

STRUCTURAL CHARACTERIZATION OF NiMnX (Sn, In) THIN FILM ALLOYS

by

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ABSTRACT

STRUCTURAL CHARACTERIZATION OF NiMnX (Sn, In) THIN FILM ALLOYS

Ferromagnetic *Ni-Mn-X* (Sn, In) alloys are predicted as potential candidates for energy efficient Magnetocaloric Effect (MCE) technologies. The MCE is the basis of magnetic refrigeration and it is expected to leads to a groundbreaking progress on conventional refrigeration methods. In our research, *NiMnX* (Sn, In) thin film alloys were for first time fabricated by co-sputter deposition method. The Mn losses due to the high Mn vapor pressure produce a deviation from the desired $Ni_{50}Mn_{37}Sn_{13}$ (Sn, In) composition, which are partially compensated by increasing power of the Mn target gun. A systematic study of thin film co-sputter fabrication was divided into three stages; (i) a *NiMnX* (Sn, In) target was evaporated at different temperatures in order to study the grain size temperature dependence, (ii) the nominal chemical composition ($Ni_{50}Mn_{37}Sn_{13}$) was reach by controlling the power value applied to the Mn target, (iii) the dependence of the phase transformation temperature with the grain size of the thin film alloys was studied. Grain size can be controlled by modifying the substrate temperature (T_s). The crystal structure is highly dependent on composition and 10-14M monoclinic crystal structure can be only found for when the Sn and In values range from 10 to 13 %. Austenite-martensite transformation, and therefore magnetocaloric effect, can only be founded for this compositional range. Our results confirm that nominal composition, $Ni_{50}Mn_{37}Sn_{13}$, can be reached in thin films for given co-sputter parameter. As expected *NiMnSn* alloys in the shape of thin films only exhibit austenite-martensite transformations in a narrow compositional range. Further studies are required to confirm the potentiality of this material as a potential candidate for magnetic cooling technology.

ÖZET

NiMnX (Sn, In) İNCE FİLM ALAŞIMLARININ YAPISAL KARAKTERİZASYONU

Enerji verimliliği açısından, Ferromanyetik $Ni-Mn-X$ (Sn, In) alaşımları Manyeto Kalorik Etki (MKE) teknolojileri için potansiyel adaydırlar. MKE manyetik soğutmanın temeli olup günümüz soğutma methodlarında yeni bir çığır açması beklenmektedir. Araştırmamızda, ikili kaplama metoduyla $Ni-Mn-X$ (Sn, In) ince film alaşımlar öncelikli olarak üretilmiştir.

Yüksek buhar basıncı nedeniyle istenen $Ni_{50}Mn_{37}X_{13}$ (Sn, In) içeriğindeki Mn oranındaki sapma Mn hedefine uygulanan güç değerindeki artışla kısmen giderilmiştir. İkili kaplama metoduyla ince film üretiminin sistematik çalışması 3 farklı kola ayrılmıştır; (i) Ince filmin yüzeyindeki granüllü yapının boyutunun sıcaklığa bağlılığını incelemek için $NiMnX$ (Sn, In) malzemesi (hedefi) farklı sıcaklıklarda buharlaştırılmıştır. (ii) Karar verilen kimyasal bileşime ($Ni_{50}Mn_{37}Sn_{13}$), Mn hedefe uygulanan güç değerini kontrol ederek ulaşılmıştır. (iii) Ince filmlerin granül boyutlarının faz değişim sıcaklığına bağlılığı çalışılmıştır.

Granüllerin boyutunun kaplama yapılan yüzeye uygulanan sıcaklık ile kontrol edilebildiği gözlemlenmiştir. Kristal yapı yüksek oranda kimyasal içeriğe bağlıdır ve 10-14M monoklinik kristal yapı sadece Sn ve In' nin alaşım içindeki yüzdesi 10% ile 13 % arasında olduğu durumda görülmektedir. Bu bileşik değerlerinde Austenite-Martensite faz dönüşümü ve dolayısıyla Manyeto Kalorik Etki gözlemlenmektedir.

Sonuçlarımız, karar verilen $Ni_{50}Mn_{37}Sn_{13}$ bileşiğine ikili kaplama için belirlenmiş olan parametrelerle ulaşılabilineceğini doğrulamaktadır. Beklendiği gibi ince film şeklindeki NiMnSn alaşımlar austenite-martensite dönüşümünü çok dar bir bileşik bandında

gös- terirler. Geniş kapsamlı araştırmamız süresince ürettiğimiz bu ince filmlerin manyetik soğutma teknolojilerinde kullanılabilecek aday malzemeler olduğunu doğrulamak için daha fazla çalışma gerekmektedir.

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LIST OF SYMBOLS

Ar	Argon
C	Heat Capacity
C_V	Heat Capacity at Constant Volume
C_P	Heat Capacity at Constant Pressure
Cr	Chromium
Cu	Copper
F	Helmholtz Free Energy
Fe	Iron
G	Gibbs Free Energy
Ge	Germanium
H	External Magnetic Field
In	Indium
M	Magnetization
Mn	Manganese
N	Number of Particles
Ni	Nickel
O	Oxygen
P	Pressure
Q	Heat Energy
S	Entropy
Si	Silicon
Sn	Tin
T	Temperature
T_c	Critical Temperature
T_s	Substrate Temperature
U	Internal Energy
V	Volume
δQ	Change in Heat Energy

δS	Change in Entropy
δS_{iso}	Change in Entropy in Isothermal Process
δT	Change in Temperature
δT_{ad}	Change in Temperature in an Adiabatic Process
μ	Chemical Potential
μ_0	Permeability of Free Space

LIST OF ACRONYMS/ABBREVIATIONS

<i>iso</i>	Isothermal Process
<i>min.</i>	Minute
μm	Micrometer
<i>nm</i>	Nanometer
<i>rpm</i>	Rotation Per Minute
<i>sccm</i>	Standard Cubic Centimeters per Minute
<i>C</i>	Celcius
<i>DC</i>	Direct Current
<i>DMCE</i>	Direct Magnetocaloric Effect
<i>EDS</i>	Energy Dispersive X-ray Spectroscopy
<i>FSMA</i>	Ferromagnetic Shape Memory Alloy
<i>GMCE</i>	Giant Magnetocaloric Effect
<i>IAD</i>	Ion Assisted Deposition
<i>IMCE</i>	Inverse Magnetocaloric Effect
<i>IP</i>	Ion Plating
<i>IVD</i>	Ion Vapor Deposition
<i>MCE</i>	Magnetocaloric Effect
<i>PVD</i>	Physical Vapor Deposition
<i>RF</i>	Radio Frequency
<i>RT</i>	Room Temperature
<i>Sbs</i>	Substrate
<i>SEM</i>	Scanning Electron Microscope
<i>SMA</i>	Shape Memory Alloy
<i>SME</i>	Shape Memory Effect
<i>VBV</i>	Vacuum Breaking Valve
<i>W</i>	Watt

1. INTRODUCTION

Magnetism is one of the most important physical phenomena and it is basically arising from the electric currents and the fundamental magnetic moments. This magnetic system causes an attraction or repulsion between particles due to the applied magnetic field. Most materials show one of these effects against an external magnetic field and the others do not exhibit any effect. This situation can be classified in the following: The strongest effect is on some materials which have permanent magnetic moments caused by an external magnetic field and this is called as ferromagnetism. Some materials which do not have permanent moments are attracted to a magnetic field and this is paramagnetism. The others are repulsed by a magnetic field (diamagnetism).

All the rest of them have a much more complex relationship with an applied magnetic field (anti-ferromagnetism). Substances that are negligibly affected by magnetic fields are known as non-magnetic substances. They include copper, aluminum, gases, and plastic. The magnetic state of a material depends on temperature, pressure, and the applied magnetic field. Ferromagnetism has a crucial place in industry and technology and it is used in many electrical and electromechanical devices such as electromagnets, electric motors, generators, transformers, and magnetic storage such as tape recorders, and hard disks [3].

New scientific discoveries in magnetism leads a broad range usage of magnetic materials, have inevitably opened magnetism based research fields. In this study, following the footsteps through one of the most important effects, which is called as MCE, is the basis of new generation cooling systems, potential underlying materials of these systems were fabricated which forms the principal part of our research.

The application of external magnetic field on particular ferromagnetic materials brings a significant change in the magnetization which interestingly alters the temperature of the system. This crucial event calls Magnetocaloric Effect (MCE) was first ob-

served in iron by Emil Warburg (1881). Therefore, the importance of this phenomenon has recently been figured out in accordance with the advancements in magnetic cooling and magnetic sensor technologies. Magnetic refrigeration has been rewarded to be one of the main applications of materials exhibiting MCE, with the advantage of being environmentally friendly and highly energy efficient materials, when compared with conventional vapor cycle refrigerator. In our research, we have studied *Ni-Mn-X* (Sn, In) ferromagnetic thin film alloys which are addressed as magnetocaloric materials.

The aim of our research is to study the relationship between structural, microstructural, and macroscopic magnetic properties in *NiMnX* (Sn, In) thin film alloys. Thin film technology offers possibilities to produce such diverse microstructures that are great opportunity to build up an alloy that can be used in magnetic cooling technology and enables us to produce these microstructures in expected composition rates with the desired thicknesses. In this study, the focused point is to use ferromagnetic materials to form a composition which can exhibit magnetocaloric effect (MCE).

Ni-Mn-In thin film alloys were deposited on p-type $\langle 100 \rangle$ silicon wafers by applying co-sputtering technique. Because of the high vapor pressure of manganese, there was a substantial loss of this element in the as-deposited *Ni-Mn-X* thin film alloys, hence a ternary target ($Ni_{50}Mn_{37}Sn_{13}$) was located on the DC cathode and pure Mn target was placed on the RF cathode.

Our study includes the synthesis of two different thin film series. The first one will be referred as power-dependent series and the aim in this case is to find the optimized power value applied to the Mn target which provides the closest chemical composition to the nominal one ($Ni_{50}Mn_{37}Sn_{13}$). The applied DC power is fixed at 100 W and kept constant throughout the entire deposition processes whereas applied RF power value is changed from 0 to 60 Watts. Substrate temperature was kept constant at $400^{\circ}C$. In the second series, called temperature-dependent series, both, applied DC and RF power value were kept constant during the entire deposition process at 100 and 60 W, respectively, while the substrate temperature (T_s) was changed from room temperature (RT) to $500^{\circ}C$ in steps of $100^{\circ}C$. Here, our aim is to study the effect

of substrate temperature on grain size of the thin film alloys and their correlation. A significant increase in the grain size was observed with increasing T_s .

Thin film chemical composition for both series was determined by EDS analysis, while scanning electron microscope (SEM) was used to determine the grain size. As expected, the first series do not show a significant change in the grain size with varying applied power value, however in second series, gradual increase of grain size was observed with increasing T_s . The preliminary results reveal that $Ni_{50}Mn_{37}Sn_{13}$ is expected as a material which may exhibit MCE and further study is required to be sure that this material is a potential candidate for magnetic cooling technology. Magnetic characterization of the samples under study is still on progress.

2. HEUSLER ALLOYS

Heusler alloys were discovered by Friedrich Heusler, German mining engineer and chemist, in 1903. The first fabricated Heusler alloy contains two parts copper, one part manganese, and one part tin, Cu_2MnSn . Currently, numerous Heusler alloys (≈ 1500) exist. One of the general features of these alloys is that magnetism of the Heusler alloys can be changed with varying heat treatment and composition [1].

Depending on the amount of contribution of each element in material, Heusler alloys have different physical properties. They can be metals, semiconductors, and semimetals and most of them exhibit ferromagnetic features [1]. In addition to these, their properties can be predicted by counting the number of valence electrons. For example, if a full Heusler alloy with X_2YZ composition has 27 valence electrons, it can be said that this alloy is superconducting and non-magnetic. Similarly, if a half Heusler alloys has 8 or 18 valence electrons with XYZ composition, this alloy is a semiconductor [4].

Before crystal structures of Heusler alloys are explained in the following paragraphs, some crystal structures or Bravais lattices should be reminded. There are 7 types of cells (cubic, tetragonal, monoclinic, orthorhombic, trigonal, triclinic, and hexagonal) and 14 kinds of Bravais Lattices. While a cubic crystal structure has the highest symmetry with three equal lattice parameters ($a = b = c$) and angles ($\alpha = \beta = \gamma = 90^\circ$), a triclinic crystal structure has the lowest one with three different lattice parameters ($a \neq b \neq c$) and angles ($\alpha \neq \beta \neq \gamma \neq 90^\circ$) [5]. As austenitic phase is related to cubic structures, martensitic phase has lower symmetric crystal structures such as tetragonal, monoclinic, or hexagonal. Their crystal structures (i.e. the arrangement of atom(s) which forms the crystal itself within a unit cell) can be seen from *Appendix A* to have a better understanding before full and half Heusler alloys.

Further constructive information related to crystal lattice structure, locating the positions of the atoms inside the crystal is one the staple steps. Wyckoff positions of

atoms show where these atoms are placed in crystal structures. There are three kinds of Heusler alloys;

- Full Heusler Alloys
- Half Heusler Alloys
- Full Quaternary Heusler Alloys

2.1. Full Heusler Alloys

Ternary Heusler alloys have X_2YZ chemical composition where X and Y are transition metals and Z is the main group element. Usually, unit cell of full Heusler alloy is $L2_1$. This crystal structure consists of four interpenetrating face centered cubic lattices. Wyckoff positions of this crystal structure for X, Y, and Z are $8c(1/4,1/4,1/4)$, $4a(0,0,0)$, and $4b(1/2,1/2,1/2)$, respectively. Many of full Heusler alloys show magnetic properties such as magneto-optical, magnetocaloric and magneto-structural characteristics [1]. Co_2MnSi , Co_2MnGe , and Co_2CrAl can be given as some examples of full Heusler alloys [6].

2.2. Half Heusler Alloys

Its chemical composition is usually XYZ . The unit cell of full Heusler Alloy is $C1_b$. This crystal structure consists of three interpenetrating face centered cubic lattices. Wyckoff positions of this crystal structure for X, Y, and Z are $8c(1/4,1/4,1/4)$, $4a(0,0,0)$, and $4b(1/2,1/2,1/2)$, respectively. $NiMnSb$, $PtMnSb$ [5], $TiNiSn$, $ZrNiSn$, and $HfNiSn$ [7] are some of half Heusler alloys.

2.3. Full Quaternary Heusler Alloys

In addition to full and half Heusler alloys, there is a third kind of Heusler alloy: Full quaternary Heusler alloys. Its chemical composition was studied by Galanakis and chemical composition of these alloys can be one of $X_2Y_{1-x}Y'_xZ$, $(X_{1-x}X'_x)_2YZ$, and $X_2YZ_{1-x}Z'_x$. $Co_2Cr_{1-x}Mn_xAl$, $Co_2Mn_{1-x}Fe_xAl$, $Co_2Cr_{1-x}V_xAl$, $Co_2V_{1-x}Fe_xAl$,

and $Co_2Cr_{1-x}Fe_xAl$ are some examples to the Heusler alloys [5].

Face centered cubic lattice (fcc), crystal structure of full Heusler alloys (4 interpenetrating fcc lattices) which are usually known as $L2_1$ and crystal structure of half Heusler alloys (3 interpenetrating fcc lattices) are called as $C1_b$ are given below (Figure 2.1 and Figure 2.2).

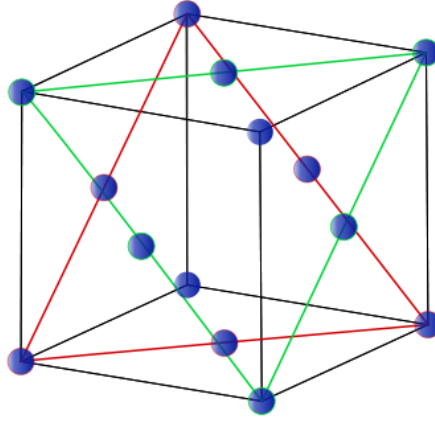


Figure 2.1. Face centered cubic lattice.

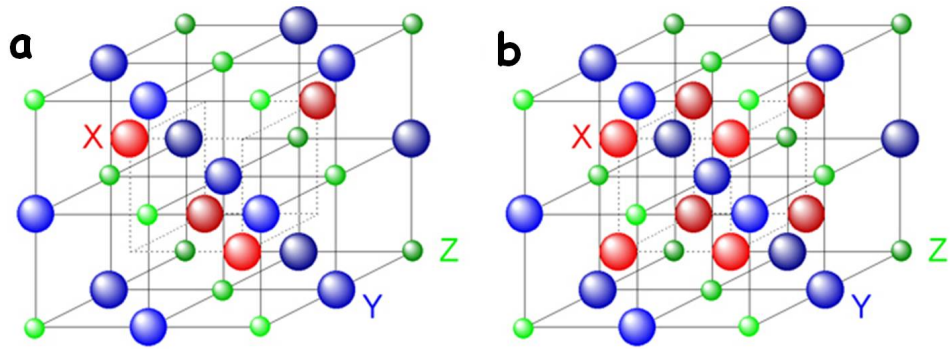


Figure 2.2. a) $C1_b$ and b) $L2_1$ crystal structure.

Periodic table which helps to create full Heusler alloy combinations can be seen from Figure 2.3. As it is mentioned before, X and Y are transition metals and these

elements are shown by red and blue parts of periodic table, respectively. Moreover, Z is the main group element and this element is indicated by green part of the periodic table. Before shape memory effect and martensitic phase transition are explained,

</

Figure 2.3. The combinations of full Heusler alloys [1].

diffusionless transformation which is the base of different atomic arrangement and crystal structure should be understood.

2.4. Diffusionless Transformation

Diffusionless transformation is a phase transformation and it causes a change in atomic arrangement by changing places of the atoms or crystal structure of the material by moving some parts of the crystal lattice. There are two different diffusionless transformations. First one is massive and second one is the martensitic phase transformation.

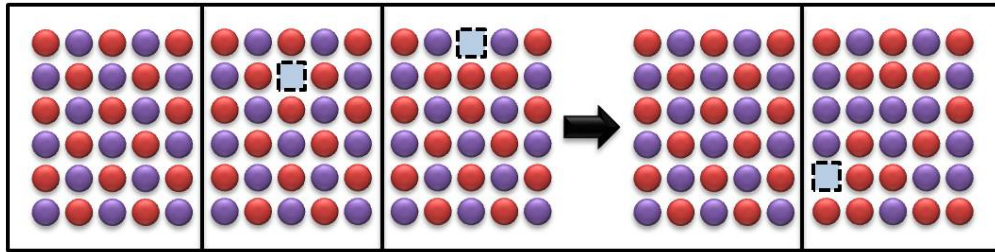


Figure 2.4. A hole can create a change in atomic arrangement and this does not cause a new crystal structure.

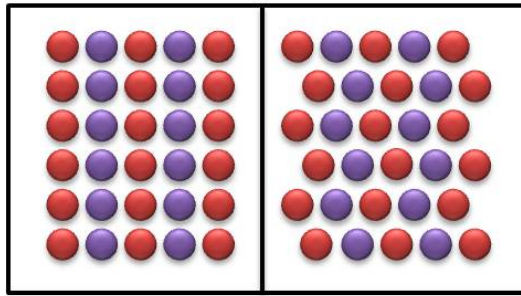


Figure 2.5. The change in lattice causes a new and low symmetric crystal structure.

Massive phase transformation is resulted by a different atomic arrangement not a new crystal structure and martensitic phase transformation is resulted by a different crystal structure. Figure 2.4 and Figure 2.5 clearly show these periods. Figure 2.4 shows the change in stacking sequence because of the movement of the atoms which is provided by a hole. In the first figure above, last two atomic arrays show the first and last version of the positions of the atoms. Figure 2.5 shows the change in crystal structure which is caused by motion of the lattices.

3. MARTENSITIC AND AUSTENITIC PHASE

Some special kinds of Heusler alloys show shape memory effect (SME) and these kinds of materials are called shape memory alloys. First of all, shape memory material or alloy can remember their predeformed or original shape after an application of heat and stress and these kind of materials are called shape memory alloys (SMA). *Cu-Ni-Al* and *Cu-Zn-Al* can be given some examples of SMAs [8]. In addition to SMAs, if an alloy or material remember their first shapes by applying a magnetic field, these materials are called magnetic (ferromagnetic) shape memory alloys (FSMA). Some examples of FSMA are *Ni-Mn-Ga*, *Ni-Fe-Ga*, *Co-Ni-Al* and *Co-Ni-Ga* [9].

The difference between SMAs and FSMAs is a degree of freedom and FSMAs has magnetic field as a degree of freedom in addition to stress and temperature [10]. For example, if Y is Mn, XYZ or X_2YZ shows the magnetic shape memory effect [8]. Figure 3.1 and Figure 3.2 explain the differences SMAs and FSMAs. If material is SMA, by applying heat or a stress, crystal structure of it can be changed. If the material is an FSMA, crystal structure of the material will change thanks to magnetic field.

All these changes in crystal structures are usually because of the martensitic transformations and these transformations can be related to some important events such as direct, inverse Magnetocaloric Effect (MCE), Giant Magnetocaloric Effect (GMCE) (all of them will be described in the next chapter, particularly), a magnetic field induced reverse martensitic transformation and a large magnetoresistance change [11].

Martensitic phase can be thought as a low temperature phase, whereas austenetic phase is high temperature phase. Austenitic phase is seen at higher temperatures than martensitic phase is. It is expected that the crystal structure of a material at austenitic phase should be low symmetry such as tetragonal, monoclinic, or orthorhombic. Materials which show the shape memory effect have an elasticity such as a plastic. So, while material at martensitic phase has lower symmetry, material at austenitic phase have

the highest symmetry like a cubic crystal structure (usually face centered cubic structure). In 1950, *Au-Cd* and *In-Tl* alloys which show SME are the first materials [12]. The shape memory effect can be understood clearly if martensitic phase transition is known.

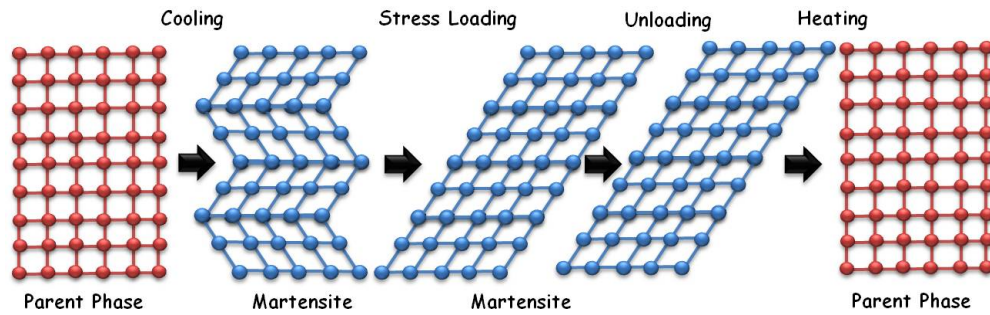


Figure 3.1. Stress or any external effect can cause a change in crystal structure. This kind of materials is called Shape Memory Alloys.

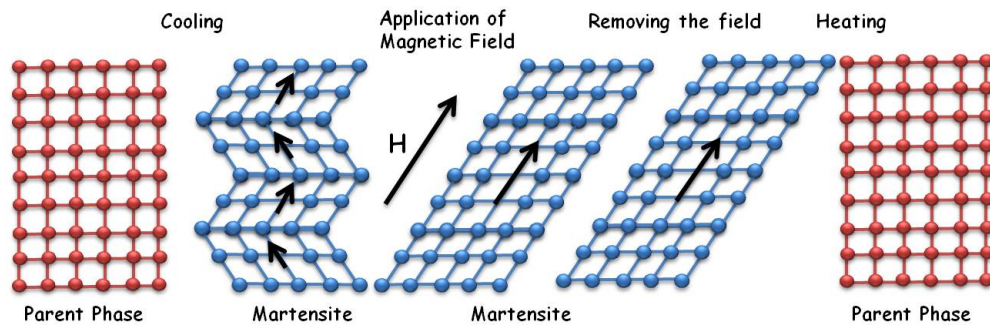


Figure 3.2. Magnetic field affects the crystal structure of the alloys. This type of SMA is Ferromagnetic Shape Memory Alloy. This event is called magnetic shape memory effect.

As it is briefly stated before, the crystal structure of austenitic phase can be described by a cubic structure. There are several kinds of martensitic phases, which are called modulated martensite such as 2M, 3M, 5M, and 7M. However, the non modulated martensite is a transformation from austenitic phase to martensitic phase.

The difference between martensitic phase and non-modulated martensitic phase is that while the former one transforms from high symmetric phase (cubic) to one of the low symmetric crystal structures (tetragonal, monoclinic, orthorhombic etc.) or vice versa, the latter one transforms from cubic structure to a tetragonal structure or vice versa.

There are some crystal structure examples related to martensitic and austenitic phase such as cubic (austenitic phase) and tetragonal structures (martensitic phase) which are created by using Powder Cell Program. This program will be explained in detail in *Appendix B*.

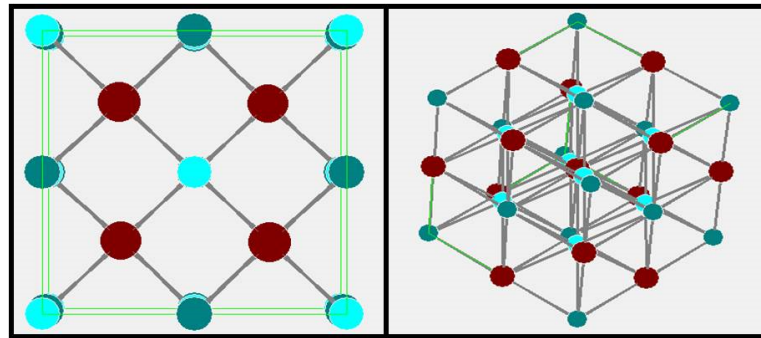


Figure 3.3. Cubic crystal structure (it defines austenitic phase).

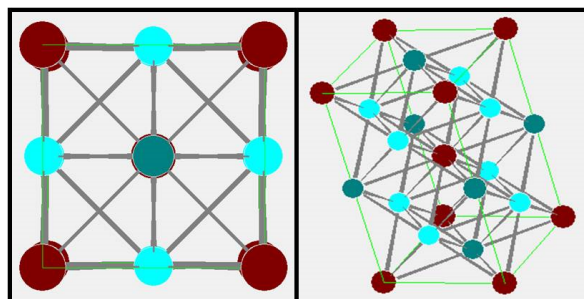


Figure 3.4. Non Modulated martensite.

