



**REPUBLIC OF TURKEY
ADANA ALPARSLAN TÜRKER SCIENCE AND TECHNOLOGY
UNIVERSITY**

**INSTITUTE OF GRADUATE STUDIES
DEPARTMENT OF MATERIALS ENGINEERING**

**INVESTIGATION OF STRUCTURAL AND MAGNETIC PROPERTIES
OF Fe AND Cu DOPED MoS₂ THIN FILMS**

**BURAK KIVRAK
MASTER OF SCIENCE**



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BURAK KIVRAK
MASTER OF SCIENCE

SUPERVISOR
ASSOC.PROF.DR. MUSTAFA AKYOL

ADANA 2021



I hereby declare that all information in this thesis has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all information that is not original to this work.

Burak KIVRAK

ABSTRACT

INVESTIGATION OF STRUCTURAL AND MAGNETIC PROPERTIES OF Fe AND Cu DOPED MoS₂ THIN FILMS

Burak KIVRAK

Department of Materials Engineering

Supervisor: Assoc. Prof. Dr. Mustafa AKYOL

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In this study, structural and magnetic properties of pure and Fe/Cu-doped Fe/Cu_x:MoS₂ (x: 0.50%, 0.75%, and 1.00%) thin film materials were investigated. Crystallizations of films were ensured decomposing of ammonium tetrathiomolybdate (ATTM) precursor at various sintering temperatures under N₂ gas flow. Structural and morphological characteristics of all produced samples were investigated by measuring X-Ray Diffraction (XRD), Raman spectroscopy and Scanning Electron Microscope (SEM). It is determined from Raman spectroscopy results that the characteristic vibration modes of 2H-MoS₂ formed after performing optimization samples. SEM images of pure sample show that MoS₂ crystals formed as back-to-back triangle shape. This shape of crystal was changed to nanorod by doping Fe atoms in to the main structure. Magnetic properties of samples were investigated by using vibration sample magnetometer (VSM). It is observed that magnetic transition temperature of samples decreases when Fe atom is added to the main structure. The magnetization transition temperatures are found as 247.6 and 95.5 K for pure (0.95% wt. ATTM) and 0.75% Fe-doped MoS₂. According to the magnetic hysteresis curves measured at 5 K, the magnetic ordering of pure and 0.75% Fe-doped samples are ferro/ferri-magnetic. For Fe-doped samples, all samples, except 0.75% Fe-doped sample, show diamagnetic characteristic at room temperature. In addition, saturation magnetization value increases with introducing of Fe atom into the main structure. For Cu-doped samples, the diamagnetic behavior was observed at room temperature.

Keywords: MoS₂, spin-coating, magnetic characteristic, thin film.

ÖZET

Fe VE Cu KATKILI MoS₂ İNCE FİMLERİNİN YAPISAL VE MANYETİK ÖZELLİKLERİNİN İNCELENMESİ

Burak KIVRAK

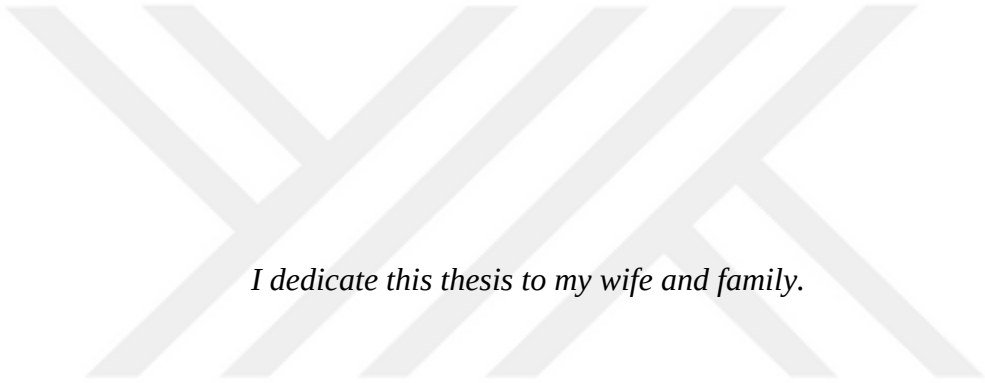
Malzeme Mühendisliği Anabilim Dalı

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Bu çalışmada, saf ve Fe/Cu katkılı Fe/Cu_x:MoS₂ (x: %0.50, %0.75 ve %1.00) ince film malzemelerin yapısal ve manyetik özellikleri incelenmiştir. Filmlerin kristalizasyonu, farklı sinterleme sıcaklıklarında N₂ gaz akışı altında amonyum tetratiyomolybdat (ATTM) öncü bileşiğinin ayrışması ile sağlanmıştır. Üretilen tüm numunelerin yapısal ve morfolojik özellikleri X-Işını Kırınımı (XRD), Raman ve Taramalı Elektron Mikroskop (SEM) kullanılarak incelenmiştir. Optimizasyon işlemlerinden sonra, Raman spektroskopi sonuçlarından 2H-MoS₂'ün karakteristik titreşim modlarının olduğu belirlenmiştir. Saf numunenin SEM görüntülerinden MoS₂ kristallerinin arka arkaya üçgen şeklinde olduğu gözlemlenmiştir. Bu kristal şekli, Fe atomunun ana yapıya katılanmasıyla birlikte nano-çubuk şeklinde dönüşmüştür. Numunelerin manyetik özellikleri, titreşim numunesi manyetometre (VSM) cihazı kullanılarak araştırıldı. Ana yapıya Fe atomu eklendiğinde Fe katkılı numunenin manyetik geçiş sıcaklığının düştüğü gözlemlenmiştir. Manyetizasyon geçiş sıcaklıkları saf (%0.95 ATTM) ve %0.75 Fe katkılı MoS₂ için 247.6 ve 95.5 K olarak bulunmuştur. 5 K'de ölçülen manyetik histerezis eğrilerine göre saf ve %0.75 Fe katkılı numunelerin manyetik yönelimleri ferro/ferri-manyetiktir. Fe katkılı numuneler için, oda sıcaklığında %0.75 Fe katkılı numune hariç tüm numuneler diyamanyetik özellik göstermektedir. Ayrıca Fe atomunun ana yapıya katılmasıyla doyum manyetizasyon değeri artmaktadır. Cu katkılı malzemeler için oda sıcaklığında diyamanyetik davranış gözlenmiştir.

Anahtar Kelimeler: MoS₂, spin-kaplama, sol-jel, manyetik karakteristik, ince film.



I dedicate this thesis to my wife and family.

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NOMENCLATURE

$\text{\AA}$	: Angstrom
$\vec{a}$	: Acceleration
$\vec{B}$	: Magnetic field
C	: Curie constant
$^{\circ}\text{C}$	: Celsius degree
D	: Crystallite size
$\vec{E}$	: Electric field
e^-	: Electron charge
EDS	: Energy-Dispersive X-Ray Spectroscopy
eV	: Electron Volts
FC	: Field Cooled
g	: Gram
hkl	: Miller indices
$\vec{H}$	: External magnetic field
H_c	: Coercive field
I	: Current
J	: Current density
$\vec{J}$	: Total angular momentum
j	: Total angular momentum quantum number
K	: Kelvin
k_B	: Boltzmann Constant
$\vec{L}$	: Orbital angular momentum
l	: Orbital angular momentum quantum number
m	: Mass
$\vec{M}$	: Magnetization vector
M_s	: Saturation Magnetization
Oe	: Oersted
PPMS	: Physical Properties Measurement System

R	: Radius
$\vec{S}$	: Spin angular momentum quantum number
SEM	: Scanning Electron Microscopy
AFM	: Atomic Force Microscopy
T	: Temperature
T_B	: Blocking temperature
T_C	: Curie temperature
T_N	: Neel temperature
VSM	: Vibrating Sample Magnetometer
ZFC	: Zero Field Cooled
XRD	: X-Ray Diffraction
Q	: Temperature constant
τ	: Relaxation time
V	: Speed
χ	: Magnetic susceptibility
λ	: Wavelength
θ	: Bragg angle
μ	: Magnetic moment
μ_B	: Bohr magnetron
μ_0	: Free space magnetic permeability
γ	: Gyromagnetic ratio
π	: Pi number

1 INTRODUCTION

Thin film technologies are a branch of science, and they continue to grow with new scientific developments for years. It refers to the layers of materials whose dimensions range from sub-nanometers to 500 nanometers. Thin film materials have been explored by researchers with the development of new deposition techniques. The thickness, quality and deposition technique determine the physical properties of thin films. The layer number of the film can be modified by changing the parameters of the system.

There are two main deposition techniques to manufacture thin films which are chemical and physical. Various techniques are composed of the parts of this two main titles. In the chemical depositions, Chemical Vapor Deposition (CVD) technique utilizes the chemical reactions to produce thin films. In contrast, the deposition of the film on substrates is ensured by the physical interactions in the Physical Vapor Deposition (PVD) process. Figure 1.1 shows the thin film production techniques.

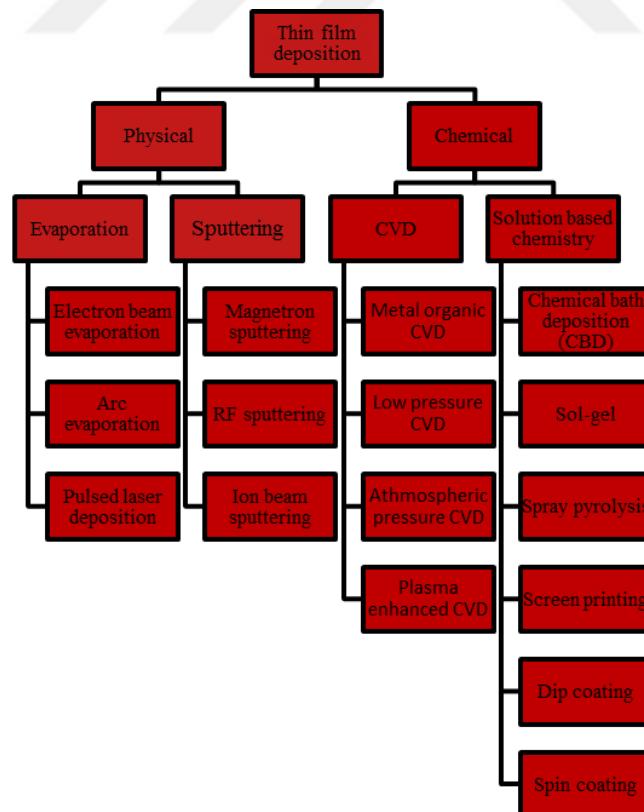


Figure 1.1. Types of thin film deposition techniques.

1.1. Transition metal dichalcogenides (TMDCs)

Transition metal dichalcogenides (TMDCs) is a kind of thin film structure which consists of one transition metal atom and two chalcogen atoms as MX_2 , where M refers to transition metal such as Ti, Zr, Hf, V, Nb, Ta, Mo, W, Tc, Re, Co, Rh, Ir, Ni, Pd, Pt and X refers to chalcogenide such as S, Se, Te. The monolayers are bonded with weak van der Waals interactions. In TMDCs system, the transition metal atom is sandwiched between two chalcogen atoms (see Figure 1.2).

Among the TMDCs, molybdenum disulfide (MoS_2) has attracted significant attention due to its various potential applications such as catalysis, electronic devices, optoelectronics, and energy storage (Ahn & Kim, 2017; Dashora, Ahuja, & Venugopalan, 2013; Ding, Chen, & Lou, 2011). The historical development of the TMDCs begins with the determination of the mineral MoS_2 structure by Linus Pauling in 1923. After this determination, the progression period of TMDCs continued with the manufacturing of monolayer MoS_2 structure by Robert Frindt in 1963. Then, MoS_2 nanotubes and nanoparticles were manufactured in 1995. The discovery of the graphene in 2004 revealed a new method to produce layered TMDCs structures (Manzeli, Ovchinnikov, Pasquier, Yazyev, & Kis, 2017; Roscoe G. Dickinson).

Generally, the crystal structures of TMDCs are formed as trigonal prismatic (2H) and octahedral (1T) phases. The difference between 2H and 1T is the stacking of the metal and chalcogen atoms (see Figure 1.2). In the 2H system, the stacking of atoms is in the A-B-A. On the other hand, the stacking of metal and chalcogen atoms of the 1T crystal system is A-B-C position. These stocking styles affect materials' physical properties. For example, 2H MoS_2 is more stable than 1T crystal orientation as thermodynamically. The stacking of atoms can be changed by the lattice distortion which results in the intermediate phase of 1T'. This 1T' crystal phase is formed by the metallic interaction between metal atoms of structure originated from the distortion (Manzeli et al., 2017). The electronic structure of these phases is completely different that the 2H phase is semiconducting with a direct band gap of 1.2-1.9 eV, whereas the 1T phase of MoS_2 shows metallic characteristics with high electrochemical activity. The schematic illustration of chemical bonding of MX_2 is shown in Figure 1.2.

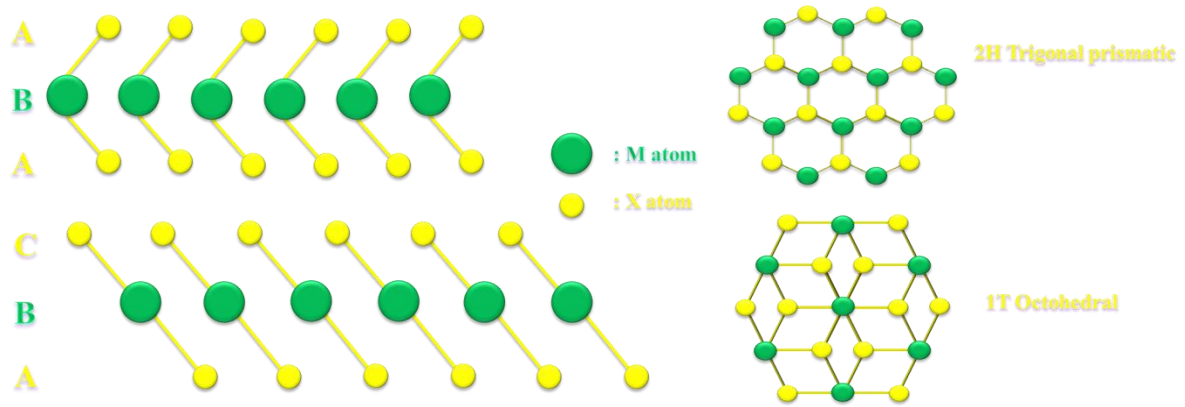


Figure 1.2. Schematic illustration of two common crystal phases of MX_2 which are trigonal prismatic (2H) and octahedral (1T).

The TMDCs have unique physical properties such as flexibility, large electrochemical active surface area, high surface tenability, rich coordination states and different electrochemical behaviors (Carroll et al., 2019; Han et al., 2019; N. Huo et al., 2015; Lim et al., 2016; Xu et al., 2019). The electrical conductivity properties of TMDCs change when their layer number decreases to a few layers. Localized d orbitals of the Mo atoms mostly occupy the states of conduction and the valence band at K point as shown in Figure 1.3(a). However, p orbitals of the S atoms give a large contribution to electronic states at the Γ point which leads to strongly affecting both valence and conduction band at Γ point by quantum confinement effects (Yazyev & Kis, 2015). As a result, the indirect band gap turns into the direct band gap (see Figure 1.3). This phenomenon affects both the optical and electrical properties of materials.

