{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 $L_{10}$ 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 $L_{10}$ 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 $L_{10}$ phase from the binary FePt phase diagram are given as dashed vertical lines.

Figure 4.36: Curie temperature of $L_{10}$ phase is plotted as a function of composition for FeMnPt films. The phase stability limits for the $L_{10}$ 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 L1\textsubscript{0} 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\textsubscript{0} phase transformation, figures of kinetic ordering temperature, activation energy and transformation enthalpy, and Curie temperature of L1\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{0} phase Curie 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 L1₀ 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 L10 phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.38: Activation energy is plotted as a function of composition for FeNiPt films. The phase stability limits for the L10 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 L10 phase from the binary FePt phase diagram are given as dashed vertical lines.

Figure 4.40: Curie temperature of L10 phase is plotted as a function of composition for FeNiPt films. The phase stability limits for the L10 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 L10 phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

**Figure 4.42**: Activation energy is plotted as a function of composition for FeNiPt films. The phase stability limits for the L10 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 L10 phase from the binary FePt phase diagram are given as dashed vertical lines.

**Figure 4.44**: Curie temperature of L10 phase is plotted as a function of composition for FeNiPt films. The phase stability limits for the L10 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 L1₀ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.46: Activation energy is plotted as a function of composition for FeCuPt films. The phase stability limits for the L1₀ 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 L1₀ phase from the binary FePt phase diagram are given as dashed vertical lines.

Figure 4.48: Curie temperature of L1₀ phase is plotted as a function of composition for FeCuPt films. The phase stability limits for the L1₀ 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 4.50: 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 4.51: 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 4.52: 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 ≥ 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-2θ XRD patterns for Fe\textsubscript{44.3}Ag\textsubscript{16.7}Pt\textsubscript{39.0} samples. The formation of the L\textsubscript{1}0 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 L₁₀ 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 L₁₀ 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 L₁₀ phase from the binary FePt phase diagram are given as dashed vertical lines.

**Figure 4.57:** Curie temperature of L₁₀ phase is plotted as a function of composition for FeAgPt films. The phase stability limits for the L₁₀ 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 4.59: 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 4.60: 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 4.61: 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 ≥ 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 as-deposited 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 L1₀ 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 L1₀ 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: 0-2θ XRD patterns for Fe$_{4.2}$ Au$_{13.8}$ Pt$_{41.0}$ samples. The formation of the L1$_0$ 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 L1₀ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.64: Activation energy is plotted as a function of composition for FeAuPt films. The phase stability limits for the L1₀ 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 L1₀ phase from the binary FePt phase diagram are given as dashed vertical lines.

Figure 4.66: Curie temperature of L1₀ phase is plotted as a function of composition for FeAuPt films. The phase stability limits for the L1₀ 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 4.68: 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 4.69: 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 4.70: 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 FeB Pt 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 L1₀ 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 \( \geq 11.8 \) 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 apparent for B contents less than 4.8 at.%. However, for Pt rich ternary films that have \( \leq 4.8 \) 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 measurable 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: 0-2θ XRD patterns for Fe$_{43.0}$ B$_{11.8}$ Pt$_{45.2}$ samples. The formation of the L1$_0$ 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 L10 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 L10 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 L10 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 L10 phase is plotted as a function of composition for FeBPt films. The phase stability limits for the L10 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 L1₀ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.77: Activation energy is plotted as a function of composition for FeBPt films. The phase stability limits for the L1₀ 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 L1₀ phase from the binary FePt phase diagram are given as dashed vertical lines.

Figure 4.79: Curie temperature of L1₀ phase is plotted as a function of composition for FeBPt films. The phase stability limits for the L1₀ 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 L1₀ 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 L1₀ 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 L10 phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.81: Activation energy is plotted as a function of composition for FeCPt films. The phase stability limits for the L10 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 L10 phase from the binary FePt phase diagram are given as dashed vertical lines.

Figure 4.83: Curie temperature of L10 phase is plotted as a function of composition for FeCPt films. The phase stability limits for the L10 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 $L_{10}$ phase from the binary FePt phase diagram are given as dashed vertical lines. The solid black curve is drawn to guide the eye.

Figure 4.85: Activation energy is plotted as a function of composition for FeCpT films. The phase stability limits for the $L_{10}$ 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 $L_{10}$ phase from the binary FePt phase diagram are given as dashed vertical lines.

Figure 4.87: Curie temperature of $L_{10}$ phase is plotted as a function of composition for FeCpT films. The phase stability limits for the $L_{10}$ 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\textsubscript{0} phase when deposited onto heated substrates over 400 °C, but the questions of what is the lowest in-situ temperature to form L1\textsubscript{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\textsubscript{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.

<table>
<thead>
<tr>
<th>Nominal Temperature (°C)</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual Temperature (°C)</td>
<td>99.7</td>
<td>150.3</td>
<td>199.5</td>
<td>249.8</td>
<td>300.9</td>
</tr>
</tbody>
</table>

Binary films that are deposited between 100 and 200 °C form both A1 and L1\textsubscript{0} phases, whereas films deposited at 250 and 300 °C form only the L1\textsubscript{0} phase. Two examples of x-ray diffraction scans of Fe\textsubscript{50.5}Pt\textsubscript{49.5} deposited at 200 °C and Fe\textsubscript{56.4}Pt\textsubscript{43.6} deposited at 300 °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 \( \text{L1}_0 \) 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 \( \text{L1}_0 \) 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 °C and a binary film (48.2 at.% Pt) deposited at 250 °C directly form \( \text{L1}_0 \) 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 \( \text{L1}_0 \) 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 \( \text{L1}_0 \) 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 L1₀ phase depending on deposition temperature.
Figure 4.88: 0-2θ XRD pattern for Fe$_{50.5}$Pt$_{49.5}$ sample. The formation of the L1$_0$ phase is evidenced by the appearance of the superlattice peak such as 001 and 110.

Figure 4.89: 0-2θ XRD pattern for Fe$_{56.4}$Pt$_{43.6}$ sample. The formation of the L1$_0$ 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 L10 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 indicate 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 L10 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 indicate 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 L10 phase from the binary FePt phase diagram are given as black dashed vertical lines. The blue and red dashed vertical lines indicate the compositions for films deposited at 200 and 300 °C, respectively.

Figure 4.93: Curie temperature of L10 phase is plotted as a function of composition for FePt films. The phase stability limits for the L10 phase from the binary FePt phase diagram are given as black dashed vertical lines.
4.5 The JMAK Models for the A1 to L1\textsubscript{0} 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 \(k_2(T)N(T)\) model, whereas the nucleation density is temperature and time dependent in \(k_2(T)N(T,t)\) model.

\textbf{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.