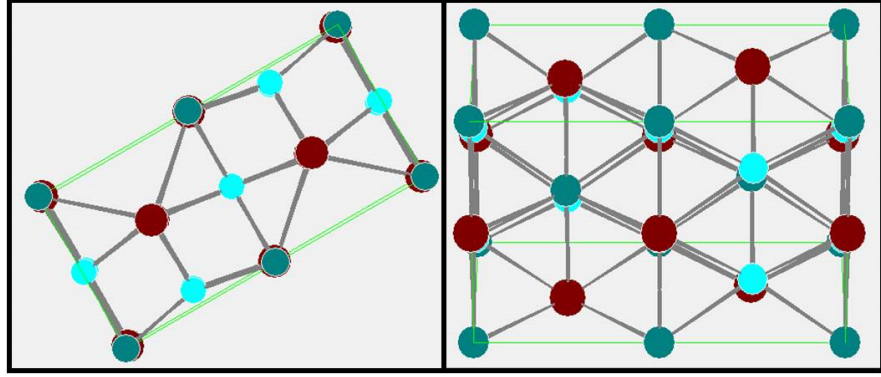


Figure 3.5. 2M-4M modulated martensite.

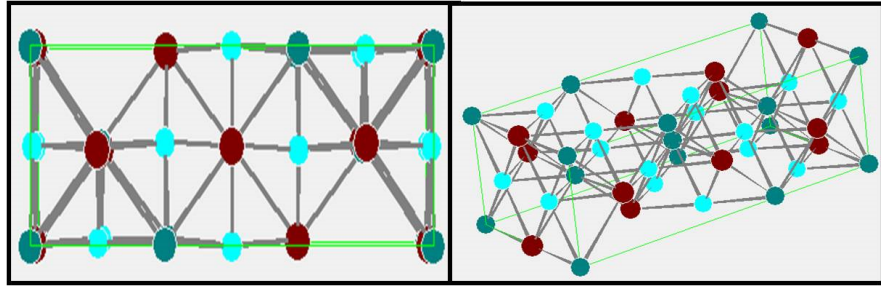


Figure 3.6. 3M-6M modulated martensite.

In addition to 2M-4M and 3M-6M (Figure 3.5 and Figure 3.6) atomic arrangements in the lattice structure of modulated martensite, 5M-10M is also created by using the same method and Figure 3.7 shows this structure. Color codes are the same for each figure and states that there three kinds of atoms exist in this structure.

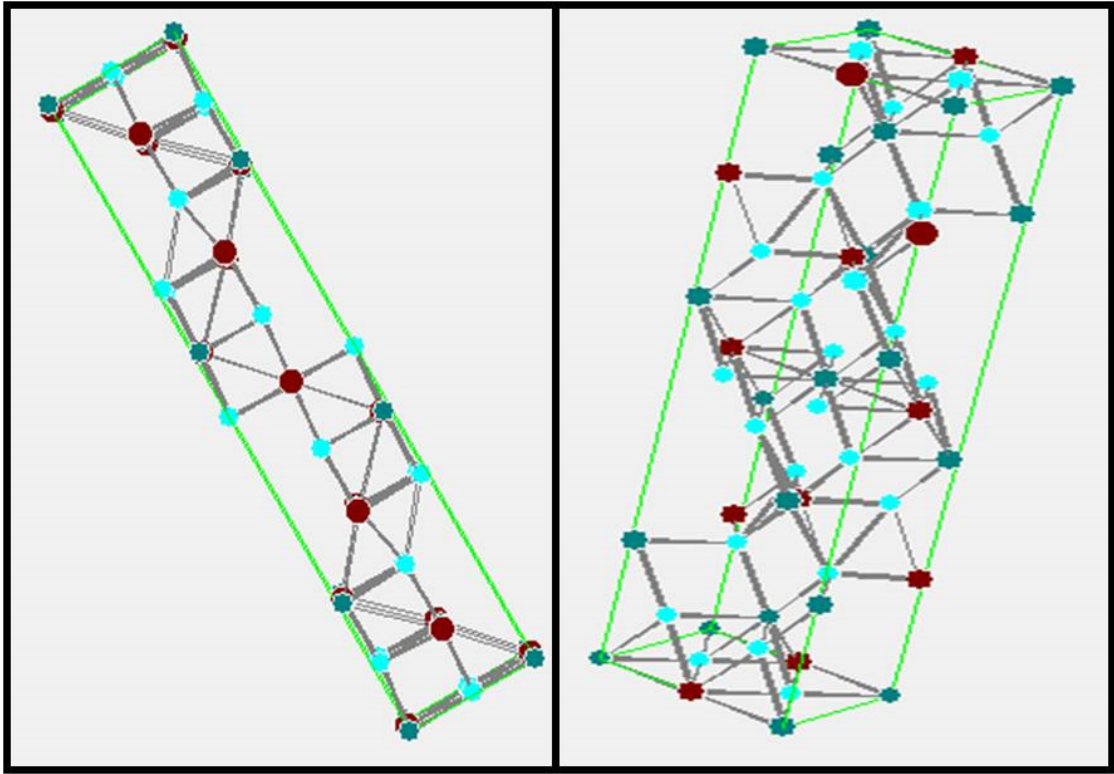


Figure 3.7. 5M-10M modulated martensite.

The last configuration is 7M-14M modulated martensite crystal structure. By using the same procedure with the previous ones, the corresponding locations of atoms in the lattice is shown as Figure 3.8.

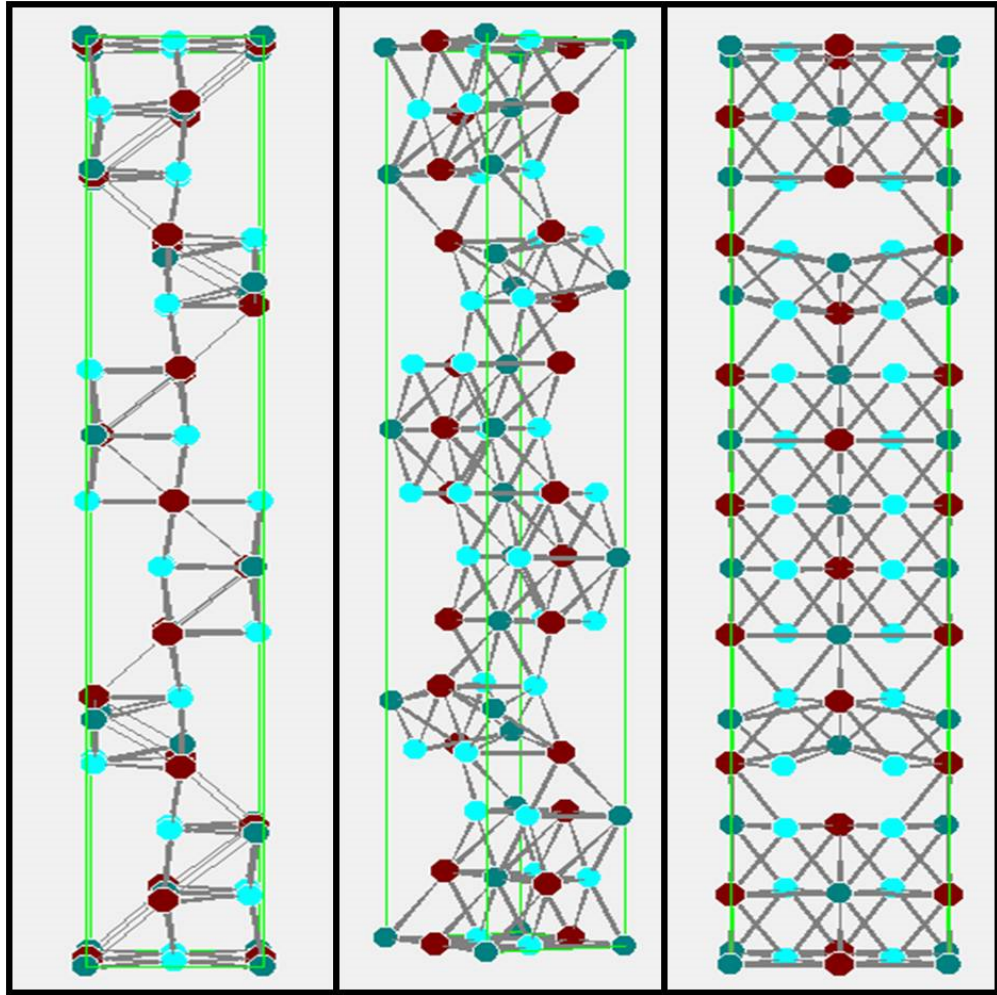


Figure 3.8. 7M-14M modulated martensite.

Before all crystal structures of austenitic and martensitic phases, their space groups, and space group numbers are combined with a table (see Figure 3.9), space groups and space groups number should be defined shortly. Space group is the one of the properties which help for the identification of the crystal structures. Space or Symmetry groups of crystal structures can be defined as the representation of the symmetry. For example, a cubic Bravais lattice can return its original shape again by rotating it 90° about a line through $\langle 100 \rangle$ direction [13]. Space group of a Bravais lattice can include one of the operations below:

- Translations which are through Bravais lattice vectors,
- Operations which leave a certain point of the lattice fixed,
- Successive operations which consist of combinations of number 1 and number 2 [13].

A unique space group number is given for each crystal structure by The International Union of Crystallography, arbitrarily and these number are between 1 and 230 [13]. All space groups and space group numbers can be found in *Appendix C*.

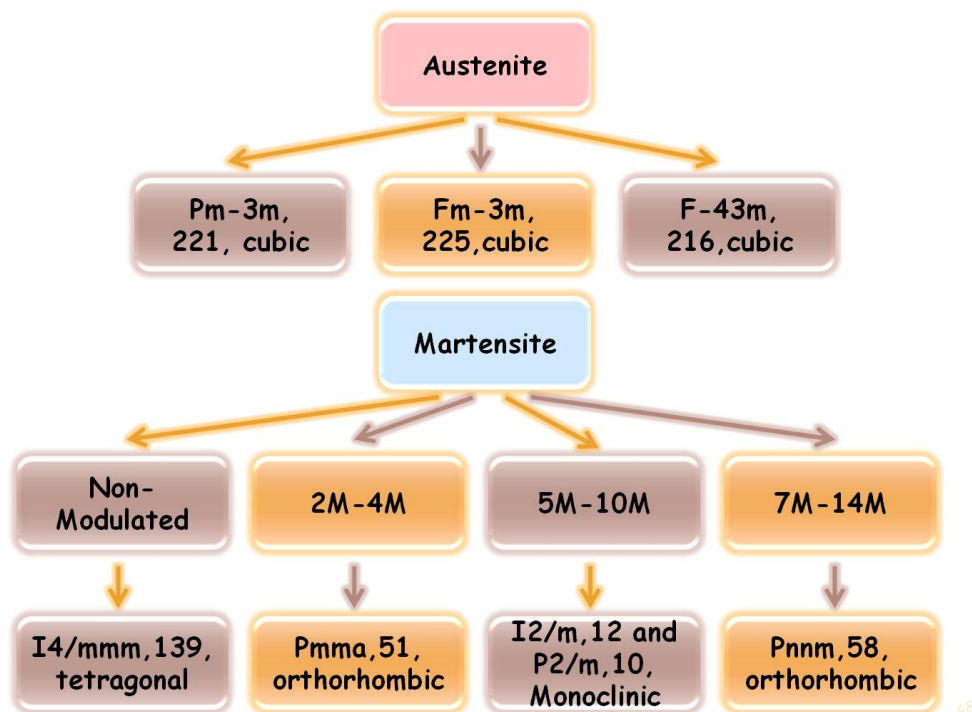


Figure 3.9. The summarization of all space groups and crystal structures related to austenitic and martensitic phase.

4. MAGNETOCALORIC EFFECT

The application of external magnetic field on particular ferromagnetic materials brings a significant change in the magnetization which interestingly alters the temperature of the system. This event is called as Magnetocaloric Effect (MCE) and it was first observed in iron by Emil Warburg in 1881 [14]. MCE can also be described, briefly as an adiabatic change in temperature ΔT or an isothermal change in entropy ΔS due to the application of magnetic field [2].

Before mentioning about the relationship between magnetic field and adiabatic and isothermal processes, in general, an adiabatic process can be expressed as follows: It is an energy transfer method by doing a work in a way except from a heating transfer to a system and its surroundings. If the surrounding of system does work on the gas, the pressure of the gas will increase and adiabatic heating will occur. For example, diesel engines work with this principle (a piston compressing the gas contained within an adiabatic cylinder). This process can be seen from Figure 4.1-a. If the gas works on the surrounding of the system (substance), a decrease in the pressure of the surrounding of system will cause adiabatic cooling. Figure 4.1-b shows a simple schematic representation of this type of cooling procedure. One of the methods which are used to reach very low temperatures is adiabatic demagnetization [15]. In isothermal process, temperature does not change. Basically, if a system is in contact with an outside thermal reservoir, an energy flow from the reservoir to the system is expected to be irrespective of a change in the temperature. Phase changes such as melting evaporation can be given as an example of isothermal process [16]. The theoretical point of view can help for further analyze of the thermodynamics potentials to have a better understanding about the behavior of the system.

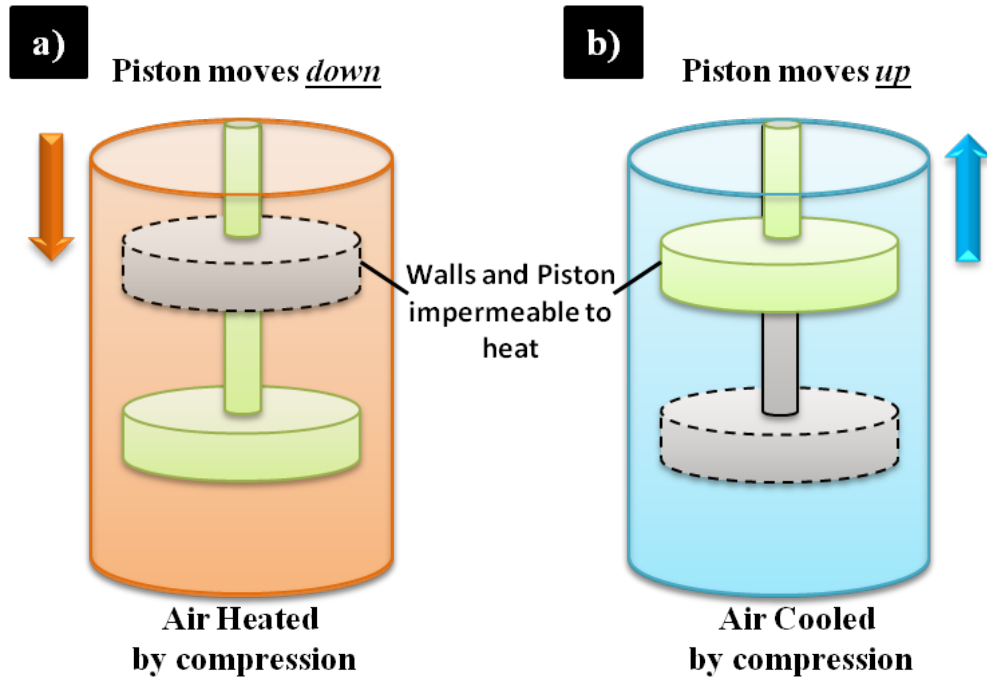


Figure 4.1. Adiabatic heating (a) and cooling (b) when a piston moves up and down in a cylinder.

4.1. Thermodynamics Potentials

4.1.1. Internal energy

Internal energy (U) is the total energy for a thermodynamics system and it is a function of entropy (S), volume (V), magnetization (M), and the number of particles (N) in the system. Differential of U is described below where μ is the chemical potential, P is the pressure of the system, T is the temperature of the system, H is the external magnetic field, and M is the magnetization [17].

$$dU = TdS - PdV + \mu dN + \mu_0 H dM \quad (4.1)$$

4.1.2. Helmholtz free energy

Helmholtz free energy (F) is used for isothermal processes and keeping the volume of system constant ($dW=0$) [17]. As it can be seen from the relation below, it is a function of T , V , M , and N . For the minimization of the Helmholtz free energy is only possible when T , V , M , and N are all constant for a specifically determined system.

$$dF = -SdT - PdV + \mu dN + \mu_0 H dM \quad (4.2)$$

4.1.3. Gibbs free energy

Gibbs free energy is also referred as available energy that measures the process initiating work obtainable from isothermal and isobaric thermodynamic systems. These kinds of systems exhibit isobaric and isothermal behavior, simultaneously. The relation written below is a general Gibbs energy in differential form and depends on T , P , H and N .

$$dG = -SdT + VdP + \mu dN - \mu_0 M dH \quad (4.3)$$

If the number of particles is constant dU , dF , and dG are reduced :

$$dU = TdS - PdV + \mu_0 H dM \quad (4.4)$$

$$dF = -SdT - PdV + \mu_0 H dM \quad (4.5)$$

$$dG = -SdT + VdP - \mu_0 M dH \quad (4.6)$$

dU , dF , and dG are the exact differentials so these equations are written as follows;

$$dU = \left(\frac{\partial U}{\partial S} \right) dS + \left(\frac{\partial U}{\partial V} \right) dV + \left(\frac{\partial U}{\partial M} \right) dM \quad (4.7)$$

$$dF = \left(\frac{\partial F}{\partial T} \right) dT + \left(\frac{\partial F}{\partial V} \right) dV + \left(\frac{\partial F}{\partial M} \right) dM \quad (4.8)$$

$$dG = \left(\frac{\partial G}{\partial T} \right) dT + \left(\frac{\partial G}{\partial P} \right) dP + \left(\frac{\partial G}{\partial H} \right) dH \quad (4.9)$$

By using the equations shown above, we come up with some new equations for F and G , respectively.

$$\left(\frac{\partial F}{\partial M} \right)_{M,T} = \mu_0 M(T, V, M) \quad (4.10)$$

$$\left(\frac{\partial F}{\partial V} \right)_{V,T} = -P(T, V, M) \quad (4.11)$$

$$\left(\frac{\partial F}{\partial T} \right)_{V,M} = -S(T, V, M) \quad (4.12)$$

and

$$\left(\frac{\partial G}{\partial T} \right)_{H,P} = -S(T, H, P) \quad (4.13)$$

$$\left(\frac{\partial G}{\partial H} \right)_{T,P} = -\mu_0 M(T, H, P) \quad (4.14)$$

$$\left(\frac{\partial G}{\partial P}\right)_{H,T} = V(T, H, P) \quad (4.15)$$

By using these equations, Maxwell's relations for thermodynamic potentials are simply obtained. For the case of Helmholtz Free Energy,

(i)

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T}\right)_{V,M}\right]_{M,T} = \left[\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V}\right)_{M,T}\right]_{M,V} \quad (4.16)$$

$$\left[\frac{\partial S}{\partial V}\right]_{M,T} = \left[\frac{\partial P}{\partial T}\right]_{M,V} \quad (4.17)$$

(ii)

$$\left[\frac{\partial}{\partial M} \left(\frac{\partial F}{\partial T}\right)_{V,M}\right]_{V,T} = \left[\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial M}\right)_{V,T}\right]_{M,V} \quad (4.18)$$

$$\left[\frac{\partial S}{\partial M}\right]_{V,T} = -\mu_0 \left[\frac{\partial H}{\partial T}\right]_{M,V} \quad (4.19)$$

(iii)

$$\left[\frac{\partial}{\partial M} \left(\frac{\partial F}{\partial V}\right)_{T,M}\right]_{V,T} = \left[\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial M}\right)_{V,T}\right]_{M,T} \quad (4.20)$$

$$\left[\frac{\partial P}{\partial M}\right]_{V,T} = -\mu_0 \left[\frac{\partial H}{\partial V}\right]_{M,T} \quad (4.21)$$

For the case of Gibbs free energy,

(i)

$$\left[\frac{\partial}{\partial H} \left(\frac{\partial G}{\partial T} \right)_{H,P} \right]_{T,P} = \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial H} \right)_{T,P} \right]_{H,P} \quad (4.22)$$

$$\left[\frac{\partial S}{\partial H} \right]_{T,P} = \mu_0 \left[\frac{\partial M}{\partial T} \right]_{H,P} \quad (4.23)$$

(ii)

$$\left[\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T} \right)_{H,P} \right]_{T,H} = \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_{T,H} \right]_{H,P} \quad (4.24)$$

$$\left[\frac{\partial S}{\partial P} \right]_{H,T} = - \left[\frac{\partial V}{\partial T} \right]_{H,P} \quad (4.25)$$

(iii)

$$\left[\frac{\partial}{\partial H} \left(\frac{\partial G}{\partial P} \right)_{H,T} \right]_{T,P} = \left[\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial H} \right)_{T,P} \right]_{H,T} \quad (4.26)$$

$$- \left[\frac{\partial V}{\partial H} \right]_{T,P} = \mu_0 \left[\frac{\partial M}{\partial P} \right]_{H,T} \quad (4.27)$$

These three important relations are written below in a compact form:

$$\left[\frac{\partial S}{\partial M} \right]_{V,T} = -\mu_0 \left[\frac{\partial H}{\partial T} \right]_{M,V} \quad (4.28)$$

$$\left[\frac{\partial S}{\partial P} \right]_{H,T} = - \left[\frac{\partial V}{\partial T} \right]_{H,P} \quad (4.29)$$

$$\left[\frac{\partial S}{\partial H} \right]_{T,P} = \mu_0 \left[\frac{\partial M}{\partial T} \right]_{H,P} \quad (4.30)$$

By using the relation between magnetic field and the magnetic field strength, $B = \mu_0 H$, the first and the last equations above can be written in the following form;

$$\left[\frac{\partial S}{\partial M} \right]_{V,T} = - \left[\frac{\partial B}{\partial T} \right]_{M,V} \quad (4.31)$$

$$\left[\frac{\partial S}{\partial B} \right]_{T,P} = - \left[\frac{\partial M}{\partial T} \right]_{M,V} \quad (4.32)$$

Heat capacity is one of the intrinsic properties of the material and expressed as an amount of required energy to change the temperature of the material. In theory, heat capacity of an object is the ratio of the transferred heat energy and temperature. The unit of the heat capacity is Joules per Kelvin [18].

$$C \equiv \frac{\Delta Q}{\Delta T} \quad (4.33)$$

The behavior of the heat capacity rests on variations in volume and pressure, therefore, the primary formalism written above can be also expressed at constant volume and pressure cases, respectively;

$$C_V \equiv \left[\frac{dQ}{dT} \right]_V \quad (4.34)$$

$$C_P \equiv \left[\frac{dQ}{dT} \right]_P \quad (4.35)$$

If these formulas are generalized where x is a constant physical quantity in the system, the heat capacity is given by:

$$C_X \equiv \left[\frac{dQ}{dX} \right]_X \quad (4.36)$$

where $x:V, P$. As a consequence, by defining dQ and TdS as the heat capacity can be written as follows;

$$C_X \equiv T \left[\frac{dS}{dT} \right]_X \quad (4.37)$$

where $x:V, P$.

4.2. Magnetocaloric Potentials

MCE is described in terms of entropy change (ΔS_{iso}) in an isothermal process and the temperature change (ΔT_{ad}) in an adiabatic process by the application of magnetic field. While ΔT_{ad} can directly be measured by using a thermometer, ΔS_{iso} can be calculated by using specific heat or magnetization data.

4.3. The Heating and Cooling Process Created By the Change in Magnetic Field

In a ferromagnetic material, magnetic moments can be fully aligned by adiabatically applying an external magnetic field. Conventional description of entropy is the measure of disorder and does not change either for an isolated system or adiabatic process [18]. It is also worth to note that both the magnetic and lattice entropies contribute significantly to the total entropy of system. The application of magnetic field causes a decrease in the magnetic contribution of entropy due to the decrease of disorder in the spin orientations. The crystalline lattice entropy simultaneously increases to keep the total entropy constant. As a consequence, the material interestingly starts to heat up. In the reversed case, if applied magnetic field is removed, it will bring that while the magnetic part of the entropy increases, the crystalline lattice part of the entropy decreases in order to compensate the variations in each of them. As a result of this, the material starts to cool down [14]. Figure 4.2 shows schematic representation of the magnetic moment orientations driven by both magnetic field and heat. First and second order phase transition will be explained in the following sections.

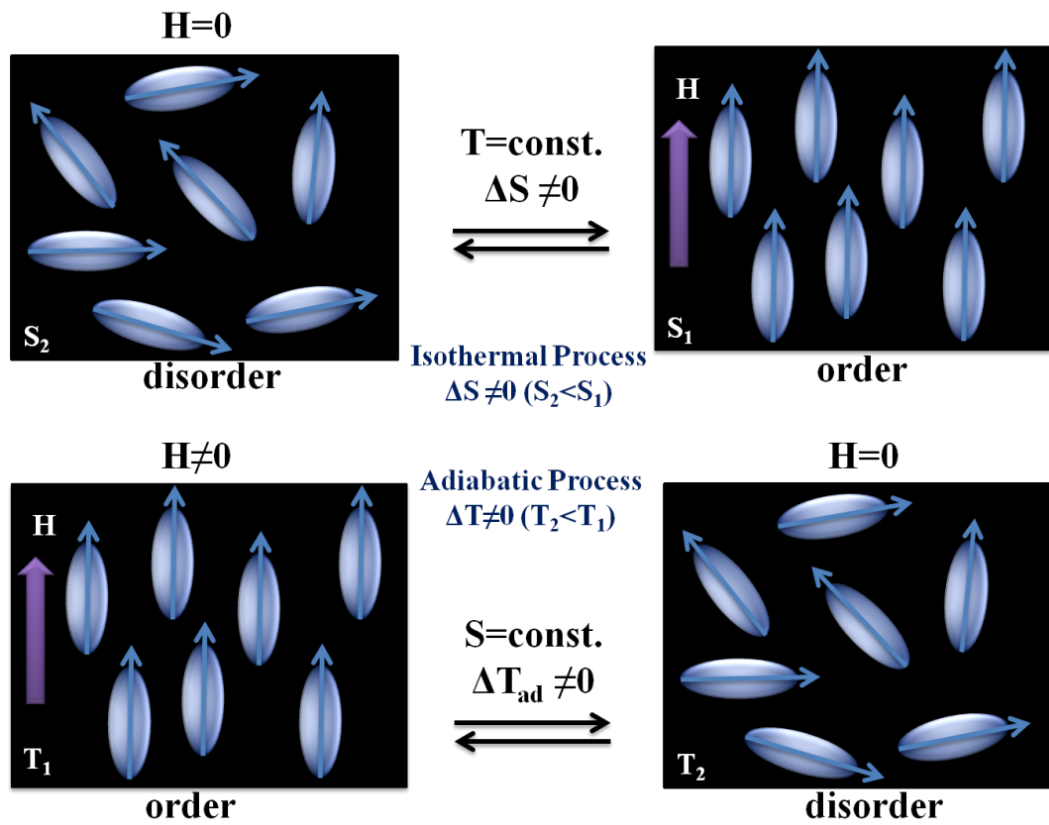


Figure 4.2. Two basic processes of the magnetocaloric effect during the application and remove of magnetic field in a magnetic material: a) isothermal process (T does not change) and b) adiabatic process ($\Delta S=0$).