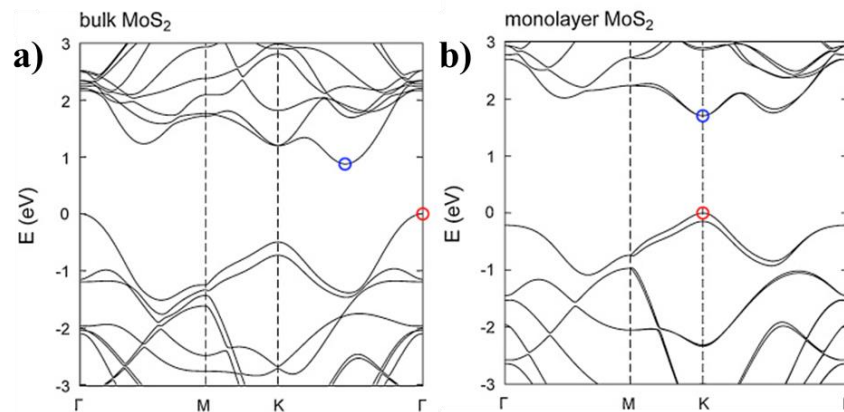


Figure 1.3. Band structure of the a) bulk and b) monolayer MoS_2 . The blue and red points show the changing position of the conduction and valence band of MoS_2 (Yazyev & Kis, 2015).

Two-dimensional (2D) TMDCs have attracted great attention to investigate and integrate to the novel electronic devices because the new generation electronic devices such as phones, detectors, circuit elements evaluate to the lower sizes (M. He et al., 2018; Hota et al., 2020; Lim et al., 2016; Z. Lin et al., 2018; Pazhamalai, Krishnamoorthy, Manoharan, & Kim, 2019). When lateral size of the material differs from nano or micrometer and its thickness is a single or few atomic layers, this kind of material system is called as two dimensional as shown in Figure 1.4. In other words, one dimension is extremely small when it is compared with the other two dimensions. Thus, the other two dimensions of the system remain large and continuity of the system is described with these two dimensions.

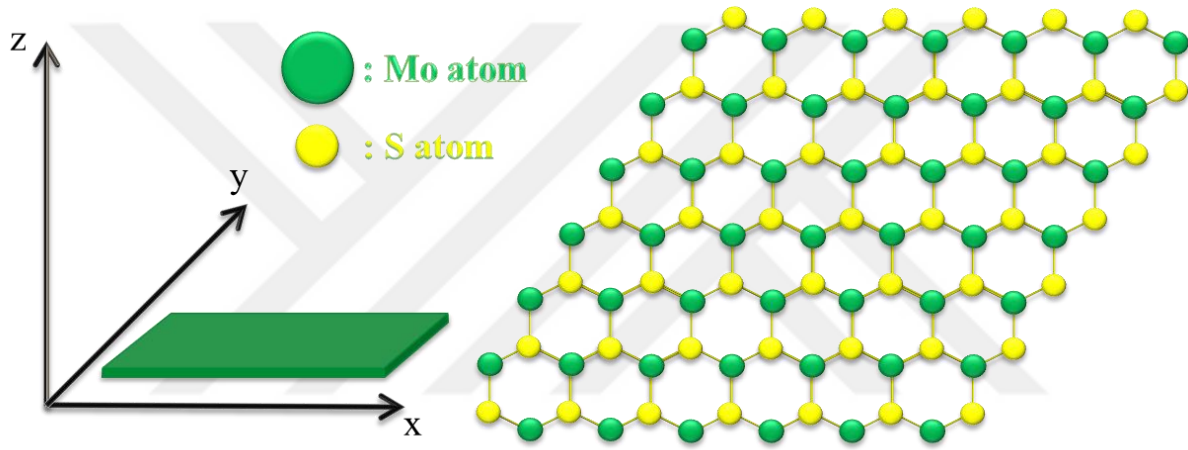


Figure 1.4. Schematic illustration of 2D system and MoS₂ monolayer.

Two-dimensional materials have more advantages than their bulk forms. The sensing and tunability properties of 2D-TMDCs are quite high due to their high surface-volume ratio and high edge ratio and surface area, respectively (Choi et al., 2017).

There are several manufacturing methods for synthesizing 2D-TMDCs such as chemical vapor deposition (CVD), mechanical exfoliation, chemical exfoliation, molecular beam epitaxy (MBE), thermal decomposition of precursor and atomic layer deposition (ALD). The film uniformity, stability, quality and cost of the system change with the method. The most effective and low cost-continuous method is thermal decomposition of the precursor material. This technique requires low temperatures and gives long-range uniformity of the films (Liu et al., 2012; O'Neill, Khan, & Coleman, 2012; Pyeon et al., 2016; Radisavljevic, Radenovic, Brivio, Giacometti, & Kis, 2011; Zhan, Liu, Najmaei, Ajayan, & Lou, 2012).

As for the application of 2D-TMDCs, gas sensors, energy storage devices, bio sensors, photonic devices and piezoelectric devices can be manufactured by producing TMDCs as 2D (Chang & Chen, 2011; Cheng et al., 2014; Choi et al., 2017; Nengjie Huo et al., 2014; W. Wu et al., 2014).

1.2. MoS₂ thin film structures

MoS₂ thin film structure is a system that consists of two sulphur (S) atoms and one molybdenum (Mo) atom in a crystal lattice. Monolayer of MoS₂ consists of Mo⁴⁺ and S²⁻ ions bonded with covalent bonding type while the bounding type between MoS₂ layers is van der Waals which allows producing easily stacked hetero-junctions. Among the TMDCs, MoS₂ has been one of the most studied layered transition metal dichalcogenides because it has been found widely in nature (X. Li & Zhu, 2015). Figure 1.5 shows the stacking behavior of 2H MoS₂ layers with van der Waals bonds. The hetero-junction systems can be produced by combining different materials with different properties using van der Waals forces.

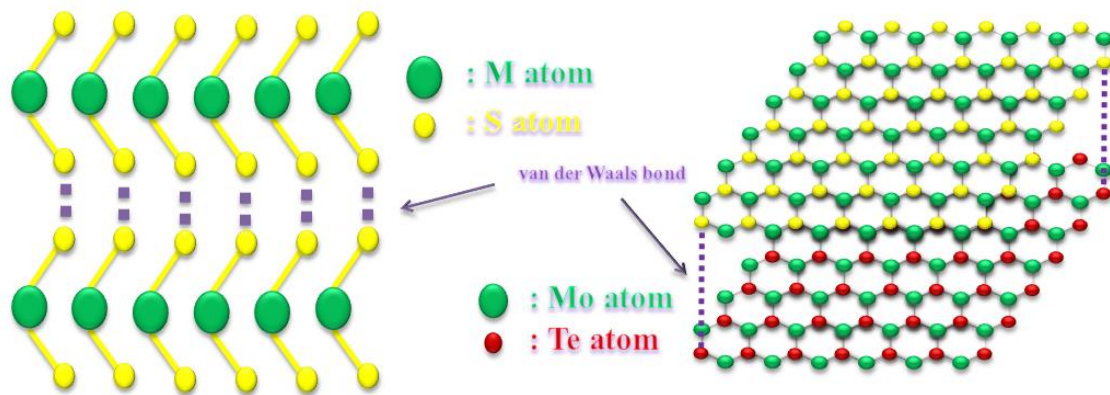


Figure 1.5. Schematic illustration of 2H-MoS₂ layers bonded with van der Waals forces and heterojunction system produced by using van der Waals interactions.

The common crystal phases of MoS₂ are 2H (trigonal prismatic) and 1T (octahedral). The crystal systems of materials specify physical properties. For example, MoS₂ behaves as semiconducting material in the 2H phase, while it behaves as metallic in the 1T phase. The electrical band structure of MoS₂ changes with the thickness. The changing in electrical band structure is controlled with quantum confinement effect. In bulk form, MoS₂ behaves as a semiconductor with indirect band gap structure. This behavior vanishes with the decreasing

number of the MoS₂ layer. Eventually, a few layers of MoS₂ behave as semiconductor materials with the band gap 1.8 eV (see Figure 1.3).

There are several approaches to produce MoS₂ thin films which are chemical vapor deposition, mechanical exfoliation, physical vapor deposition, thermal decomposition of precursors. The most common method to produce MoS₂ thin film structure is thermal decomposition of precursor and CVD technique. The thermal decomposition method enables the manufacture of highly crystalline and good quality films at low temperatures by using a mixture of H₂ and inert gases (Ar/N₂). The CVD technique also enables highly crystalline film structure. The differences between these techniques are the coating method and precursor. The precursor is generally chosen as the MoO₃ and S source for CVD method while the precursor of thermal decomposition method is chosen ATTU.

MoS₂ has desirable properties for sensing applications, field effect transistors, hydrogen evolution reaction (HER), photovoltaic devices, energy-storage devices and phototransistors due to its band gap value $\cong 1.8$ eV (Chang & Chen, 2011; Nengjie Huo et al., 2014; Nengjie Huo, Yang, & Li, 2017; Y. Li et al., 2011; Y. C. Lin et al., 2012; Radisavljevic et al., 2011). A few layers of MoS₂, each MoS₂ layer has 0.65 nm thickness, have weakly bonded with each other by van der Waals bonding and this property allows us to use these materials as a lubricant (X. Zhang et al., 2009). Few-layered MoS₂ can also be used in piezoelectricity applications because few-layer MoS₂ causes oscillation in piezoelectric voltage and current outputs (Han et al., 2019; W. Wu et al., 2014). The Young modulus value and crystal straightness allow bending to the film without any signal loss and this feature encourages the film to be used in flexible applications (Akinwande, Petrone, & Hone, 2014).

1.3. Introduction to magnetism

Classical atomic model suggests that moving of electrons around a nucleus having radius R with a velocity V create a current (I) in the opposite direction to motion of electrons (see Figure 1.6). As a result, a loop of current generates a magnetic moment $\vec{\mu} = I\vec{A}$ (where $\vec{A}$ is a normal area vector).

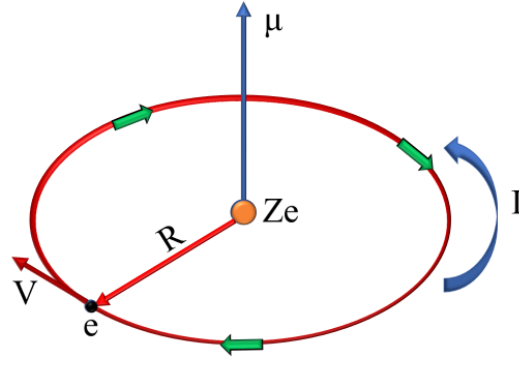


Figure 1.6. Magnetic moment produced by current loop (Akyol, 2011).

Figure 1.6 shows the schematic illustration of electron nucleus interaction. For a simple atom having one electron (H:hydrogen), this electron-nucleus interaction is described as following,

$$I = \frac{eV}{2\pi R} \quad (1)$$

where V is the velocity of electron and e is the charge of electron. The magnetic dipole is written as follows.

$$|\vec{\mu}| = |I\vec{A}| = \frac{eV}{2\pi R} \pi R^2 |\hat{A}| \quad (2)$$

Orbital angular momentum is included the magnetic dipole term, following equation is obtained.

$$\vec{L} = m\vec{V} \times \vec{R} \quad (3)$$

$$|\vec{\mu}| = \frac{1}{2} eVR |\hat{A}| = \frac{e}{2m_e} |\vec{L}| = \gamma |\vec{L}| \quad (4)$$

where γ is gyromagnetic ratio. The electrons not only have orbital angular momentum but also have a spin angular momentum that can be written with the operator $\hat{S}^2$.

$$\hat{S}^2 \chi = \hbar^2 s(s+1) \chi \quad (5)$$

Following equation gives the quantized angular momentum.

$$|\vec{S}| = \hbar\sqrt{s(s+1)} \quad (6)$$

Thus, spin magnetic moment can be written as in equation (7);

$$|\mu_s| = \gamma|\vec{S}| = \gamma\hbar\sqrt{s(s+1)} \quad (7)$$

The magnetic dipole created by the orbital and spin angular momentum can be written in terms of Bohr magneton which is $\mu_B = e\hbar/2m_e$;

$$|\mu_s| = \gamma|\vec{S}| = \mu_B\sqrt{s(s+1)} \quad (8)$$

$$|\mu_l| = \gamma|\vec{L}| = \mu_B\sqrt{l(l+1)} \quad (9)$$

Then, total contribution of orbital and spin angular momentum to magnetic dipole is given as follows,

$$|\mu_j| = \gamma|\vec{J}| = \mu_B\sqrt{j(j+1)} \quad (10)$$

where (j) refers to the total angular momentum quantum number which is equal to the sum of the orbital angular momentum and spin angular momentum as given in equation 11.

$$\vec{J} = \vec{L} + \vec{S} \quad (11)$$

1.4. Classification of magnetic materials

The magnetic behavior of materials originates from orbital and spin movements of electrons and the interactions between electrons in orbitals. There are different kinds of magnetic behaviors which can be determined by the interaction of material to applied magnetic fields.

These magnetic behaviors of materials are expressed as diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism.

1.4.1. Diamagnetism

Diamagnetism is a magnetic behavior that causes an opposite alignment of spins of materials to applied magnetic field that means diamagnetic materials have negative magnetic susceptibility. When the applied field is removed, the magnetic susceptibility disappears and magnetization vanishes.

In a circular wire, an electromotive force is induced by the changing of the current. Then, the electromotive force starts to shift the state of the current previous condition. In this situation, electrons can be expressed as a current passing through the wire and the wire is orbital of the atom. The magnetization occurs when an external magnetic field is applied. The direction of magnetization and external magnetic field are opposite to each other. As a result, the applied magnetic field is pushed by the material (Akyol, 2011). Materials having this structural behavior are called "diamagnetic" materials. DNA, water, petroleum and a great deal of plastic materials show diamagnetism.

When an external magnetic field is applied, a small amount of negative magnetic moment is induced which is proportional to the magnitude of the applied field. Figure 1.7 shows the schematic illustration of diamagnetic behavior of material with and without external field.

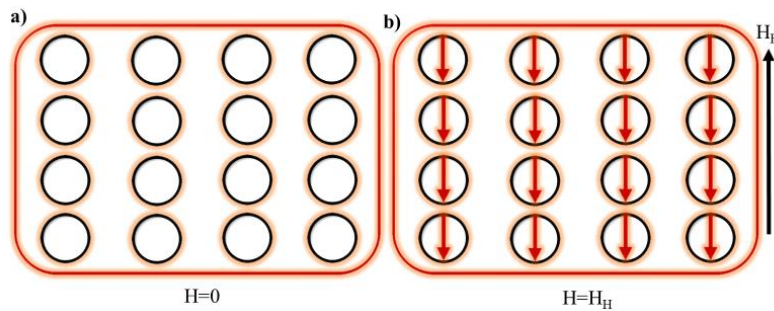


Figure 1.7. Arrangement of the magnetic moments of a diamagnetic material a) without an external magnetic field and b) an external magnetic field is applied (Gülkesen, 2020).

Figure 1.8 shows the behavior of magnetization under applied magnetic field for the diamagnetic materials. As can be seen in Figure 1.8, an opposite directional magnetization is

formed by the diamagnetic material on the applied area. When the external magnetic field is increased, the magnetization of a diamagnetic material increases in the opposite direction. On the other hand, the net magnetic moment of a material turns to zero when the applied field is removed. The magnetic susceptibility in a diamagnetic material is expressed by the mathematical relationship as $\chi = M/H$ where M is magnetization and H is applied magnetic field.