<table>
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<th>Athermal Nucleation</th>
<th>Burst Nucleation</th>
<th>Continuous Nucleation</th>
</tr>
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<td><strong>k_2</strong></td>
<td>Constant</td>
<td>Temperature Dependent</td>
<td>Temperature Dependent</td>
</tr>
<tr>
<td>Nucleation Density</td>
<td>Constant</td>
<td>Temperature Dependent</td>
<td>Temperature and Time Dependent</td>
</tr>
</tbody>
</table>

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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 (ΔH), and the frequency factor, ν, 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 Fe52.9Pt47.1 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-time-transformation (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 Fe46.7Cu2.4Pt50.9 that is calculated by using these four models. The TTT diagrams that acquired by MD, k2(T) and k2(T)N(T) models are
calculated by implementing EDS composition, and corresponding \( T_c \) temperatures and equilibrium temperatures. It is worth noting that the interfacial energy (\( \gamma \)) in \( k_2(T)N(T,t) \) 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 \( \gamma \), 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 \( \gamma \) values is given in Table 4.7. The TTT curves calculated using \( k_2(T)N(T,t) \) as well as isothermal transformation curves remain the same no matter which set of \( S \) and \( \gamma \) is chosen. As \( S \) goes to zero, the continuous nucleation model reaches its limit, where no energy barrier exists for nucleation. The \( k_2(T) \) model is one implementation of this limit, for which the nucleation activation energy is zero.

\[
\frac{\Delta G_{\text{Het}}^*}{\Delta G_{\text{Hom}}^*} = S(\theta) \tag{4.1}
\]

<table>
<thead>
<tr>
<th>( S )</th>
<th>1</th>
<th>0.9</th>
<th>0.8</th>
<th>0.7</th>
<th>0.6</th>
<th>0.5</th>
<th>0.4</th>
<th>0.3</th>
<th>0.2</th>
<th>0.1</th>
<th>0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma ) (mJ/m(^2))</td>
<td>136</td>
<td>141</td>
<td>147</td>
<td>153</td>
<td>161</td>
<td>171</td>
<td>185</td>
<td>203</td>
<td>233</td>
<td>293</td>
<td>369</td>
</tr>
<tr>
<td>( SY^3 ) (mJ/m(^2))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Constant = ( 2.52 \times 10^6 )</td>
</tr>
</tbody>
</table>
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 from 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 cannot 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 $T_0 = T_e$ (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 value 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 L1$_0$ phase ($\gamma$) used for calculating isothermal and TTT curves for $k_2(T)N(T,t)$ model. Table 4.11 lists the 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, $T_e$, estimated from the phase diagrams, and transformation enthalpy, $\Delta H$, 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 $\Delta H$ is also provided.

<table>
<thead>
<tr>
<th>Composition (EDS)</th>
<th>$T_e$ (°C)</th>
<th>$\Delta H$ (kJ/g-atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD fitting</td>
<td>Experiment</td>
</tr>
<tr>
<td>Fe (at.%) Cu (at.% Pt (at.%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52.9 0 47.1</td>
<td>1287</td>
<td>5.8 ± 0.8</td>
</tr>
<tr>
<td>51.4 0 48.6</td>
<td>1295</td>
<td>7.2 ± 0.4</td>
</tr>
<tr>
<td>46.7 2.4 50.9</td>
<td>1287</td>
<td>8.1 ± 0.8</td>
</tr>
<tr>
<td>44.5 0 55.5</td>
<td>685</td>
<td>6.6 ± 0.5</td>
</tr>
</tbody>
</table>

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-L12 interfacial energy, $\gamma$, the growth velocity, $v$, at 300 and 500 °C, respectively, and the critical nucleus volume, $V^*$, are calculated after the fitting. The values of $\gamma$ from this table are used in the $k_2(T)$ and $k_2(T)N(T)$ models.

<table>
<thead>
<tr>
<th>Composition (EDS)</th>
<th>$v$ (s$^{-1}$)</th>
<th>$N$ (m$^{-3}$)</th>
<th>$v$ at (nm/s)</th>
<th>$\gamma$ (mJ m$^{-2}$)</th>
<th>$V^*$ (unit cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (at.%) Cu (at.% Pt (at.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52.9 0 47.1</td>
<td>1.34 × 10$^{10}$</td>
<td>6.89 × 10$^{17}$</td>
<td>1.34</td>
<td>1595.42</td>
<td>144</td>
</tr>
<tr>
<td>51.4 0 48.6</td>
<td>4.24 × 10$^{10}$</td>
<td>1.23 × 10$^{19}$</td>
<td>0.51</td>
<td>1080.40</td>
<td>142</td>
</tr>
<tr>
<td>46.7 2.4 50.9</td>
<td>2.57 × 10$^{11}$</td>
<td>1.53 × 10$^{21}$</td>
<td>0.08</td>
<td>292.93</td>
<td>134</td>
</tr>
<tr>
<td>44.5 0 55.5</td>
<td>1.97 × 10$^{12}$</td>
<td>1.66 × 10$^{24}$</td>
<td>7.8 × 10$^{-5}$</td>
<td>1.02</td>
<td>65</td>
</tr>
</tbody>
</table>
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 L1_0 phase ($\gamma$) used for calculating isothermal and TTT curves by using the $k_2(T)N(T,t)$ model. $\gamma$ is a fitting parameter for this model.

<table>
<thead>
<tr>
<th>Film Composition (EDS)</th>
<th>$Q_G$ (eV)</th>
<th>$Q_N$ (eV)</th>
<th>$\gamma$ (mJ/m$^2$)</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (at.%) Cu (at.%) Pt (at.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52.9 0.0 47.1</td>
<td>1.6</td>
<td>1.4</td>
<td>103</td>
<td>0.7</td>
</tr>
<tr>
<td>51.4 0.0 48.6</td>
<td>1.6</td>
<td>1.6</td>
<td>112</td>
<td>0.7</td>
</tr>
<tr>
<td>46.7 2.4 50.9</td>
<td>1.5</td>
<td>1.7</td>
<td>136</td>
<td>0.865</td>
</tr>
</tbody>
</table>

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>
<thead>
<tr>
<th>Composition (EDS)</th>
<th>N (m$^3$)</th>
<th>v at (nm/s)</th>
<th>$V^*$ (unit cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (at.%) Cu (at.%) Pt (at.%)</td>
<td>300 °C</td>
<td>500 °C</td>
<td>300 °C</td>
</tr>
<tr>
<td>52.9 0.0 47.1</td>
<td>$3.54 \times 10^{25}$</td>
<td>$1.56 \times 10^{12}$</td>
<td>0.22</td>
</tr>
<tr>
<td>51.4 0.0 48.6</td>
<td>$2.09 \times 10^{20}$</td>
<td>$3.22 \times 10^{26}$</td>
<td>0.22</td>
</tr>
<tr>
<td>46.7 2.4 50.9</td>
<td>$3.03 \times 10^{18}$</td>
<td>$2.44 \times 10^{22}$</td>
<td>1.40</td>
</tr>
</tbody>
</table>
Figure 4.94: The fitting of MD model with four non-isothermal DSC traces for the A1 to L1₀ transformation in Fe₅₂.₉Pt₄₇.₁ 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 L1₀ transformation in Fe₄₆.₇Cu₂.₄Pt₅₀.₉ calculated using the (a) MD, (b) k₂(T), (c) k₂(T) N(T) and k₂(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. Tₑ 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) $k_3(T)$ N(T) and (d) $k_5(T)$ 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 $k_5(T)$ 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 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.
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.
For thin films such as recording media (~ 10 nm), the fraction transformed can be calculated by implementing a geometry correction term \( \psi \), yielding