4.4. First and Second Order Phase Transitions

Phase transitions from one stable state to another can be classified into two principle types: first order and second order transitions. In order to explain the phase transitions, it is indispensable to look for the exchange interactions in between the free energy in the system and the thermodynamic variables of the system. These interactions bring about certain extraordinary discontinuities at particular points which are entitled as phase transition points.

This empirical point of view can be defined theoretically in terms of the first and second order derivatives of the free energy with respect to thermodynamic variables. By looking at the boundary conditions evaluated at the transition points which can be obtained experimentally, we can simply define the phase transitions.

As it is mentioned above, mainly, there are two types of phase transitions which can be identified depending on how the order parameter varies during the transition state. In ferroelectrics, the order parameter is taken as polarization. A first order transition is the one which has a discontinuity in the order parameter itself. Although the polarization itself is a continuous function of temperature, the second order transition is the one which has a discontinuity in the derivative of the order parameter with respect to temperature [19].

More specifically, such as in a ferromagnetic material, the state of the magnetization can be regarded as an order parameter, which helps in a separation of magnetic phase (ie. nonzero magnetization) from non-magnetic phase (ie. zero magnetization) [19]. As it is stated above, this separation is expressed in terms of the derivative of the free energy with respect to the magnetic field (which is the key thermodynamic variable of this case and it is referred as magnetization (M)). The further searching issue is the discontinuity at the phase transition point. The first order differentiation of the free energy of entire system indicates a jump in the magnetization and serves the wanted discontinuity in the system behavior. This is called as first order transition. As opposed to the first order transition, the second order transition is defining a kind

of continuity in the second order differentiation in the free energy which is similar to polarization's temperature trend in the second order phase transition.

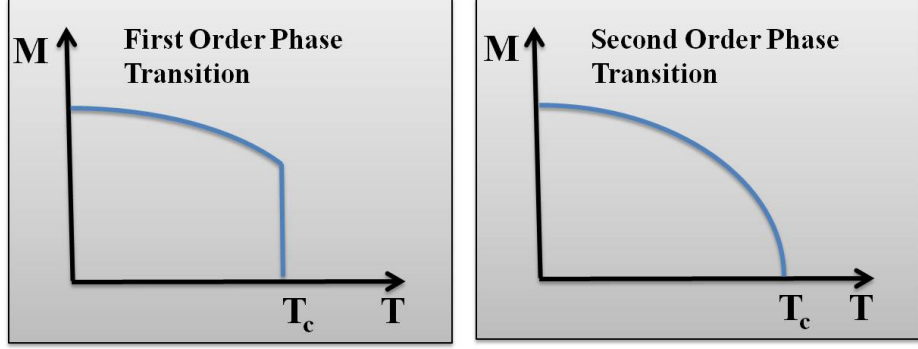


Figure 4.3. a) The discontinuous behavior of M at the critical temperature (T_c) is the base for the first order phase transition b) the continuous trend of M with T enhancement up to a critical point identifies the second order phase transition.

4.5. Magnetocaloric Potentials: ΔS and ΔT

The crystalline lattice, the conduction electrons, the atomic magnetic moments, and the atomic nucleus have contributions to the system entropy [2]. Frequently, the atomic nucleus, is neglected which led us to write down the total entropy in the following form;

$$S(T, B, P) = S_E(T, B, P) + S_M(T, B, P) + S_{LAT}(T, B, P) \quad (4.38)$$

Usually, $S_E(T, B, P)$ and $S_{LAT}(T, B, P)$ do not depend on applied external magnetic field, so they can be neglected from Equation 4.38. For both isothermal and adiabatic processes, the change in the temperature as a function of system entropy is shown in Figure 4.4. In theory, for isothermal process, the change of external magnetic field at constant pressure is defined as

$$[\Delta S_{MM}(T)]_{(T,P)} = [[\Delta S_{MM}(T)]_{B_2} - [\Delta S_{MM}(T)]_{B_1}]_{(T,P)} \quad (4.39)$$

For adiabatic process, the change of the temperature at the constant pressure is defined as

$$\Delta T_{ad}(S) = T_{ad}(S)_{(B_2)} - T_{ad}(S)_{(B_1)} \quad (4.40)$$

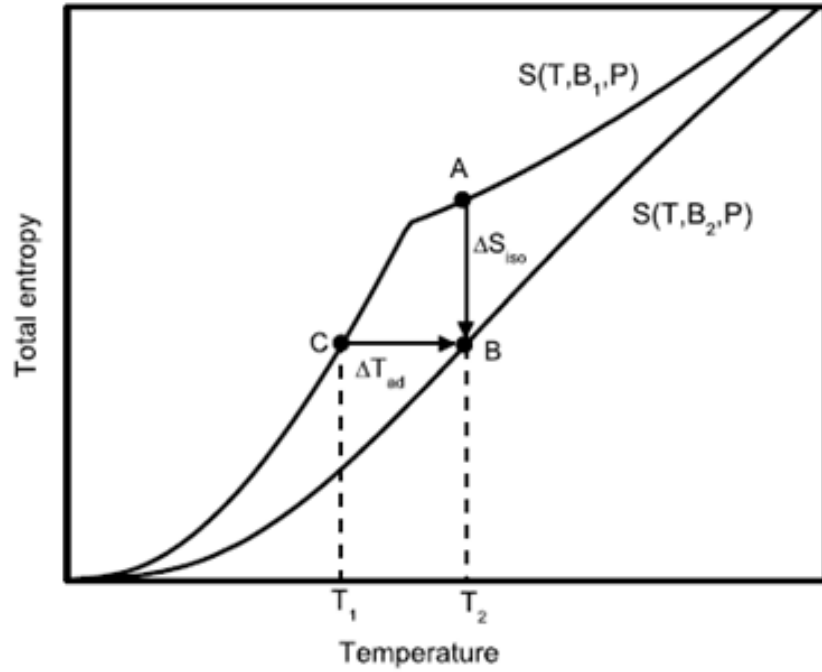


Figure 4.4. Change of temperature in an adiabatic process and change of magnetic field in an isothermal process [2].

4.6. Determination of Magnetocaloric Potentials

If the entropy is considered as a function of B (Magnetic Field) and T (Temperature), a small entropy change can be shown in terms of an increment in the temperature δT and the magnetic field δB . Thus, it can be written as follows;

$$\delta S_{MM}(T, B) = S_{MM}(T + \delta T, B + \delta B) - S_{MM}(T, B) \quad (4.41)$$

By using the mean value theorem, $\delta S_M M(B, T)$ turns into the following form;

$$\delta S_{MM}(B, T) = [(\partial S_{MM}(T_C, B))/\partial T]_B \delta T + [(\partial S_{MM}(T, B_C))/\partial B]_T \delta B \quad (4.42)$$

$$\left[\frac{\partial S_{MM}(T_C, B)}{\partial T} \right]_B = \left[\frac{\partial S_{MM}(T, B)}{\partial T} \right]_B + \left[\frac{\delta S_{MM}(T_C, B)}{\delta T} \right]_B \quad (4.43)$$

$$\left[\frac{\partial S_{MM}(T, B_C)}{\partial B} \right]_T = \left[\frac{\partial S_{MM}(T, B)}{\partial B} \right]_T + \left[\frac{\delta S_{MM}(T, B_C)}{\delta B} \right]_T \quad (4.44)$$

$\left[\frac{\delta S_{MM}(T_C, B)}{\delta B} \right]_T$ shows the difference between the exact derivatives of S_{MM} with respect to T variable at the points T_C and T as the magnetic field is kept constant. Similarly, is the difference between the exact derivatives of with respect to B_C variable at the points and B as the temperature is kept constant. In the infinitesimal limit,

$$\begin{aligned} dS_{MM}(T, B) &= \left\{ \left[\frac{\partial S_{MM}(T, B)}{\partial T} \right]_B + \left[\frac{\delta S_{MM}(T_C, B)}{\delta T} \right]_B \right\} dT + \dots \\ &\quad \dots + \left\{ \left[\frac{\partial S_{MM}(T, B)}{\partial B} \right]_T + \left[\frac{\delta S_{MM}(T, B_C)}{\delta B} \right]_T \right\} dB \quad (4.45) \\ &= \left[\frac{\partial S_{MM}(T, B)}{\partial T} \right]_B dT + \left[\frac{\partial S_{MM}(T, B)}{\partial B} \right]_T dB \end{aligned}$$

The entropy change in an isothermal process with varying magnetic field (there is no change of temperature, so $dT = 0$) is given by the following relations;

$$\begin{aligned} dS_{MM}(T, B) &= \left[\frac{\partial S_{MM}(T, B)}{\partial T} \right]_B 0 + \left[\frac{\partial S_{MM}(T, B)}{\partial B} \right]_T dB \\ \Delta(S_{MM})_{iso}(T, \Delta B) &= \int_{B_1}^{B_2} \left[\frac{\partial S_{MM}(T, B)}{\partial B} \right]_T dB \\ \Delta(S_{MM})_{iso}(T, \Delta B) &= S(T, B_2) - S(T, B_1) \end{aligned} \quad (4.46)$$

For an adiabatic process ($dQ = 0$ so $dS_{MM}(T, B) = 0$),

$$0 = \left[\frac{\partial S_{MM}(T, B)}{\partial T} \right]_B dT + \left[\frac{\partial S_{MM}(T, B)}{\partial B} \right]_T dB \quad (4.47)$$

$$\left[\frac{\partial S_{MM}(T, B)}{\partial T} \right]_B dT = - \left[\frac{\partial S_{MM}(T, B)}{\partial B} \right]_T dB \Rightarrow dT = \frac{- \left[\frac{\partial S_{MM}(T, B)}{\partial B} \right]_T}{\left[\frac{\partial S_{MM}(T, B)}{\partial T} \right]_B} dB$$

By using the relation for heat capacity ($C_X \equiv T(dS/dT)_X$ where X is P or V), the determination of temperature change in the adiabatic case can be carried out, easily.

$$\frac{C_B(T, B)}{T} = \left[\frac{\partial S_{MM}(T, B)}{\partial T} \right]_B \quad (4.48)$$

$$\Delta T_{ad}(T, \Delta B) = - \int_{B_1}^{B_2} \frac{T}{C_B(T, B)} \left[\frac{\partial S_{MM}(T, B)}{\partial B} \right]_T dB$$

At constant magnetic field, the temperature change can be expressed as follows;

$$\Delta T_{ad}(T, \Delta B) = [T(B_2) - T(B_1)] \quad (4.49)$$

The calculation of $\Delta(S_{MM})_{iso}$ for the first order phase transition, Gibbs free energy ($G(T, B)$) should be used. Accordingly, similar to the previous case, an infinitesimally small change in the entropy G can be expressed as infinitesimally small increments in both temperature δT and magnetic field δB and therefore, it can be given as follows

$$\delta G(T, B) = G(T + \delta T, B + \delta B) - G(T, B) \quad (4.50)$$

By using the mean value theorem, $\delta G(T, B)$ is

$$\delta G(T, B) = \left[\frac{\partial G(T_C, B)}{\partial T} \right]_B \delta T + \left[\frac{\partial G(T, B_C)}{\partial B} \right]_T \delta B \quad (4.51)$$

As $T \rightarrow T_C$ we can come up with a separate equation for the differentiation of the Gibbs free energy with respect to temperature at constant magnetic field. The same case is valid for the magnetic field as $B \rightarrow B_C$. Therefore, we can obtain the following

relations for them;

$$\begin{aligned}\left[\frac{\partial G(T_C, B)}{\partial T}\right]_B &= \left[\frac{\partial G(T, B)}{\partial T}\right]_B + \left[\frac{\delta G(T_C, B)}{\delta T}\right]_B \\ \left[\frac{\partial G(T, B_C)}{\partial B}\right]_T &= \left[\frac{\partial G(T, B)}{\partial B}\right]_T + \left[\frac{\delta G(T, B_C)}{\delta B}\right]_T\end{aligned}\tag{4.52}$$

$\left[\frac{\delta G(T_C, B)}{\delta T}\right]_B$ and $\left[\frac{\delta G(T, B_C)}{\delta B}\right]_T$ show the difference between the derivatives at the points T and T_C and B and B_C , respectively. In the infinitesimal limit,

$$\begin{aligned}dG(T, B) &= \left\{ \left[\frac{\partial G(T, B)}{\partial B}\right]_T + \left[\frac{\delta G(T, B_C)}{\delta B}\right]_T \right\} dB + \dots \\ &\dots + \left\{ \left[\frac{\partial G(T, B)}{\partial T}\right]_B + \left[\frac{\delta G(T_C, B)}{\delta T}\right]_B \right\} dT\end{aligned}$$

Similar to the Free Helmholtz energy, the second part of the each differential will be zero:

$$dG(T, B) = \left[\frac{\partial G(T, B)}{\partial T}\right]_B dT + \left[\frac{\partial G(T, B)}{\partial B}\right]_T dB\tag{4.53}$$

By using these thermodynamic relations and compare it with the first law of thermodynamics, we come up with basic definitions for both entropy and the magnetization as follows;

$$\begin{aligned}dG(T, B) &= \boxed{\left[\frac{\partial G(T, B)}{\partial T}\right]_B} dT + \boxed{\left[\frac{\partial G(T, B)}{\partial B}\right]_T} dB \\ &\quad \uparrow \qquad \qquad \qquad \uparrow \\ dG(T, B) &= \boxed{-S(T, B)} dT + \boxed{-M(T, B)} dB\end{aligned}$$

In this way, S(T,B) and M(T,B) can be obtained as follows;

$$S(T, B) = -\left[\frac{\partial G(T, B)}{\partial T}\right]_B \qquad M(T, B) = -\left[\frac{\partial G(T, B)}{\partial B}\right]_T$$

$G(T,B)$ is an exact differential so the following relation can be simply written;

$$\left[\frac{\partial}{\partial B} \left[\frac{\partial G(T,B)}{\partial T} \right]_B \right]_T = \left[\frac{\partial}{\partial T} \left[\frac{\partial G(T,B)}{\partial B} \right]_T \right]_B$$

$$\left[\frac{\partial S(T,B)}{\partial B} \right]_T = \left[\frac{\partial M(T,B)}{\partial T} \right]_B$$

$$\Delta S_{iso}(T, \Delta B) = \int_{B_1}^{B_2} \left[\frac{\partial S(T,B)}{\partial B} \right]_T dB = \int_{B_1}^{B_2} \left[\frac{\partial M(T,B)}{\partial T} \right]_B dB$$

By using $M \times T$ curves, the value of ΔS_{iso} can be calculated.

$$\begin{aligned} \Delta T_{ad}(T, \Delta B) &= - \int_{B_1}^{B_2} \frac{T}{C_B(T, B)} \left[\frac{\partial S(T, B)}{\partial B} \right]_T dB \\ &= - \int_{B_1}^{B_2} \frac{T}{C_B(T, B)} \left[\frac{\partial M(T, B)}{\partial T} \right]_B dB \end{aligned} \quad (4.54)$$

As a result of this relation, in an adiabatic process, the temperature variation ΔT_{ad} can be calculated. Signs of $\Delta S_{iso}(T, \Delta B)$ and $\Delta T_{ad}(T, \Delta B)$ change depending on the signs of components into the integrals. This refers to two types of MCE and these are:

4.7. Direct and Inverse Magnetocaloric Effect (MCE and IMCE)

Depending on the sign of both entropy and temperature change, MCE has a different behavior. If $\Delta S_{iso}(T, \Delta B)$ is negative and $\Delta T_{ad}(T, \Delta B)$ is positive for a positive magnetic field change, this is called direct magnetocaloric effect or if $\Delta S_{iso}(T, \Delta B)$ is positive and $\Delta T_{ad}(T, \Delta B)$ is negative for a positive magnetic field change, this is called inverse magnetocaloric effect [4].

4.8. Giant or Colossal Magnetocaloric Effect (GME)

The total magnetic entropy change ΔS_H during the isothermal magnetization process can be written in the following form;

$$\Delta S_{iso}(T, \Delta B) = \int_{B_1}^{B_2} \left[\frac{\partial M(T, B)}{\partial T} \right]_B dB \quad (4.55)$$

$$\Delta T_{ad}(T, \Delta B) = - \int_{B_1}^{B_2} \frac{T}{C_B(T, B)} \left[\frac{\partial M(T, B)}{\partial T} \right]_B dB \quad (4.56)$$

In MCE, there is a magnetic disorder-order transition and orientations of the magnetic moments turns from random to aligned one by means of the applied magnetic field. Second-order transition occurs gradually as the magnetic moments come into alignment whereas the first-order transition occurs suddenly from one state to another. As expected, this transition gives rise to a considerable alteration in the structural properties. Consequently, the heat capacity, entropy, and magnetization show a jump at the point of transition [20]. The result of this can be larger than the result of MCE, with a change in ΔS_M of up to 600 % [21]. The size of the effect is huge, so this effect is called giant or colossal magnetocaloric. where R is the gas constant and j is the total angular momentum of the magnetic ion. The upper limit of the magnetic entropy is

$$\Delta S_{iso}^{max}(T, \Delta B) = R \ln(2j + 1) \quad (4.57)$$

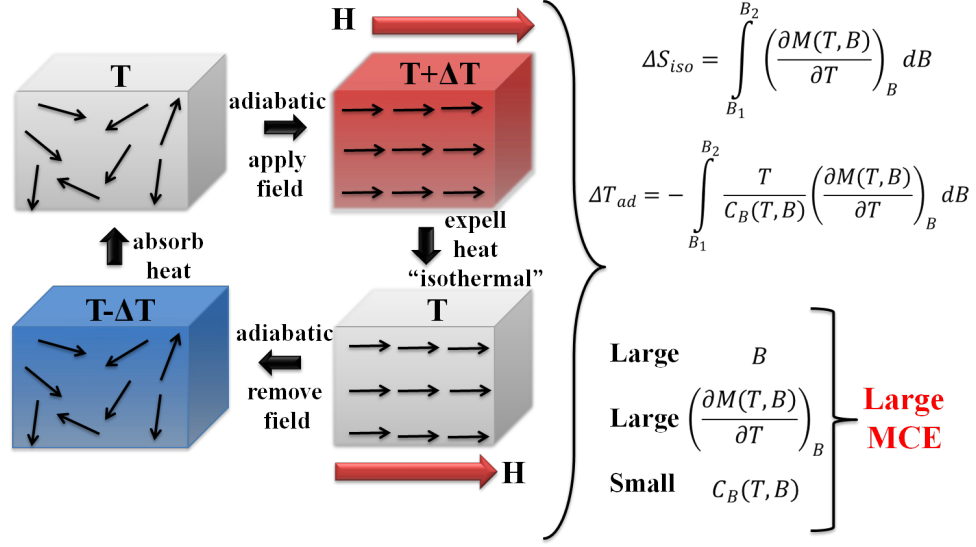


Figure 4.5. Giant Magnetocaloric Effect.

4.9. Some examples of materials which show MCE, GMCE, and IMCE

Some special kinds of Ni-Mn based Heusler Alloys with specific chemical compositions are reported as ferromagnetic materials exhibit MCE. These kinds of alloys usually transform from austenite to martensite. *Ni-Mn-Ga* is one of the most studied alloys to create this outstanding effect. As a different example, *Ni₅₀ Mn_{50-x} Sn_x* alloys show structural and magnetic phase transformations where x is ranging from 0.13 to 0.15 [22]. *Gd₅ (Si_xGe_{1-x})₄* shows Giant Magnetocaloric effect (adiabatic demagnetization via cooling effect) [23]. GMCE, firstly, was observed in *Gd₂ Si₂ Ge₂* in 1997. When an external magnetic field was applied to this material, entropy change was huge [23]. *La(Fe_{0.88}Si_{0.12})₁₃* can be given as one example of the materials which show GMCE [24].

The expected change in the lattice parameters can also result in inverse magnetocaloric effect (this is a large change in the entropy with opposite sign i.e. adiabatic magnetization via cooling effect). *Mn_{1.96} Cr_{0.05} Sb* is one of the examples which show inverse magnetocaloric effect [22]. In addition to the examples given above, *La_{0.67} Ca_{0.33} MnO₃* and *La_{0.604} Ca_{0.33} Y_{0.07} MnO₃* was studied by Zhang et al due to their

prominent magnetocaloric properties [2]. Many materials provide important contributions to be shown magnetocaloric effect in materials [15].

4.10. Applications of Magnetocaloric Effect

There are many technological application areas of magnetocaloric effect such as physical treatment of some types of cancer, magnetic refrigeration, and magnetic sensors. Cancer treatment is a method, based on nanoparticles which can be absorbed by cancerous cells. Applying magnetic field bring about an elevation in the temperature which causes to kill the cancerous cells. Interestingly, during this process, neither these nanoparticles nor heating damages the healthy cells. However, further study is required to apply this method on the human beings. In addition to treatment of cancer method, magnetic refrigeration which is an environmentally friendly technology is one of the applications of the MCE. Its magnetic compounds can be used as cooling materials. When a conventional vapor cycle refrigerator and magnetic refrigeration are compared (see Figure 4.6), the latter one can use an energy which is less than the first one can use [12].

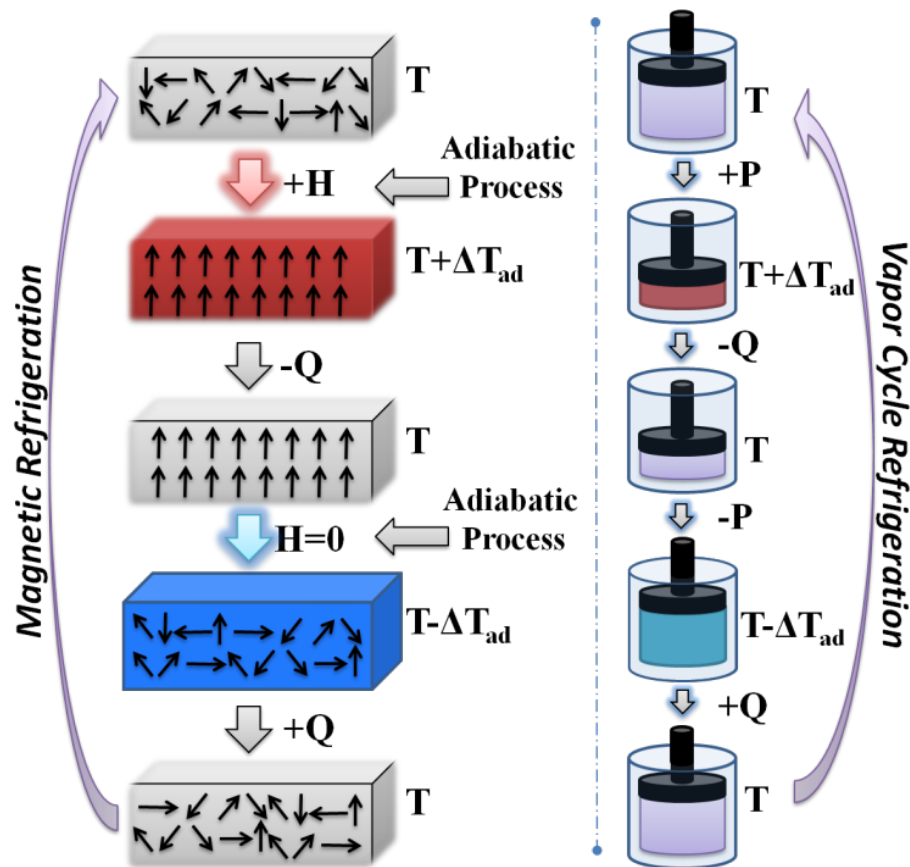


Figure 4.6. Difference between magnetic refrigeration and vapor cycle or conventional refrigeration where magnetic field (H), heat (Q); pressure (P); adiabatic temperature variation (ΔT_{ad})

5. EXPERIMENTAL SET-UP

5.1. Grain Size Measurement Method

Depending on the external conditions, the specific composition rates give rise to a granular surface. The further analysis of SEM images rests on a study about this granular structure of the sample surfaces. Moreover, the most important step is to decide the grain size of the samples. By using the SEM images, the grain size can be measured, easily. This measurement can be carried out in the following way: Via a

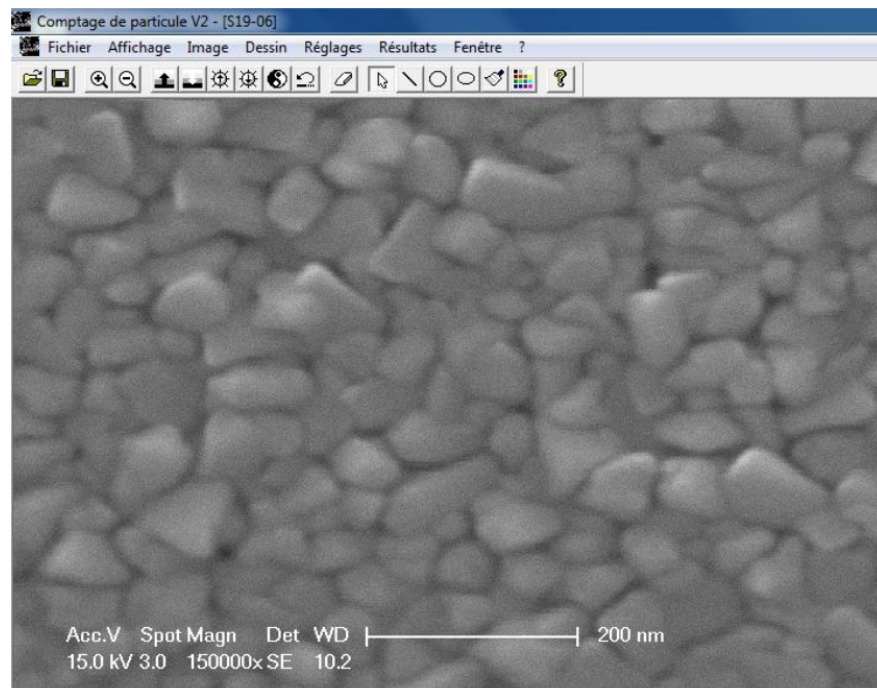


Figure 5.1. SEM image of a sample in granular structure by means of grain size calculation problem.

software program, so called Counting the Number of Particles (comptage de particule), the length of any object can be measured.

In this section, we will be making use of this program to measure the grain sizes, precisely. The first step is to determine a pixel value which is a kind of segment for

the image. It is important to note that the image needs to be in BMP format.