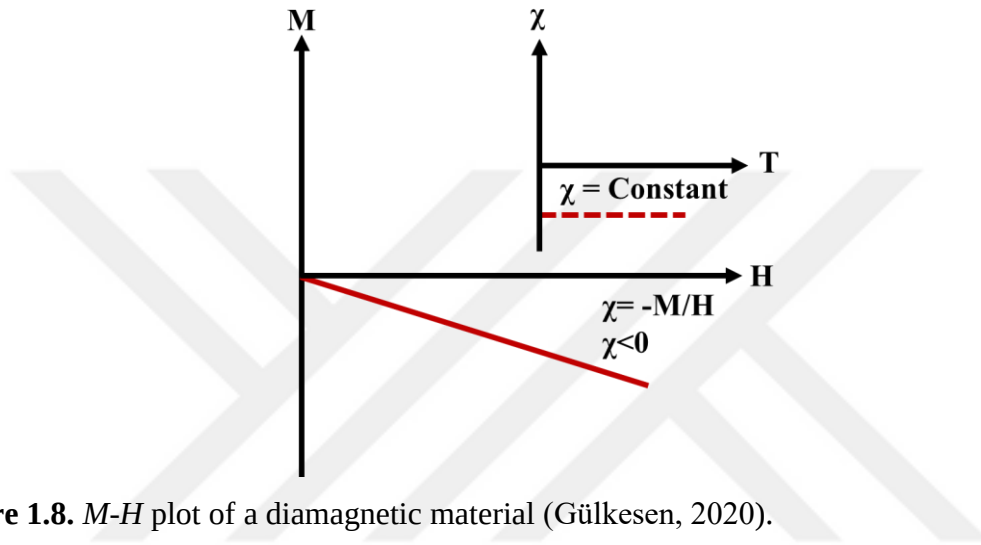


Figure 1.8. M - H plot of a diamagnetic material (Gülkesen, 2020).

1.4.2. Paramagnetism

Paramagnetism is a magnetic behavior that creates a small amount of magnetic moment in the direction of an applied magnetic field. There is a net magnetic moment for paramagnetic atoms in the absence of an applied magnetic field. Although each atom of material has net magnetic moment, an interaction between these atoms does not occur due to the presence of unpaired electrons in the orbits of atoms and this leads to occurrence of no net magnetic moment for paramagnetic materials without an applied field.

As can be seen in Figure 1.9, magnetic moments of atoms are randomly oriented in lattice when there is no external magnetic field. The orientations of magnetic moments are constantly changed by the thermal fluctuation in the system which causes the net magnetic moment to be approximately zero. In the presence of an external magnetic field, some of the moments are lined up in the direction of the applied field but the spin orientation remains random which causes a small amount of net magnetization. Figure 1.9(b) shows the saturation state of the magnetization in the presence of an applied strong magnetic field. In other cases,

when the magnitude of the external magnetic field is low, the moments cannot be oriented as seen in Figure 1.9 (Akyol, 2011).

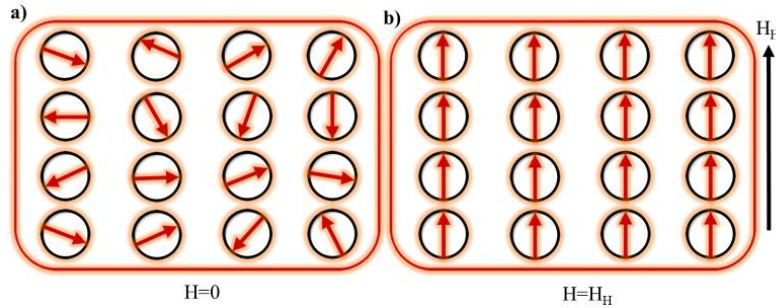


Figure 1.9. Arrangement of the magnetic moments of a paramagnetic material a) absence of external field and b) presence of external field (Gülkesen, 2020).

Figure 1.10 shows the behavior of a paramagnetic material to the external magnetic field. The magnetic moments of paramagnetic material, which are randomly orientated, begin to arrange in the same direction of the applied field. The magnetization is relaxed by the magnetic moments in the same direction of the external field. A linear increase is observed when the amount of external field increases. This linear increase is caused by the regulation of magnetic moments by the increasing external field amount. The saturation magnetization is observed if the external field is of adequate value.

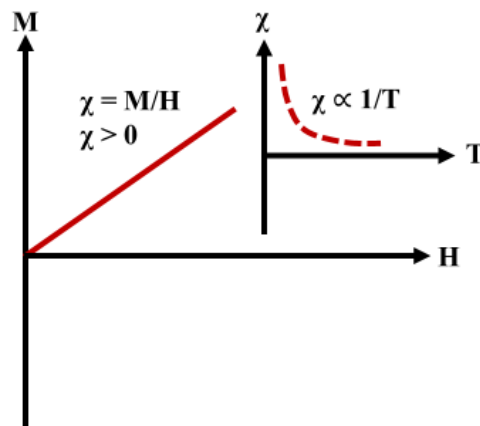


Figure 1.10. M - H plot of a paramagnetic material (Gülkesen, 2020).

1.4.3. Ferromagnetism

In ferromagnetism, there is a net magnetic moment of atoms even if there is no external magnetic field. The spin coupling which is formed by unpaired electrons in the d -shell of transition metals resulting from exchange energy which causes spin sorting leads to formation

of long distance magnetic moment order. The thermal fluctuations cause the changing magnetic behavior of ferromagnetic materials at a certain temperature which is called Curie temperature (T_C). The long distance atomic order of ferromagnetic materials is ensured by the domains which are caused by unpaired electron spins lined up parallel to each other in regions. In the absence of an external magnetic field, the domains having internal magnetization remain present. Figure 1.11(a-b) shows a ferromagnetic material's magnetic moment alignments under zero and applied magnetic fields, respectively.

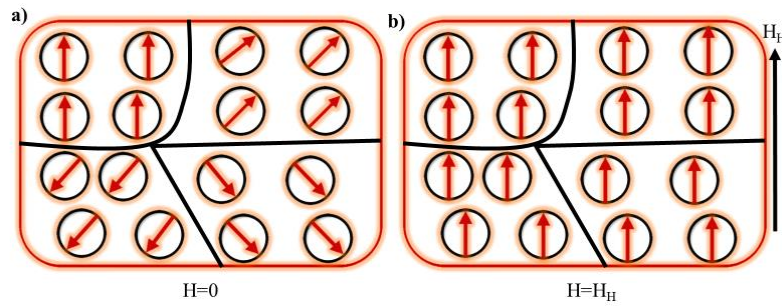


Figure 1.11. Arrangement of the magnetic moments of a ferromagnetic material a) external magnetic field is not applied and b) external magnetic field is applied (Gülkesen, 2020).

The ferromagnetic materials show an irreversible and nonlinear magnetization in the field-dependent direction in the presence of an applied field. This behavior is identified by the hysteresis loop. Figure 1.12(a) shows the magnetic moments' reaction of ferromagnetic materials against applied magnetic fields. The hysteresis loop of hard and soft ferromagnetic materials is shown in Figure 1.12(b-c), respectively (Coey, 2010).

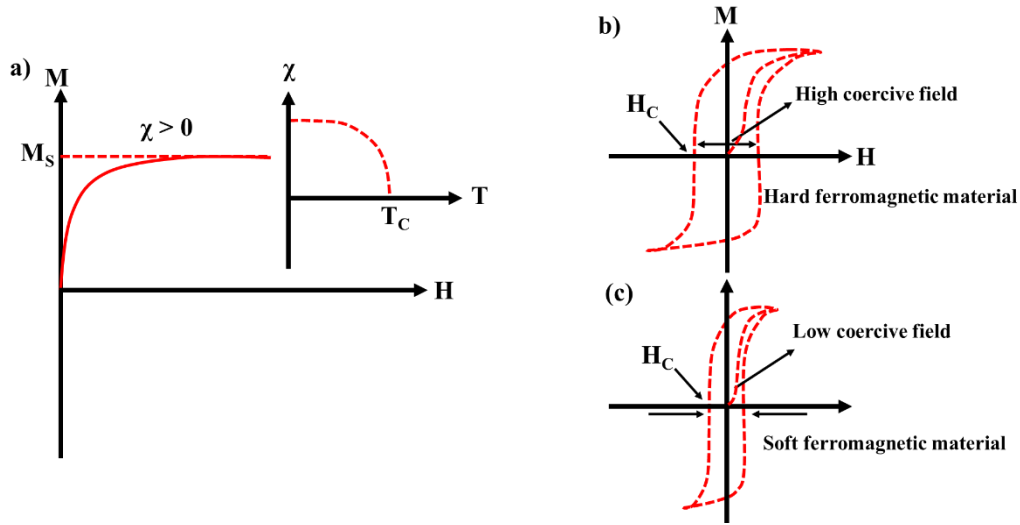


Figure 1.12. a) M - H plot of a ferromagnetic material. Hysteresis curves of b) hard and c) soft ferromagnetic material (Gülkesen, 2020).

In the presence of an external field, the atoms in the ferromagnetic material begin to rotate and regulate rapidly in the applied field direction. The total magnetization of the material increases abruptly due to this response. The magnetization of ferromagnetic material reaches saturation magnetization (M_s) value by increasing external magnetic field value (Coey, 2010). Figure 1.12(b) shows that the behavior is hard ferromagnetic materials having large coercive field (H_C) value. The soft ferromagnetic materials behavior is shown in Figure 1.12. In the presence of external fields, these materials have small coercive field values. When the external field is removed, the magnetization value of these materials disappears. Because of this, they are called temporary magnets. In order to reveal the spontaneous/natural ferromagnetic order that already exists on the scale of microscopic domains, an external magnetic field is used (Coey, 2010).

1.4.4. Antiferromagnetism

The alignment of neighboring magnetic moments in antiferromagnetic material is anti-parallel in sequence due to the super exchange interaction. Thus, the nearest neighboring magnetic moments cancel each other (Coey, 2010). Due to the anti-parallel-aligned spins, antiferromagnetic materials have a small positive magnetic susceptibility. The long range order for these materials is present. The orientation of the magnetic moments of the atoms with and without applied field is shown in Figure 1.13.

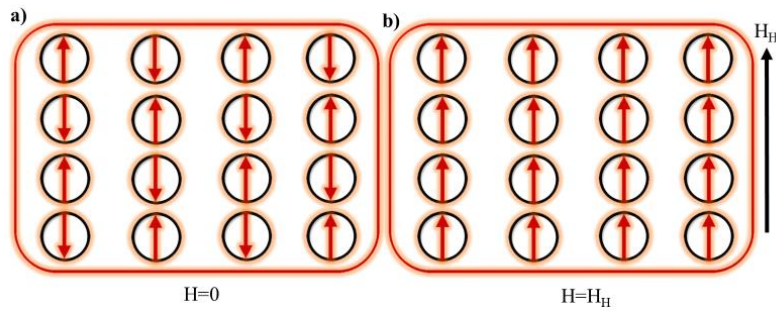


Figure 1.13. Arrangement of the magnetic moments of an antiferromagnetic material a) in the absence of external field and b) in the presence of applied field (Gülkesen, 2020).

If magnetic moments in an antiferromagnetic material are equally strong, each moment cancels the other moment as seen in Figure 1.13(a). Figure 1.13(b) shows the atomic moments under an applied magnetic field. In the presence of an external magnetic field, the opposite oriented magnetic moments become lined up and the magnetization value occurs in the same direction as the applied field. When the applied field increases, the total magnetization value increases. When the external magnetic field reaches sufficient values, the magnetization of the material is expected to reach its saturation value. Figure 1.14 shows the M - H curve of antiferromagnetic materials.

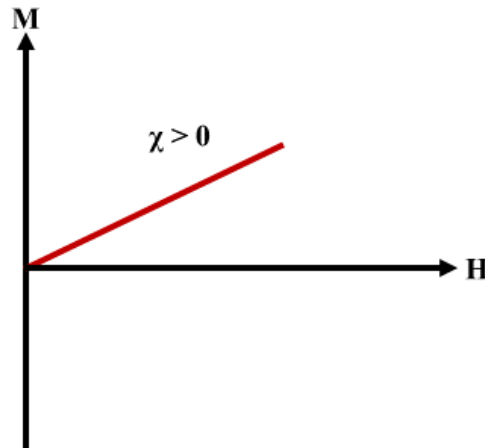


Figure 1.14. M - H plot of an antiferromagnetic material (Gülkesen, 2020).

1.4.5. Ferrimagnetism

In ferrimagnetism, the moment alignment with the neighboring magnetic moments is anti-parallel in sequence, but their magnitudes are different. With these characteristics, ferrimagnetic materials are separated from antiferromagnetic materials. The magnetic moments of ferrimagnetic materials do not cancel because of the different magnitudes. The

saturation magnetization value of ferromagnetic materials is bigger than ferrimagnetic materials. In terms of hysteresis behavior, these materials are similar to ferromagnets. Two different types of atoms form the structure of ferrimagnetic materials. Due to the super-exchange interaction between magnetic moments, the anti-parallel alignment of the magnetic moments occurs. Figure 1.15 shows the alignment of magnetic moments before and after a sufficiently high external magnetic field is applied from the outside.

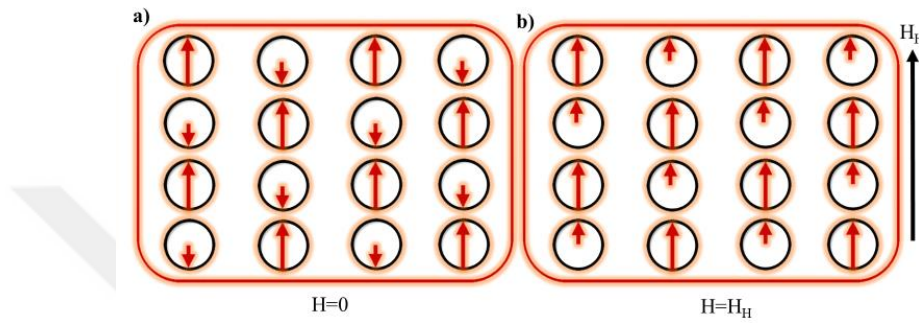


Figure 1.15. Arrangement of the magnetic moments of a ferrimagnetic material under a) zero magnetic field and b) applied magnetic field (Gülkesen, 2020).

The response of a ferrimagnetic material to the applied field is seen very similar to the response of a ferromagnetic material but the saturation magnetization value is different. The M_s value of ferromagnetic materials is bigger than ferrimagnets. The magnetization value increases with the increasing applied field. After some point where the applied field is high and sufficient, the material's magnetization saturates which means all moments are aligned with the same direction of the applied external field. M - H plot of a ferrimagnetic material is shown in Figure 1.16.

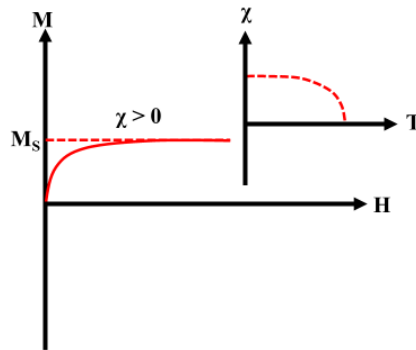


Figure 1.16. M - H plot of a ferrimagnetic material (Gülkesen, 2020).