\[
X_f = 1 - \exp(-X_E)\psi
\]  (4.2)

\[
\psi = \frac{I}{\sqrt[3]{Nd_{film}}} \left[ \int_0^{\sqrt[3]{Nd_{film}}} \exp \left( X_E f \left( \frac{z}{\sqrt[3]{N}r} \right) \right) \exp \left( X_E f \left( \frac{\sqrt[3]{Nd_{film}} - z}{\sqrt[3]{N}r} \right) \right) \right] dz
\]  (4.3)

\[
f(s) = \frac{I}{4} \left( 2 - 3s + s^2 \right) \Theta(1 - s)
\]  (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 defines the volume of a spherical cap and \( \Theta(1-s) \) is the Heaviside step function, which accounts for 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 \( \mu \)m 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 k\(_2(T)\) 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 $\text{L}_1_0$ 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 L1$_0$ 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 μm and 10 nm thick Fe_{51.4}Pt_{48.6} film using (a) $k_2(T)$, (b) $k_2(T)\cdot N(T)$ and (c) $k_2(T)\cdot N(T,t)$ 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 L1_0 is the thermodynamically stable phase.
Temperature (°C)

(a) \( k_2(T) \)

Fe\(_{51.4}\)Pt\(_{48.6}\)

L1\(_0\)

Laser Annealed 10%

Furnace Annealed 90%

Furnace Annealed 50%

Furnace Annealed 10%

time (s)

\( \mu s \)  \( ms \)  \( s \)  \( min \)  \( h \)  \( day \)  \( year \)  \( month \)
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%, 50% and 90% ordering, respectively.[Inaba 2010]
Figure 4.104: The calculated fraction transformed curve at 700 °C for Fe₅₁.₄Pt₄₈.₆ 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 \( k_2(T) \) model, the only energy barrier for the transformation is the activation energy for growth.

\[
\begin{array}{|c|c|c|c|c|}
\hline
& \text{Equilibrium temperature, } T_e & \text{Coherent stability temperature, } T_k & \text{Coherent instability temperature, } T_s \\
\hline
\text{°C} & K & °C & K & °C & K \\
\hline
\text{AuCu} & 410 & 683 & 375 & 648 & 357 & 630 \\
\hline
\text{FePt} & 1300 & 1573 & 1219 & 1492 & 1178 & 1451 \\
\hline
\end{array}
\]