After saving the image, software program is recalled and Figure 5.1 is the image that initial state. From the result tab (resultat tab), the length of the segment can also be seen. Now, the first thing is to find the corresponding number of pixels to the length bar of the SEM image. The screenshot of corresponding interface is shown in Figure 5.2. In this case, the drawn segment (red solid line) equals to 728 pixels and the scale bar of the SEM image is 200 nm, so one pixel is $200/728$ nm. Thus, we have determined the size of a pixel for the SEM image. Yet, this measurement is repeated at least 5 times to decrease the error in the calculations. As a next step, we can proceed

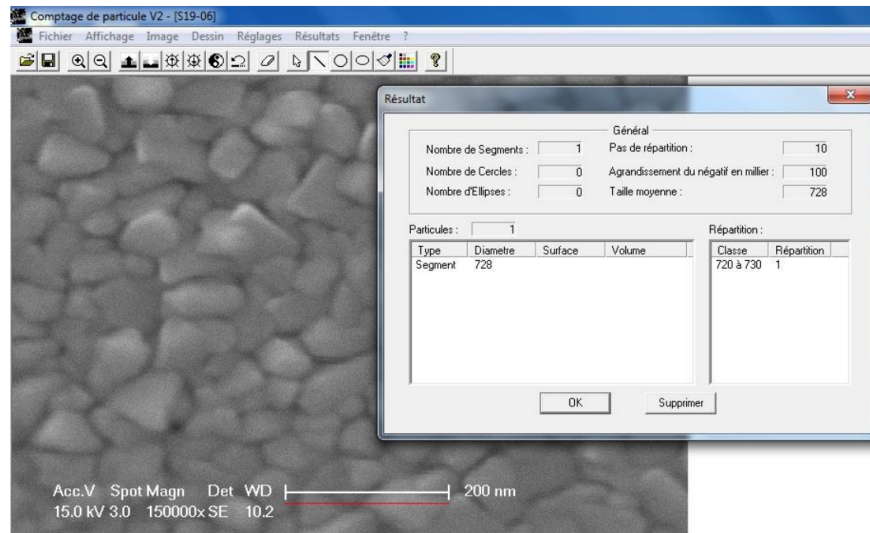


Figure 5.2. Fitting the segment (red solid line) to the scale bar of the SEM image (gray solid line) to find the length of each pixel.

to the grain size measurement. As it can be seen from Figure 5.1, grains are typically in the circle-like shape. However, they are not equal to each other, so we chose more than 50 to 150 grains to obtain an average value for the grain size of the each SEM image in order to prevent a significant error in the analysis. Another important thing is to measure each grain twice by drawing a cross on the image which is shown in Figure 5.3. A standard deviation from the average value is also calculated for each grain. Since the measured distance is the diameter of the grains, we can also calculate the radius of the grains and the volume of the grains (by regarding them in a spherical

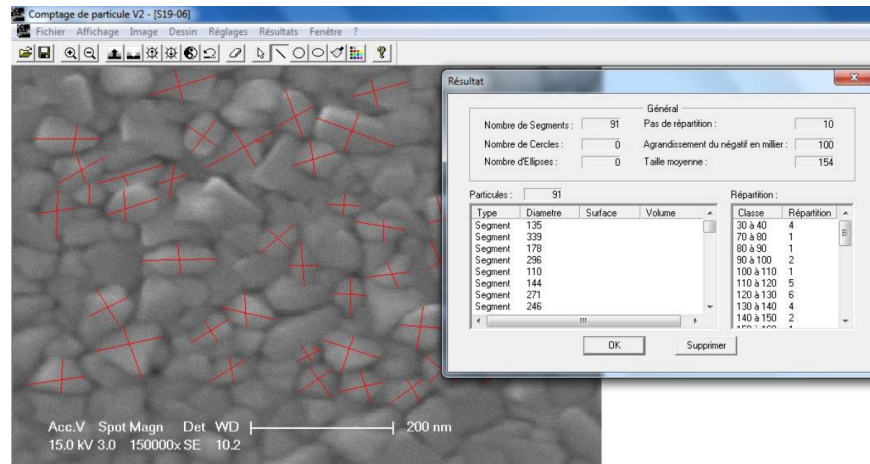


Figure 5.3. The red solid lines on each grain are drawn to determine an average grain size. The interface is showing the corresponding number of pixels to the segments.

shape), as well. All in all, a precise measurement with a negligible error is achieved.

5.2. EDS Analysis

EDS and SEM analysis were done by using the Philips XL30 ESEM-FEG/EDAX system at Boğaziçi University Advanced Technologies R&D Center, Electron Microscopy and Microanalysis Unit. Well adjustment of the X-Ray beam energy is required to avoid



Figure 5.4. ESEM device.

from burning of the thin film surfaces. In our case, 15 keV was the default value for EDS analysis. Although some burns on the samples with small spot size are expected during the e-beam bombardment, they do not affect the other analysis such as XRD, SEM, SQUID etc., considerably. EDS analysis is a fitting method of the theoretical peak positions to the experimental peaks. These theoretical peak positions are also matched with the elements. Therefore, the elements and/or molecules, which are deposited on the substrate, are chosen by the user from ‘the lists of possible elements’ corresponding to each peak to form the right configuration for alloy. There is an example of EDS spectrum below to have a better understanding of the situation.

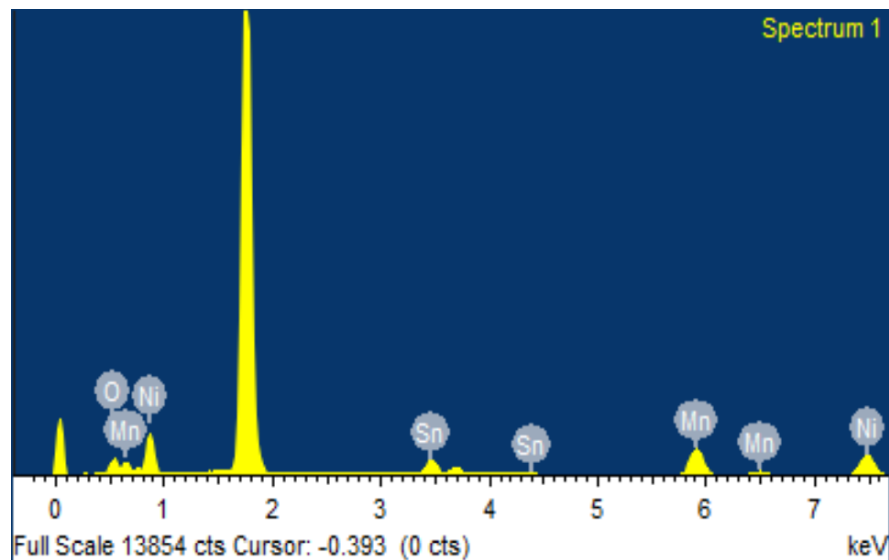


Figure 5.5. EDS spectrum plot of NiMnSn (in order to see the oxidization level, Oxygen peak is also labeled).

In our case, the chemical compositions of thin films are $NiMnSn$ and $NiMnIn$, so EDS results should include the peaks corresponding to Ni, Mn, Sn, and In elements. However, in addition to these elements, Silicon (Si) and Oxygen (O) are among the other two elements which have strong peaks in X-ray energy spectrum plot. The substrate preference is Silicon wafer and the existence of ferromagnetic materials gives rise to the oxidization are the reasons in behind of having the peaks of Si and O, respectively. Since O and Si are not included in our alloy, their peaks are subtracted

from the X-ray spectrum.

As it can be seen from Figure 5.5, peaks are named by following the aforesaid rule. The greatest peak is possessed by Si. However, since it is not among the alloy elements, the peak is not taken into account. Therefore, disregarding the existence of Silicon but considering Oxygen existence, O peaks are named during the EDS analysis in order to see the oxidization level. The table below shows the atomic and weight percentages in fabricated *NiMnSn* alloy.

Table 5.1. Atomic and Weight percentages of each element in NiMnSn.

<i>Element</i>	<i>Weight%</i>	<i>Atomic%</i>
O	16.27	43.46
Mn	27.99	21.78
Ni	39.94	29.08
Sn	15.79	5.69

It is important to note that results may vary from a chosen region to another. Therefore, to decrease the error, we chose from 10 to 15 different regions and took the average of these Figure 5.5 EDS spectrum plot of *NiMnSn* (in order to see the oxidization level, Oxygen peak is also labeled) values. Before presenting the EDS result of an individual thin film alloy, EDS results of two *NiMnSn* ternary targets are shown from Table 5.2.

Table 5.2. Comparison of two NiMnSn targets.

<i>Target</i>	<i>Ni</i>	<i>Mn</i>	<i>Sn</i>
1. Target	51.05 ± 0.35	36.20 ± 0.26	12.76 ± 0.18
2. Target	50.81 ± 0.40	36.16 ± 0.32	13.04 ± 0.32

Table 5.2 shows the differences between two targets by comparing the quantity of each element in the alloy. When the deviations are taken into account, it can be said that the differences are not significant. Table 5.3 shows the composition rates for each element in the alloy. We have chosen 15 different regions on the substrate and calculated the composition rate of each element, for chosen regions. By using these data, calculation of average composition rate was carried out. This leads to prevent from having a considerable error.

Table 5.3. An example to the calculation of average composition rate is carried out by choosing 15 different regions on the substrate (ACC: Atomic Chemical Composition).

<i>Elements/#of Reg.</i>	Ni	Mn	Sn
1.	50.19	39.64	10.16
2.	50.48	39.41	10.11
3.	49.90	39.86	10.24
4.	50.33	39.65	10.02
5.	49.67	40.27	10.06
6.	49.85	40.16	9.99
7.	49.91	40.04	10.05
8.	49.83	40.12	10.04
9.	50.08	39.87	10.05
10.	49.93	40.27	9.80
11.	49.79	40.15	10.07
12.	50.95	39.27	9.78
13.	50.68	39.57	9.75
14.	50.10	39.89	10.00
15.	49.49	40.25	10.26
ACC (at%)	50.08 ± 0.39	39.89 ± 0.32	10.03 ± 0.15

5.3. Sputtering

$NiMnX$ (Sn, In) thin films were fabricated at Center of Life Sciences and Technologies Boğaziçi University by using Vaksis (Angora series) Sputter System. Sputtering machine can be seen from the Figure 5.6.



Figure 5.6. Vaksis Sputtering machine.

Thanks to a Lab-VIEW(short for Laboratory Virtual Instrument Engineering Workbench) program, all changes and settings related to sputtering machine such as chamber and substrate temperature, pressure, gas flow inside the chamber, vacuuming the chamber etc. are automatically controlled. Before mentioning about the coating process, Lab-VIEW interface of sputtering machine is introduced for the purpose of stating the significant adjustments together with the vital steps which needs to be followed before and during the deposition. Figure 5.7 is the Lab-VIEW interface.

- Black circled numbers indicate the particular units of sputtering machine. The

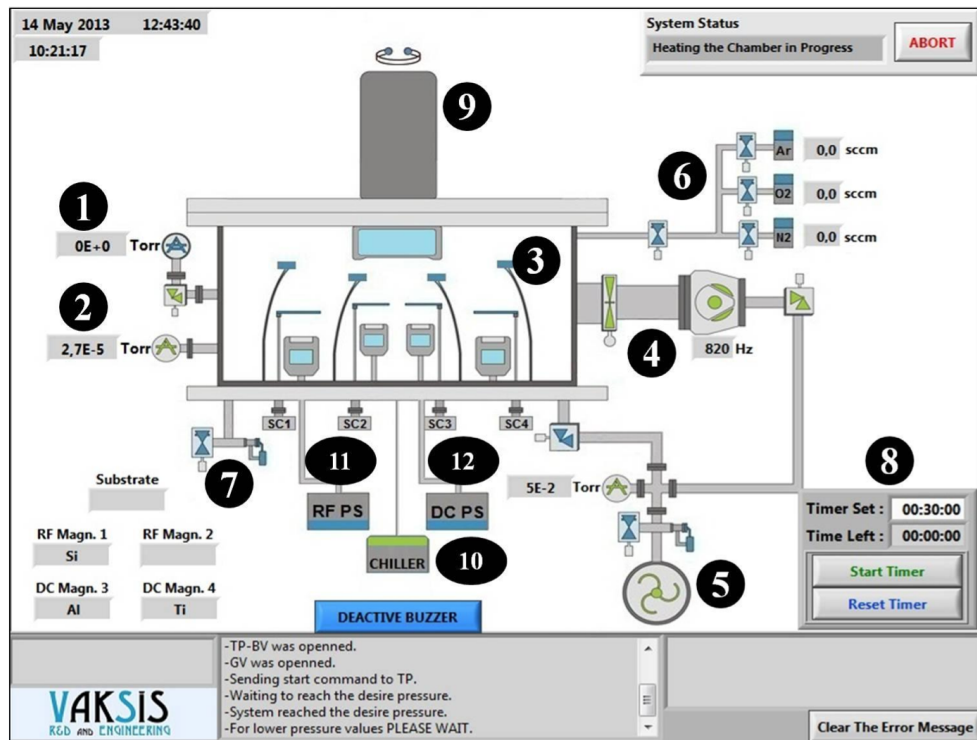


Figure 5.7. Lab-VIEW interface of the VAKSIS Sputter.

first two units (Units 1 and 2) are the pressure indicators. However, second unit measures the pressure more precisely than the first unit.

- The inner part of the chamber is Unit 3 which is highlighted at the Lab-VIEW screenshot. This unit includes two RF and two DC magnetrons together with their shutters.
- The fourth and fifth units are pumping sections of the device together with their valves. Turbo pump and its block valve (Unit 4) enable to regulate the pressure especially inside the chamber and the branches connected to the chamber.
- Scroll pump and its block valve are the Unit 5. This pumping engine has the same mission with the turbo pumping which has different strength. However, Scroll pump decreases the pressure up to a certain level. As soon as the scroll pump reduces the pressure, the turbo pump is activated to decrease the pressure more.
- Conventionally, gas can also be injected to the chamber via gas (it can be Ar, N_2 , or O_2) flow unit (Unit 6). On the other hand, the gas injection is another

way of controlling the pressure inside the chamber.

- Unit 7, vacuum breaking valve, is the key element in the opening procedure. When it is opened, the inner pressure of the chamber reaches to the atmosphere pressure.
- The duration of coating is determined by using the timer set (Unit 8). Thus, the remaining time can be followed, easily.
- The top of the chamber together with a rotator engine is the section of unit 9. The rotator enables more uniform coating on the substrate. The rotation speed can be adjusted via Lab View program. Top of the chamber is automatically opened / closed.
- The chiller, which is responsible for the distribution of water flow, Unit 10, supplies the water to substrate, magnetrons, chamber etc.
- Units 11 and 12 are the power suppliers of RF and DC magnetrons, respectively.

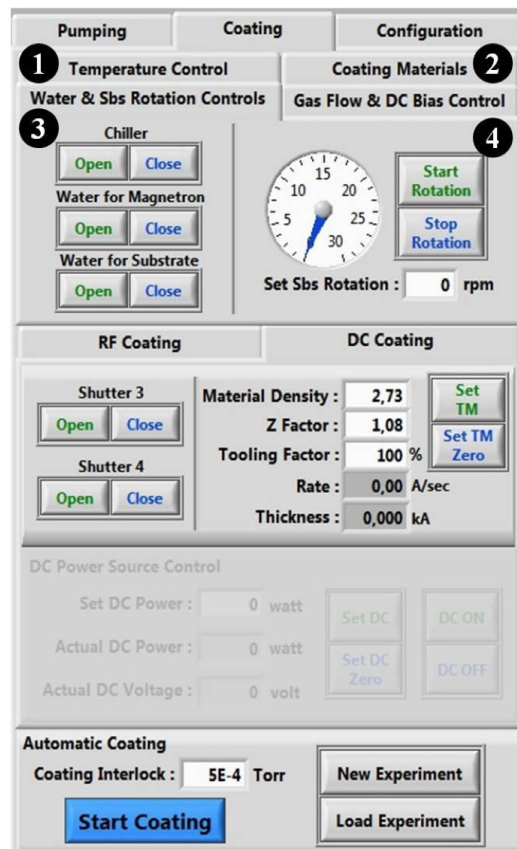


Figure 5.8. Water and substrate rotation control panel of the Lab-VIEW interface.

One of the important parts of this Lab-VIEW interface is Control panel and it can be seen from Figure 5.8 which is shown above.

Control panel has 3 important tabs. These tabs are pumping, coating, and configuration. Coating part consists of 4 significant sections: Temperature control (i), coating materials (ii), water and substrate rotation control (iii), and gas and DC bias control (iv). Figure 5.8 shows the water and substrate rotation control panel. During all coating processes, chiller, water for both magnetron, and substrate should be opened not to cause any overheating of the sputter machine. As it is stated above, rotation of the substrate is crucial to get a homogeneous and uniform film. Rotation speed can be varied from 0 to 30 rpm (rotation per minute).

Pumping		Coating		Configuration	
Water & Sbs Rotation Controls		Gas Flow & DC Bias Control			
Temperature Control		Coating Materials			
Set Substrate Temperature :	0 °C	Set Sbs Temp.	Set Temp. Zero		
Substrate Temperature :	36 °C				
Set Chamber Temperature :	50 °C	Set Ch. Temp.	Set Temp. Zero		
Chamber Temperature :	28 °C				
Target Ch. Temperature :	50 °C	Heating			
Heating Time :	60 min				

Figure 5.9. Temperature control panel of the Lab-VIEW interface.

Figure 5.10 shows the temperature control panel. By using this part, both substrate and chamber temperatures together with their heating time can be adjusted and checked/controlled from the same interface. Available substrate temperature values range from 0 to 500°C. Figure 5.11 is the screenshot of the Coating materials panel. Both target and substrate (Sbs.) names are written in the blanks on right side of the panel. For example, if *NiMnIn* target and silicon wafer are used and target is placed on DC magnetron, *NiMnIn* is written in the third or fourth blank and Si is written in the fifth/Sbs. blank.

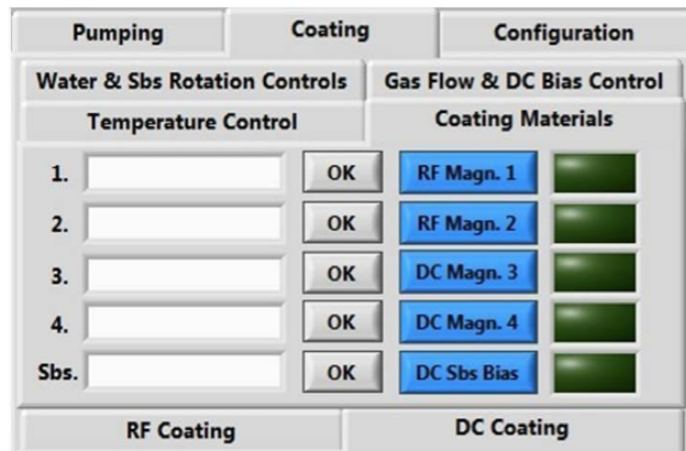


Figure 5.10. Coating material panel of the Lab-VIEW interface.

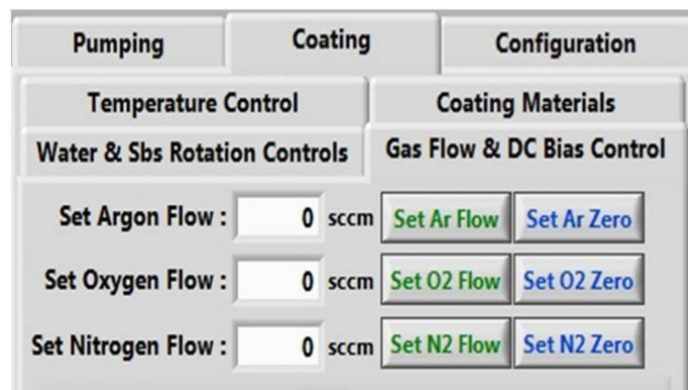


Figure 5.11. Gas Flow and DC Bias Control segment of Lab-VIEW interface.

Gas Flow and DC Bias Control interfaces (Figure 5.11) set gas flow through the chamber and the other branches. In our experiment, Argon (Ar) is used and its value is 50 sccm (Standard Cubic centimeters per minute). By the time the deposition process ends, the Set Ar Zero (blue) button should be checked to cease the gas flow from the interface.

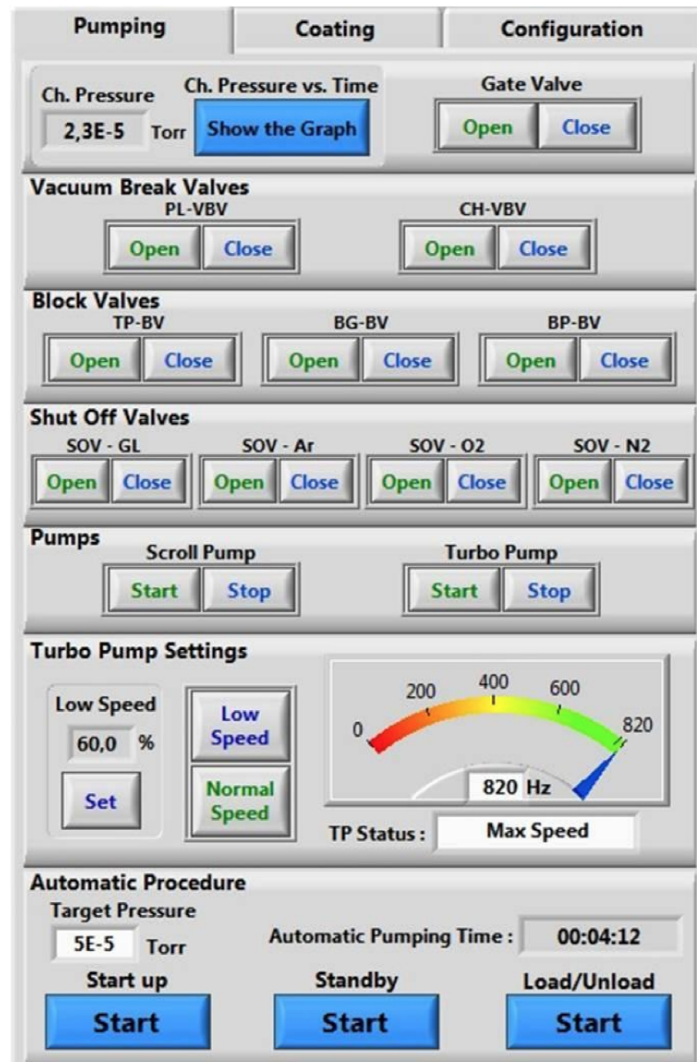
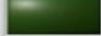
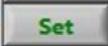


Figure 5.12. The Lab-VIEW interface which automates both pumps and valves conditions.

Pumping tab of the Lab-VIEW interface makes easy for the adjustments about pumps and their valves. The details of this tab can be seen from Figure 5.12. Vacuum break valves, block valves, shut off valves can be opened / closed from this tab. Similar to valves, turbo and scroll pumps can also be started / stopped from the pumping tab. In addition to this, setting the speed of turbo pump can also be carried out with this interface.

Pumping	Coating	Configuration
Vkss_Cnt_1 I%COM11	Vkss_Cnt_2 I%COM12	Thickness Sensor 1 I%COM59
Vkss_Cnt_3 I%COM13	Turbo_Pump I%COM14	Thickness Sensor 2 I%COM9
Pid I%COM15	RF Generator I%COM16	Thickness Sensor 3 I%COM32
Servo I%COM17	Servo 2 I%COM18	Thickness Sensor 4 I%COM33

Pressure Control Gate Valve		
Actual Position :	0 %	Pressure Control Active 
Set Position :	0 %	
Set Pressure :	0 mTorr	
		 

Thickness Monitors Properties		
Thickness Monitor 1:	Crystal Status	Crystal Life Time 0
Thickness Monitor 2:	Crystal Status	Crystal Life Time 0
Thickness Monitor 3:	Crystal Status	Crystal Life Time 0
Thickness Monitor 4:	Crystal Status	Crystal Life Time 0

Figure 5.13. Configuration part of the Lab-VIEW interface.

Figure 5.13 shows a screenshot of configuration tab which has three subsections. The pressure value can be changed from the control mechanism of gate valve subsection. For example, second pressure indicator should typically show 3×10^{-2} Torr for all experiments. Yet, in order to reach this pressure level, *set position* needs to be set as 82%-83%. The other subsections are left by default conditions.

Up to now, we have given a brief introduction on EDS and SEM analysis, PVD systems, Lab-VIEW interface of the sputter machine etc. In our experiment, we have used sputtering and co-sputtering technique and from now on, some important points during the deposition will be mentioned, clearly.

During the cleaning procedure, wearing gloves is compulsory. The chamber ring is vulnerable to the dust and it needs to be cleaned by using isopropanol and methanol. This also eradicates the oil or other liquids from the surface of the ring. Another crucial thing is to be careful while placing the substrate. Silicon wafer has a delicate surface so while placing it, we need to use tweezers.

One of the important segments of sputtering machine is Vacuum Breaking Valve (VBV). In order to break the vacuum inside the chamber, this valve needs to be opened, initially. However, another vital point is the screws which hold the top of chamber, tightly. Therefore, while the air flow is allowed inside the chamber, the chamber pressure increases and reaches to air pressure. If the screws are still tight, there will be a big problem with opening the chamber. These screws should be opened before the air is allowed to get inside. Then, samples and substrate are placed in sputter, chamber is closed, and screws are tightened.

Pressure value is also another notable point. During the deposition of a magnetic thin film, the pressure should be less than 4×10^{-7} Torr. To decrease the pressure up to this value, two pumping systems are employed in VAKSIS sputter machine. While the first one is called as turbo pump, the second one is scroll pump. The turbo pumping is stronger than scroll pumping, so initially the scroll pumping is turned on to decrease the pressure up to 10^{-5} Torr. Right after both pressure inside the chamber and other segments of the device see 10^{-5} Torr value, turbo pumping starts to pump up the system to reach an available pressure value for the magnetic deposition.

In order to refrain from any humidity or other remaining contaminations, the chamber can be heated up to 70°C when the chamber pressure reaches around 5×10^{-5} Torr. The duration of this heating process is 120 min. After the heating procedure,

the chamber is left to cool down back to room temperature ($T_{room}=300K$ or $24^{\circ}C$).



Figure 5.14. Blue and purple plasma which are created NiMnX (Sn, In) ternary target and pure Mn target.

The RF magnetron has a segment, so called rump timer, which gives a rising/falling time while the power is on/off. Having a smoothed type of power prevents the target from being fractured due to the abrupt turning on/off the power. For the power application on the RF magnetron case of our experiment, the rump (up/down) time is set to 10 seconds. This means that it rises up to the peak value in 10 seconds and for another 10 seconds, it will goes from the peak value to zero. This situation continues until the coating finishes. In order to fabricate a uniform film, substrate rotation is used and its value is chosen as 20 rpm. Coating duration (45 min.) is written in timer set and coating is started. When the coating finishes, the following processes should be applied, sequentially:

- Set temperature zero, thus both substrate and chamber will cool down back to the room temperature.

- Close gas flow (Ar gas).
- All the other steps except from the first two points are straightforward and automatic closing procedure.