1.5. Curie temperature and Curie-Weiss law

There is a critical temperature point where the behavior of ferromagnetic materials changes from ferromagnetic to paramagnetic which is called Curie temperature, T_c . Increasing temperature values cause the thermal vibrations which affects the magnetic orientation of ferromagnetic moments. Then, material behaves as paramagnetic above T_c . The magnetic susceptibility (χ) can also be expressed in terms of temperature by following equation;

$$\chi = \frac{M}{H} = \frac{C}{T} \quad (12)$$

where C is Curie constant. Magnetic moment per unit volume or mass is defined as magnetization of material which depends on the individual magnetic dipole of the atoms in material and interactions between these dipoles. The relations of moments of ferromagnetic materials cause an influence of single moments by the average molecular field formed by other magnetic moments. This expression was first described by Weiss (Weiss, 1906) with the molecular field theory. When the temperature is above the Curie temperature, materials behave as paramagnetically, the equation is written as follows.

$$\chi = \frac{C}{T - \theta} \quad (13)$$

This equation is called Curie-Weiss law (Weiss, 1906). θ is a temperature constant which takes negative, positive and zero values changing with the type of magnetic materials such as antiferromagnetic, ferro/ferri-magnetic and paramagnetic, respectively.

- If $\theta = 0$, Curie law (equation 12) takes over.
- If $\theta > 0$, the material is ferromagnetic below Curie critical temperature, T_c .
- If $\theta < 0$, the material is antiferromagnetic below the Neel critical temperature, T_N .

The magnetic transition temperature of ferromagnetic and antiferromagnetic materials which are Curie and Neel temperatures respectively can be seen in Figure 1.17. A ferromagnetic (antiferromagnetic) material behaves as paramagnetic materials when the temperature is above the Curie (Neel) temperature (Coey, 2010).

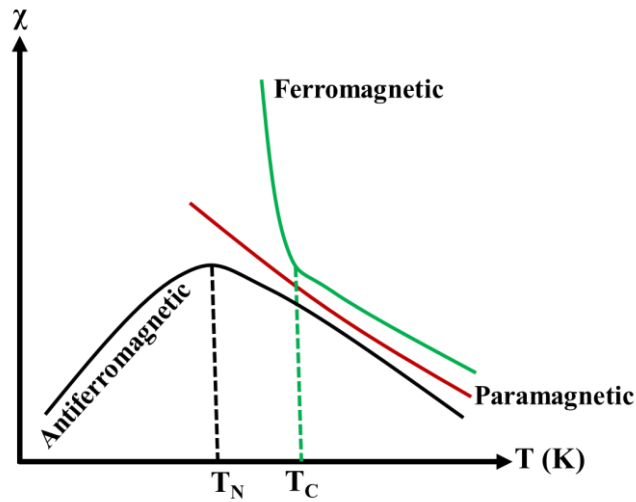


Figure 1.17. Magnetic transition of antiferromagnetic and ferromagnetic materials (Gülkesen, 2020).

1.6. Magnetic Hysteresis loop

When an external magnetic field is applied to ferrimagnetic or ferromagnetic materials, the magnetization value becomes a complex situation. The hysteresis loops of materials allow understanding and analyzing the change in magnetization. The saturation magnetization (M_s), remenant magnetization (M_r) and coercive field (H_c) of a magnetic material can be obtained from hysteresis loops. The hysteresis loops of multi-domain magnetic material are shown in Figure 1.18.

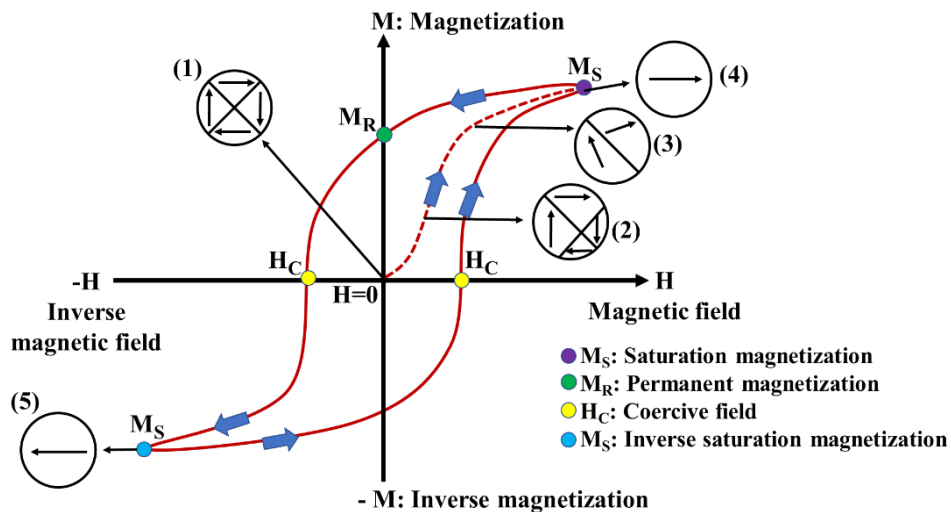


Figure 1.18. Hysteresis loop of a multi-domain magnetic material (Gülkesen, 2020).

In the absence of external magnetic field, ferrimagnetic and ferromagnetic materials give net magnetization value. When the external field is applied, their magnetization values increase with the increasing field ending with a point which is called saturation magnetization. Most of the ferromagnetic materials show remanent magnetization (the green point at Figure 1.18) when the applied external field is removed. When the applied magnetic field is changed to opposite direction, the magnetization is forced to be zero at coercive value (yellow point) which is the half width of the hysteresis loop. This point leads to understanding how to magnetize material easily or difficulty. The H_c value of materials describes the types of magnetic behavior which are called “hard magnetic materials” and “soft magnetic materials”. The coercive field larger (lower) than 100 Oe (10000 A/m) is called as hard (soft) magnetic material.

1.7. Thesis objectives

In this thesis, the objectives are to produce crystalline ferromagnetically doped MoS₂ thin films and investigate structural and magnetic characteristics of produced samples. In order to deposit MoS₂ thin films, we used spin coating technique. First, optimization samples were produced by changing parameters of the system. Then, main samples of the thesis were manufactured after selecting optimal parameters and their properties were investigated.

2. LITERATURE REVIEW

In this chapter, the studies that carried out manufacturing and characterizing of MoS₂ thin films are mentioned. At the beginning of this chapter, the research about manufacturing pure MoS₂ thin film structure takes place, then theoretical and experimental research about doped MoS₂ thin film materials will be given. At the end of chapter, studies on device manufacturing by using MoS₂ thin films as the main or supportive material in the device structure will take place.

Liu et al. produced high quality and large area MoS₂ films by thermolysis of (NH₄)₂MoS₄ (ATTM) at high temperature with addition of sulphur. The solution containing Dimethylformamide (DMF) and ATTM was prepared with a ratio of 1.25%wt then coated on to the sapphire and Si/SiO₂ substrates by dip coating system with slow pulling (0.5 mm/s). Two-step heat treatment process was applied on the coated films. In the first step, the thermal process was applied at 500°C under Ar/H₂ (flow rate is 4:1) flow at pressure of 1 torr for 1 hour. Then, samples were heated up to 1000°C temperature with a mixture of Ar and sulphur at the pressure of 500 torr for 30 minutes. In order to show the impact of the additional sulphur, they made Raman measurements of the films before and after the second step of the thermal process in order to compare properties of films. According to results, the intensity of the two characteristic Raman peaks of the MoS₂ E_{2g}^1 and A_{1g} significantly increases with additional sulphur at 1000°C. Raman shifts of bilayer MoS₂ stay at 384.6 cm⁻¹ and 404.6 cm⁻¹ for more diluted solution with fast pulling times. On the other hand Raman shifts of the trilayer MoS₂ stays at 383.1 cm⁻¹ and 405.4 cm⁻¹ for normally prepared solution and normal pulling times. They carried out photoluminescence (PL) measurement for trilayer MoS₂ annealed at 1000°C with sulphur addition which shows stronger PL intensity compared to trilayer MoS₂ annealed at 1000°C without sulphur addition. They also examined the MoS₂ films annealed at 800, 900, 950°C temperatures. The results of these samples show that 1000°C has the strongest PL intensity. In order to examine the quality of films, they produced trilayer MoS₂ coated on sapphire and Si/SiO₂. They reported that the film grown on sapphire substrate shows better quality than the film grown on Si/SiO₂ substrate. The thickness and topography of the trilayer MoS₂ annealed at 1000°C were found as 2 nm and uniformly flat by performing atomic force microscope (AFM) measurements. The high resolution tunneling

electron microscopy (HRTEM) and selected area electron diffraction (SAED) pattern show that film is highly crystalline and MoS₂ lattice parameters belong hexagonal P₆₃/mmc symmetry group with constants of $a = b = 3.1 \text{ \AA}$, $c = 12.8 \text{ \AA}$. The lateral size of the crystal domain of the film grown on sapphire with sulphur addition is larger than 160 nm. The domain size of the film grown on sapphire at 1000°C with Ar is bigger than the samples grown on Si/SiO₂ at 1000°C with Ar+H₂. They used grazing incidence angle X-ray diffraction (GIA-XRD) and in-plane X-ray diffraction (in-plane XRD) measurements to show the effect of sulphur addition on crystal properties of the films. According to GIA-XRD measurements, there are two peaks for sample annealed in the Ar+S atmosphere at $2\theta = 50.6^\circ$ and 56.1° for diffraction planes (105) and (106), respectively. These peaks did not emerge for sample grown in pure Ar atmosphere. As for the in-plane XRD measurement, the peaks which stay at $2\theta = 33.1^\circ$ and 58.9° for diffraction (100) and (110) are similar for both samples. The X-ray photoelectron spectroscopy (XPS) shows the appearance of the Mo 3d at 229.3 and 232.5 eV which mean the doublet Mo 3d_{5/2} and Mo 3d_{3/2}, respectively. The sulfide ions (S²⁻) peaks which are S 2p_{1/2} and S 2p_{3/2} are observed at 163.3 and 162 eV, respectively. According to the XPS and TEM-based energy dispersive spectroscopy (TEM-EDS), the films grown in pure Ar show high oxygen content (22.2 atomic %) compare to samples grown on sulphur addition (~6.7 atomic %). They fabricated bottom-gate transistor based trilayer MoS₂ grown on sapphire transferred to Si/SiO₂ substrate. According to the typical transfer curves of devices produce from trilayer MoS₂ with and without sulphur addition, the on/off current ratio of device annealed with Sulphur (1.6×10^5) is bigger than the device annealed without Sulphur (2.4×10^3) (Liu et al., 2012).

Lim et al. fabricated wafer-scale, homogenous MoS₂ thin films by using a two-step thermal decomposition process of (NH₄)₂MoS₄ (ATTM) as a single source precursor at low temperature under H₂. They used solution-processed technique for synthesizing MoS₂ thin films on different substrates such as Si/SiO₂ (300nm), polyimide and glass. They investigated both the structural properties of the MoS₂ thin films on different substrates and photoelectric device properties of MoS₂ thin film by producing MoS₂-based visible light detector and electrochemically gated MoS₂ field effect transistors (FETs). At the solution part of this research, this team used ethylene glycol (EG) as solvent material. They prepared 1.25 %wt. (NH₄)₂MoS₄ solution to produce thin films. They used this solution to coat on different substrates by a spin-coating system. The two step thermal process used to crystallize thin

films. First, samples annealed at 280°C under N₂ flow at pressure of 1.8 torr for 30 minutes. Then, the heat increased 450°C and samples annealed at this temperature under 100 sccm H₂ and N₂ gases flow at the same pressure for 30 minutes. According to the Raman spectra of films, typical vibration modes of hexagonal MoS₂, E_{2g}¹ and A_{1g} were observed at 382.4 cm⁻¹ and 405.8 cm⁻¹, respectively. The difference between these peaks corresponds to layer number of MoS₂ thin films is $\cong 23.4$ cm⁻¹. TEM results of the study shows that number of the layer and interlayer spacing of MoS₂ thin film which are 5 and $\cong 6$ Å, respectively. The optical transmittance of films was found to be 90.8% at 550 nm. This team also fabricated thin film produced from the solution containing N,N-dimethylformamide and showed the XRD results of films. According to XRD results of these films, main peaks of MoS₂ were observed at 14°, 24° and 44° corresponding to (002), (100) and (104) crystal planes, respectively. In order to examine photo electrical performance of MoS₂ thin films, they produced MoS₂-based visible light detector arrays on 4 inch Si/SiO₂ wafer and MoS₂-based visible light detector on flexible polyimide. According to the photo electrical measurements of films, the spatial distribution of all devices showed a homogenous photocurrent independent of device location. The photocurrent of the flexible photo detector coated on polyimide decreased 5.6% after 10⁵ cycles at 5 mm radius bending (Lim et al., 2016).

Qi *et al.* reported a study about manufacturing large-area MoS₂ thin film grown on Si/SiO₂ substrate using thermal decomposition of (NH₄)₂MoS₄ at 500°C and investigated the effect of the H₂ on thin films. They prepared 40mM solution including (NH₄)₂MoS₄ and DMF. They used (H₂SO₄/H₂O₂~7/3) piranha solution in order to clean films. The coating parameter of films was chosen as 3000 rpm for 20 s and 6000 rpm for 60 s. The Ar/H₂ mixture gas was introduced to the system under a 3×10^{-3} Pa vacuum atmosphere. The heat treatment was carried out at 500°C for 60 min. According to the Raman results of study, E_{2g}¹ and A_{1g} (in-plane and out of plane) vibration modes of MoS₂ were observed at 382.4 cm⁻¹ and 405.7 cm⁻¹, respectively. The difference between vibrations modes were calculated as 23.3cm⁻¹ which equals trilayer MoS₂. The AFM results show that the surface roughness and height of the film are 0.48 nm and 2.4 nm, respectively. The binding energies of Mo 3d were observed at 229.7 eV and 232.9 eV corresponding to 3d_{5/2} and 3d_{3/2}, respectively which shows the Mo⁴⁺ state. In order to examine the effect of H₂ on MoS₂ thin films, the H₂ flow was set as 0 to 100 sccm. According to the S/Mo ratio of films, the 2.0 ratio can be reached by introducing 100 sccm H₂ flow into the system. According to the XPS results of samples exposed different H₂ flow from

0-100 sccm, the Mo^{+6} state corresponds to the MoO_3 peak decreasing with increasing H_2 flow (Qi et al., 2015).

Gong et al. fabricated flexible MoS_2 thin films at 450°C via chemical vapor deposition (CVD) method by using polyimide as substrate. They used $(\text{NH}_4)_2\text{MoS}_4$ as a precursor of the system and they carried out a heat treatment procedure under Ar/H_2 gas flow. In order to fabricate MoS_2 thin films, they selected parameters of the CVD system as 250°C for low temperature zone and 450°C for high temperature zone for 10 minute deposition. They fabricated a flexible light-detector device in order to investigate photo-electronic properties of MoS_2 thin films. According to the Raman results of flexible films, the layer number of MoS_2 found monolayer film from 20.1 cm^{-1} Raman peaks width. The AFM results showed the layer thickness of MoS_2 as 1.4 nm and fish-net wrinkles of film surface. According to the study, these kinds of wrinkles are caused by the cooling process. The scanning transmission electron microscope (STEM) and annular dark field STEM results of films showed that the structure has high quality and the continuous hole-free films. According to the mechanical-optoelectrical properties of structure, the enhancement in photocurrent was observed when the strain reached 0.79%. After this value, the photocurrent begins to decrease. They clarified this phenomenon as the reason for this can be that the band gap value of 2D structure decreases when strain applied (Gong et al., 2017).