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 $\text{A1 to } \text{L1}_0$ 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 $\sim 357 \, ^\circ\text{C}$ 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 $\text{L1}_0$ 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 $\text{A1 to } \text{L1}_0$ 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 were annealed, in addition to XRD peaks for the L1\(_0\) phases, fcc Ag and Au peaks were seen for $\text{Ag} \geq 6.9$ at.% and $\text{Au} \geq 7.2$ 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 L1\(_0\) FePt and Ag or Au was not measurably different than that for transformation of the A1 phase to the L1\(_0\) 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\textsubscript{o} 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\textsubscript{o} phase or speedup the growth rate of the L1\textsubscript{o} 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 L\textsubscript{10} 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 energy \(Q\), the transformation enthalpy \(\Delta H\) for the A1 to L1\(_0\) transformation, and AA-1 to 11 are the lattice parameters and grain size for the A1 and L1\(_0\) phases in FePt, FeMgPt, FeVPt, FeMnP, FeNiPt, FeCuPt, FeAgPt, FeAuPt, FeB Pt and FeCPt, respectively. For those films, of which the Curie temperature of L1\(_0\) 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 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 (ΔH) for the A1 to L1₀ transformation in ambient temperature deposited binary FePt films. The Curie temperature of the L1₀ phase (Tₖ) 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.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
<th>KOT</th>
<th>Tₖ</th>
<th>Q</th>
<th>ΔH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe (at.%)</td>
<td>Pt (at.%)</td>
<td>(°C)</td>
<td>(°C)</td>
<td>(eV)</td>
</tr>
<tr>
<td>900</td>
<td>57.0</td>
<td>43.0</td>
<td>372</td>
<td>452±1</td>
<td>1.5</td>
</tr>
<tr>
<td>901</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>902</td>
<td>54.3</td>
<td>45.7</td>
<td>379</td>
<td>453±2</td>
<td>1.7</td>
</tr>
<tr>
<td>903</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>876</td>
<td>52.4</td>
<td>47.6</td>
<td>364</td>
<td>451±2</td>
<td>1.5</td>
</tr>
<tr>
<td>877</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>852</td>
<td>47.7</td>
<td>52.3</td>
<td>388</td>
<td>-</td>
<td>1.6</td>
</tr>
<tr>
<td>853</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>874</td>
<td>43.9</td>
<td>56.1</td>
<td>486</td>
<td>-</td>
<td>2.2</td>
</tr>
<tr>
<td>875</td>
<td></td>
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</tbody>
</table>
Table AA-1: Film composition measured by EDS, the lattice parameters of A1 (a) and L1₀ (a and c) phases, and grain sizes of as-deposited and annealed in ambient temperature deposited binary FePt films.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
<th>Lattice parameters(Å)</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe (at.%)</td>
<td>Pt (at.%)</td>
<td>A1 (a)</td>
</tr>
<tr>
<td>900 901</td>
<td>57.0</td>
<td>43.0</td>
<td>-</td>
</tr>
<tr>
<td>902 903</td>
<td>54.3</td>
<td>45.7</td>
<td>3.83</td>
</tr>
<tr>
<td>876 877</td>
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<td>47.6</td>
<td>3.81</td>
</tr>
<tr>
<td>852 853</td>
<td>47.7</td>
<td>52.3</td>
<td>3.83</td>
</tr>
<tr>
<td>874 875</td>
<td>43.9</td>
<td>56.1</td>
<td>-</td>
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</table>
Table A-2: Deposition Temperature ($T_D$), film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy ($Q$) and the enthalpy ($\Delta H$) for the A1 to L1$_0$ transformation in binary FePt films deposited at elevated temperature. The Curie temperature of the L1$_0$ 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.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>$T_D$ (°C)</th>
<th>Composition (EDS)</th>
<th>ETDPT</th>
<th>$T_C$ (°C)</th>
<th>$Q$ (eV)</th>
<th>$\Delta H$ (kJ / g - atom)</th>
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<td>426 ± 2</td>
<td>1.9</td>
</tr>
<tr>
<td>1079</td>
<td>100</td>
<td>54.4</td>
<td>45.6</td>
<td>413</td>
<td>442 ± 4</td>
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</tr>
<tr>
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<td>51.2</td>
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<td>457 ± 3</td>
<td>1.5</td>
</tr>
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<td>53.5</td>
<td>415</td>
<td>419</td>
<td>1.6</td>
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<td>418 ± 1</td>
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<td>372</td>
<td>454 ± 2</td>
<td>1.5</td>
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<td>43.6</td>
<td>440</td>
<td>418</td>
<td>1.6</td>
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<tr>
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<td>449 ± 1</td>
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</tr>
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<td>49.5</td>
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<td>458 ± 1</td>
<td>1.5</td>
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<td>-</td>
<td>1.7</td>
</tr>
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<td>250</td>
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<td>-</td>
<td>451</td>
<td>-</td>
</tr>
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<td>-</td>
<td>-</td>
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<tr>
<td>1055</td>
<td>300</td>
<td>46.4</td>
<td>53.6</td>
<td>-</td>
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Table AA-2: Deposition Temperature ($T_D$), 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 binary FePt films deposited at elevated temperature.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>$T_D$ ($^\circ$C)</th>
<th>Composition (EDS)</th>
<th>Lattice parameters ($\AA$)</th>
<th>Grain Size (nm)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe (at.%)</td>
<td>Pt (at.%)</td>
<td>A1 (a)</td>
</tr>
<tr>
<td>1078 1079</td>
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<td>56.2</td>
<td>43.8</td>
<td>3.80</td>
</tr>
<tr>
<td>1046 1047</td>
<td>100</td>
<td>54.4</td>
<td>45.6</td>
<td>3.80</td>
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<tr>
<td>1030 1031</td>
<td>100</td>
<td>51.2</td>
<td>48.8</td>
<td>3.81</td>
</tr>
<tr>
<td>1044 1045</td>
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<td>53.5</td>
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<td>42.4</td>
<td>3.80</td>
</tr>
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<td>47.7</td>
<td>3.81</td>
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<td>42.4</td>
<td>-</td>
</tr>
<tr>
<td>1076 1077</td>
<td>200</td>
<td>56.4</td>
<td>43.6</td>
<td>3.79</td>
</tr>
<tr>
<td>1036 1037</td>
<td>200</td>
<td>53.1</td>
<td>46.9</td>
<td>3.80</td>
</tr>
<tr>
<td>1032 1033</td>
<td>200</td>
<td>50.5</td>
<td>49.5</td>
<td>3.81</td>
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<td>1038 1039</td>
<td>200</td>
<td>46.0</td>
<td>54.0</td>
<td>3.82</td>
</tr>
<tr>
<td>1054 1055</td>
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<td>48.2</td>
<td>-</td>
</tr>
<tr>
<td>1080 1081</td>
<td>300</td>
<td>56.4</td>
<td>43.6</td>
<td>-</td>
</tr>
<tr>
<td>1034 1035</td>
<td>300</td>
<td>51.5</td>
<td>48.5</td>
<td>-</td>
</tr>
<tr>
<td>1042 1043</td>
<td>300</td>
<td>46.4</td>
<td>53.6</td>
<td>-</td>
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Table A-3: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (ΔH) 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.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
<th>KOT</th>
<th>T_c</th>
<th>Q</th>
<th>ΔH</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Fe (at.%)</td>
<td>Pt (at.%)</td>
<td>Mg (at.%)</td>
<td>(°C)</td>
<td>(°C)</td>
</tr>
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<td>0.7</td>
<td>384</td>
<td>448 ± 2</td>
</tr>
<tr>
<td>938</td>
<td>52.1</td>
<td>46.2</td>
<td>1.8</td>
<td>413</td>
<td>435 ± 2</td>
</tr>
<tr>
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<td>46.3</td>
<td>0.0</td>
<td>373</td>
<td>449 ± 2</td>
</tr>
<tr>
<td>896</td>
<td>53.3</td>
<td>46.4</td>
<td>0.3</td>
<td>382</td>
<td>447 ± 3</td>
</tr>
<tr>
<td>940</td>
<td>48.8</td>
<td>48.6</td>
<td>2.6</td>
<td>436</td>
<td>419 ± 2</td>
</tr>
</tbody>
</table>
Table AA-3: 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 FeMgPt films.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
<th>Lattice parameters(Å)</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
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<td>Fe (at.%)</td>
<td>Pt (at.%)</td>
<td>Mg (at.%)</td>
</tr>
<tr>
<td>898 899</td>
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<td>42.1</td>
<td>0.7</td>
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<tr>
<td>938 939</td>
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<td>46.2</td>
<td>1.8</td>
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<td>53.8</td>
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<td>0.0</td>
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<td>0.3</td>
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<tr>
<td>940 941</td>
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<td>48.6</td>
<td>2.6</td>
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</table>
Table A-4: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (ΔH) 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.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
<th>KOT</th>
<th>T_c</th>
<th>Q</th>
<th>ΔH</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Fe (at.%)</td>
<td>Pt (at.%)</td>
<td>V (at.%)</td>
<td>(°C)</td>
<td>(°C)</td>
</tr>
<tr>
<td>1016</td>
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<td>44.8</td>
<td>12.2</td>
<td>502</td>
<td>-</td>
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<tr>
<td>1017</td>
<td>47.7</td>
<td>46.5</td>
<td>5.8</td>
<td>413</td>
<td>451 ± 1</td>
</tr>
<tr>
<td>906</td>
<td>53.6</td>
<td>45.7</td>
<td>0.7</td>
<td>382</td>
<td>461 ± 1</td>
</tr>
<tr>
<td>907</td>
<td>48.3</td>
<td>48.6</td>
<td>3.1</td>
<td>386</td>
<td>462 ± 1</td>
</tr>
</tbody>
</table>
**Table AA-4:** 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 FeV Pt films.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
<th>Lattice parameters (Å)</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe (at.%)</td>
<td>Pt (at.%)</td>
<td>V (at.%)</td>
</tr>
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<td>1016</td>
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<td>48.3</td>
<td>48.6</td>
<td>3.1</td>
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</table>
Table A-5: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (ΔH) 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.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
<th>KOT</th>
<th>T_c</th>
<th>Q</th>
<th>ΔH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe (at.%), Pt (at.%), Mn (at.%)</td>
<td>(°C)</td>
<td>(°C)</td>
<td>(eV)</td>
<td>(kJ / g - atom)</td>
</tr>
<tr>
<td>1020-1021</td>
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<td>525</td>
<td>-</td>
<td>2.3</td>
<td>10.0 ± 0.3</td>
</tr>
<tr>
<td>1022-1023</td>
<td>47.2, 46.8, 6.0</td>
<td>442</td>
<td>381 ± 2</td>
<td>2.0</td>
<td>10.7 ± 2.0</td>
</tr>
<tr>
<td>1024-1025</td>
<td>49.1, 48.6, 2.2</td>
<td>388</td>
<td>425 ± 2</td>
<td>1.8</td>
<td>9.0 ± 2.0</td>
</tr>
<tr>
<td>854-855</td>
<td>42.6, 53.1, 4.3</td>
<td>443</td>
<td>-</td>
<td>1.9</td>
<td>10.5 ± 3.4</td>
</tr>
<tr>
<td>856-857</td>
<td>28.3, 55.4, 16.3</td>
<td>555</td>
<td>-</td>
<td>3.2</td>
<td>8.1 ± 1.5</td>
</tr>
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</table>
Table AA-5: 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 FeMnPt films.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
<th>Lattice parameters(Å)</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe (at.%)</td>
<td>Pt (at.%)</td>
<td>Mn (at.%)</td>
</tr>
<tr>
<td>1020 1021</td>
<td>45.7</td>
<td>43.6</td>
<td>10.7</td>
</tr>
<tr>
<td>1022 1023</td>
<td>47.2</td>
<td>46.8</td>
<td>6.0</td>
</tr>
<tr>
<td>1024 1025</td>
<td>49.1</td>
<td>48.6</td>
<td>2.2</td>
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<td>854 855</td>
<td>42.6</td>
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<tr>
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<td>55.4</td>
<td>16.3</td>
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Table A-6: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (ΔH) 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.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
<th>KOT</th>
<th>T_c</th>
<th>Q</th>
<th>ΔH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe (at.%)</td>
<td>Pt (at.%)</td>
<td>Ni (at.%)</td>
<td>(°C)</td>
<td>(°C)</td>
</tr>
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<td>47.7</td>
<td>46.2</td>
<td>6.1</td>
<td>421</td>
<td>441 ± 2</td>
</tr>
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<td>589</td>
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</tr>
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<td>445</td>
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<td>6.7</td>
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<td>446</td>
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<td>401</td>
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<td>430</td>
<td>359 ± 1</td>
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Table AA-6: 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 FeNiPt films.