When the substrate reaches a temperature less than 30°C , coated sample can be removed from the chamber.

6. SEM and EDS ANALYSIS of Ni-Mn-X (In and Sn) THIN FILM ALLOYS

The goal of this thesis is to study the relationships between structural, microstructural, and macroscopic magnetic properties in NiMnX (Sn, In) thin films alloys obtained by co-sputtering deposition technique.

Our study will focus on the magnetic and structural properties of thin films with composition $Ni_{50}Mn_{37}In_{13}$ and $Ni_{50}Mn_{37}Sn_{13}$. The origin of our interest in this particular composition lies on structural transformation from the martensitic and austenitic phase and vice versa.

Thin film fabrication procedure can be divided into the following stages; (i) $NiMnSn$ target was evaporated at different temperatures in order to study the grain size temperature dependence. During the thin film fabrication process, we encounter several difficulties. One of them is the deviation from the expected growth rate due to the manganese vapor pressure. Because of this problem, the first goal was to prepare samples which have the same or the nearest chemical composition to the decided one. (ii) In order to compensate manganese losses during evaporation and to obtain the desired nominal composition, a Mn target, placed on RF magnetron, was co-sputtered together with the $Ni_{50}Mn_{37}Sn_{13}$ or $Ni_{50}Mn_{37}In_{13}$ target, placed on DC magnetron. Here, 100 W DC power value was kept constant throughout the experimental process while RF power value was changed from 0 to 60 W. (iii) The substrate temperature was changed from room temperature (RT) to 500 °C in steps of 100 °C to study possible variations in grain sizes and find a relationship between grain size and austenitic/martensitic phase transformation.

In addition to $NiMnSn$ thin film series based study, $NiMnIn$ series were deposited on silicon wafers. However, unlike the fabrication process of $NiMnSn$ thin film series, which was comprised of three separate series (temperature dependent sput-

ter, power dependent co-sputter, and temperature dependent co-sputter series), only two different *NiMnIn* series (power dependent co-sputter and temperature dependent co-sputter series) were deposited. The primary step for the *NiMnIn* thin films was eliminated because it was expected that Mn composition rates in both *NiMnSn* and *NiMnIn* thin film alloys will have similar behaviors. According to EDS results of the first *NiMnSn* series, Mn assisted sputtering is required in order to reach the decided composition. In this sense, the remaining two fabrication steps were repeated for *NiMnIn* series.

It is worth stating that the first series of *NiMnSn* provided us to have a better understanding about structural point of view such as the loss of Mn because of the high vapor pressure, the possibility of having a correlation between substrate temperature and the loss of Mn, the increase of the grain size with rising substrate temperature etc. In consequences of these reasons, the second and third steps were carried out.

We delve into the structural analysis by doing two independent studies; (i) Energy-Dispersive X-Ray Spectroscopy (EDS) analysis was performed to determine the chemical composition of the fabricated thin film. A comparison with the nominal composition values can provide information of each element losses. (ii) Scanning Electron Microscopy (SEM) analysis provided information of the homogeneity of thin film surfaces and the grain size.

NiMnIn thin films were fabricated at Center of Life Sciences and Technologies Boğaziçi University by using Vaksis (Angora series) Sputter System. EDS and SEM analysis were done by using the Philips XL30 ESEM-FEG/EDAX system at Boğaziçi University Advanced Technologies R&D Center, Electron Microscopy and Microanalysis Unit. Thicknesses of thin films are measured by using Bruker Dektak XT Profilometer at Center of Life Sciences and Technologies Boğaziçi University.

6.1. Structural Analysis

Following the fabrication process, a structural analysis was performed to determine the deposition rates, the effects of external conditions (temperature, pressure etc.) on the fabricated samples, and the compositional homogeneity of the alloys.

The chemical composition of thin film alloys was controlled through the RF power value during co-sputter deposition in case the composition rates may change due to some factors such as vapor pressure of components and low RF power value during co-sputter (less than 50 Watts) etc. Their compositions were confirmed by EDS analysis, revealing whether there is any loss of components in thin film alloys or not. EDS analysis was performed in, at least, 15 different locations of the each thin film.

SEM results of $NiMnX$ (Sn, In) show the homogeneity of thin film surfaces and granular structures revealing a direct relation between substrate temperature and grain size.

6.2. Ni-Mn-Sn Thin Films

This section is devoted to give detailed information about the fabrication process and the structural analysis of the $NiMnSn$ alloys. Furthermore, the fabrication processes of the magnetic thin films are stated below.

6.2.1. Structural Properties of Thin Films Fabricated by NiMnSn target

- Only one target ($Ni-Mn-Sn$) was used during this process.
- The Substrate temperature was changed from RT to $500^{\circ}C$ (RT , 200 , 300, 400, and $500^{\circ}C$).
- The power value, which was applied on $Ni-Mn-Sn$ target, was kept constant at 100W.

The first fabricated series of the $NiMnSn$ based magnetic thin films were analyzed by using EDS technique to determine its compositions' rates and compare with the decided composition.

Table 6.1. Deposition conditions.

Name	Condition
Substrate	$Si\langle 100 \rangle$ type P
Chamber pressure before preheating	5×10^{-6} Torr
Chamber pre-heating temperature	$70^\circ C$
Chamber pre-heating duration	30 min
Chamber pressure after pre-heated	2×10^{-7} Torr
Chamber temperature after pre-heated	$25^\circ C$
Substrate pre-heating temperature	$200^\circ C$
Substrate pre-heating duration	30 min
Substrate temperature while coating	$RT - 200 - 300 - 400 - 500^\circ C$
Target Clean power	$100W - DC$
Target Clean duration	2 min
Chamber Coating Start Pressure	5×10^{-6} Torr
Coating power	100 W for $Ni_{50}Mn_{37}Sn_{13}$ target
Chamber Coating Pressure	3×10^{-2} Torr
Coating inert gas	Argon – 50 scc/m
Coating Duration	45 min
Rotation speed	20 rpm
Target-substrate distance	5cm

EDS results can be shown as a percentage of either the weight of each element (wt (%)) or the number of atoms of each element in the composition (at %). From now on, experimental data will be shown in (at %). As shown in both Table 6.2 and Figure 6.1, the chemical composition of the $NiMnSn$ based thin films is independent of the substrate temperature.

Table 6.2. Average chemical composition percentages (at %) of elements (Ni, Mn, and Sn) for each substrate temperature.

Substrate Temperature (°C)	Ni %	Mn %	Sn %
RT	60.43 ± 0.34	26.93 ± 0.37	12.64 ± 0.28
200	60.66 ± 0.32	27.09 ± 0.24	12.25 ± 0.17
300	62.15 ± 0.61	26.57 ± 0.45	11.93 ± 0.38
400	61.50 ± 0.53	27.09 ± 0.24	12.25 ± 0.17
500	61.55 ± 0.46	26.40 ± 0.55	12.05 ± 0.31
Decided Composition	50	37	13

The deviations from the average values are ranging from $\pm 0.17\%$ to $\pm 0.61\%$ which implies a relatively uniform thin film deposited on the Si substrate.

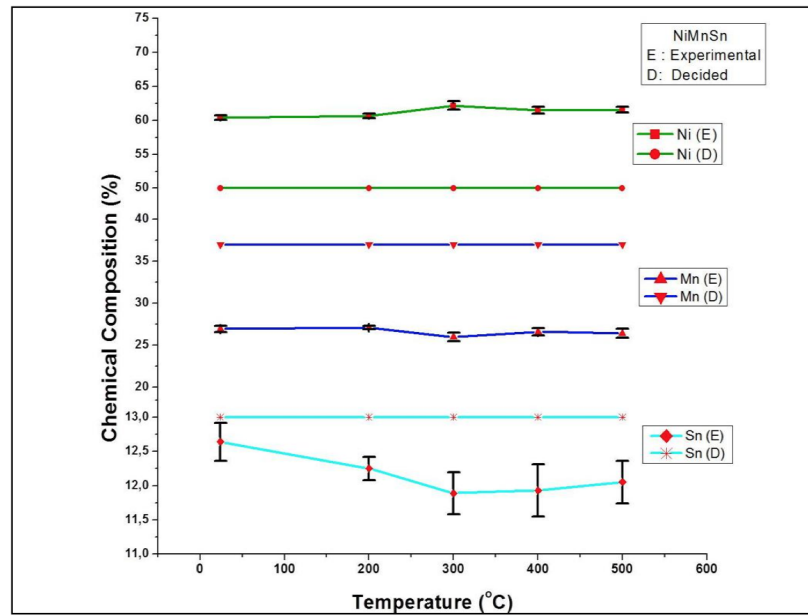


Figure 6.1. The difference between nominal (or decided) and experimental chemical composition (%) of each element is plotted versus the substrate temperature.

The cross section of the thin film fabricated with a substrate temperature of 400°C is shown in Figure 6.2. The thickness of the thin film was roughly estimated using the cross sectional SEM image providing a value of about 164 nm.

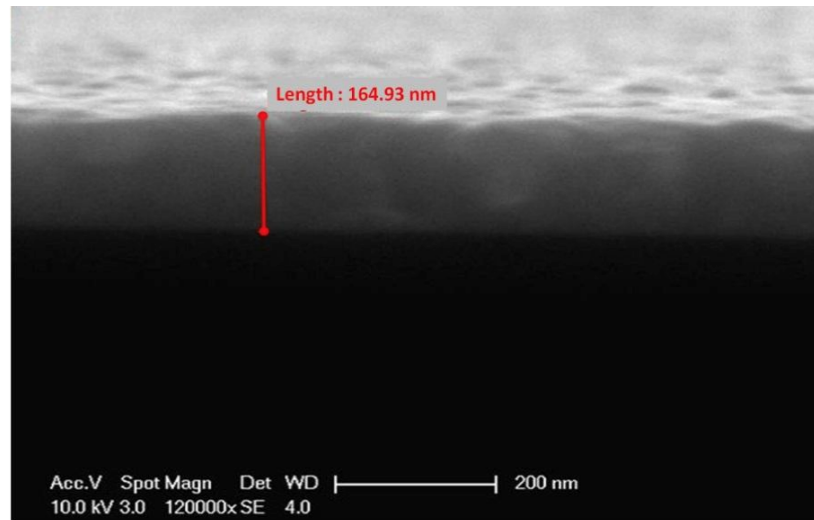


Figure 6.2. Cross section of the thin film at 400°C.

SEM images at Figure 6.3 show an increase of the grain size when the thin films are fabricated at different substrate temperatures. While Figure 6.3 shows the SEM images for different temperature values, Table 6.3 and Figure 6.4 indicate the qualitative analysis of the grain size.

Each grain was assumed as a sphere with a given diameter (average of the edge to edge distance) to estimate their dimensions. Between 50 and 150 different grains were measured for each temperature value. A nonlinear increase in the grain size with increasing temperatures is observed via a detailed analysis of SEM images.

Table 6.3. Average grain size of the thin films at different substrate temperatures.

Substrate Temperature (°C)	Grain Diameter (nm)
RT	37.11 ± 1.05
200	45.27 ± 0.47
300	55.84 ± 1.96
400	101.80 ± 1.40
500	116.36 ± 1.76

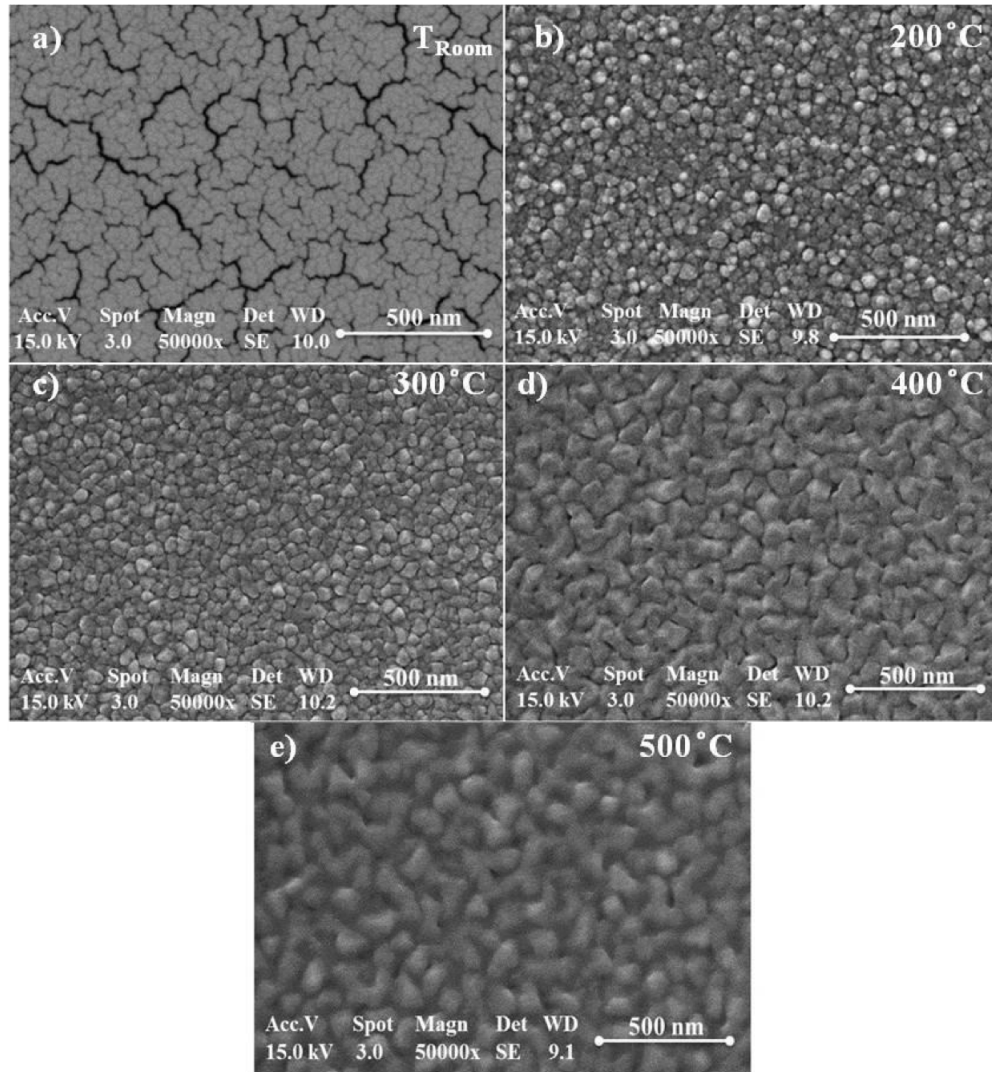


Figure 6.3. SEM images with the same magnification rates at different substrate temperature.

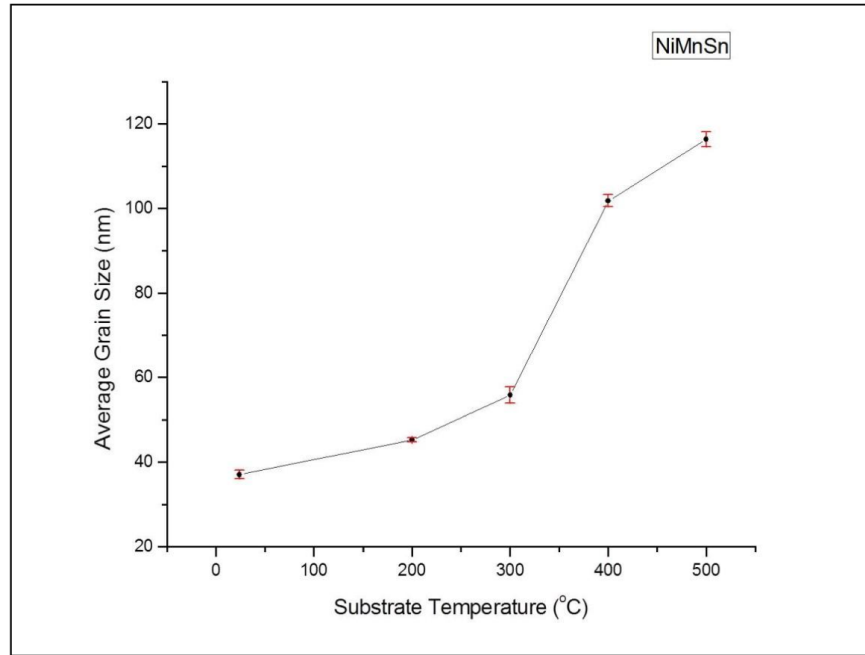


Figure 6.4. The relation between grain size and substrate temperature.

6.2.2. RF Power Dependent Structural Properties of Thin Films Fabricated by co-sputtered NiMnSn and Mn target

- A ternary (*Ni-Mn-Sn*) and a pure (Mn) target were used during this process.
- Since any other variations were excluded to study the power dependence of the chemical composition, the substrate temperature was kept constant at 400°C.
- While the power applied on *Ni-Mn-Sn* target was 100 Watts and it was constant during the experiment, power applied on Mn target was changed from 0 to 60 Watts.

Despite the fact that all of the thin films almost have the same deposition conditions, some of the key parameters will be the variables of the system, such as substrate temperature and power applied on RF magnetron. Furthermore, from now on, only the variable parameters will be shown in the table to define the deposition conditions.

Table 6.4. Deposition Conditions.

Substrate Heating Temperature	400°C
Coating power	100 W for $Ni_{50}Mn_{37}Sn_{13}$ target 0, 10, 20, 30, and 60 W for pure Mn target

The composition rates of fabricated $NiMnSn$ thin film alloys, obtained by means of EDS, and their corresponding RF power values are given in Table 6.4 and Figure 6.5 .

Table 6.5. Average chemical composition percentages (at %) of elements (Ni, Mn, and Sn) for each power applied on RF magnetron.

RF Power Value (W)	Ni %	Mn %	Sn %
0	61.56 ± 0.43	26.15 ± 0.44	12.29 ± 0.15
10	61.66 ± 0.83	26.26 ± 0.81	12.08 ± 0.35
20	60.56 ± 0.44	27.65 ± 0.34	11.79 ± 0.26
30	54.57 ± 0.61	30.48 ± 0.57	14.95 ± 0.37
60	$50, 08 \pm 0, 39$	$39, 89 \pm 0, 32$	$10, 03 \pm 0, 15$
Decided Composition	50	37	13

Figure 6.5 below shows the dependence of the composition rates of each element on applied RF power of Mn target. According to the analysis results, the experimental composition rates became closer to the decided composition rates by depending on the increasing applied power on RF magnetron.

However, the experimental composition rate for various power values (less than 50 W) is not showing a good agreement with the corresponding decided composition rates. It is demonstrated that for higher power values (up to 60 W), the experimental results approaches to the decided results. This significant result affected the other fabrication series and led us to focus in the vicinity of 60 W rather than the values far away from the 60 W.

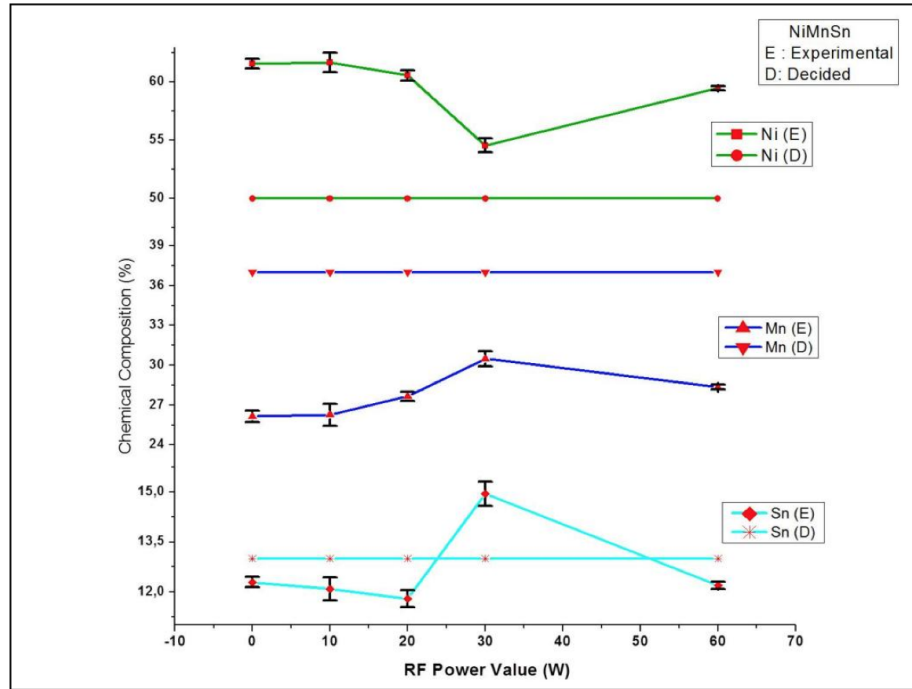


Figure 6.5. The difference between nominal (or decided) and experimental chemical composition (at %) of each element with changing RF power values of the Manganese target.

Figure 6.6 is divided into five individual parts and each part shows the different alloy at the same temperature but different power values. Figure 6.6a is corresponding to an alloy, where no Mn was sputtered. The chemical composition of this alloy is far away from the decided one.

The fabrication of *NiMnSn* thin films in the presence of different applied power values on the RF magnetron was carried out for the purpose of observing whether any effect of the power application on the structural properties of the alloys exists or not. Therefore, we have chosen 10, 20, 30, and 60 Watts values whose corresponding SEM images are shown in the Figure 6.6a, Figure 6.6b, Figure 6.6 c, and Figure 6.6d, respectively.

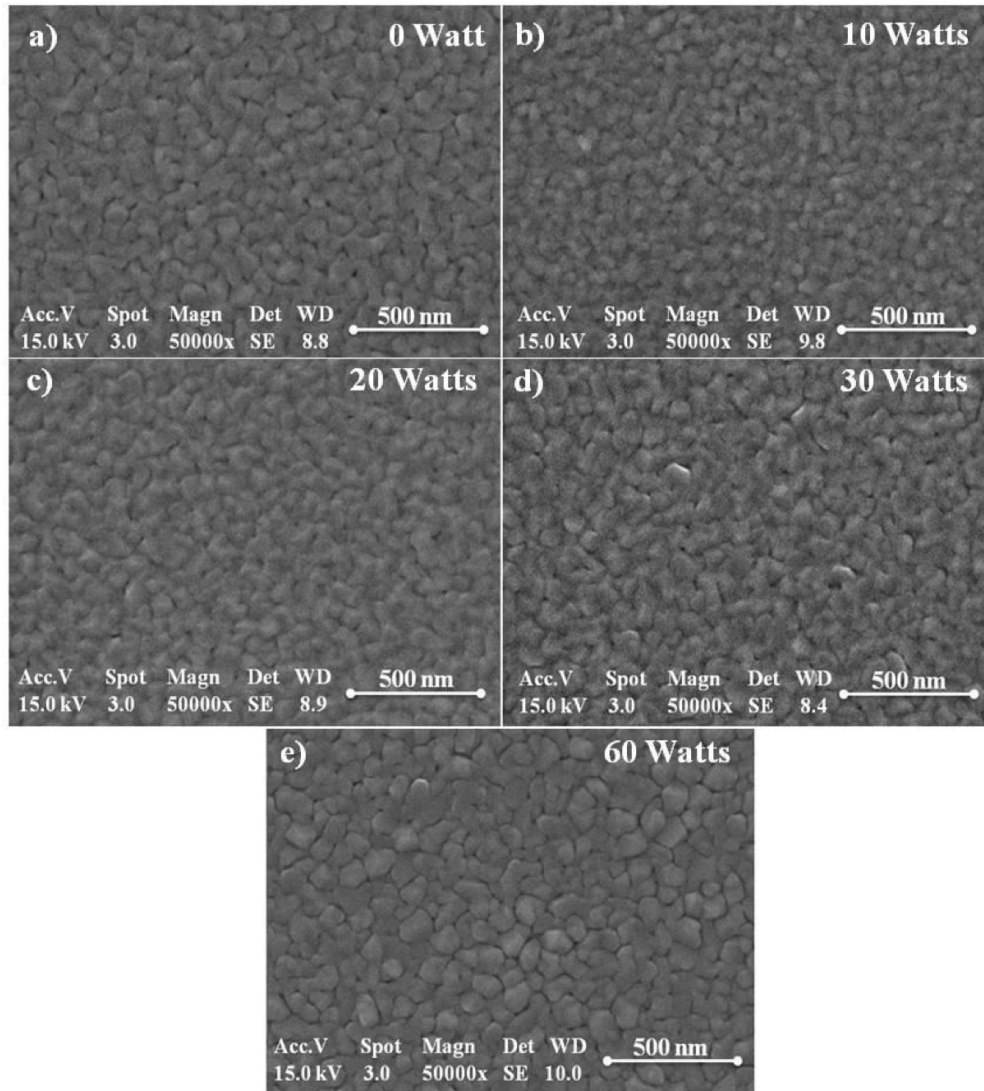


Figure 6.6. SEM images with the same magnification rates at different RF power values.

The substrate temperature is the key parameter in grain growth process rather than the applied power on RF magnetron, so the fabrication of samples for different power values was not implemented for explaining the grain growth process. However, the main objective of this section is to find a power value which enables an agreement in between experimental and decided composition rates. As it can be seen from Figure 6.7 or Table 6.7 which are shown below, the grain size has no particular dependence on RF power value.

Table 6.6. Average grain size for each power applied on RF magnetron.

RF Power Value (W)	Grain Size (nm)
0	84.16 ± 2.13
10	80.47 ± 0.95
20	80.99 ± 1.82
30	83.79 ± 0.26
60	87.86 ± 2.40

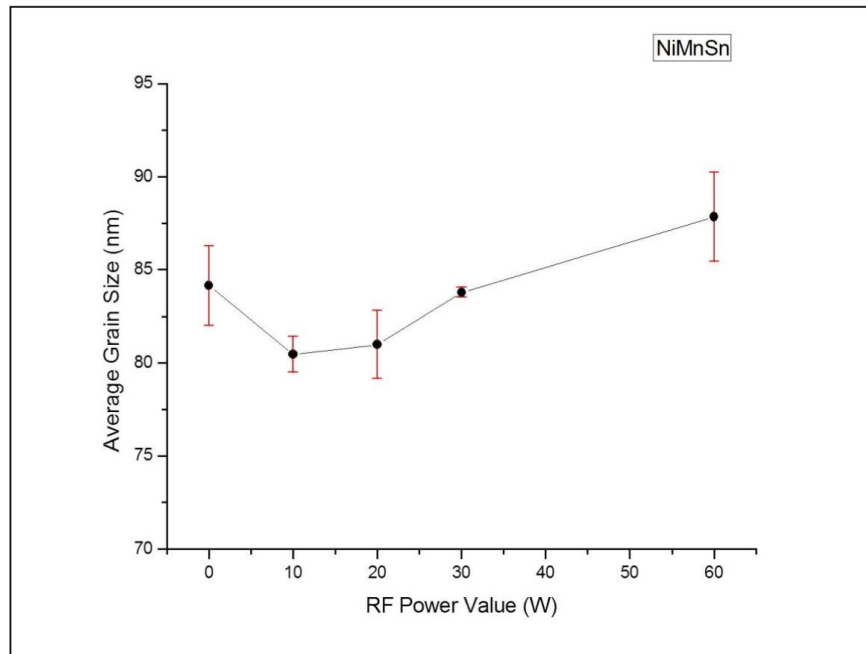


Figure 6.7. The relation between grain size and RF power.