George et al. produced atomically thin MoS_2 via thermolysis of $(\text{NH}_4)_2\text{MoS}_4$ precursor coated by using spin coating technique. In order to prepare a solution of MoS_2 thin films, they dissolved $(\text{NH}_4)_2\text{MoS}_4$ in n-methylpyrrolidone (NMP). They used toluene, acetone and isopropanol to clean Si/SiO_2 substrates by 45 minutes waiting period for each solvent in sequent. Then, RCA clean SC-1 (5 parts DI water, 1 part NH_4OH , 1 part H_2O_2) was used as last cleaning procedure for 15 minutes. The spin coating parameter of the system was chosen as 3000 rpm for 1 min. The heat treatment procedure was applied in 3 steps. The first step is heating films at 100°C in order to remove residual NMP. The second step is annealing at 480°C under (200/400 sccm) Ar/H_2 gas flow for 1 hour and the third step is another annealing process at 1000°C under Ar gas flow in order to enhance crystallinity of the films. According to the AFM results of films, the thickness is $\cong 1.3 \text{ nm}$ corresponding to bilayer MoS_2 and the surface roughness of films 0.25 nm. High-angle annular dark-field scanning TEM (HAADF-STEM) results of films proved that the films have AB stacking corresponding to the 2H

MoS₂. The Mo 3d peaks were observed at 232.2 and 235.5 eV corresponding to the 3d_{3/2} and 3d_{5/2} binding energies for the Mo⁴⁺ state, respectively. The binding energies of sulphur were observed at 232.5 eV and 229.3 eV. According to the Raman results of MoS₂ thin films, the difference between two characteristic MoS₂ peaks is 19.3 cm⁻¹ which corresponds to monolayer MoS₂. The PL spectra of MoS₂ showed that the band gap energy was 1.84 eV. They fabricated few-layer MoS₂ FETs on Si/SiO₂ substrate in order to evaluate transport properties of structure. The mobility and on/off current ratio of the device were found as 0.1 cm² V⁻¹ s⁻¹ and 108, respectively. MoS₂ film shows n-type switching behavior and the threshold voltage is ≈70 V (George et al., 2014).

Wu *et al.* fabricated MoS₂ monolayer structure via catalyst-free vapor-solid mechanism on different substrates such as Si/SiO₂, glass and sapphire. The crystal quality and defect of the MoS₂ thin films was investigated by valley polarization approach. They used MoS₂ powder as the material supplement of the system. The substrates were cleaned with acetone, isopropyl alcohol and deionized water then the precursor and substrate was placed in the cool zone of the furnace (650°C). Then, Ar gas was introduced to the furnace and the system was pumped at 20 torr. After the pump started to clear the system from oxygen, the furnace temperature was set as 900°C. System waited at this temperature for 15-20 minutes, and then it cooled down. According to the SEM images of the films, the lateral dimension of crystals is 25 μm and their shapes were observed as triangles. Optical microscope images shows that the films grow on sapphire denser than other substrates (glass and Si/SiO₂). The layer thickness of the film grown Si/SiO₂ is 0.75 nm. The two characteristic Raman peaks of MoS₂ were observed at 386 cm⁻¹ and 405 cm⁻¹ for Si/SiO₂ substrate, 384 cm⁻¹ and 404 cm⁻¹ for sapphire substrate, 385 cm⁻¹ and 404 cm⁻¹ for glass substrate. The differences between these peaks are 19 cm⁻¹, 21 cm⁻¹ and 19 cm⁻¹ for Si/SiO₂, sapphire and glass, respectively. According to the polarization-resolved photoluminescence spectra of samples, there is only a single emission peak at 1.9 eV for Si/SiO₂ substrate which corresponds to the absence of impurity. The degree of polarization of Si/SiO₂ sample is almost unity. On the other hand, this value is 95% for sapphire substrate. The PL polarization at room temperature approaches maximum of 35% at 1.92 eV for Si/SiO₂ and sapphire samples which is quite as good as mechanically exfoliated MoS₂ thin films (S. Wu et al., 2013).

Lin et al. fabricated atomically thin MoS₂ film structure by two-step thermal processes of reduction of MoO₃ thin films as precursor material. They used sapphire substrate to deposit MoO₃ powders on the surface. Piranha solution was used to clean substrate. The MoO₃ film was coated by introducing MoO₃ powder quartz tube from cold zone to 500°C temperature zone under Ar/H₂ (4/1) gas flow at 1 torr for 1 hour. After 1 hour, the film was taken to the cold zone of the furnace. Then sulphur powder was introduced to the furnace and the heat set as 1000°C. The film was annealed at this temperature under 70 sccm Ar flow at pressure 600 torr for 30 minutes. According to the AFM results of film, the root-mean-square roughness is 0.2 nm and the thickness of the layer ranges from 1.8 to 2.0 nm. The thickness of each layer was observed as 0.65 nm at TEM measurements. The SAED measurements approve the thickness of the film as 1.9 nm. The XPS measurements show that binding energies of Mo 3d peaks are observed at 232.5 and 229.3 eV corresponding to Mo 3d_{3/2} and Mo 3d_{5/2} for Mo⁴⁺ state, respectively. The two characteristic Raman peaks of MoS₂ are observed at 385.5 cm⁻¹ and 406.5cm⁻¹. In order to investigate electrical properties of MoS₂ films, they fabricated a bottom-gate transistor grown on Si/SiO₂. According to the drain current and drain voltage measurements, on/off ratio of device showed n-type behavior is $\approx 10^5$ and field electron mobility is 0.8 cm²V⁻¹s⁻¹ (Y. C. Lin et al., 2012).

Xie et al. fabricated heavy metal/transition metal ferromagnet structure built on MoS₂ and they investigated the structural and magnetic characteristics of film. They used magnetron sputtering technique to produce samples which are Si/SiO₂/MoS₂(2L)/Pt(t_{pt}:0.5-15nm)/[Co/Ni]₂ and Pt(t_{pt}:0.5-15nm)/[Co/Ni]₂ [Co/Ni]. In addition, they produced various samples consisting of different layer thickness combinations to investigate spin orbit torque (SOT) efficiency and perpendicular magnetic anisotropy (PMA) values of the structures further. The thickness of the [Co/Ni] layers is 0.76 nm for both samples. According to the Raman results of sputtered MoS₂ film, two characteristic peaks E_{2g}^1 and A_{1g} were observed at 384.3 cm⁻¹ and 405.1cm⁻¹. The frequency difference between two peaks is 20.8 cm⁻¹ which corresponds to the two layers (2L) of MoS₂. PL peak position of MoS₂ was observed at 1.87 eV corresponding bilayer film. The binding energies of Mo 3d_{5/2} and 3d_{3/2} observed at 229.1 eV and 233.6 eV, respectively. These results show that the chemical state of Mo in the MoS₂ structure which is Mo⁺⁴. On the other hand, the binding energies of S 2p_{3/2} and 2p_{1/2} peaks were observed at 162.5 and 163.4 eV, respectively. The cross sectional TEM images of samples MoS₂ (2L)/Pt(4)/[Co/Ni]₂ and Pt(4)/[Co/Ni]₂ shows that the interface between MoS₂

and Pt clear and Pt in both samples shows good texture (111). In order to investigate magnetic properties of two different structures, they used a superconducting quantum interference device (SQUID). The out of plane (OOP) and in-plane (IP) hysteresis loops of samples shows good PMA. They observed that the OOP coercivity of samples was quite different. The OOP coercivity value of a sample having MoS₂ under-layer is 1078 Oe, while the OOP value of sample without MoS₂ under-layer is 120 Oe. The effects of the MoS₂ under-layer were also observed at changing anisotropy field value from 6000 to 19 000 Oe for samples without MoS₂ and with MoS₂ under-layer, respectively. Anisotropy constants of structures are 3.57×10^6 erg cm⁻³ and 1×10^7 erg cm⁻³ for samples without and with MoS₂ under-layer, respectively. In further investigation, the effects of MoS₂ on PMA as a function of Pt thickness were shown. The anisotropy field and constant values of samples without MoS₂ increase with the increasing Pt thickness. On the contrary, the sample anisotropy field and constant values fabricated with MoS₂ under-layer increases at some point (Pt:2), then these values decrease. They explained this phenomenon with two mechanisms which are the interface roughness and interface hybridization. The increasing value of anisotropy field and anisotropy constant was explained with the interfacial hybridization of Pt/Co interface. On the other hand, decreasing value of anisotropy field and constant for sample with MoS₂ was explained with impact of MoS₂ on electronic band structure of Pt. In order to investigate spin-orbit torque characteristic of samples, they carried out harmonic Hall measurements. According to the Hall measurements of samples with and without MoS₂ under-layer, the SOT efficiencies are 0.51 and 0.029, respectively. The changing in SOT efficiency with thickness of Pt was observed for sample MoS₂. When Pt thickness is 2 nm, the SOT efficiency reaches maximum value. The PMA enhancement in sample having MoS₂ under-layer was explained by performing Vienna ab initio simulation package (VASP). The calculations were carried out with MoS₂/Pt/Co/Ni and Pt/Co/Ni. The magnetic anisotropy energy values of these structures are 1.4 and 0.60 erg cm⁻², respectively. According to the X-ray absorption spectrum of samples, the intensity difference between L2 and L3 main peaks of sample with MoS₂ under-layer I ($\theta = 90^\circ$) is higher than the sample without MoS₂ under-layer I ($\theta = 20^\circ$). This means more electrons occupy the OOP orbitals for sample with MoS₂. The effect of the MoS₂ on the electronic band structure of Pt and Co at the interface were clarified with these results which means MoS₂ causes the redistribution of electronic states and modulates the orbital hybridization at these interfaces (Pt and Co). They conclude that the effect of MoS₂ on

materials orbital hybridization leads to enhancement of SOT efficiency by effecting spin transparency at Pt/Co interface (Xie et al., 2019).

Zhang et al. fabricated Cr-doped MoS₂ nano-sheets by using hydrothermal method and investigated absorption and magnetic properties of nano-sheets. In order to produce nano-sheets, they used Na₂MoO₄ and CH₃CSNH₂ as precursor materials. The amounts of precursors were determined as 100 mg Na₂MoO₄, 200 mg CH₃CSNH₂ and CrCl₃ with different amounts such as 3 mg, 7 mg, 10 mg and 15mg. They dissolved precursors in 80 ml distilled water and stirred for 5 minutes. Then, the solutions are transferred into the autoclave for heat treatment which is under 260°C for 1 hour. After heat treatment, solutions were dried at 60°C. They also produced pure MoS₂ nano-sheets to compare samples. According to the XRD results of undoped and Cr-doped MoS₂ nano-sheets, there is no impurity or different phases in patterns. The Raman results showed that the two main peaks of MoS₂ stay at 375 cm⁻¹ and 400 cm⁻¹ for undoped samples. According to the results, the height of these peaks decreases when the Cr concentration increases (from 0 to 6% by 2% step) which was explained the hindering effect of Cr atoms on MoS₂ lattice structure and these effects leads to forming atomic defects. The XPS spectra of undoped samples showed that the binding energies of Mo 3d_{5/2} and 3d_{3/2} observed at 229 eV and 232 eV, respectively. When the Cr is added to structure, these two peaks stay at lower energy levels and this phenomenon is explained with two reasons which are occupying of the S states by Cr atoms and organizing of defects and S vacancies by Cr atoms. The SEM images of undoped and Cr doped samples showed that the nano-sheets are ultrathin and flower-like. The distance between nano-sheets was measured at 0.23 nm corresponding to the (103) MoS₂ plane by evaluating high-resolution transmission electron microscope (HRTEM). In order to investigate magnetic properties of samples, they used the SQUID system. The *M-H* measurements of samples were carried out under room temperature (292 K). They carried zero field cooled and field-cooled measurements for 4.24% Cr-doped sample. These measurements showed that the Curie temperature of this sample is above the room temperature and shows no blocking temperature which means there is no ferromagnetic cluster in the doped sample. According to the *M-H* curves, the undoped sample showed weak ferromagnetic behavior, while the 4% Cr-doped sample showed high saturation magnetization behavior compared to the other samples. They conclude that when Cr concentration increases, antiferromagnetic coupling increases, then saturation magnetization decreases. The electromagnetic properties of films were measured by

using a network analyzer in transmission mode in 2-18 GHz. In order to investigate absorption properties of films, they fabricated paraffin mixed samples with concentration of powder 20%. According to the results, the undoped MoS₂ showed frequency dependent behavior in which its real (ϵ') and imaginary (ϵ'') parts decreases from 104.3 and 92.6 to 15.8 and 31.7 with increasing frequency, respectively. The maximum reflection loss (RL) value was observed for 4.24% Cr-doped MoS₂/paraffin sample as - 43 dB with the band width of 7.2 GHz (R. Zhang, Du, Han, & Gao, 2018).

Tongay et al. reported a study on MoS₂ single crystal magnetic properties. They used commercial MoS₂ as material for study. According to the Raman results of the sample, the two main peaks of MoS₂ E_{2g}^1 (in-plane vibration mode) and A_{1g} (out-of-plane vibration mode) observed at 378 cm⁻¹ and 402 cm⁻¹, respectively. The XPS results of the sample showed that the elemental ratio of Mo and S as (1:2). The (002) plane of MoS₂ was observed in XRD measurement. According to the full width half-maximum calculation, the average crystallite size was found as 76 nm. SEM measurements carried out to confirm grain sizes of samples which are larger than 100 nm. In order to investigate magnetic properties of MoS₂, they used the SQUID system. They carried out magnetic hysteresis measurements under 10 and 300 K. According to the M - H measurements of single crystal MoS₂, diamagnetic background was superimposed onto ferromagnetic loop onto ferromagnetic loop which means total susceptibility includes both diamagnetic and ferromagnetic parts. They calculated parallel diamagnetic susceptibility as $\chi_{dia}^{\parallel} = 1 \times 10^{-6}$ emu/g and the magnetic anisotropy value of the sample ($\chi_{dia}^{\parallel}/\chi_{dia}^{\perp}$) is between 1.2–1.5. In order to make observations of ferromagnetic behavior, they subtracted the diamagnetic part of magnetic results and they plotted ferromagnetic contribution at different temperatures by means of applied magnetic field parallel to the c -axis. According to the results, the saturation magnetization did not change with the temperature. On the other hand, the coercive field increased from 100 Oe to 400 Oe. They found that the zig-zag edges are ferromagnetic signals by using average grain size from XRD measurements as 2×10^{-6} emu/g and the total magnetization value is $\cong 4 \times 10^{-3}$ emu/g. This ferromagnetic contribution might be the result of magnetic impurities. In order to clarify this situation, they examined XPS measurement but no impurity peaks were observed. According to the magnetic results of MoS₂, they connected the ferromagnetic behavior to the existence of zig-zag edges within grain boundaries. They also

connected this behavior to magnetic impurities that might be present beyond the detection limit of XPS measurements (Tongay, Varnoosfaderani, Appleton, Wu, & Hebard, 2012).



3. MATERIALS AND METHODS

Solution assisted spin coating is one of the commonly used methods for growing thin films. This technique allows the depositing of thin films on the surface of substrate. The aim of this method is to disperse the prepared solution that contains trace materials basis on the surfaces of the substrate. On the other hand, the thermal decomposition of the films is the second step of manufacturing thin films in solution assisted spin coating systems. In this method, heat is used for decomposing the precursor material.