<table>
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<th>Lattice parameters(Å)</th>
<th>Grain Size (nm)</th>
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</thead>
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<td>Ni (at.%)</td>
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Table A-7: Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (ΔH) for the A1 to L1₀ transformation in FeCuPt films. The Curie temperature of the L1₀ phase (Tₐ) 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.

<table>
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<th>Tc</th>
<th>Q</th>
<th>ΔH</th>
</tr>
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<td>Cu (at.%)</td>
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<td>(°C)</td>
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<td>368</td>
<td>397 ± 3</td>
</tr>
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<td>43.2</td>
<td>48.8</td>
<td>8.0</td>
<td>362</td>
<td>335 ± 3</td>
</tr>
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<td>366</td>
<td>386 ± 2</td>
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</tr>
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<td>50.8</td>
<td>12.0</td>
<td>370</td>
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</tr>
<tr>
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<td>50.9</td>
<td>2.4</td>
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<td>407 ± 1</td>
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<td>1.3</td>
<td>384</td>
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</tr>
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<td>54.1</td>
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<td>402</td>
<td>362</td>
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<td>54.4</td>
<td>4.9</td>
<td>410</td>
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<td>55.0</td>
<td>9.2</td>
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<tr>
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<td>12.9</td>
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Table AA-7: 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 FeCuPt films.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
<th>Lattice parameters(Å)</th>
<th>Grain Size (nm)</th>
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<tbody>
<tr>
<td></td>
<td>Fe (at.%)</td>
<td>Pt (at.%)</td>
<td>Cu (at.%)</td>
</tr>
<tr>
<td>SG3</td>
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<tr>
<td>SG2</td>
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<td>31.7</td>
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**Table A-8:** Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (ΔH) for the A1 to L1₀ transformation in FeAgPt films. The Curie temperature of the L1₀ phase (Tₐ) 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.

<table>
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<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
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<th>Tₐ</th>
<th>Q</th>
<th>ΔH (kJ/g-atom)</th>
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<td>Ag (at.%)</td>
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<td>(°C)</td>
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<td>460</td>
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</tr>
<tr>
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<td>43.1</td>
<td>6.9*</td>
<td>441</td>
<td>446 ± 3</td>
</tr>
<tr>
<td>946 947</td>
<td>49.1</td>
<td>47.5</td>
<td>3.4</td>
<td>410</td>
<td>454 ± 1</td>
</tr>
<tr>
<td>988 989</td>
<td>50.5</td>
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<td>0.0</td>
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<td>457 ± 2</td>
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<td>49.8</td>
<td>1.5</td>
<td>406</td>
<td>440 ± 2</td>
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*: films decompose into L1₀ FePt and Ag upon annealing.
**Table AA-8:** 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 FeAgPt films.

<table>
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<th>Run ID</th>
<th>Composition (EDS)</th>
<th>Lattice parameters(Å)</th>
<th>Grain Size (nm)</th>
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<td>Pt (at.%)</td>
<td>Ag (at.%)</td>
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<td>16.7*</td>
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<tr>
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<td>994</td>
<td>50.0</td>
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<td>6.9*</td>
</tr>
<tr>
<td>995</td>
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<tr>
<td>946</td>
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<td>47.5</td>
<td>3.4</td>
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</table>

*: 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 (ΔH) 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.

<table>
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<th>T_c</th>
<th>Q</th>
<th>ΔH</th>
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<td>Au (at.%)</td>
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<td>(°C)</td>
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<td>1002 1003</td>
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<td>444</td>
<td>467 ± 2</td>
</tr>
<tr>
<td>1000 1001</td>
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<td>45.0</td>
<td>4.1</td>
<td>408</td>
<td>463 ± 1</td>
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<td>45.6</td>
<td>7.2*</td>
<td>430</td>
<td>465 ± 3</td>
</tr>
<tr>
<td>998 999</td>
<td>52.2</td>
<td>45.9</td>
<td>1.9</td>
<td>386</td>
<td>455 ± 2</td>
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*: films decompose into L1₀ FePt and Au upon annealing.
Table AA-9: 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 FeAuPt films.

<table>
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<th>Grain Size (nm)</th>
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<td>1003</td>
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<td>998</td>
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</table>

*: 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 (ΔH) for the A1 to L1₀ transformation in FeB₉t films. The Curie temperature of the L1₀ phase (T�stalk) 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.

<table>
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<th>Run ID</th>
<th>Composition (EDS)</th>
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<th>Q</th>
<th>ΔH</th>
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<td>B (at.%)</td>
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<td>(°C)</td>
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<td>452 ± 3</td>
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<tr>
<td>932 933</td>
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<td>42.7</td>
<td>12.3</td>
<td>484</td>
<td>456 ± 1</td>
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<td>45.2</td>
<td>11.8</td>
<td>466</td>
<td>442 ± 1</td>
</tr>
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<td>368</td>
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</tr>
<tr>
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<td>452 ± 2</td>
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<td>4.8</td>
<td>442</td>
<td>391 ± 4</td>
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<td>2.4</td>
<td>438</td>
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<td>870 871</td>
<td>44.3</td>
<td>54.5</td>
<td>1.2</td>
<td>454</td>
<td>386</td>
</tr>
</tbody>
</table>
Table AA-10: 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 FeBPt films.