6.2.3. Substrate Temperature Dependent Structural Properties of Thin Films Fabricated by co-sputtered NiMnSn and Mn targets

- A ternary (*Ni-Mn-Sn*) and a pure (Mn) target were used during this process.
- Substrate temperature was changed from room temperature to 400°C (*RT*, 200, 300, and 400°C).
- While the power applied on *Ni-Mn-Sn* target was 100 Watts, the power applied on pure Mn target was 60 Watts. Both of them were stable and did not vary in time throughout the experiment.

Table 6.7. Deposition conditions.

Substrate Heating Temperature	$RT - 200 - 300 - 400^{\circ}C$
Coating power	100 W for $Ni_{50}Mn_{37}Sn_{13}$ target 60 W for pure Mn target

$NiMnSn$ thin film alloy composition rates with respect to substrate temperature values are given in Table 6.8. The substrate temperature dependence of each element's

Table 6.8. Change in the chemical composition rates depending on substrate temperatures and decided composition rates.

Substrate Temperature ($^{\circ}C$)	Ni %	Mn %	Sn %
RT	51.23 ± 0.39	38.70 ± 0.18	10.07 ± 0.40
200	52.39 ± 0.40	37.87 ± 0.37	9.75 ± 0.40
300	51.31 ± 0.45	$38.85 \pm 0, 39$	9.84 ± 0.20
400	50.08 ± 0.39	39.89 ± 0.32	10.03 ± 0.15
Decided Composition	50	37	13

chemical composition is shown in Figure 6.8.

At $400^{\circ}C$ the experimentally obtained compositional rate is approximately the decided one. For the fabrication of $Ni-Mn-Sn$ thin films, 4 different temperature values (RT, 200, 300, and $400^{\circ}C$) have been determined. SEM images of $NiMnSn$ thin films show how increasing substrate temperature values led us to observe larger grain sizes, which can be seen in Figure 6.9. No data are provided at room temperature due to

Table 6.9. Substrate temperatures versus grain size values.

Substrate temperature $^{\circ}C$	Grain Size (nm)
RT	—
200	$21, 30 \pm 0, 14$
300	$44, 49 \pm 0, 22$
400	$78, 20 \pm 0, 21$

limitations in the equipment accuracy to determine sizes below. However; a monotonic increase is obtained with the enhanced substrate temperature.

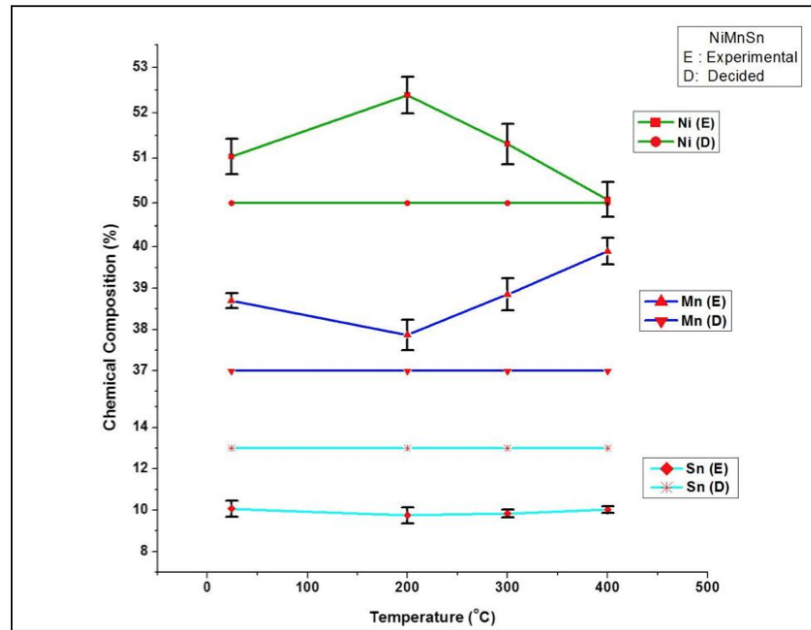


Figure 6.8. Plot of chemical composition rates as a function of substrate temperature.

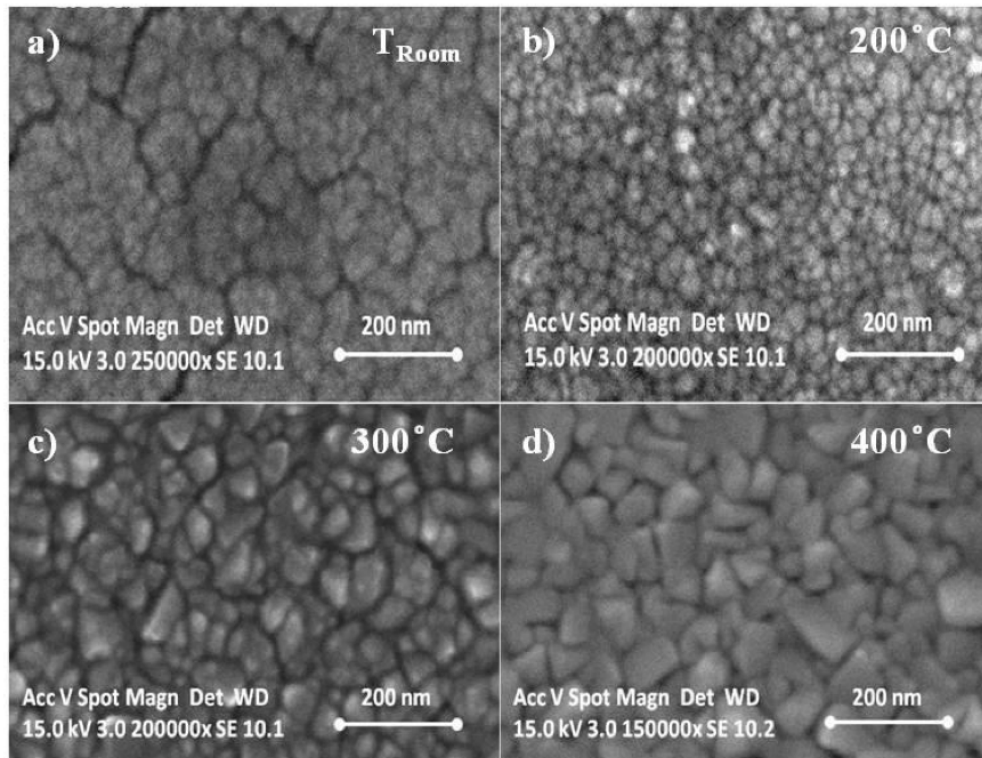


Figure 6.9. SEM images of NiMnSn alloys fabricated at different substrate temperatures.

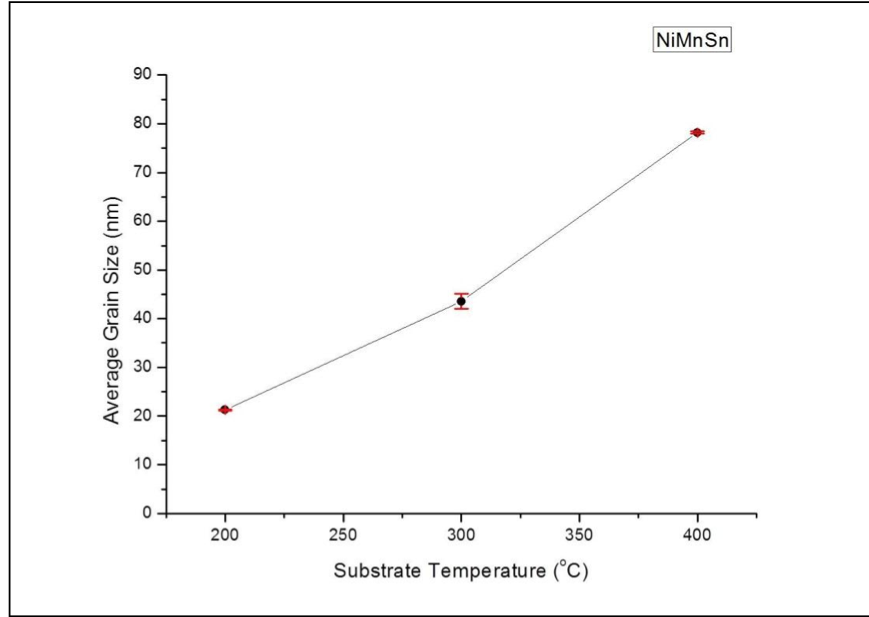


Figure 6.10. Extraction of average grain size values from the SEM images of thin film alloys fabricated at different substrate temperatures.

6.3. Ni-Mn-In Thin Film Alloys

Another Heusler type ferromagnetic shape memory alloy which is expected to exhibit magneto-caloric properties [24], *NiMnIn*, is the second part of this research. Similar to *NiMnSn* thin film analysis procedure, the SEM images and EDS results of *NiMnIn* alloys which were fabricated under different conditions will be shown in this section. We therefore gain detailed information about the surface and chemical composition of *NiMnIn* thin films. Similarly to the previous section, the same process was implemented for *NiMnIn* thin film alloy fabrication process and their structural analysis.

6.3.1. RF Power Dependent Structural Properties of Thin Films Fabricated by co-sputtered NiMnIn and Mn target

- A ternary (*Ni-Mn-In*) and a pure (Mn) target were used during this process.

- Substrate temperature was kept constant at 400°C throughout this experimental process.
- While power applied on *Ni-Mn-In* target was constant and 100 W, power applied on Mn target was changed from 0 to 60 W.

Table 6.10. Deposition conditions:

Substrate Heating Temperature	400°C
Coating power	100 W for $\text{Ni}_{50}\text{Mn}_{37}\text{In}_{13}$ target 0, 10, 20 30, and 60 W for pure Mn target

Table 6.11 shows EDS analysis of the average composition rates of the fabricated thin films for different applied power values.

Table 6.11. Average chemical composition percentages (at %) of elements (Ni, Mn, and In) for each power applied RF magnetron.

Substrate Temperature ($^{\circ}\text{C}$)	Ni %	Mn %	In %
0	57.673 ± 0.637	28.01 ± 0.457	14.317 ± 0.322
10	56.020 ± 0.483	29.253 ± 0.460	14.728 ± 0.222
20	56.616 ± 0.402	28.827 ± 0.351	14.557 ± 0.296
30	54.551 ± 0.314	31.368 ± 0.345	14.081 ± 0.291
50	52.227 ± 0.590	35.098 ± 0.517	12.678 ± 0.263
60	51.321 ± 0.655	36.67 ± 0.575	12.010 ± 0.255
Decided Composition	50	37	13

A trend of composition dependence on RF power can be observed at Figure 6.11 which includes both decided and experimentally obtained data.

For further clarification, a comparison between two samples which have greater possibility of exhibiting phase transition merits a special importance. One sample fabricated at 50 Watts, the composition rate of In was closer to the decided rate of this element than the other two elements (Mn, Ni). The other sample which was fabricated at 60 Watts, while In was making a small deviation from the decided composition rate, the remaining two elements became closer to the nominal values. Therefore, 60 Watts

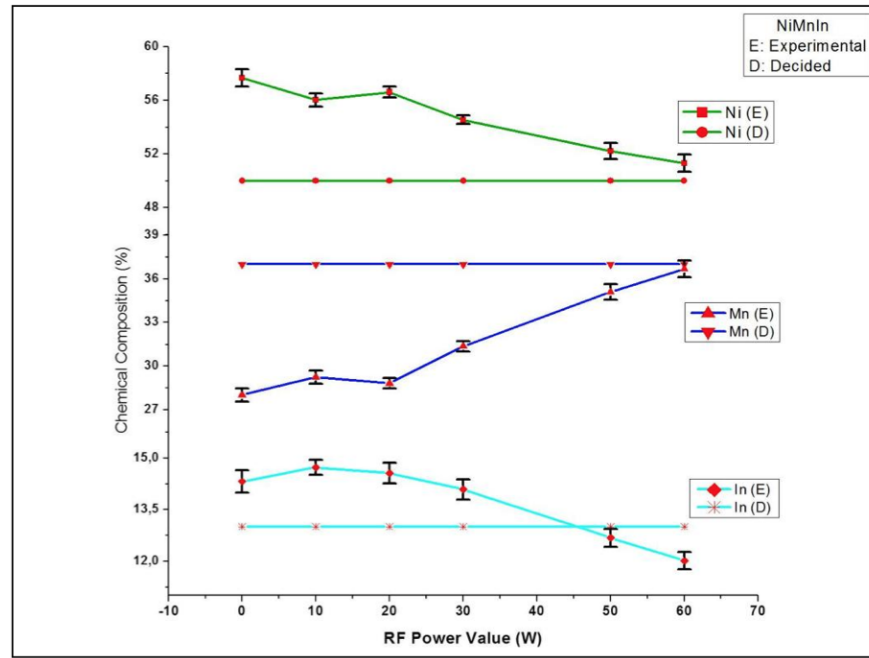


Figure 6.11. The difference between nominal (or decided) and experimental chemical composition (at %) of each element with changing RF power values.

was determined as the best power value which enables to reach decided composition rates. For the following series, 60 W was used as power value of RF magnetron.

The composition rate of Mn was controlled by the application of power on the RF magnetron to reach the decided composition rate for the alloy elements. Figure 6.12 shows SEM images for different power values. While Figure 6.12a shows the SEM image of *NiMnIn* thin film in the absence of RF power application, Figure 6.12b, Figure 6.12c, and Figure 6.12d are the images of *NiMnIn* thin film corresponding to 10, 20, 30, and 60 Watts, respectively.

All SEM images were taken with the same magnification (50000x) at different RF power values and they showed that there was no significant variation of grain sizes with the RF power. As it is seen from Figure 6.13 and the cross section of the thin film, thickness of the sample is roughly about 157.56 nm.

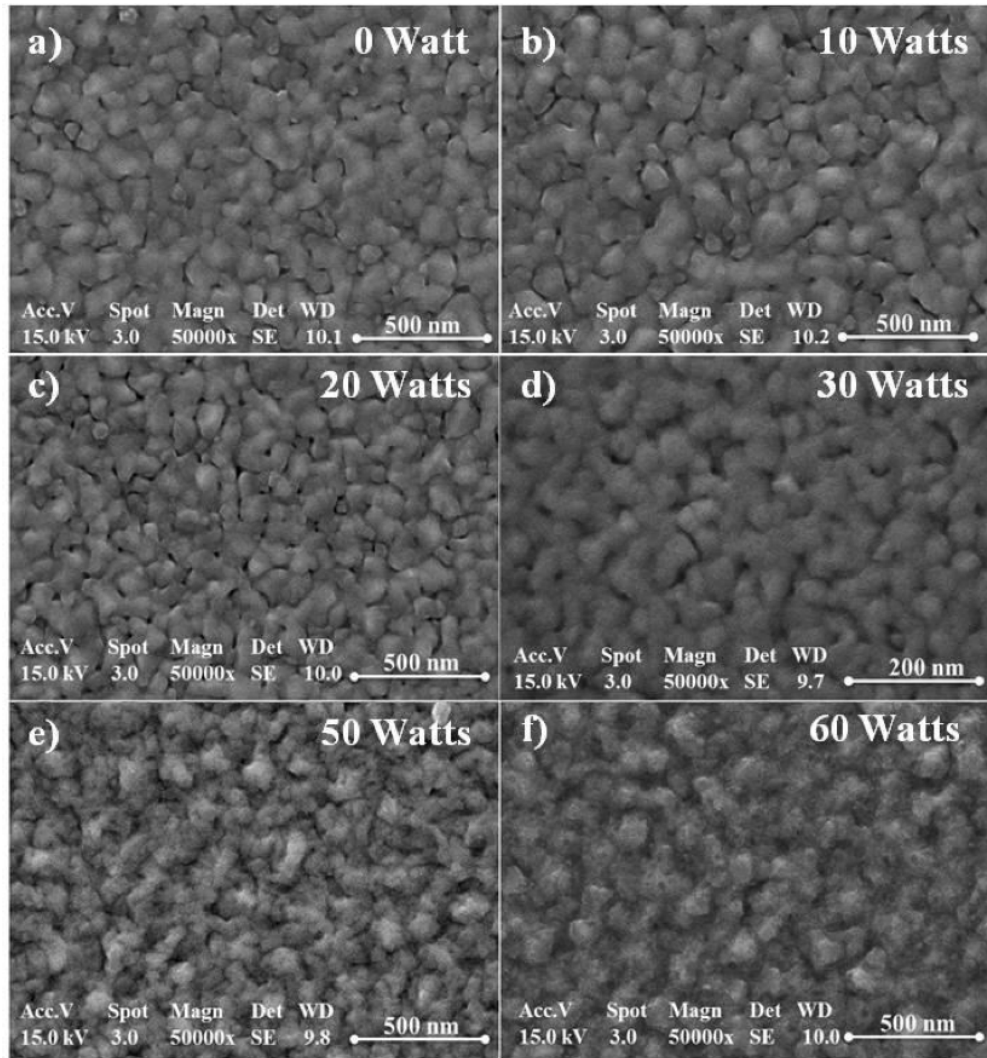


Figure 6.12. SEM images of NiMnIn thin film alloys at different RF power values.

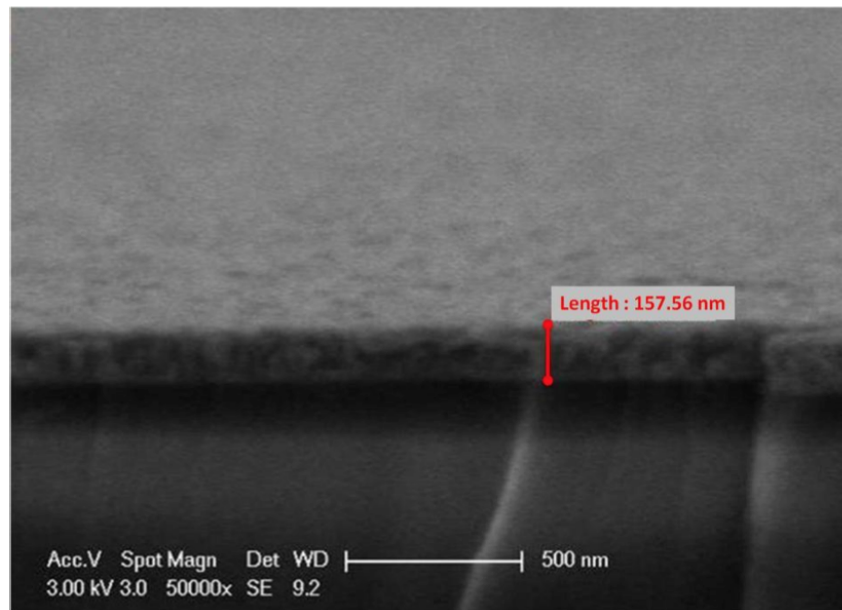


Figure 6.13. Profile and thickness of the thin film at 60 Watts.

Table 6.12. Average grain size for each power applied on RF magnetron.

RF Power Value (W)	Grain Size (nm)
0	135.90 ± 2.62
10	141.99 ± 9.72
20	123.84 ± 3.07
30	138.56 ± 8.51
50	132.50 ± 4.33
60	139.44 ± 2.99

Table 6.12 and Figure 6.14 show RF power values and corresponding average grain size together with its standard deviations which is obtained detailed analysis based up on SEM images. The deviation from the average value is about 3.84 % and it can be concluded that the grain growth does not depend on the RF power value. Whilst the black dots are showing experimental data and their values are listed in Table 6.12, the solid dark gray line is just to connect the experimental data which can be regarded as a linear interpolation to each of two consecutive values. Figure 6.14 shows the dependence of grain size on RF power.

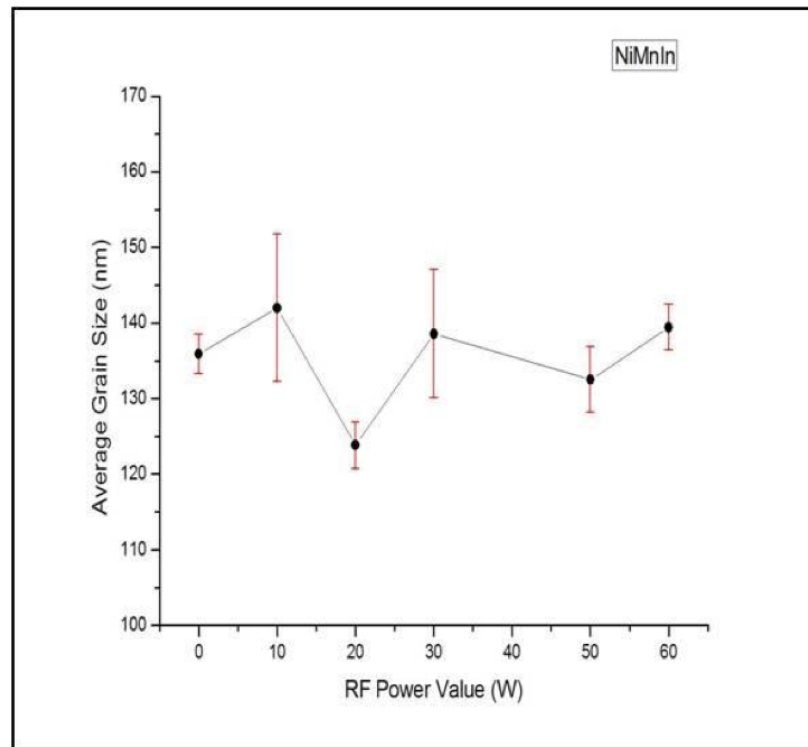


Figure 6.14. The relation between grain size and RF power value with average grain size at 20 W.

6.3.2. Substrate Temperature Dependent Structural Properties of Thin Films Fabricated by co-sputtered NiMnIn and Mn targets

In this section, the principle aim is to figure out the behavior of the thin films deposited under different temperatures values. Thereby, a difference in the grain size and morphology of the grain can be observed at Figure 6.16.

Table 6.13. Deposition conditions:

Substrate Heating Temperature	$RT - 100 - 200 - 400^{\circ}C$
Coating power	100 W for $Ni_{50}Mn_{37}In_{13}$ target 60 W for pure Mn target

The other important conditions of this turn can be stated as follows;

- A ternary ($Ni-Mn-In$) and a pure (Mn) target were used during this process.

- The substrate temperature was changed from RT (Room Temperature) to 400°C (RT, 100, 200, and 400°C).
- While power applied on *Ni-Mn-In* target was constant and 100 W, power applied on Mn target was changed from 0 to 60 W.

Table 6.14. Average chemical composition percentages (at %) of elements (Ni, Mn, and In) for each substrate temperature.

Substrate Temperature (°C)	Ni %	Mn %	In %
RT	49.91 ± 0.45	36.85 ± 0.46	13.23 ± 0.24
100	48.83 ± 0.36	37.91 ± 0.41	13.27 ± 0.18
200	50.97 ± 0.65	38.56 ± 0.57	10.46 ± 0.28
400	51.32 ± 0.65	36.67 ± 0.57	12.01 ± 0.25
Decided Composition	50	37	13

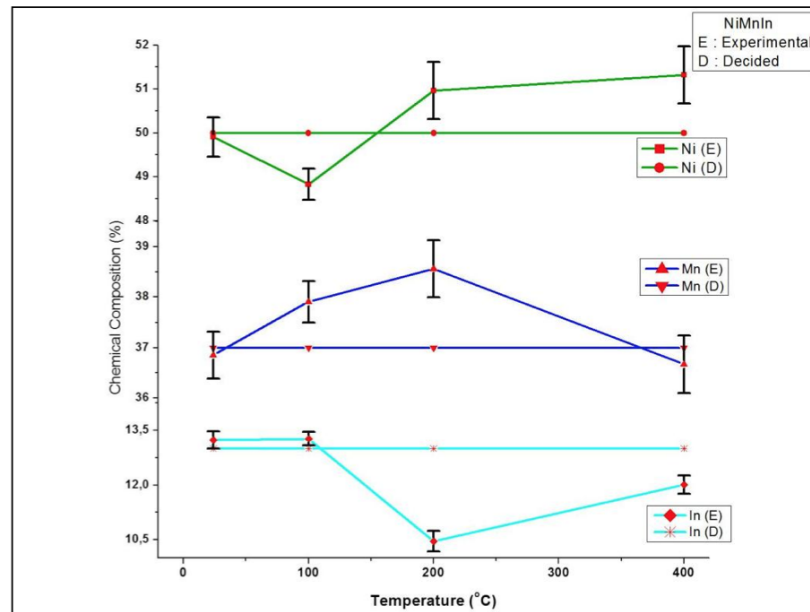


Figure 6.15. The difference between nominal (or decided) and experimental chemical composition (at %) of each element with changing substrate temperature.

Table 6.14 and Figure 6.15 show the experimental composition rates and the plot of both decided and experimental composition rates versus substrate temperature, respectively. Except from the thin film fabricated at 200°C, a significant increment in the grain size was observed.