In this chapter, the preparation procedures of pure and Fe-doped MoS₂ thin film structures within the scope of the thesis and the measurement systems used to examine the structural and magnetic properties of the materials will be given in detail. This chapter also includes all of the productions during the specifying parameters such as solutions, cleaning procedures, substrates and coating parameters.

We used a couple of different chemical processes to obtain the optimum MoS₂ films. (ATTM) 99.97% trace metals basis as a precursor material and different solvents such as EG, 2-methoxyethylamine (M), N,N-dimethylformamide (DMF) were used to create MoS₂. The fundamental working scheme of thin film production by using solution assisted spin coating technique is given in Figure 3.1. Here, the whole process is summarized in four steps. These are solution preparation, substrate cleaning, film coating and heat treatment.



Figure 3.1. Schematic illustration of flow cart of the film manufacturing process.

3.1. Thin film production process

3.1.1. Preperation of chemical solutions

In this part of the thesis, all steps of preparing chemical solutions and consumables used in the thin film making process are mentioned elaborately. The process starts with weighing precursor and solvent material. Precursor material is added to the beaker and solvent is poured on the precursor. Then, magnetic fish is added to the beaker. After that, the solution is added on a hot plate/mixer to ensure homogeneity of solution. Hot plate is set to 50°C and 600 rpm. Various solvent materials were used in the production part of this thesis which are EG, M and DMF.

Figure 3.2 shows the whole devices and chemical materials used in the manufacturing process. In Figure 3.2(b), chemical solution prepared by mixing powder precursor and different kinds of solvent material is shown in other figures. The brim of the beaker was rolled up with parafilm and left an aging process on the hot plate.

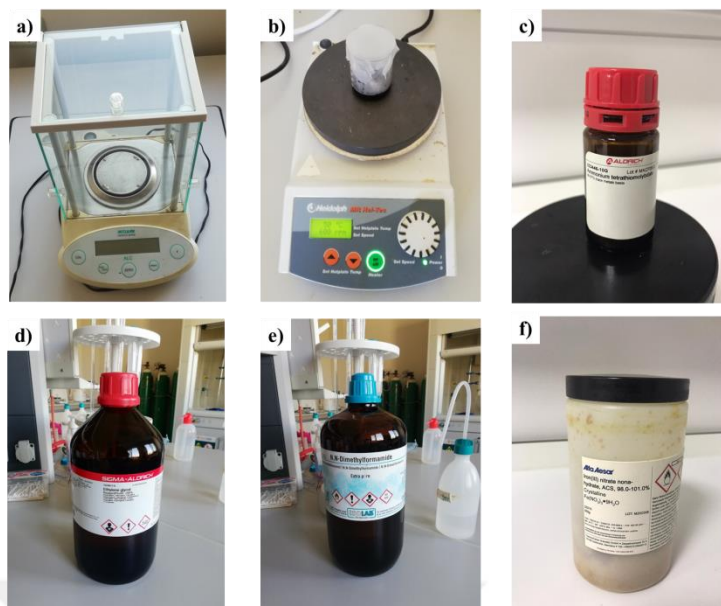


Figure 3.2. a) Sensitive scale device, b) hot-plate having magnetic stirrer option, c) ATTM precursor material, d) EG, e) N,N-dimethylformamide and f) Fe-precursor.

3.1.2. Substrate cleaning

The substrates, first, were cut to the desired size (generally 10 mm × 10 mm), and then the cleaning process was applied in various combinations. In the overall cleaning process, ethyl alcohol, detergent, N₂ (nitrogen), piranha solution, ultrasonic bath and hot plate were used. Different variations of the cleaning process were prepared to obtain best results.

First combination of the cleaning process was prepared by arraying detergent-cotton bud-ethyl alcohol-acetone in this order. At first, detergent was applied by circling with cotton bud on substrates. Then, ethyl alcohol and acetone were applied by spraying in an array. Second combination of the cleaning process consists of piranha solution. The piranha solution (7/3) was prepared by using 7 ml H₂SO₄ (sulphuric acid) and 3 ml H₂O₂ (hydrogen peroxide). The array of chemicals of piranha solution is crucial for security. H₂O₂ must be added to H₂SO₄ slowly to avoid explosion. First, H₂SO₄ is added to the beaker on a hot plate, then, temperature is set to 110°C. After that, H₂O₂ is added to H₂SO₄ slowly by dropping. Substrates were added to the beaker consisting of piranha solution and left to vibrate in an ultrasonic bath for 15 minutes. After 15 minutes, substrates were pulled off and detergent agent was applied on substrates. Then pure water was sprayed on substrates to remove detergent residual. After pure water, ethyl alcohol was used to remove water droplets on substrate. Then, N₂ gas was applied on substrates to ensure there were no ethyl alcohol

residuals. At the end of the process, the substrates were left on a hot plate for 1-2 minutes. Two different cleaning processes that are used in thesis productions are listed in Table 3-1.

Table 3.1. The details of cleaning process, abbreviations and meanings.

Cleaning process	Code	Content of process
First process	n (normal)	Detergent-cotton bud-ethyl alcohol-acetone-dry
Second process	PD (piranha and detergent)	15 min piranha in ultrasonic bath-ethyl alcohol dripping-detergent-pure water-ethyl alcohol-N ₂ -hot plate

3.1.3. Film growing by spin-coating system

To deposit films on the substrate, a spin coating system was used. Spin coating deposition technique utilizes centrifugal force to disperse prepared solution at the surface of the samples. This method consists of three steps:

1. Precursor particles dissolve in a solvent, then solution is dropped by micro-pipe on the substrate surface (Figure 3.3(a-b)),
2. Spinning up the substrate adjusted values (Figure 3.3(c)),
3. Evaporation of the solvent (Figure 3.3(d)).

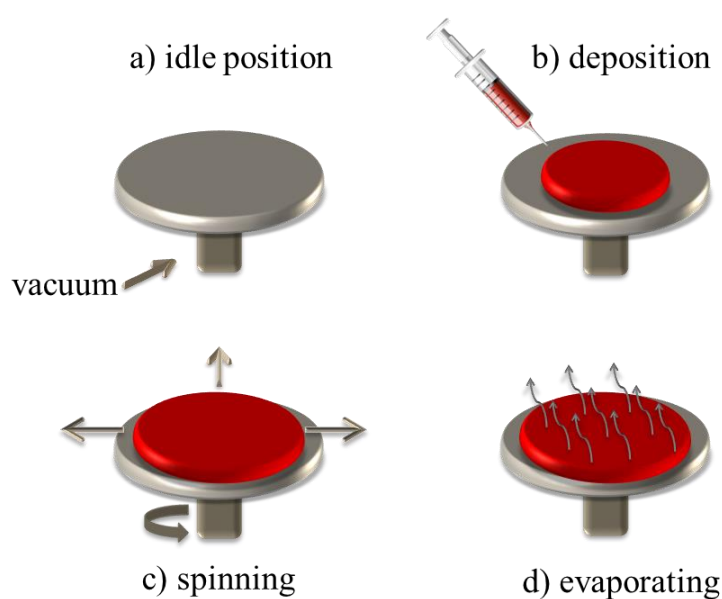


Figure 3.3. Spin-coating process steps.

The solvent material is removed from the surface rapidly by spinning motion and solid films stay onto the substrate surface (Nguyen, 2012). The speed of the spinning causes the formation of a thin layer on the surface. There are main parameters to specify thin film quality. The speed of the device and the viscosity of the solution determine the uniformity and the thickness of the film (Yilbas, Al-Sharafi, & Ali, 2019). The spin coating system that is used in this thesis study is shown in Figure 3.4.



Figure 3.4. The spin-coating system.

Four different coating parameters were used in film manufacturing processes which are listed in Table 3-2 with their abbreviations and explanations. All processes consist of two steps. The time, speed and acceleration of steps are different from each other. These parameters are determined by considering the quality of the film right after the spin coating system. Various parameters of coating systems lead to depositing of liquid solution with different forms on the surface of substrate. For example, high angular speed causes the rapidly removing liquid solution from the surface of the substrate. In contrast, low angular speed of the system leads to formation of thick films. In order to avoid these improper situations, various coating parameters were tried.

Table 3.2. The coating abbreviations and their explanations.

Coating Abbreviations	Codes Meaning
X	5 seconds 500 rpm acceleration 500 15 seconds 2000 rpm acceleration 1000
Y	5 seconds 500 rpm acceleration 500 15 seconds 2500 rpm acceleration 1000
Z	5 seconds 500 rpm acceleration 500 15 seconds 3000 rpm accelerations 1000
T	15 seconds 500 rpm accelerations 500 30 seconds 2500 rpm accelerations 1000
W	10 second 800 rpm acceleration 500 20 second 3500 rpm acceleration 1000

3.1.4. Heat treatment process

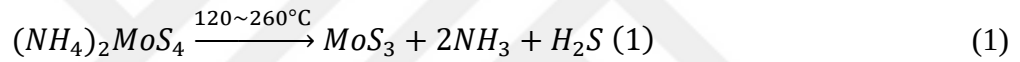
Thermal decomposition of ATTM precursor is a common method for producing MoS₂ thin films. The decomposition of MoS₂ thin films can be carried out at high and moderately low temperatures. The main difference between these temperatures is experiment conditions. At a high temperature process, the system temperature can be reached up to 1000°C at atmospheric pressure. Since this temperature is above the melting point of the glass, the high temperature decomposition process cannot be used for glass substrates. On the other hand, at moderately low temperatures, the temperature of the system does not exceed 600°C under vacuum atmosphere and gas flow is needed during the decomposition process. Nitrogen (N₂), nitrogen-hydrogen mixture H₂/N₂ and argon (Ar) are generally used as carried gas which is inserted into the system (Joaquin L. Brito 1995; Lim et al., 2018; Lim et al., 2016; Liu et al., 2012). The decomposition process is performed in our home-made high temperature furnace system shown in Figure 3.5.

In this process, first of all, the sample is placed in the middle of the furnace. Secondly, the furnace door is closed and the work part of the furnace is vacuumed with the vacuum pump mounted on the left side. Then, nitrogen gas is sent inside and the interior of the furnace is swept with this gas. Finally, the temperature settings of the furnace are made and the heat treatment process is started.



Figure 3.5. The compact system to be carried out heat treatment.

Heat treatment parameters were determined after literature research by taking consideration of MoS₂ thermodynamic properties (H. W. WANG, 1998; H.W. WANG, 1997; Lim et al., 2018; Richard I. Walton, 1998);



The formation of MoS₂ from ATTM is shown in Equation 1 and 2. Thermal decomposition of ATTM consists of two steps, one is forming of MoS₃ and second one is forming of MoS₂. The first step of decomposition from ATTM to MoS₃ occurs between 120°C and 260°C temperatures (Richard I. Walton, 1998). To ensure the occurrence of MoS₃ phase, the first step of thermal decomposition was selected as 280°C for 30 minutes. According to the literature, the second transform of the process starts at around 600°C for 40 minutes under N₂/H₂ flow (Lim et al., 2018). To obtain crystallinity of MoS₂ films, samples in this thesis study are heated 570°C for 40 minutes under N₂ flow.

The decomposition process during heat treatment can be explained by the following. At the first step of heat treatment (Figure 3.6), the temperature reaches 280°C (T₁) by the 4°C/min step. The system's temperature is kept at this temperature for 30 minutes (t₂-t₁). At the third step, the furnace temperature reaches 570°C (T₂) by the 4°C/min step. And then, the furnace temperature is kept at this temperature for 40 minutes (t₄-t₃). After that the furnace is allowed to cool down to room temperature (t₄-t₅).

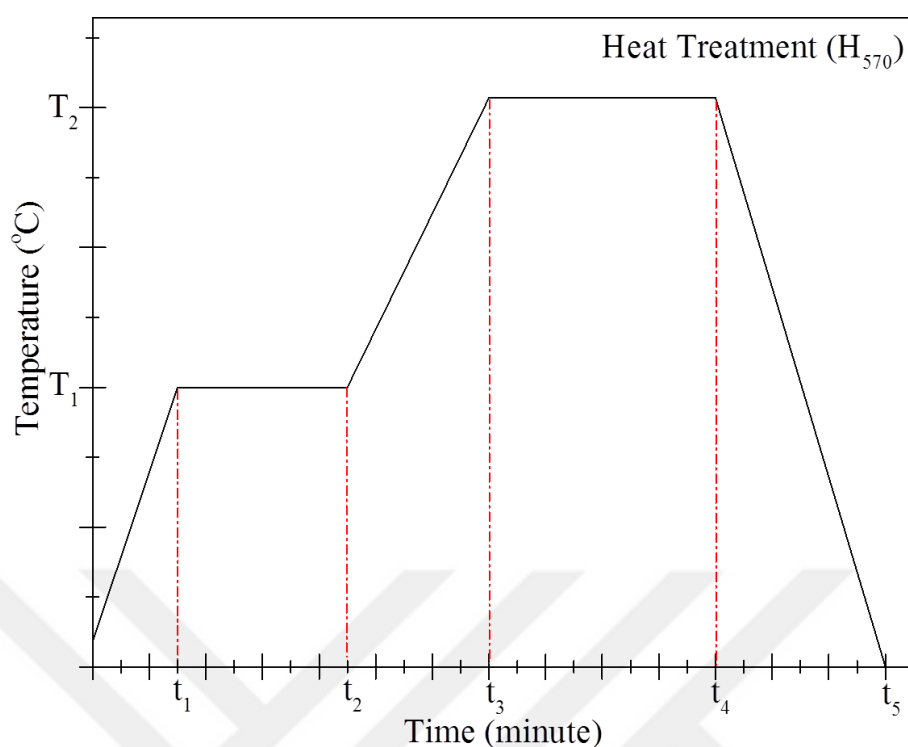


Figure 3.6. Diagram of the heat treatment process.

3.2. Optimization of MoS₂ thin film production

The optimizations of MoS₂ thin film productions were performed by taking into account the substrate cleaning procedure, solvents (EG, DMF, 2-methoxyethylamine) concentration of ATTM, coating parameters and heat treatment process. In this section, we will summarize all of these parameters to find out the optimum thin film production process. Before doing the optimization points, we will introduce sample codes' abbreviations in the following table.

Table 3-3 shows the different letters having various meanings used in coding of samples. The letters of coating parameters which were mentioned in the previous section were not added to code of produced samples to avoid the complication of the codes (see Table 3-2). These parameters are informed in the manufacturing process of the samples.

Table 3.3. The letters used in sample codes, their abbreviations and meanings.

Sample Code Abbreviations	Codes Meaning
G	Glass substrate
Q	Quartz substrate
S	Si/SiO ₂ substrate
M	2-Methoxyethylamine
EG	Ethylene Glycol
DMF	N,N-dimethylformamide

3.2.1. Optimization of EG, DMF, 2-Methoxyethylamine

The solvent optimization was done by using various solvent materials which are EG, 2-Methoxyethylamine (M) and DMF. First of all, we worked with EG as a solvent material to disperse the ATTM. The ATTM weight percent was selected 3.5% according to literature research. First, ATTM was weighted (0.1765 gram) and placed in a beaker. Then, the EG (4.44 ml) was added onto the ATTM precursor in the beaker. Then, magnetic fish was added into the beaker. The solution was left for a 48 hours age period at 50°C under 600 rpm. Second solution contains 2-methoxyethylamine solvent. We used the same process with the first production one. In the second bunch of production, 0.1614 gram ATTM and 4 mL 2-methoxyethylamine solvent were added into the beaker. Then, the solution was left for a 48 hours age period 50°C under 600 rpm. After the solution aging process is finished, two different substrates (glass and quartz) were cut into the pieces.