<table>
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<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
<th>Lattice parameters(Å)</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
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<td>Fe (at.%)</td>
<td>Pt (at.%)</td>
<td>Au (at.%)</td>
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<td>46.3</td>
<td>40.8</td>
<td>12.9</td>
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<tr>
<td>932 933</td>
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<td>44.3</td>
<td>54.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>
**Table A-11:** Film composition measured by EDS, the kinetic ordering temperature (KOT), the activation energy (Q) and the enthalpy (ΔH) for the A1 to L1₀ transformation in FeCPt films. The Curie temperature of the L1₀ phase (Tᵥ) 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.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>Composition (EDS)</th>
<th>KOT</th>
<th>Tᵥ</th>
<th>Q</th>
<th>ΔH</th>
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<tr>
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<td>Fe (at.%)</td>
<td>49.8</td>
<td>Pt (at.%)</td>
<td>48.8</td>
<td>C (at.%)</td>
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</table>
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 L1₀ 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 L1₀ 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]

\[
I = \frac{I_0}{16\pi R} \left( \frac{e^4}{m^2 c^4} \right) \frac{\lambda^2 M_{hkl} F_{hkl}^2}{2 \mu \nu_a^2} \left( 1 + \frac{\cos^2 2\theta \cos^2 2\theta_m}{\sin \theta \sin 2\theta} \right) \exp(-2M)
\]

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, \( \lambda \) is the wavelength of X-ray radiation, \( M_{hkl} \) is the multiplicity, \( \nu_a \) is the unit volume of the unit cell. The term
\[ \frac{1 + \cos^2 \theta \cos^2 2\theta_m}{\sin \theta \sin 2\theta} \] 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 monochromator is 26.57°.

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

\[
F_{hk} = \sum_{j=1}^{N} \text{# of atoms in unit cell} f_j \exp\left(-2\pi i\left(hx_j + ky_j + lz_j\right)\right) \quad \text{B-2}
\]

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 \( (f_0) \) 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 \( 2.0 \ \text{Å}^{-1} < \sin \theta / \lambda < 6.0 \ \text{Å}^{-1} \). [Wilson 1992]

\[
f_j^2 = (f_0 + \nabla f')^2 + (f_0 + \nabla f'')^2 \quad \text{B-3}
\]

\[
f_0\left(\frac{\sin \theta}{\lambda}\right) = \left(\sum_{i=1}^{4} a_i \exp\left(\frac{b_i \sin^2 \theta}{\lambda}\right) + c_i\right) \quad \text{B-4}
\]
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] \( \lambda \) is the wavelength of X-ray radiation and \( \theta \) is the angle of x-ray incoming beam.

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

\[
\mu = \left( \frac{\mu_{Fe}}{\rho_{Fe}} \right) \text{wt.% Fe} + \left( \frac{\mu_{Pt}}{\rho_{Pt}} \right) \text{wt.% Pt} \times \left[ X_{Fe} \rho_{Fe} + X_{Pt} \rho_{Pt} \right]
\]

\[B-5\]

\( X_{Fe} \) and \( X_{Pt} \) are the atomic percentage of Fe and Pt in the sample, respectively. The values of \( \mu/\rho \) can be find for Fe and Pt in Warren’s book. Warren 1990] \( \rho \) is the density of each element.

The temperature term \( M \) is given as

\[
M = \frac{(Q\sigma)^2}{2}
\]

\[B-6\]

Where \( \sigma \) 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]

$$F_{\text{fund}} = 4 \left( X_{Fe} f_{Fe} + X_{Pt} f_{Pt} \right)$$  \hspace{1cm} \text{B-8}

$$F_{\text{sup}} = 2S \left( f_{Fe} - f_{Pt} \right)$$  \hspace{1cm} \text{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 L1$_0$ FePt sample.

Table B-1 is the calculation of 20 angles and corresponding peak intensities for randomly oriented Si and L1$_0$ 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 L1$_0$ 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 L1$_0$ FePt, respectively.
Table B-1. The calculation of 2θ 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.

<table>
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<tr>
<th>h k l</th>
<th>2θ (Degree)</th>
<th>Normalized Intensities (%)</th>
<th>h k l</th>
<th>2θ (Degree)</th>
<th>Normalized Intensities (%)</th>
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</thead>
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<td>0 0 1</td>
<td>24.06</td>
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<td>2 0 1</td>
<td>53.76</td>
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<td></td>
<td></td>
<td>3 1 0</td>
<td>78.74</td>
<td>2.73</td>
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</table>
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) L1₀ 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 X-ray 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, θ/2θ 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, θ/2θ 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 2θ 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.

![XRD pattern of Seagate large-thick sample](image1)

![XRD pattern of CMU large-thick sample](image2)

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

<table>
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<tr>
<th>(2\theta) (Degree)</th>
<th>Experimental (Seagate) Normalized Intensities</th>
<th>Theoretical Normalized Intensities</th>
<th>Experimental (CMU) Normalized Intensities</th>
<th>Ratio of Theoretical / Experimental</th>
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</thead>
<tbody>
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<td>100.00</td>
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<tr>
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<td>1.04/1.09</td>
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<td>39.50</td>
<td>1.22/1.18</td>
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<td>10.46</td>
<td>1.23/1.29</td>
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<td>8.48</td>
<td>136.90</td>
<td>9.12</td>
<td>1.08/1.09</td>
</tr>
</tbody>
</table>

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.

![XRD pattern of CMU large-thick sample](image)

**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 2\(\theta\) 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.
Table C-2: The comparison of peak intensities between the theoretical calculations and randomly orientated small-thick Si samples that are provided by Seagate and fabricated at CMU.

<table>
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<tr>
<th>20 (Degree)</th>
<th>Theoretical Normalized Intensities</th>
<th>Experimental (Seagate) Normalized Intensities</th>
<th>Experimental (CMU) Normalized Intensities</th>
<th>Ratio of Theoretical / Experimental</th>
<th>Seagate</th>
<th>CMU</th>
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<tr>
<td>47.31</td>
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<td>101.15</td>
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</tr>
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<td>76.51</td>
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<td>0.45</td>
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<td>0.32</td>
<td>0.46</td>
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<td>106.71</td>
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<td>0.37</td>
<td>0.45</td>
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<tr>
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<td>34.98</td>
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<td>0.44</td>
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<td>0.44</td>
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</table>
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 $2\theta$, shown in Fig. C-5.

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.

\[
\text{Theoretical Value} = 2.24 \times \exp \left( - \frac{\text{Intensity from small sample}}{20.78} \right) + 0.43 \quad \text{C-1}
\]
The intensity ratios of (001) / (002) and (110) / (220) for large 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

\[
\text{Intensity ratio (superlattice / fundamental) for large sample} = 1.11 \times \text{Intensity ratio (superlattice / fundamental) for small sample}
\]

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

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 validated by the Si result from both samples from Seagate and prepared at CMU. The area correction should be based on the result from CMU sample. The scale factor of 1.11 that was 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 $2\theta$ equal (a) 28.47 and (b) 47.32.