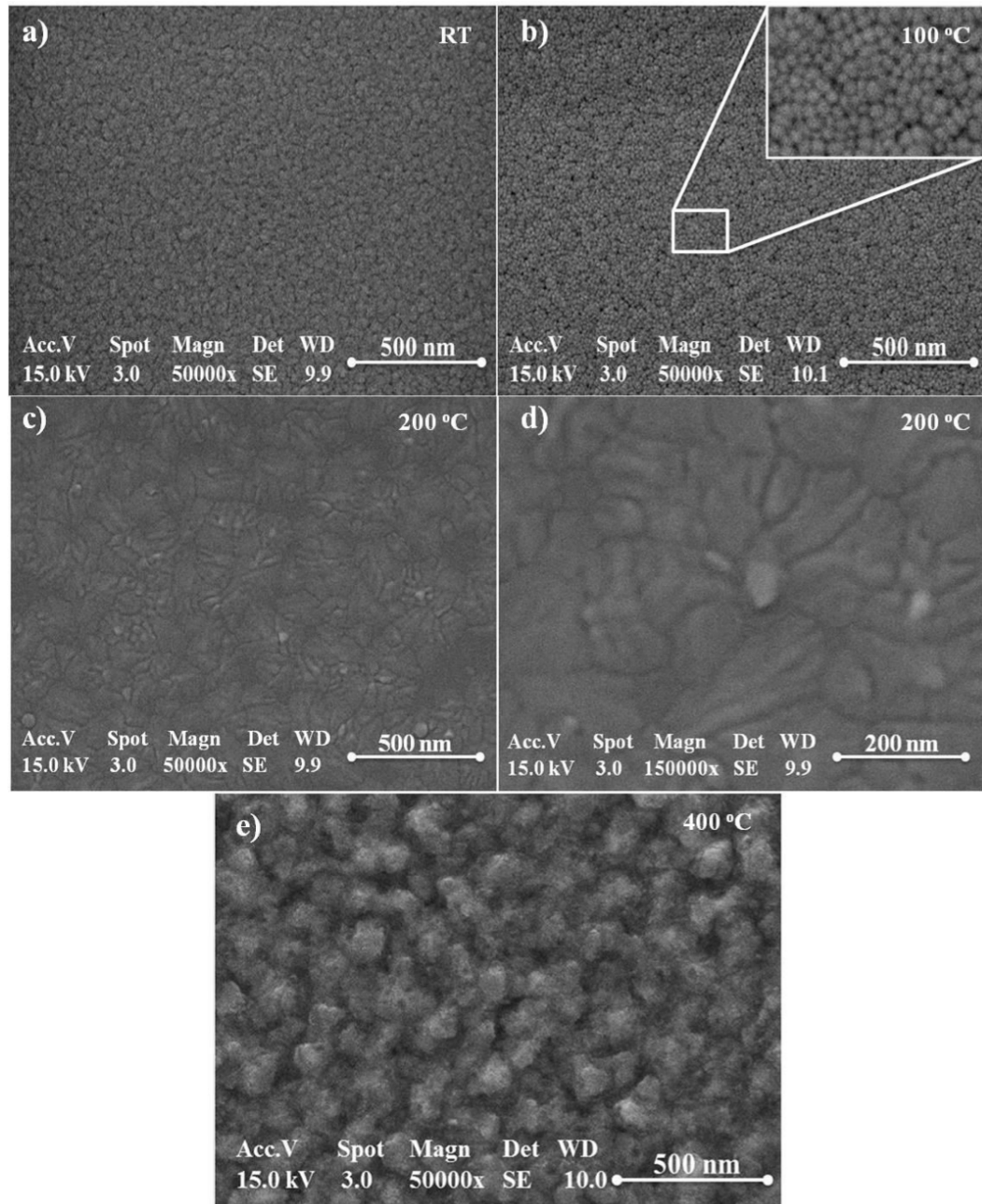


Figure 6.16. SEM images of thin films at RT, 100, 200 and 400°C.

The thin film deposition implemented at room temperature is shown in Figure 6.16a at 50000x. Temperature effect on the deposition was also studied at different temperatures. The difference between grains on the surface at RT and 100 can clearly be seen from Figure 6.16a and Figure 6.16b, respectively. The last part of Figure 6.16 is the SEM image of thin film for $400^{\circ}C$ which has precise grains.

7. CONCLUSION

7.1. NiMnSn Thin film Alloys Structural Properties of Thin Films Fabricated by NiMnSn target

For the first series of *Ni-Mn-Sn*, sputter technique was applied and only one ternary (*NiMnSn*) target was used. The aim of this step was to investigate the change in grain size and chemical composition rates due to an external heating or power application on Mn target during the deposition. Thereby, a successful verification of grain growth process, which is an increase in grain size with rising temperature, implemented/obtained for the samples of this serie. Their corresponding SEM and EDS analysis will be shown in the following pages. Due to the high vapor pressure possession of Mn element, a significant amount of material loss occurs during their fabrication processes. There were considerable deviations from the decided chemical composition (Ni: 50, Mn: 37, and Sn: 13) when only one ternary target (*NiMnSn*) was used. Additionally, the effect of substrate temperature on chemical composition was examined in detail. It was concluded that substrate temperature did not affect the chemical composition of the thin films and therefore almost all thin film alloys had a close chemical composition rate.

7.2. RF Power Dependent Structural Properties of Thin Films Fabricated by co-sputtered NiMnSn and Mn target

The second series of *Ni-Mn-Sn* series, unlike the first step, co-sputter technique was carried out and one ternary and one pure Mn target were co-sputtered as a way to compensate the Mn loss of Mn in alloy. As it was mentioned before, Mn target was placed on RF magnetron and power value applied on this magnetron was changed from 0 to 60 W. It was understood that 60 Watts was the optimized power value to reach the decided composition. Grain size shows no dependence with the power applied on RF magnetron.

7.3. Substrate Temperature Dependent Structural Properties of Thin Films Fabricated by co-sputtered NiMnSn and Mn target

The next series was prepared to study the dependence or relationship between substrate temperature and grain size. Once experimental EDS results of the samples approached to the decided composition rates, Similar to first series, there was an increase in grain size when substrate temperature was risen and substrate temperature has no effect on the chemical composition of the thin film alloys. *NiMnIn* Thin film Alloys

7.4. RF Power Dependent Structural Properties of Thin Films Fabricated by co-sputtered NiMnIn and Mn target

After three *NiMnSn* series were completed, *NiMnIn* based thin film alloys were studied to see structural properties. It was expected that *NiMnIn* and *NiMnSn* thin films have similar structural properties. Because chemical composition rates of *NiMnSn* thin film series were far away from decided composition, first step of *NiMnSn* was not repeated for *NiMnIn* thin films. Power value applied on RF magnetron was changed from 0 to 60 Watts to see the change in chemical composition.

A comparison with the rates of each other, the average chemical composition of Mn corresponding to 30, 50, and 60 Watts power applications are 31.368 ± 0.345 (at %), 35.098 ± 0.517 (at %), and 36.67 ± 0.575 (at %), respectively. However, the decided value is 37. Therefore, the result at 60 Watts is closer to the decided one. After the 50 W, a decrease in the average chemical composition of In was observed while Mn and Ni were approaching to their decided composition rates. Second significant result is that the grain growth does not have a direct relationship with RF power applied on Mn target. Moreover, SEM results show the polycrystalline nature of our samples, as well.

7.5. Substrate Temperature Dependent Structural Properties of Thin Films Fabricated by co-sputtered NiMnSn and Mn target

The most appropriate power value which gave the decided composition was 60 Watts and which was applied as a constant power to this series. Only variable parameter was the substrate temperature and results did not show any change: An increase in the grain size with rising temperature occurred in *NiMnIn* thin film similarly to the *NiMnSn*. Substrate temperature did not have any obvious effect on the chemical composition of thin films.

APPENDIX A: TYPES OF BRAVAIS LATTICES

In this appendix the images of 14 different Bravais lattice shapes are shown in Figure A.1.

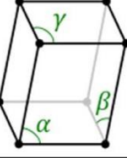
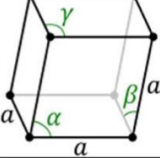
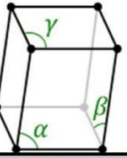
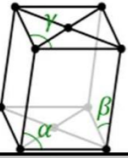
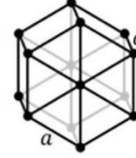
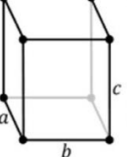
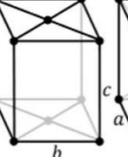
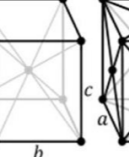
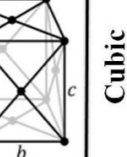
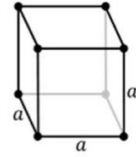
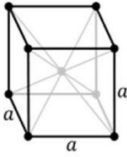
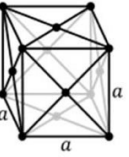
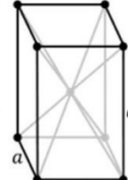
Triclinic	$\alpha, \beta, \gamma \neq 90^\circ$ 	Rhombohedral	$\alpha = \beta = \gamma \neq 90^\circ$ 
Monoclinic	$\beta \neq 90^\circ, \alpha, \gamma = 90^\circ$  $\beta \neq 90^\circ, \alpha, \gamma = 90^\circ$ 	Hexagonal	
Orthorhombic	$a \neq b \neq c$  $a \neq b \neq c$  $a \neq b \neq c$  $a \neq b \neq c$ 	Cubic	  
Tetragonal	$a \neq c$  $a \neq c$ 		

Figure A.1. Types of Bravais Lattices.

APPENDIX B: POWDER CELL PROGRAM

According to the explanation about martensitic and austenitic phases, there can be some changes in the crystal structure of the material during the phase transitions because of the following reasons: temperature and stress if the material is shape memory alloy or magnetic field if the material is a ferromagnetic shape memory alloys.

Change in one of the degrees of freedom (temperature, stress, or magnetic field) can create a different crystal structure. The change in the crystal structure usually makes the material more sensitive to external stimuli and provides a wide range of potential applications.

The identification of a crystal structure can be done by using several ways. One way of searching the closest crystal structure is to utilize Powder cell program which is typically used the following purposes;

- find the crystal structure of sample
- 3D representation of crystal structure
- compare experimental with theoretical XRD pattern

In the following, we will briefly explain this program supported by screen shots. In the first place, Figure B.1 is the initiation screen of the Powder Cell program. In this screenshot, the bottom level shows the powder pattern and the crystal structure will be shown at the top of this pattern.

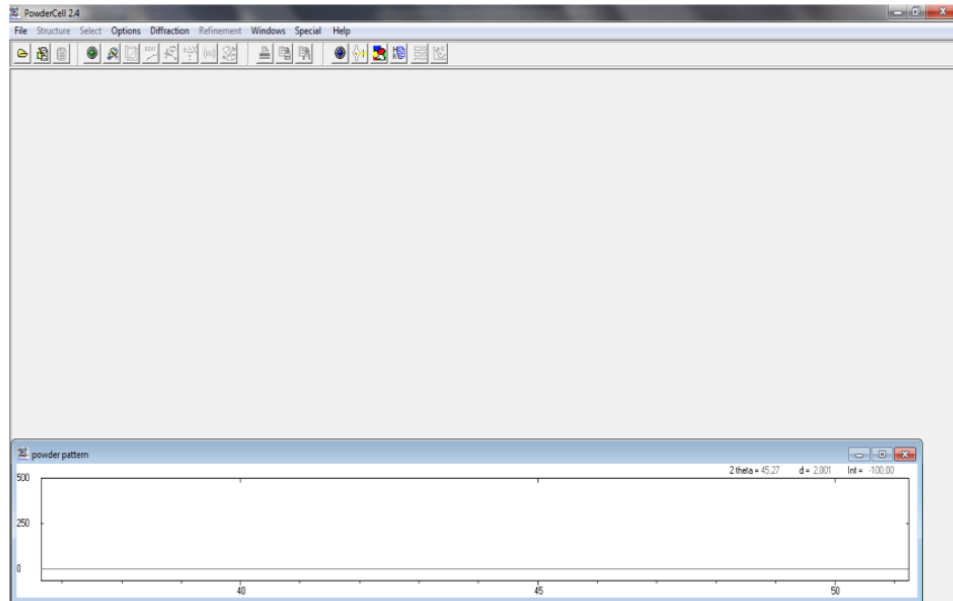


Figure B.1. Initial screen of the Powder sell program.

B.1. Edit Initial Data

First of all, we need to know the space group number of the sample. As it is stated before, space groups which can be also called as the crystallographic or symmetry groups show the symmetry of the crystals [25].

For example, the space group number is 225 for a cubic structure with Fm-3m space group. There are two important set of parameters, which needs to be chosen by hand, the space group number and lattice parameters. For example, we should put one lattice parameter ($a=b=c$) and one angle value ($\theta=\beta=\gamma=90^\circ$) for a cubic structure. Additionally, we should enter the names and atomic numbers of the atoms. There are some blanks which should be filled to get 2D or 3D representation of crystal structure or theoretical XRD pattern of the sample. These blanks are belong to Wyckoff position, SOF, and B values and these values are described below.

structure data

initial data

noname

lattice constants

space-group No setting P 1 atoms in cell: 0.0 (0 pos)

a b c α β γ

cell vol: 0.000 Å³ density: 0.000 g/cm³ rel. mass: 0.000 mass abs coef: 0.000 cm²/g

name	Z	ion	Wyck	x	y	z	SOF	B (temp)

Figure B.2. Structure Data.

B.2. Wyckoff Position

Wyckoff position can be regarded as a point which belongs to a set of points defines the space group used in calculations of crystal properties. Wyckoff positions provide information about the positions of each atom. Therefore, defining the positions of each individual atoms in the crystal enables the structural analysis. Mainly, Wyckoff positions can classified into two groups as general and special positions.

- General positions: while there is only one general position, just the identity operation left invariant.
- Special positions: while there are more than two operations of space groups, they are left invariant by the identity operation.

Crystallography tables present the Wyckoff positions for different space groups. There is a particular parameter, so called SOF, which is the occupancy of a given site (a fraction of specifically determined crystallographic site is occupied by a given atom). The other important parameter, so called B, is the temperature factor (a degree of

movement of the specified atom due to thermal agitations) [25]. When the SOF and B values of the alloys or thin films are determined, data part of structure is completed.

For the case of cubic structure, information such as its space group, crystal structure, space group number (Appendix B), lattice parameter, angles between each two edges etc. should be known drawing crystal structure of the sample by using powder cell program. For example, there should be some values to get the 2D and 3D crystal structure representation of the full-heusler alloy: $NiMnGa_2$.

PDF index name:	Gallium Manganese Nickel
Empirical formula:	Ga_2MnNi
Chemical formula:	$MnNiGa_2$
<u>Crystallographic parameters</u>	
Crystal system:	Cubic
Space group:	Fm-3m
Space group number:	225
a (Å):	5.8400
b (Å):	5.8400
c (Å):	5.8400
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	90.0000
Volume of cell (10^6 pm^3):	199.18

Figure B.3. Theoretical information about NiMnGa sample.

Structure								
No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	GA1	Ga	0.25000	0.25000	0.25000	0.5000	1.0000	8c
2	MN1	Mn	0.50000	0.50000	0.50000	0.5000	1.0000	4b
3	NI1	Ni	0.00000	0.00000	0.00000	0.5000	1.0000	4a

Figure B.4. Wyckoff positions, B, and SOF values of NiMnGa sample.

structure data

initial data |

lattice constants

space-group No setting F 4/m -3 2/m atoms in cell: 0.0 (0 pos)

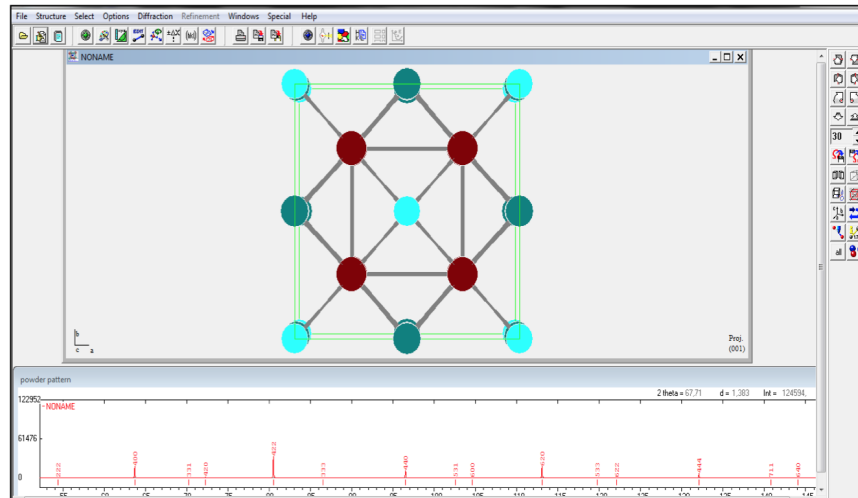
a b c α β γ

cell vol: 0.000 Å³ density: 0.000 g/cm³ rel. mass: 0.000 mass abs coef: 0.000 cm²/g

name	Z	ion	Wyck	x	y	z	SOF	B (temp)
Ga	31	Ga	8c	0.25	0.25	0.25	1	0.5
Mn	25	Mn	4b	0.5	0.5	0.5	1	0.5
Ni	28	Ni	4a	0	0	0	1	0.5

Figure B.5. Complete structure data.

When we chose OK tab on the right corner of the interface, 2D cubic structure of $NiMnGa_2$ can be seen as follows:



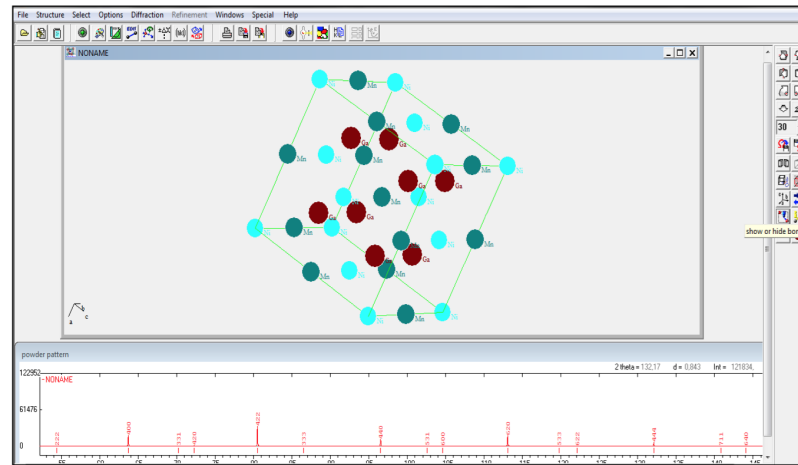


Figure B.8. Crystal structure (different side) and theoretical diffraction result.

We can turn off the representation part of the system and turn on the diffraction part or vice versa. For example, we turned off the representation part just to examine diffraction part. This led us to see the following screen: $\langle hkl \rangle$ are the Miller indices

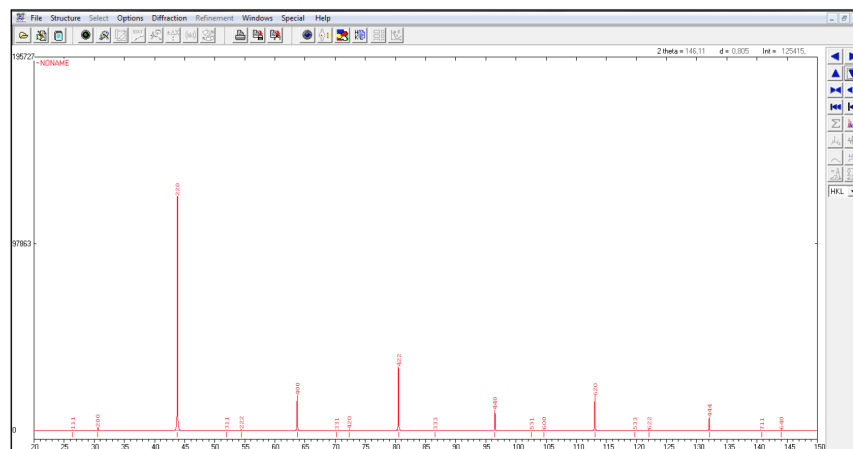


Figure B.9. Theoretical diffraction result of the sample.

which lead us to identify not only crystal orientations, but also individual directions defined in the crystal lattice system. However, unlike the Miller indices based crystal orientation, in the powder cell program this is done by using the lattice parameter d for each peak.

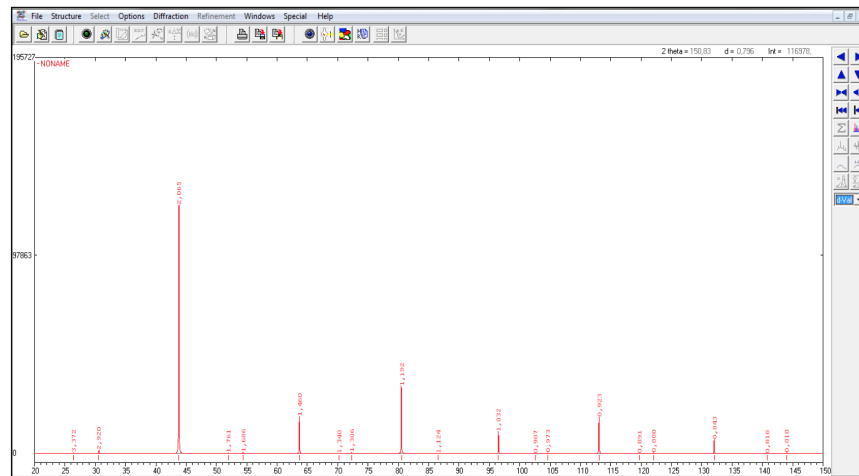


Figure B.10. Theoretical diffraction result of the sample (d value).

By choosing diffraction section, it will be available to obtain hkl list of the peaks.

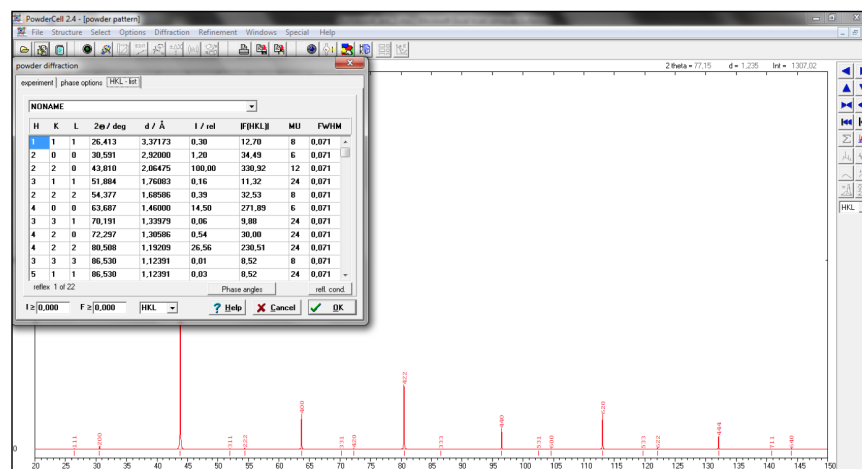


Figure B.11. hkl list of the theoretical diffraction result of the sample.

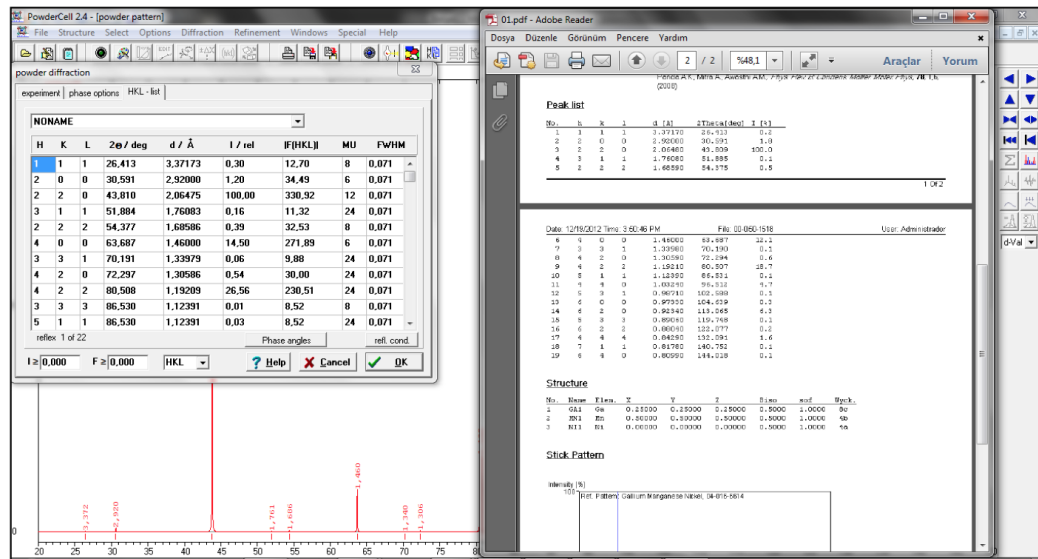


Figure B.12. The comparison hkl lists (first list is theoretical and second list is experimental).

APPENDIX C: SEM (Scanning Electron Microscopy)

The early history of Scanning Electron Microscopy begins with a researcher Max Knoll, who produced a photo with a 50 mm object by means of an electron beam scanner. However, in 1937, Manfred von Ardenne invented true microscope configuration with high magnification by scanning a very small space by using a magnified and precisely focused e-beam [26].

Right after this invention, Ardenne upgraded the electron microscope and further examined the various detection modes, and the theory behind the SEM device. Additionally, he is the inventor of the first high magnification SEM device [27]. Further improvements in the SEM instrument were achieved by the different groups, especially Zworykin's group and the Cambridge groups, in the middle of the 20th century. Yet, in 1965 the first commercial SEM so called Stereoscan (delivered to DuPont) by Cambridge Scientific Instrument Company supervised by Charles Oatley, all of which led the SEM device to be the marketing of the commercial detection instrument [27].

C.1. The Prominent Features of SEM Image

- Focal depth is greater than that of an optical microscope. On the other hand, SEM images are in black and white (lack of color based information).
- Advanced techs turn the brightness based gray images into artificially colorful image.
- All kinds of solid surfaces can be scanned and imaged with a broad range magnification orders.
- A typical SEM image includes secondary electron and backscattered electron data.
- A cross sectional probing can be carried out via backscattered electron detector.
- The combination of SEM with X-ray analyzer permits compositional analysis of a microscopic area.

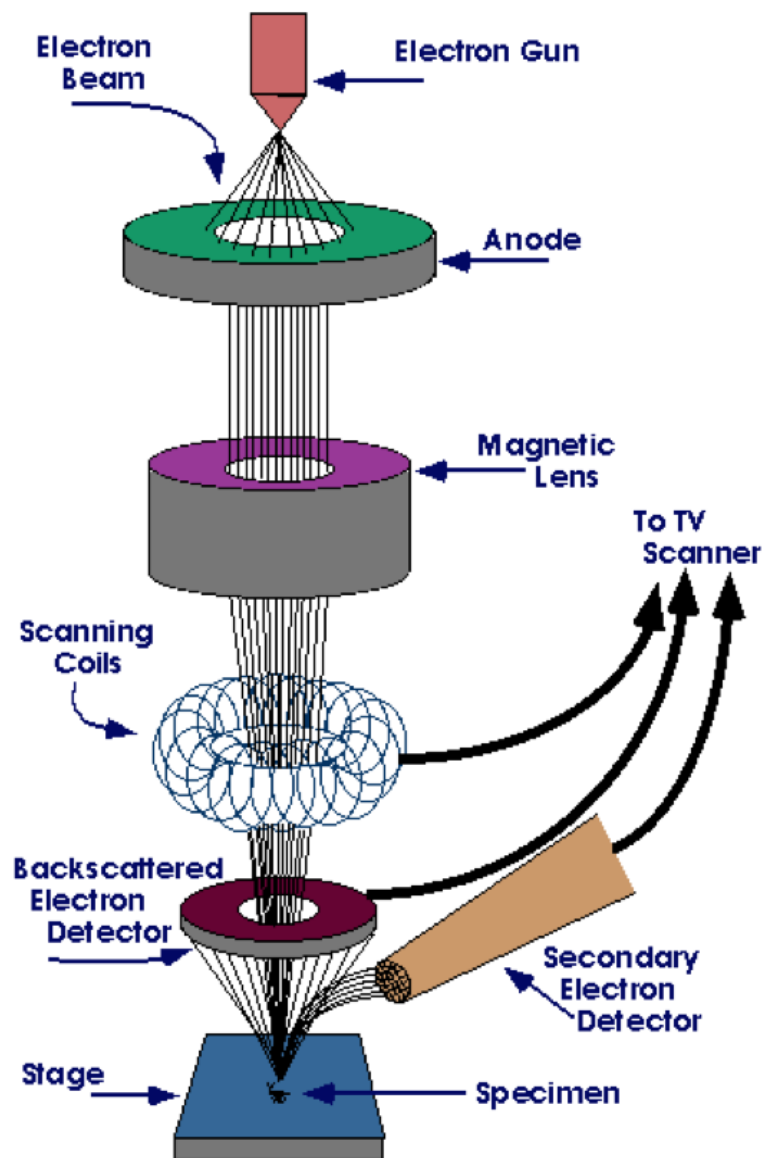


Figure C.1. Entire structure of SEM device.