To clean the surface of the substrates, cleaning procedure ‘n’ was used (see Table 3.1). After the cleaning process finished, the coating process was started using a spin coater. The produced samples list is given in Table 3-4. The details and amounts of solution of sample MoS₂-DMF3-G were given in section 3.2.4. In contrast to sample MoS₂-DMF3-S in section 3.2.4, this sample was produced using glass as substrate. In addition, the ‘PD’ cleaning process was used to clean the surface of this sample. For these samples, the letters of coating and heat treatment parameters were not mentioned at the code of the samples to avoid complication. To clarify the sample’ codes, the first part of the code indicates the structure of film (f.e.: ‘MoS₂’). The second part of code (f.e.: ‘M’) shows the solvent type of solution. The last part of the code (f.e.: ‘G’) indicates the substrate type of sample.

Five different coating parameters were used in order to stabilize the processes which are X, Y, Z, T and W. In order to see details of parameters see Table 3-2. The coating parameters X, Y, Z, T and W were used to produce sample MoS₂-M-G, MoS₂-EG-Q, MoS₂-M-Q, MoS₂-EG-G, MoS₂-DMF3-G, respectively.

Table 3.4. Table of first production of samples and their codes.

Sample Code	ATTM content	ATTM (g)	Substrate
MoS ₂ -M-G	4.0%	0.1614	Glass
MoS ₂ -EG-Q	3.5%	0.1765	Quartz
MoS ₂ -M-Q	4.0%	0.1614	Quartz
MoS ₂ -EG-G	3.5%	0.1765	Glass
MoS ₂ -DMF3-G	1.08%	0.0520	Glass

In order to ensure crystallinity of the films, heat treatment procedures under vacuum atmosphere with flow of N₂ gas at 570 and 600°C were applied on samples. MoS₂-EG-G is the only sample that is exposed to a 570°C heat treatment procedure. Other sample' heat treatments were carried out at 600°C. The details of heat treatments are given in Table 3-5.

3.2.2. Optimization of heat treatment process

In this part of the thesis, temperature of heat treatment was determined to reach best results for film quality and crystallinity. Three different heat treatment temperatures were applied on samples. Regardless of coating parameters, three different samples were produced to make comparison of heat treatments. These samples were produced by using the solution containing 3.5% wt. ATTM. The amount of precursor and solvent is mentioned in the previous section (see section 3.2.1). The produced samples' list is given in Table 3-5.

Table 3.5. The samples codes produced for optimization of heat treatment process.

Sample Code	Heat Treatment Process
MoS ₂ -EG-G-H ₅₅₀	Heat treatment at 550°C 30 min to 280°C 30 min stay 280°C 46 min to 550°C 30 min stay at 550°C and cooled to room temperature
MoS ₂ -EG-G-H ₅₇₀	Heat treatment at 570°C 30 min to 280°C 30 min stay 280°C 46 min to 570°C 30 min stay at 570°C and cooled to room temperature
MoS ₂ -EG-G-H ₆₀₀	Heat treatment at 600°C 30 min to 280°C 30 min stay 280°C 46 min to 600°C 30 min stay at 600°C and cooled to room temperature

These samples given in Table 3-5 with heat treatment letters (H₅₅₀, H₅₇₀ and H₆₀₀) are different from the samples mentioned before. The coating parameters are the same as samples mentioned in Table 3-4, but these are completely different samples. The coating parameters are Z, X and Y for samples MoS₂-EG-G-H₅₅₀, MoS₂-EG-G-H₅₇₀, MoS₂-EG-G-H₆₀₀, respectively.

3.2.3. Optimization of ATTM concentration in EG

Three new solutions having 1.25, 2.25 and 3.25% wt. ATTM were prepared by mixing precursor and solvent materials in precise ratio. The steps of preparing solutions are similar to previous solutions. The components were weighed, stirred and left for the 1 hour aging process. The new cleaning procedure (PD) and coating parameter (W) were used to manufacture new samples. The amounts of components are given in Table 3.6.

Table 3.6. The sample codes, ATTM content and substrate for the optimization of ATTM concentration in EG.

Sample Code	ATTM content (EG)	ATTM (g)	Substrate
MoS ₂ -EG1-G	1.25% (4.6 mL)	0.0625	Glass
MoS ₂ -EG2-G	2.25% (4.5 mL)	0.1125	Glass
MoS ₂ -EG3-G	3.25% (4.3 mL)	0.1628	Glass

The new cleaning process which is piranha solution created smooth films. 15 minute piranha cleaning gives extraordinary improvement in surface quality of substrates. To enhance this improvement, a few more steps were applied. The reason that detergent is used is to enhance the surface activity with a surface active material. The N_2 was also used to reinforce dryness of films. In order to see details of the cleaning process; you may see Section 3.1.2.

In addition to the new cleaning process, a new coating process was created to reach best results and these coating parameters will be the last parameters starting from this production. This new coating process ('W') has the following parameters; 10 seconds 800 rpm acceleration 500, 20 seconds 3500 rpm acceleration 1000. To enhance crystallinity of films, 570°C heat treatment was applied to the produced films.

In order to make a visual comparison of thin film quality before the heat treatment process, their images were given in Figure 3.7. According to the images, the darkness of the films increases with increasing concentration of ATTM from 1.25% to 3.25%. This increase in darkness not only causes film quality but also causes increasing thickness of films. In the next Chapter, the characterization results of these films will be discussed in detail.

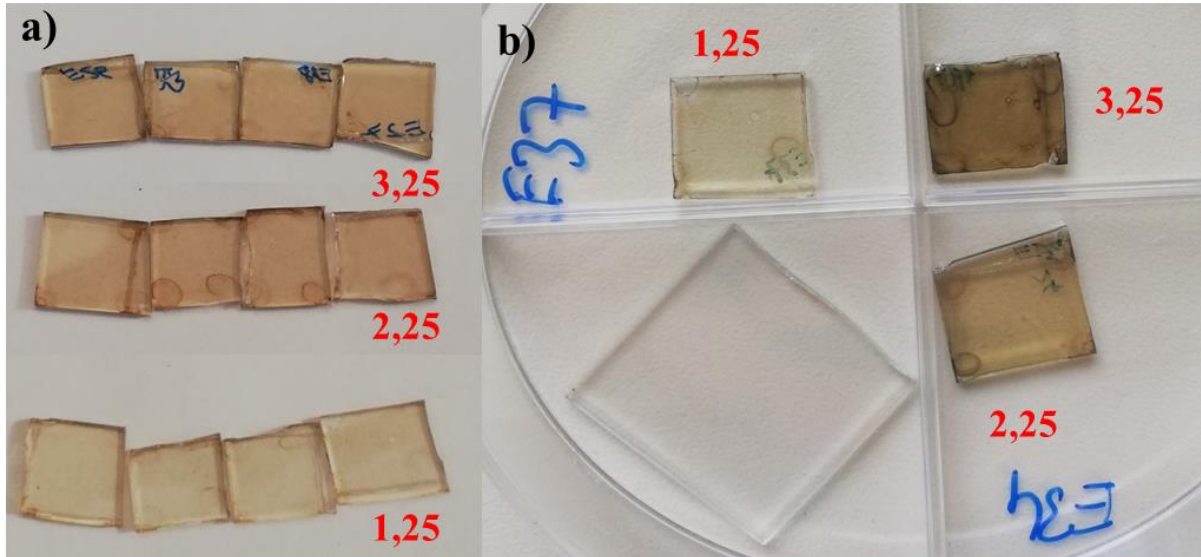


Figure 3.7. The images of films coated with three different solutions (ATTM wt. 1.25/2.25/3.25 in EG) a) before heat treatment, b) after heat treatment process.

3.2.4. Optimization of ATTM concentration in DMF

In this part, the ATTM concentration was optimized by using DMF as a solvent. The DMF was used to create more stable solutions in terms of solubility and surface quality. The reasons for using DMF instead of EG are solubility, film quality and aging time of solutions. Aging time of solutions which contain EG is quite longer than the solution containing DMF solvent. In addition, EG solutions began to create some impurities inside of the solutions in a time interval. In addition, the density of EG (1.11 g/mL) is much higher than DMF (0,944 g/mL) which affects the homogeneity of solution and homogeneity directly affects the quality of the films. Therefore, we used DMF instead of EG in our new productions.

In this part of the thesis, different pure solutions containing only ATTM and DMF were produced by selecting the proper percent ratio. According to the literature, the ratio of 40 mM corresponds to the 1.08% wt. ratio is suitable for producing MoS₂ thin films (Qi et al., 2015). Pure solutions were produced based on this value and a new ratio of solutions was created to change film layer properties. PD cleaning, W coating and H₅₇₀ heat treatment processes selected in the previous chapter were applied to all of the new samples. Three different solutions having different ATTM concentrations were produced to compare results. Table 3-7 shows the sample codes, ATTM contents and substrates. In this bunch of samples, we used Si/SiO₂ as a substrate.

The same solution preparation was used as we explained in the previous sections. For 1.08% (40mM) ATTM concentration, 0.0520 gram ATTM was weighed and added into the beaker. Then, 5 mL DMF was poured into the baker and the solution was put into the ultrasonic bath for 60 minute for sonication. For 0.95% wt. concentration, 0.04525 gram ATTM was weighed and it is added into the beaker. 5mL DMF was added onto the ATTM precursor. The aging process is the same with the previous one. To create 0.82% wt. solution, 0.03925 ATTM was weighed and 5 mL DMF was added to the beaker. Then, the solutions were left for the 1 hour aging process.

Table 3.7. The sample codes, ATTM content and substrate for the optimization of ATTM concentration in DMF.

Sample Code	ATTM content (DMF)	ATTM (g)	Substrate
MoS ₂ -DMF1-S	0.82% (5mL)	0.0392	Si/SiO ₂
MoS ₂ -DMF2-S	0.95% (5mL)	0.0452	Si/SiO ₂
MoS ₂ -DMF3-S	1.08% (5mL)	0.0520	Si/SiO ₂

Once the sonication process was completed, the cleaning of Si/SiO₂ substrates was done by using the PD process. As we mentioned before, substrates was left into the 7/3 Piranha solution (7:H₂SO₄, 3:H₂O₂) for 15 minutes in an ultrasonic bath. Then, they were taken out of the piranha solution and washed with pure water. After that, the detergent was applied on substrates by sliding cotton buds on the sample surfaces. Then, the substrates were washed with pure water again. In order to remove water from substrates, ethyl alcohol was used. N₂ was sprayed to remove ethyl alcohol from substrates surfaces. Finally, the substrates were left on a hot plate to dry.

After the substrates were dried, the films were coated on the substrates by using a spin coating system with W process. At the first stage of the coating process of films, rotational motion of the spin coater begins with the 800 rpm under 500 acceleration for 15 seconds then reaches 3500 rpm under 1000 acceleration for 20 seconds then the coating process finishes. After the coating process, thin films were transferred to the furnace to apply heat treatment H₅₇₀.

3.3. Production of Fe-doped MoS₂ thin films

After interpreting the results of the pure samples that contain different amounts of ATTM in DMF, 0.95% were selected and all of the synthesizing parameters for doped solutions were determined by based on this value. The Fe doped MoS₂ samples were prepared by using 0.95% ATTM in the DMF solutions. Three different Fe concentrations were synthesized in this section. The precursor amount and sample codes of all samples are given in Table 3.7.

Table 3.8. The sample codes, Fe-content, precursor amount and substrates used in Fe-doped MoS₂ films.

Sample Code	Fe-content	Precursor amount		Substrate
Fe _{0.50} :MoS ₂ -S	0.50%	ATTM	0.18035 g	Si/SiO ₂
		Fe-pre	0.00140 g	
		DMF	20 mL	
Fe _{0.75} :MoS ₂ -S	0.75%	ATTM	0.18001 g	Si/SiO ₂
		Fe-pre	0.00211 g	
		DMF	20 mL	
Fe _{1.00} :MoS ₂ -S	1.00%	ATTM	0.17967 g	Si/SiO ₂
		Fe-pre	0.00281 g	
		DMF	20 mL	

Substrates of the films (S), cleaning (PD), coating process (W) and heat treatment (H₅₇₀) are the same as the pure samples that were mentioned before. To see details of processes visit Table 3-1, Table 3-2, Table 3-3 and Table 3-5.

3.4. Production of Cu-doped MoS₂ thin films

Cu-doped MoS₂ thin films were prepared by taking 0.95% concentration of ATTM into consideration. The same values of doping Fe atoms in thin films were used for Cu-doped samples. Prepared Cu- doped samples are shown in Table 3-9.

Table 3.9. The sample codes, Cu-content, precursor amount and substrates used in Cu-doped MoS₂ films.

Sample Code	Fe-content	Precursor amount		Substrate
Cu _{0.50} :MoS ₂ -S	0.50%	ATTM	0.180309	Si/SiO ₂
		Cu-pre	0.00065	
		DMF	20 mL	
Cu _{0.75} :MoS ₂ -S	0.75%	ATTM	0.179947	Si/SiO ₂
		Cu-pre	0.00098	
		DMF	20 mL	
Cu _{1.00} :MoS ₂ -S	1.00%	ATTM	0.179585	Si/SiO ₂
		Cu-pre	0.001307	
		DMF	20mL	

3.5. Characterization techniques

In this thesis, x-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy measurements were performed to analyze structural properties of the produced pure and Fe-doped MoS₂ thin films.

3.5.1. X-Ray diffraction (XRD) method

X-ray diffraction method is used to characterize lattice properties of crystal structures. This technique utilizes interference between x-ray beam and crystal structure and reveals the fundamental lattice parameters of crystals. For example, lattice type of crystal, the amount of crystallinity, dimensions of the unit cell, the lattice parameter, the distances and the angles between atoms can be determined by XRD method (Chauhan, 2014; Eckert, 2012). German physicist Max von Laue discovered the reflection of the X-ray from a crystal. He expressed the diffraction of the X-ray from crystal on the photographic plate. His experiment showed that the X-rays are waves in nature and atoms are arranged in the crystal periodically. Laue won the Nobel Prize in physics in 1914 for his discovery. Laue's experiments were supported by the British physicist W.L Bragg. He revealed the mathematical relation required for occurrence of diffraction conditions. This mathematical relation is known as "Bragg's Law".

$$n\lambda = 2d\sin\theta \quad (3)$$

n is an integer. If the wavelength of the incident beam is smaller and equal than the $2d$ ($\lambda \leq 2d$), Bragg reflection occurs.

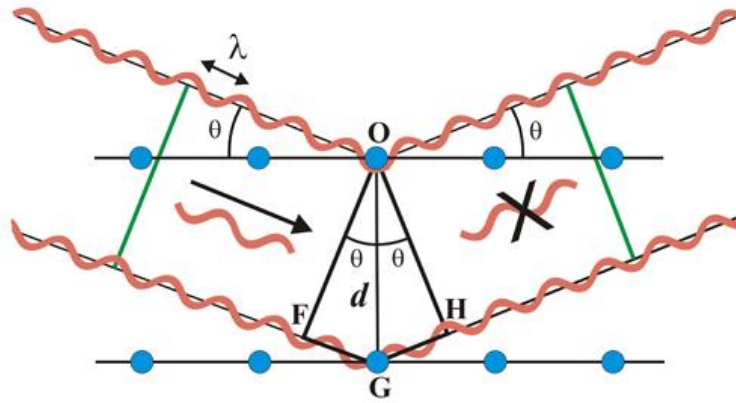


Figure 3.8. Diffraction of the incident X-ray beams from the crystal planes.