Figure C-11: Psi scan of randomly oriented small Si samples at $2\theta$ equal (a) 28.47 and (b) 47.32.
Appendix D:

Order Parameter of FePt System

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

\[ S = \frac{r_\alpha - X_A}{y_\beta} \]  \hspace{1cm} \text{D-1} \]

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

\[ \frac{I_{\text{sup}}}{I_{\text{fund}}} = \frac{AF_{\text{sup}}^2 LP \exp(-2M)}{AF_{\text{fund}}^2 LP \exp(-2M)} \]  \hspace{1cm} \text{D-2} \]

Where \( I_{\text{sup}} \) and \( I_{\text{fund}} \) are intensities for superlattice and fundamental peaks, respectively. And \( F_{\text{sup}} \) and \( F_{\text{fund}} \) 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.

\[ F_{\text{final}} = 4 \left( X_{Fe} f_{Fe} + X_{Pt} f_{Pt} \right) \]  

\[ F_{\text{sup}} = 2S \left( f_{Fe} - f_{Pt} \right) \]  

\[ A = 1 - \exp \left( \frac{-2 \mu t}{\sin(\theta) \cos(\psi)} \right) \]  

where \( \psi \) 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 \( \sigma \) is fitted to be 0.16 for the purpose of minimum the standard deviation of S values obtained form {001}/(002) and {110}/(220).

<table>
<thead>
<tr>
<th>Run ID</th>
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<th>Composition Pt (at.%)</th>
<th>ψ (degree)</th>
<th>Peak Intensity</th>
<th>S_ave</th>
<th>S_ave / S_max</th>
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<td>(110)</td>
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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$_{\text{max}}$) 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$_{\text{max}}$) are calculated and presented.
Appendix E:

Fitting of $k_2(T)N(T,t)$ model

To simulate the non-isothermal DSC traces at four heating rate, three parameters, namely $Q_g$, $m$ and $\gamma$, were used in $k_2(T)N(T,t)$ model. The fitting quality was determined from root mean square (RMS). Examples of the impact of $Q_g$, $m$ and $\gamma$ 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 $\gamma$ for same activation energy $Q_g$, whereas Figs. E-1 and E-3 illustrates the interaction of $Q_g$ and $\gamma$ for same $m$. These examples are served for demonstrating the impact of fitting parameters on the RMS.
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 Fe₅₂.₉Pt₄₇.₁ 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 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.
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 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.
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.
Fe$_{56.2}$Pt$_{43.8}$

(a)

Exothermic down (mW)

-15
-10
-5
0
5
10
15

Temperature (°C)

20 K/min
40 K/min
80 K/min
160 K/min

Counts/s

(b)

Fe$_{56.2}$Pt$_{43.8}$

As-deposited
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.
Fe_{54.4}Pt_{45.6}

(a)

Exothermic down (mW)

Temperature (°C)

-15
-10
-5
0
100 200 300 400 500 600 700

-20 K/min
-40 K/min
-80 K/min
-160 K/min

Counts/s

(b)

Fe_{54.4}Pt_{45.6}
As-deposited
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.
Fe$_{51.2}$Pt$_{48.8}$

(a)

Exothermic down (mW)

Temperature ($^\circ$C)

-50 -40 -30 -20 -10 0

20 K/min
40 K/min
80 K/min
160 K/min

(b)

Fe$_{51.2}$Pt$_{48.8}$
As-deposited

Counts/s

0 40000 160000 360000

Position [°2Theta]
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.
Fe_{46.5}Pt_{53.5}

(a)

Exothermic down (mW)

Temperature (°C)

20 K/min
40 K/min
80 K/min
160 K/min

(b)

Fe_{46.5}Pt_{53.5}
As-deposited
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.
Fe$_{57.6}$Pt$_{42.4}$

Exothermic down (mW)

Temperature ($^\circ$C)

-15

-10

-5

0

20 K/min

40 K/min

80 K/min

160 K/min

Counts/s

22500

10000

2500

0

Fe$_{57.6}$Pt$_{42.4}$

As-deposited

Position [^2Theta]
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.
(a) \text{Fe}_{52.3}\text{Pt}_{47.7}

(b) \text{Fe}_{52.3}\text{Pt}_{47.7} 
As-deposited
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
Fe\textsubscript{56.4}Pt\textsubscript{43.6}

(a) Exothermic down (mW)

Temperature (°C)

-15
0
5
10
20 K/min
40 K/min
80 K/min
160 K/min

Counts/s

(b) Fe\textsubscript{56.4}Pt\textsubscript{43.6}
As-deposited

Position [°2Theta]

0
2500
10000

193
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.
Fe$_{53.1}$Pt$_{46.9}$

Exothermic down (mW)

Temperature (°C)

Counts/s

(b) Fe$_{53.1}$Pt$_{46.9}$
As-deposited
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.
Fe$_{50.5}$Pt$_{49.5}$

![Graph showing exothermic down (mW) vs. Temperature (°C) for different heating rates.](image)

Counts/s

(b) Fe$_{50.5}$Pt$_{49.5}$ As-deposited

![Graph showing scatter plot of counts/s vs. Position [°2Theta].](image)
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.
Fe$_{46.0}$Pt$_{54.0}$

(a) Exothermic down (mW)

(b) Fe$_{46.0}$Pt$_{54.0}$
As-deposited
Fig. F-11: (a) the DSC traces for Fe\textsubscript{46.0}Pt\textsubscript{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.
Fe$_{51.8}$Pt$_{48.2}$

Exothermic down (mW) vs. Temperature ($^\circ$C) for Fe$_{51.8}$Pt$_{48.2}$ at 40 K/min.

Counts/s vs. Position ($^\circ 2\text{Theta}$) for Fe$_{51.8}$Pt$_{48.2}$ as-deposited.
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.
Fe$_{56.4}$Pt$_{43.6}$

Exothermic down (mW)

Temperature ($^\circ$C)

40 K/min

Counts/s

(b) Fe$_{56.4}$Pt$_{43.6}$
As-deposited
Fig. F-13: (a) the DSC traces for Fe\textsubscript{56.4}Pt\textsubscript{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.
Fe_{51.5}Pt_{48.5}

(a)

Exothermic down (mW) vs. Temperature (°C)

(b)

Counts/s vs. Position [°2Theta]

Fe_{51.5}Pt_{48.5}
As-deposited
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.
Fe$_{46.4}$Pt$_{53.6}$

Exothermic down (mW)

Temperature (°C)

40 K/min

Counts/s

(b) Fe$_{46.4}$Pt$_{53.6}$
As-deposited
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
Fe$_{54.3}$Pt$_{45.7}$

Exothermic down (mW)

Counts/s

(b) 
Fe$_{54.3}$Pt$_{45.7}$
As-deposited
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 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.
Fe$_{52.4}$Pt$_{47.6}$

(a)

Exothermic down (mW)

Temperature (°C)

-40
-35
-30
-25
-20
-15
-10
-5
0
5

20 K/min
40 K/min
80 K/min
160 K/min

(b)

Fe$_{52.4}$Pt$_{47.6}$
As-deposited

Counts/s

0
10000
30000
90000

30
40
50
60
70

Position [°2Theta]
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.
The diagram shows the exothermic down (mW) versus temperature (°C) for Fe_{47.7}Pt_{52.3} with different cooling rates: 20 K/min, 40 K/min, 80 K/min, and 160 K/min. The graph illustrates the thermal behavior of the material under these conditions.