C.2. Principles of SEM

SEM is an instrument which scans the sample surface with an almost fully converged e-beam in a vacuum (i.e. highly sensitive adjustment e-beam). This beam is the core of SEM which strikes the sample and creates distinct signals that includes secondary electrons, backscattered electrons, X-rays and cathode luminescence together with auger electrons, simultaneously. Commonly, by using the first one leads us to get the high resolution image of the sample on the monitor screen [28].

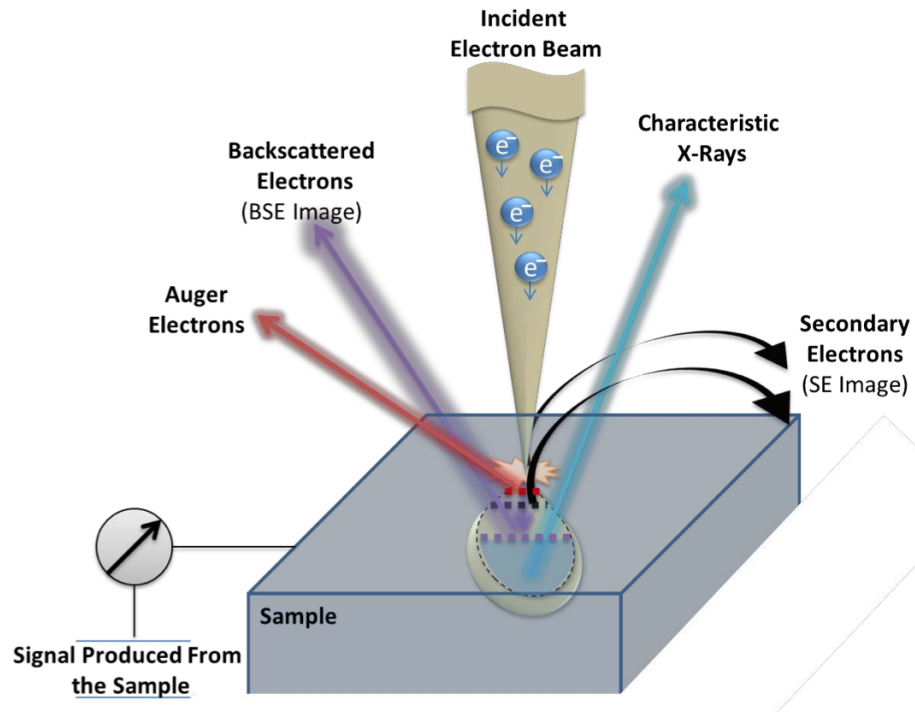


Figure C.2. The interaction of the incoming fine e-beam and the sample.

The physics behind the theory of SEM technology starts with the primary electron beam - sample interaction. During this interaction, electrons lose their energy, as expected. This energy is transferred to both the atomic structure and the lattice system of sample. Both random scattering of incident electrons and their energy absorption within a teardrop-shaped volume shown in the figure. We can see it clearly in the schematic drawing of the sample electron beam interaction which is shown above

(Figure C.2). This tear drop shape volume is also referred as the interaction volume, which varies from 100 nm to approximately $5\mu\text{m}$ into the surface [28]. The table below shows the outputs of the interaction between primary electrons and sample.

After Striking on Surface	Depth
Auger Electrons	<5nm
Secondary Electrons	5 nm
Back Scattered Electrons	400 nm
X-Rays	microns

Table C.1. The interaction of the incident electron beam and the sample creates versatile outputs which are from different depths.

The size of the interaction volume rests on the following three important points [29].

- The landing energy of the incident electron
- The atomic number of the specimen
- The specimen's density

When the object is exposed to the e-beam radiation under the vacuum condition, the interaction directly gets started. The energy exchange between the electron beam and the sample causes [30].

- high-energy electron reflection by elastic scattering
- secondary electron emission by inelastic scattering
- electromagnetic radiation emission

Each of these can be detected with high efficiency by specialized detectors. Electronic amplifiers are utilized in amplifying the signals. These signals are the spot intensities and their intensities may vary. These alterations in the intensity levels causes brightness changes and seen from the computer monitor. From the monitor, each pixel is synchronized with the beam position on the sample. The resulting image

is full map of the intensity distribution which corresponds to the signals taken from the scanned area of the specimen.

As a conclusion, the creation of a sample surface image is obtained by utilizing either backscattered electron signals or secondary electron signals for SEM device. Since the secondary electrons are the ones which are created closer to the sample surface, probing these secondary electrons generates the SEM image which represents the topological image of the sample.

The other main portions of the electrons, so-called back-scattered electrons that are scattered from the atoms of sample just are beneath the surface. Therefore, depending on the types of atoms in the sample, scattered electron population varies. This significant conclusion leads us to determine the compositional distribution of samples by using the backscattered electrons based image of the sample [29].

In addition to these, by means of attaching the X-ray detector to the SEM device, this enables to figure out the sample structure, as well. In other words, employing the X-ray analyzer to the SEM device helps in determining which types of elements are included in the sample and what are the portions of each element in the sample.

C.3. Segments of SEM

To reach a high resolution surface topography (does not represent colorful image), SEM device has a complex structure. In this section, main segments of the SEM will be stated in detail and the remaining smaller units will also be introduced, briefly [31].

Mainly, SEM device consists of the following parts;

- Column
- Specimen
- Chamber
- Display

- Operating Section

It is important to note that the pressure value is so low (i.e. kept in a high vacuum) inside chamber. Before the e^- beam strikes the sample, it is converted into a fine beam via electromagnetic lenses (which are listed as objective and condenser lenses). Application of the scan signal to the deflection coils lead us to probe the surface of the sample by using the e-beam which is created via e-gun [32].

As a kind of secondary electron detector, the specimen chamber employs another unit. This detector is responsible for detecting the signals coming from the sample which is under the influence of e-beam. This significant detection can be simply regarded as the topographical image of the surface when the e beam travels along the surface.

As it has been mentioned before, the backscattered electron detector and/or X-ray detector can also be mounted in order to get further information about both the surface of sample and composition rates of individual each element. A vacuum pump plays a key role in keeping at a certain pressure (low pressure) in the chamber where the sample is placed and the interior of the column [31].

Conventionally, an SEM device has the following individual units, which are:

- Electron Gun

Electron Gun which can also be called as electron emitter is a mechanism emits narrow and collimated electrons (which are traveling in space as a parallel) and then accelerates them in a strong electric field trough the sample.

- Deflection Coils

Basically, an SEM image presents a surface image (i.e. topography of the sample surface). In order to compile the image, we need data which is the accumulation of signals coming from the sample when e-beam scans the entire surface. However, the collimated e-beam needs to be moved in both x and y directions. This is done by the deflection coils.

Furthermore, the deflection coils change the size of the area on the sample surface which is scanned by the e-beam. One of the essential ability of a microscope is the magnification adjustment. In other words, the employment of these coils, the SEM device enables to make precise magnification adjustments. The qualitative calculation of magnification for a SEM imaging is given with the ratio of display area (L) to the width of the e-beam scan on the sample (w).

- Electron Lenses

In principle, electron beams can be focused by either electric field or magnetic field. Thereby, the electron beam which is controlled by the magnetic field with smaller noise effect. That is why, SEM system is having small aberrations due to the employment of magnetic field. In order to carry out the magnification of electron beam diameter, the electron lenses are mostly employed. Because of having variable strength, focal length can be adjusted depending on the strength. In the case of SEM, the electron lenses are made use of magnifying the image of the emission source. It means that a narrow probe is necessary, which can be performed by employing the optical lenses. There are two types of electron lenses which are employed in the SEM device.

(i) Condenser Lens

(ii) Objective Lens

Both condenser and objective lenses are electromagnetic lenses and they are employed for the purpose of converging the e-beam emitted from the electron gun into a fine beam and then make it focused onto the sample surface [32]. The e-beam is converged and brought into a relatively parallel stream via the condenser lens, [32]. Incoming e-beam to the condenser lens is magnified up to certain rate. After this part, e-beam deflected thru the condenser aperture. Objective lenses are employed not only to condense the electron beam into a probe point on the substrate surface, but also to gain further demagnification [33]. To sum up, in a conventional SEM instrument, the generated e-beam diameter is shrunk down and condensed by using both of these lenses. Figure C.3 shows the schematic drawing of e-beam trajectory and the positions of the lenses.

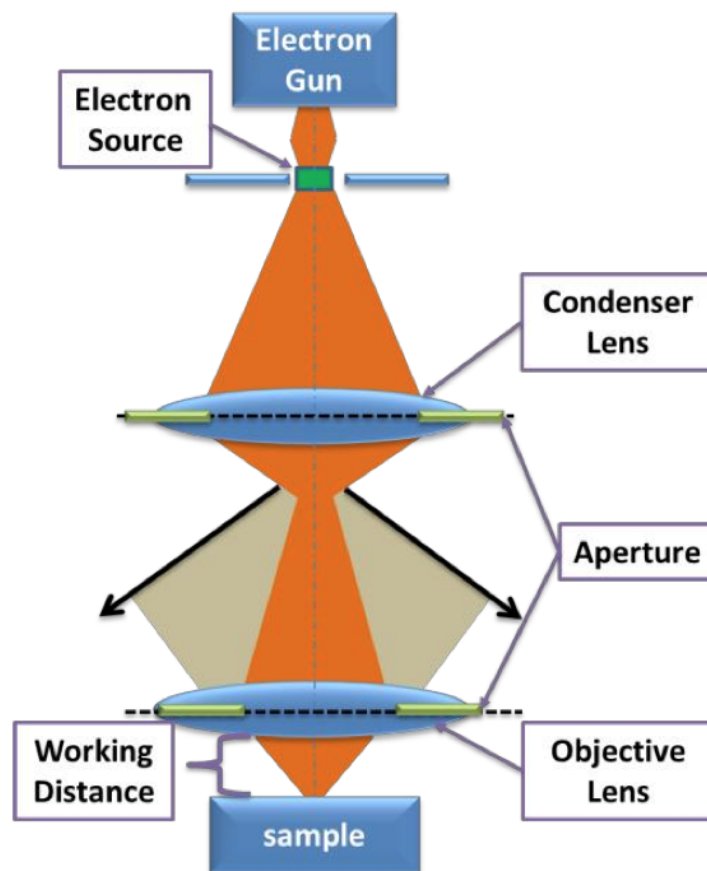


Figure C.3. Schematic illustration of the e beam path: Obtaining the Fine Electron Beam.

- Secondary Electron Detector

This detector is the output of the SEM imaging system. By means of this detector, secondary electrons are found out and efficiently captured in order to turn them into electric signals. After that it amplifies the secondary electrons obtained from the sample itself.

- Display

The display is required to see the signals. The signal values change the level of brightness. Thus, it provides a high resolution and enlarged image.

- Vacuum Pump

This segment is an inevitable part of the SEM system since it regulates the pressure inside the chamber. The vacuum level is varying from 10^{-4} to 10^6 Pa [34].

C.4. Possible Encountered Problems Related to SEM

- Electron microscopes are expensive from the point of both maintenance and purchasing.
- In order to prevent any possible electron scattering from the air molecules imaging the sample surface is implemented under the vacuum condition. (Apart from the others, the environmental type of SEM is able to view the hydrated samples in a low-pressure level (up to 20 Torr or 2.7 kPa) and/or wet environment).
- Under high-vacuum condition, SEM works to take the image of conductive specimens. However, a conductive coating (for example gold/palladium alloy, carbon, and osmium etc.) for non-conductive materials is necessary for the purpose of making possible to take SEM image of them .
- It is worth to note that another way out to take the image of non-conductive samples without coating is to employ the conventional low-voltage mode of modern microscopes. Non-conductive materials can also be viewed by using a variable pressure (or environmental) scanning electron microscope.
- In addition to the aforestated problems, for micro or nano range specimens such as carbon nanotubes do not necessitate a particular treatment before being imaged via SEM tech.

- However, these processes may cause undesirable artifacts, but these can usually be identified by comparing the results obtained by using radically different specimen preparation methods.

APPENDIX D: COATING TECHNIQUES

Surface engineering deals with modifying or changing the surface and near-surface region properties in a desirable way and can be regarded as either an overlay process or a surface modification process.

In overlay processes, a specimen is coated with a material and not detectable on the surface. On the other hand, the surface modification process changes the properties of the surface, but the substrate material is still present on the surface [35]. For the purpose of above mentioned modifications or changes on the substrate can be created by using one of the Physical Vapor Deposition (PVD) techniques.

D.1. Physical Vapor Deposition (PVD) Processes

Physical Vapor Deposition (PVD) technique are a kind of atomistic scale deposition process. During the process, the material is vaporized from a solid or liquid phase in the form of atoms or molecules. Right after that they are transported in the form of a vapor through a vacuum or low pressure gas environment to the substrate where it is condensed back. The conventional PVD processes make available to deposit films with thicknesses in the range of a few nanometers to a few micrometers. However, this PVD technique can also be used to form multilayer coatings and thicker depositions. The size of the substrates is ranging from very small to very large such as the 10" x 12" glass panels used for architectural glass [34]. PVD deposition rates are typically 10-100Å (1/10 nanometers) per second.

One of the types of PVD processes, so-called reactive deposition processes is made use of depositing either elements or alloys [36]. In reactive coating techniques, the reaction of depositing materials with the stable gas environment such as nitrogen (e.g. titanium nitride, argon) forms the compounds. They can also be in the form of a co-depositing material (e.g. titanium carbide, TiC) [34].

There are different PVD systems but the main types are:

- Vacuum Deposition
- Sputter Deposition
- Arc Vapor Deposition
- Ion Plating

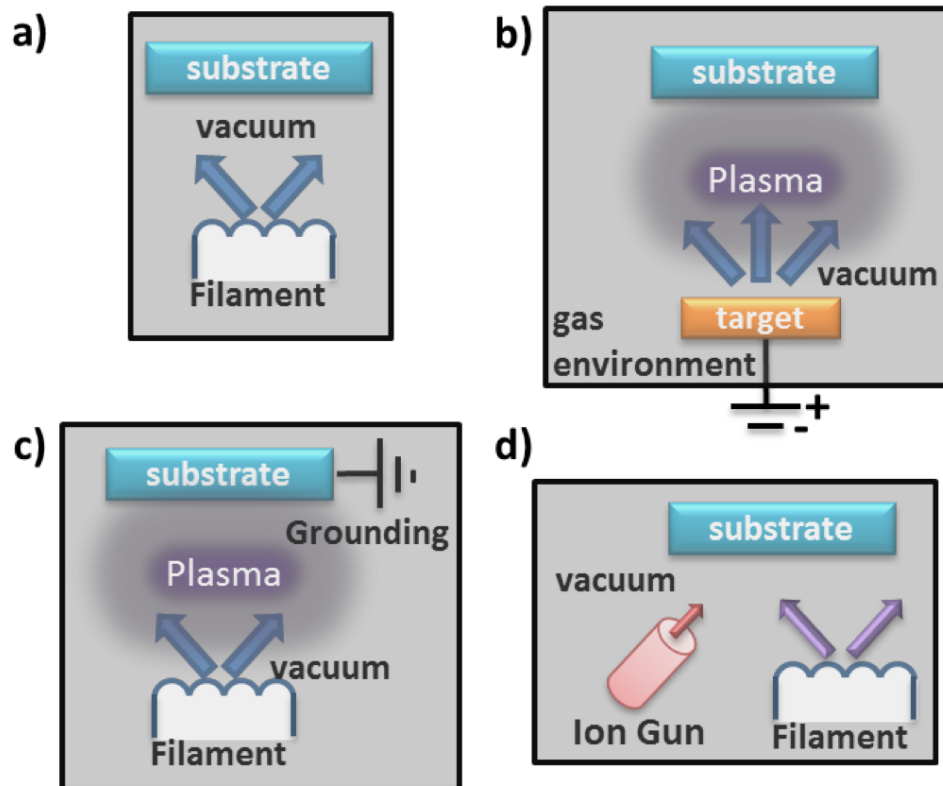


Figure D.1. Schematic drawing for the each type of PVD process.

This chapter covers not only all crucial parts of one of the widely used PVD technologies so-called Sputter Deposition System, but also covers the characterizing and preparing the substrate together with the coating process. Additionally, we will be getting introduced on film characterization and post deposition processing. A brief introduction to the other types of PVD systems will also be the last subject of this chapter.

D.2. Vacuum Evaporation / Deposition

Vacuum evaporation is also addressed as vacuum deposition. By thermally vaporizing the material in a vacuumed place is the main idea behind this method. This thermal energy is provided via a direct voltage application on the holder/pot of the material which will be vaporized. The vacuumed chamber is usually filled with a type of gas leads to control both the pressure and deposition velocity. Furthermore, under the vacuum condition, the contamination by other gases is significantly reduced. The vacuum levels are ranging from 10^{-5} to 10^{-9} Torr [34]. Figure D.2 shows a detailed schematic illustration of vacuum deposition as the evaporation of the material is coated on the substrate. If the gas contamination inside the vacuum chamber can

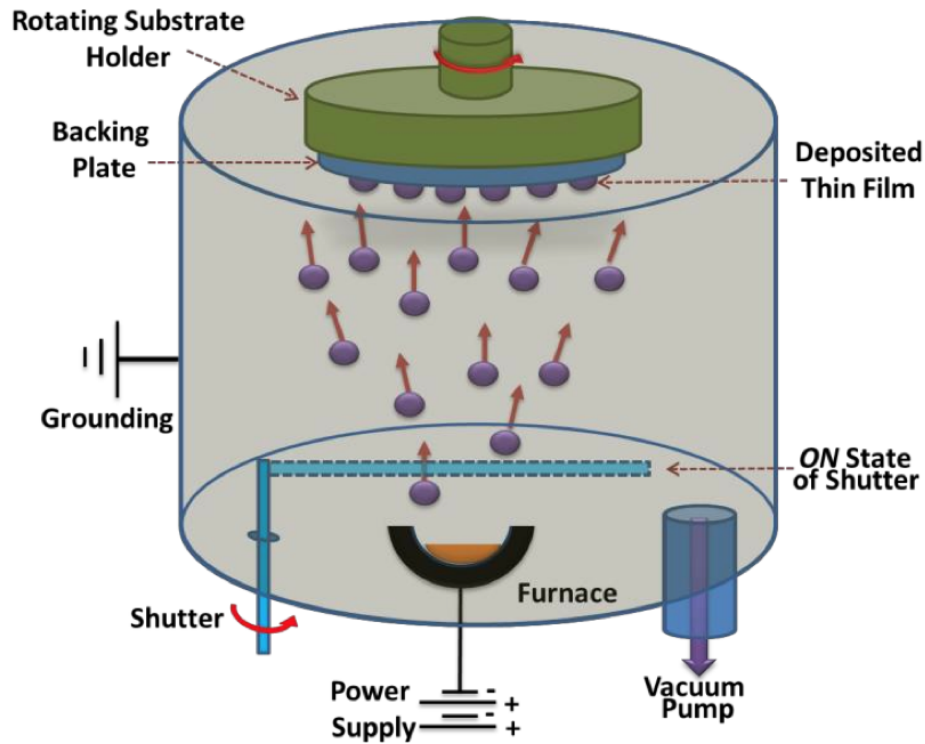


Figure D.2. Schematic illustration of Vacuum Chamber during evaporation.

be controlled, the deposition rate is predicted to be much higher as compared to the other methods. Conventional vacuum evaporation technique employs either resistive coils or a high energy electron beam to evaporate the material. However, the substrate

is placed at a larger distance from the source against radiant heat transfer.

D.3. Arc Vapor Deposition

The arc vapor deposition technique is able to deposit with a high level of adhesion and a dense structure. Moreover, it provides a smooth macro particle free surface [36]. During the deposition, it utilizes a high current, low-voltage arc in order to vaporize either a cathodic electrode (cathodic arc) or anodic electrode (anodic arc). However, the target is highly ionized and because of that reason, the substrate is usually biased so as to accelerate the ions to the substrate surface [35].

D.4. Ion Assisted Deposition

Ion Assisted Deposition (IAD) which is also known as Ion Vapor Deposition (IVD) or Ion Plating (IP) is a kind of deposition process that makes use of periodic or concurrent depositing material bombardment in order to control or modify the properties of the film.

In ion plating system, the important variables are the energy, flux, and the mass of the bombarding species together with ratio of both bombarding particles. The depositing particles needs to be taken into account for desired deposition [36].

For IAD, the vaporization method can be a different kind of tech such as chemical vapor decomposition, sputtering, or evaporation. This process can be implemented where ions for bombardment are received from a separate ion gun or from the plasma itself. The separate ion gun process is sometimes known as Ion Beam Assisted Deposition (IBAD).

Ion plating is another way of deposition tech and is able to coat hard materials. Additionally, it is adherent to metal, optical with and conformal coatings on complex surfaces [36].

D.5. Sputter Deposition

Sputter deposition is the process where the material is not thermally vaporized and the atoms are physically redirected from the source material (which is called as target) to the substrate by collision from a bombarding particle. In the other way around, physical sputtering is a kind of vaporization process without thermal heating application. During the process, surface atoms are physically ousted from the target surface by transferring the momentum from an atomic-sized bombarding particle. This atomic sized bombarding particles is usually a gas ion accelerated from plasma state. This PVD process is sometimes just called sputtering. Figure D.3 is showing each part inside the chamber.

Another particular feature of this PVD type is the traveling distance of the particles. The distance ranges from the particles of the target are pulled apart from the surface to the surface of the sample which will be coated. The distance between the targets to the substrate is much shorter than that of vacuum deposition. Under a higher plasma pressure, such as $5\text{--}20 \times 10^{-3}$ Torr, the sputter deposition can be carried out.

Generally, the range from source to substrate is reduced when it is compared it with that of the vacuum deposition tech. Thus, the performance of energetic ion bombardment thru the sputtering target in a vacuum using an ion gun or low pressure plasma ($< 5 \times 10^{-3}$ Torr) depends on this distance. Moreover, the sputtered particles make negligible collisions in gas phase during their travel in the space between the target and the substrate.

Sputtering can also be carried out in a higher plasma pressure which is ranging from 5 Torr to 30×10^{-3} Torr. At this plasma pressure is sufficient for the energetic particles in order to be sputtered on the substrate or to be reflected from the sputtering target. The plasma condition has an adjustable nature which can not only be confined near the sputtering surface or to fill the space inbetween the target and the substrate. It is important to note that the presence of plasma activates the reactive gas (plasma

activation) which leads itself to become more chemically reactive.

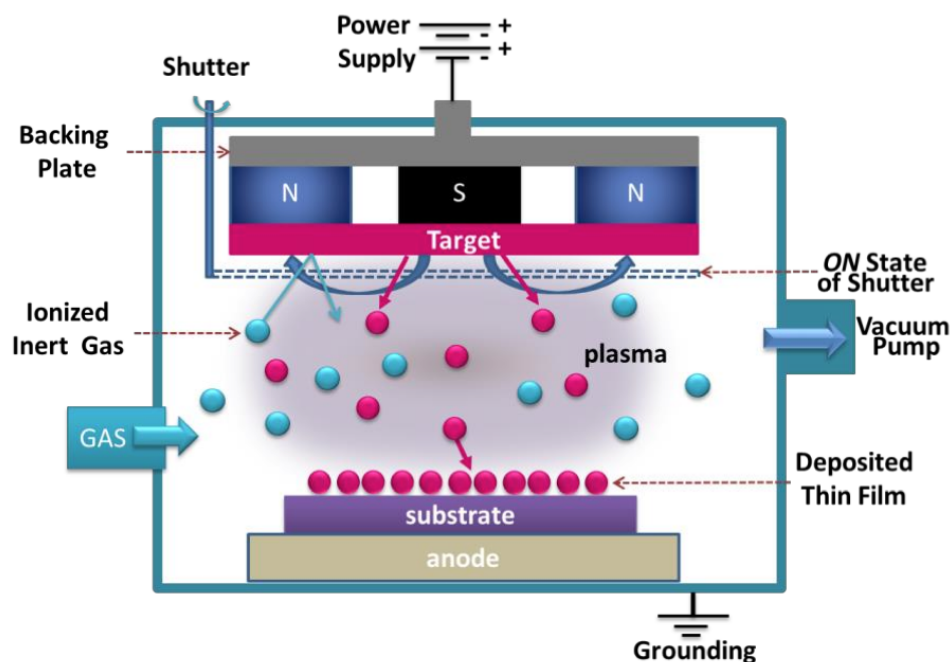


Figure D.3. Each segment of the Sputtering technique during the deposition.

This form of deposition is commonly used in semiconductor manufacturing, architectural glass, reflective coatings, compact discs (CDs), magnetic films, dry film lubricants, and decorative coatings [36].

Advantages of sputter deposition:

- Elements, alloys and/or compounds can be coated.
- The sputtering target provides a stable, long-lived vaporization source.
- The sputtering source can be a defined shape such as a line or the surface of a rod or cylinder.
- Reactive deposition can be easily accomplished by using reactive gaseous species that are activated in plasma.
- There is very little radiant heat in the deposition process.
- The source and substrate needs to be close to each other.
- Having smaller chamber is favorable for the sputter deposition.

Disadvantages of sputter deposition:

- Sputtering rates are low when it is compared it with those that can be attained in thermal evaporation.
- Sputtering targets are often expensive and material use may be poor.
- Most of the incoming energy on the target leads the plasma environment, target, and substrate to become heated, which is an undesirable situation and additional power is spent to remove the heating.
- Gaseous contaminants always exist in the evaporation process. In the plasma based evaporation, this is a problematic case since this contamination is mostly activated gives rise to make film contamination.
- In reactive sputter deposition technique, controlling the contribution of gas to the composition is a must in order to prevent poisoning the target.

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