Below the main graph, there is a smaller graph showing the counts/s for Fe_{47.7}Pt_{52.3} in an as-deposited state.
Fig. F-19: (a) the DSC traces for Fe<sub>47.7</sub>Pt<sub>52.3</sub> 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 film at 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.
Fe\textsubscript{52.1}Mg\textsubscript{1.8}Pt\textsubscript{46.2}

Exothermic down (mW)

Temperature (°C)

Counts/s

Fe\textsubscript{52.1}Mg\textsubscript{1.8}Pt\textsubscript{46.2}
As-deposited
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$_{46.3}$

Exothermic down (mW)

Temperature (°C)

Counts/s

Fe$_{53.8}$Mg$_{0.0}$Pt$_{46.3}$
As-deposited
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\textsubscript{48.8}Mg\textsubscript{2.6}Pt\textsubscript{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.
Fe\textsubscript{43.0}V\textsubscript{12.2}Pt\textsubscript{44.8}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Exothermic down (mW) vs. Temperature (°C) for Fe\textsubscript{43.0}V\textsubscript{12.2}Pt\textsubscript{44.8}.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Counts/s vs. Position [°2Theta] for Fe\textsubscript{43.0}V\textsubscript{12.2}Pt\textsubscript{44.8} As-deposited.}
\end{figure}
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 film at 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 $0^\circ$ tilt (d) the XRD pattern for the annealed at film $36.5^\circ$ tilt and (e) the XRD pattern for the annealed film at $53.7^\circ$ 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.
The graph shows the exothermic down (mW) for \( \text{Fe}_{48.3}\text{V}_{3.1}\text{Pt}_{48.6} \) at different heating rates: 20 K/min, 40 K/min, 80 K/min, and 160 K/min. The temperature is given in °C. The graph indicates a peak at around 400 °C for all heating rates, indicating a phase transition or a reaction that releases energy.
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.
Fe\textsubscript{47.2}Mn\textsubscript{6.0}Pt\textsubscript{46.8}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig_f-31}
\caption{(a) the DSC traces for Fe\textsubscript{47.2}Mn\textsubscript{6.0}Pt\textsubscript{46.8} film.}
\end{figure}
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$_{55.4}$

(a)

Exothermic down (mW)

Temperature (°C)

Counts/s

(b) Fe$_{28.3}$Mn$_{16.3}$Pt$_{55.4}$ As-deposited
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.
Fe_{44.2}Ag_{16.7}Pt_{39.1}

(a)

Exothermic down (mW)

Temperature (°C)

-15

-10

-5

0

100 200 300 400 500 600 700

20 K/min

40 K/min

80 K/min

160 K/min

(b)

Fe_{44.2}Ag_{16.7}Pt_{39.1}

As-deposited

Counts/s

640000

360000

160000

40000

0

30 40 50 60 70

Position [°2Theta]
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$_{43.1}$

(a)

Temperature (°C)

Exothermic down (mW)

Counts/s

(b) Fe$_{50.0}$Ag$_{6.9}$Pt$_{43.1}$
As-deposited
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$_{47.5}$

![Graph showing exothermic down (mW) vs. Temperature (°C) for different cooling rates: 20 K/min, 40 K/min, 80 K/min, and 160 K/min.](a)

Counts/s

![Graph showing counts/s vs. Position [°2Theta] for Fe$_{49.1}$Ag$_{3.4}$Pt$_{47.5}$ as-deposited.](b)
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 film with 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.
Fig. F-39: (a) the DSC traces for Fe\textsubscript{48.7}Ag\textsubscript{1.5}Pt\textsubscript{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.
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}

(a)

(b) Fe_{50.9}Au_{4.1}Pt_{45.0}
As-deposited
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 film at 36.5° tilt and (e) the XRD pattern for the annealed film at 53.7° tilt.
Fe$_{47.2}$Au$_{7.2}$Pt$_{45.6}$

![Exothermic down (mW) vs. Temperature (°C)](image)

- 20 K/min
- 40 K/min
- 80 K/min
- 160 K/min

Counts/s

Fe$_{47.2}$Au$_{7.2}$Pt$_{45.6}$

As-deposited
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$_{54.2}$

(a) Exothermic down (mW) vs. Temperature ($^\circ$C) with 40 K/min.

(b) Fe$_{38.6}$Au$_{7.2}$Pt$_{54.2}$ As-deposited.
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 $0^\circ$ tilt (d) the XRD pattern for the annealed film at $36.5^\circ$ tilt and (e) the XRD pattern for the annealed film at $53.7^\circ$ tilt.
Fig. F-45: (a) the DSC traces for Fe$_{46.3}$B$_{12.9}$Pt$_{40.8}$ film.
Fe_{45.1}B_{12.3}Pt_{42.7}

(a)

Exothermic down (mW)

Temperature (°C)

Counts/s

(b)

Fe_{45.1}B_{12.3}Pt_{42.7}
As-deposited
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$_{45.2}$

(a)

Exothermic down (mW)

Temperature ($^\circ$C)

-80 -70 -60 -50 -40 -30 -20 -10 0

-80 -70 -60 -50 -40 -30 -20 -10 0

20 K/min
40 K/min
80 K/min
160 K/min

(b)

Counts/s

Fe$_{43.0}$B$_{11.8}$Pt$_{45.2}$
As-deposited
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.
Fe$_{49.9}$B$_{4.8}$Pt$_{45.3}$

(a) Exothermic down (mW)

Temperature (°C)

-50  -40  -30  -20  -10   0

-50 -40 -30 -20 -10  0  10  20  30  40  50  60  70

Position [°2Theta]

Counts/s

(b) Fe$_{49.9}$B$_{4.8}$Pt$_{45.3}$

As-deposited
Fig. F-48: (a) the DSC traces for Fe\textsubscript{49.9}B\textsubscript{4.8}Pt\textsubscript{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.
Fe$_{50.9}$B$_{2.6}$Pt$_{46.5}$

Exothermic down (mW) vs. Temperature ($^\circ$C)

- 20 K/min
- 40 K/min
- 80 K/min
- 160 K/min

Counts/s vs. Position [°2Theta]

Fe$_{50.9}$B$_{2.6}$Pt$_{46.5}$
As-deposited
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.
**Fe_{44.1}B_{4.8}Pt_{51.2}**

(a) Exothermic down (mW) vs Temperature (°C) for different heating rates: 20 K/min, 40 K/min, 80 K/min, 160 K/min.

(b) Count/s vs Position [°2Theta] for Fe_{44.1}B_{4.8}Pt_{51.2} As-deposited.
Fig. F-50: (a) the DSC traces for Fe\textsubscript{44.1}B\textsubscript{4.8}Pt\textsubscript{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.
Fe_{44.3}B_{1.2}Pt_{54.5}

Exothermic down (mW)

Temperature (°C)

Counts/s

(b) Fe_{44.3}B_{1.2}Pt_{54.5}
As-deposited
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 $0^\circ$ tilt (d) the XRD pattern for the annealed at film $36.5^\circ$ tilt and (e) the XRD pattern for the annealed film at $53.7^\circ$ tilt.
Fig. F-53: (a) the DSC traces for Fe\textsubscript{49.8}C\textsubscript{1.4}Pt\textsubscript{48.8} film.
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VITA

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