Figure 3.8 shows the description of Bragg's law. λ is the wavelength of the incident beam, θ is the angle between incident beam and crystal plane and d is the distance between two planes of crystal structure. If the path differences of the scattered beams between two consecutive planes have the same value with the wavelength of incident beams, the constructive interference occurs. These scattered beams strength reinforce each other and cause the formation of diffraction beams. The XRD device gathers the information of these beams and

analyzes properties of crystal structure. X-ray diffraction pattern is shown in a graph of the diffracted beam's intensity as a function of the reflection angle (2θ). XRD measurements of the samples in this study were done by using the PANalytical EMPYREAN X-ray diffraction system (see Figure 3.9) with Cu-K α (1.5405 Å) X-ray source. Measurements were carried out at room temperature.



Figure 3.9. Image of the PANalytical EMPYREAN X-ray diffraction (XRD) system.

3.5.2. Scanning electron microscope (SEM) imaging

Scanning electron microscopy method utilizes the electron interference with the materials atoms to produce morphology images of the samples. The morphological properties of the materials can be evaluated by the scanning electron images. The shape of the nanomaterial or the surface of the thin film can be examined by the SEM images. Figure 3.10 shows the schematically illustrated working scheme of SEM. The electron beams are produced by an electron gun. Then, an electron beam passes through the lenses. The aim of the lenses is to gather electrons and focus them on the sample. After the lenses, there is a scanning coil which is used for adjusting the orbits of the electrons. Then, an electron hits the sample and creates interference with the sample's atoms. The detectors in the system gather the scattered electrons from the sample and create the high resolution image.

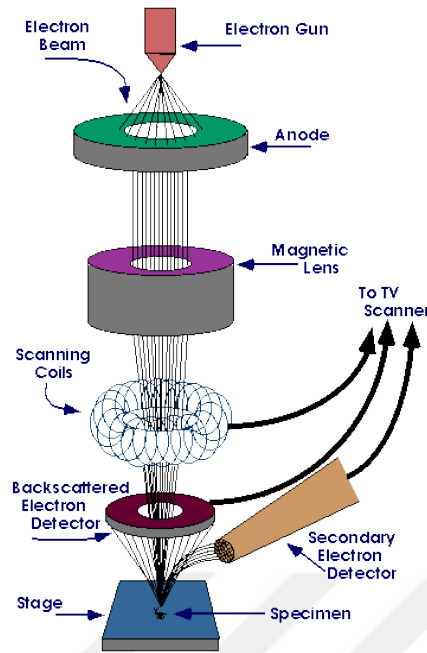


Figure 3.10. Schematic illustration of working scheme of SEM (Honglin Li et al., 2015).

Backscattered and secondary electrons are required for SEM to create an image. The source of back scattering electrons is elastic collision between incident beam and sample's atoms. Backscattered electrons carry high energy and they are scattered from deep regions (50-300nm) of the samples. The composition information about the sample can be provided by the backscattered electrons. Secondary electrons are created by the inelastic collision between the incident electron and sample's atom. These electrons carry low energy because of the inelastic collision. The depth of the area which secondary electrons emerge from is 5-50nm. The topological information of the sample is obtained from the secondary electrons.

3.5.3. Raman spectroscopy

The materials show the unique vibrational modes at different directions and dimensions. Raman spectroscopy utilizes inelastic light scattering to specify structural conditions of the materials such as chemical condition, layer number or dimension of material and crystal orientations. If the incident laser beam wavelength has a different value with the scattered beam by phonons, Raman scattering occurs. Figure 3.11 shows the laser interference with atoms in Raman scattering.

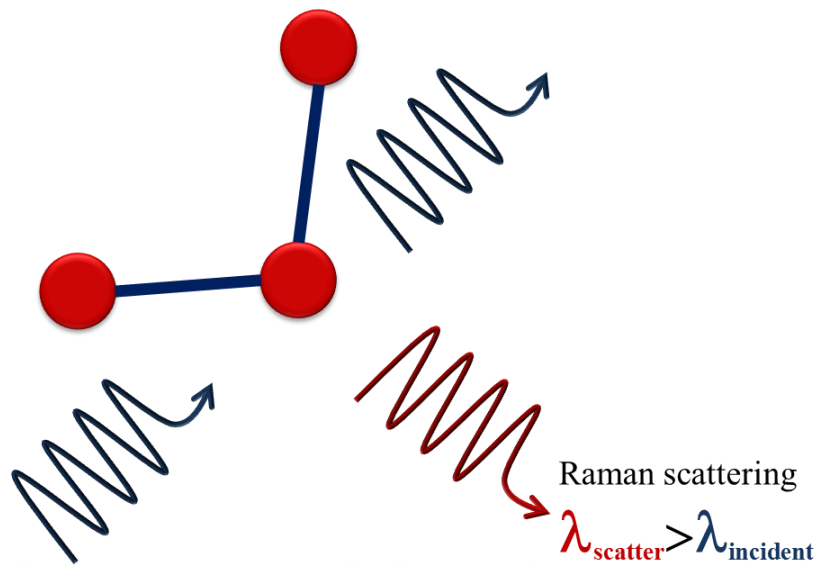


Figure 3.11. Schematic illustration of Raman scattering.

3.5.4. Magnetic analysis

The Physical Property Measurement System (Quantum Design Dyna-Cool, PPMS) is an integrated measurement system designed to specify the physical properties of the material. The diversity of modules is attached to the PPMS system. Vibrating sample magnetometer (VSM) is one of the modules that measure the moment value of material under various conditions, f.e. temperature and magnetic field.

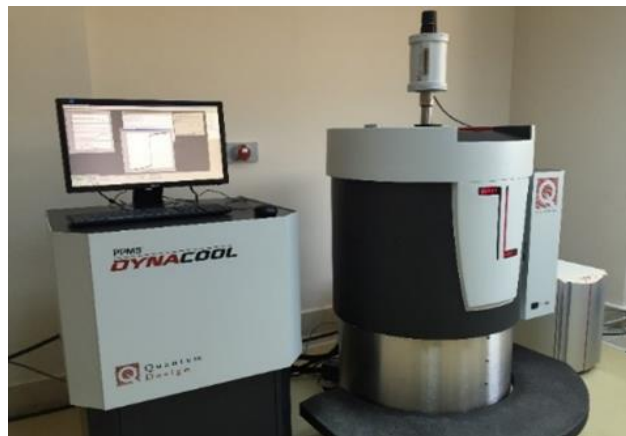


Figure 3.12. Quantum Design Dyna-Cool Physical Property Measurement System (PPMS).

The PPMS system is used for the determination of physical properties at the high sensitivity at wide temperature range and magnetic fields required. The working temperature of the system is between 2 K (-271°C) - 400K (127 °C) and the system ensures heat flow controlling

at sample area. Both continuous and discontinuous modes can be used through the magnet control system which also configures the power supply current in order to produce a ± 9 T magnetic field. In this study, magnetic measurements of all samples were carried out using the vibrating sample magnetometer in PPMS.



4. RESULTS AND DISCUSSIONS

In this thesis, pure MoS₂ thin films were produced by solution assisted spin coating method. In order to ensure the aim of this study, Fe and Cu atoms were doped onto the MoS₂ film structure. The optimization process and structural characterizations of samples were discussed in Section 4.1. The structural and magnetic analysis of optimized samples and Fe/Cu-doped MoS₂ samples of this thesis were discussed in Section 4.2, 4.3 and 4.4.

4.1. Structural results of optimization samples

In this section, the results of produced MoS₂ thin films with different solutions, heat treatment and coating parameters were discussed. The samples' structural properties were investigated by using x-ray diffraction (XRD) and Raman spectroscopy.

4.1.1. XRD results of optimization samples

The XRD measurements were performed by sweeping the diffraction angle between 10° and 90°. According to the XRD result of MoS₂-M-G sample which was grown glass substrate by using 2-Methoxyethylamine as a solvent (see Figure 4.1, there are four peaks stay at ~12.7°, 25.6°, 38.9° and 67.6° with diffraction plane (020), (040), (060) and (0100), respectively. These peaks indicate that Mo formed as orthorhombic α -MoO₃ for this sample (H. Hu, Deng, Xu, Zhang, & Sun, 2015; Krishna, Hussain, & Guillen, 2008). The XRD analysis indicates that the film is completely formed by MoO₃ which means the sulfur atoms are evaporated and swept by N₂ gas during the heat treatment process.

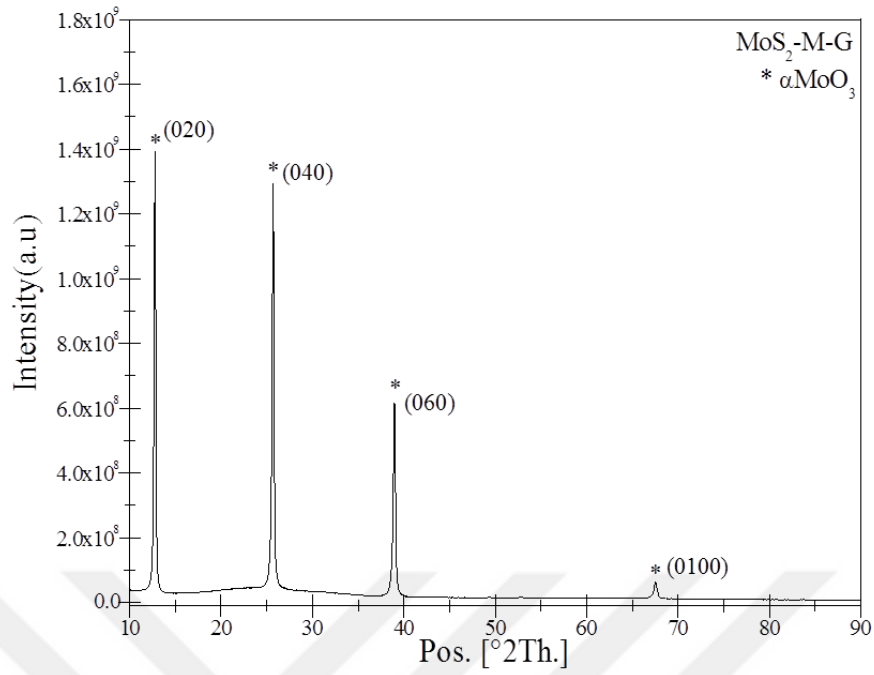


Figure 4.1. XRD result of sample MoS₂-M-G annealed at 600°C.

The same solvent (2-Methoxyethylamine) was also used to grow film on quartz substrates. Figure 4.2 shows the XRD result of sample MoS₂-M-Q. Similar to the sample MoS₂-M-G, we observed orthorhombic α -MoO₃ diffraction peaks. In addition to these peaks, a new diffraction peak oriented in (002) and (112) planes are observed in the MoS₂-M-Q sample (H. Hu et al., 2015).

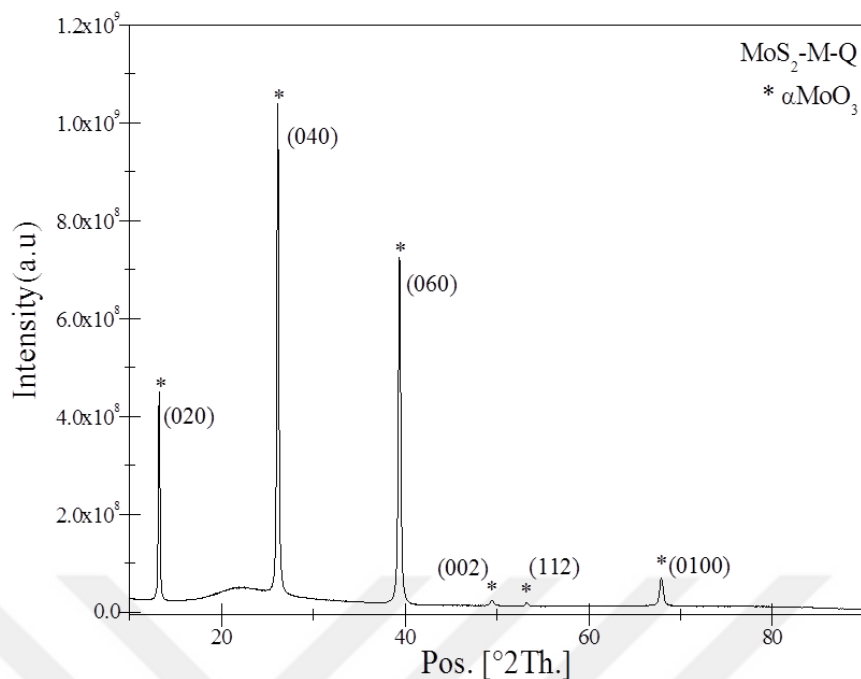


Figure 4.2. XRD result of MoS₂-M-Q annealed at 600°C.

Next, we used ethylene-glycol as a solvent for ATTm and observed the same crystal property in the MoS₂-EG-Q sample. But, the corresponding orthorhombic α -MoO₃ phase peaks are shifted to the right side in the spectrum (see Figure 4.3).

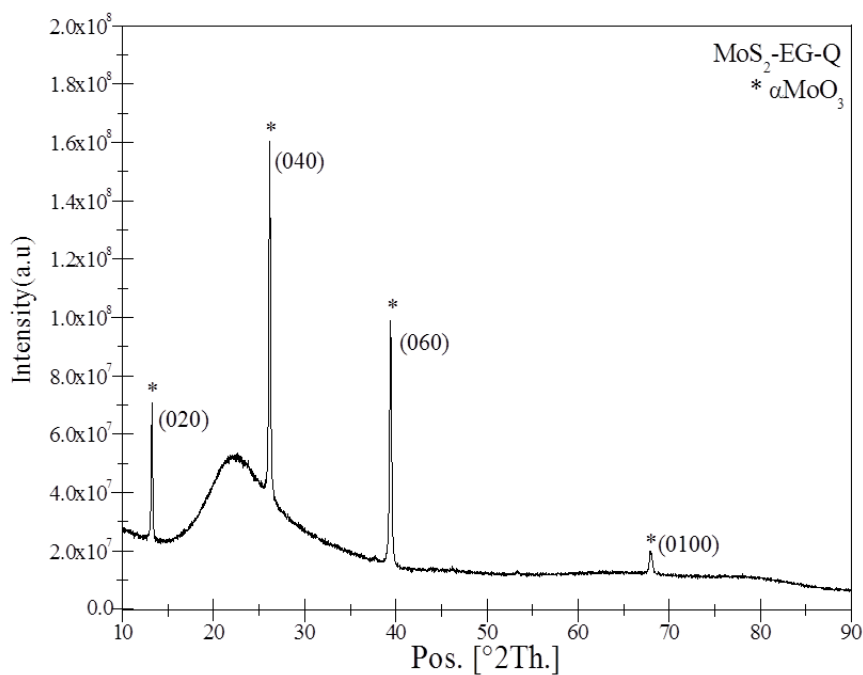


Figure 4.3. XRD result of MoS₂-EG-Q sample annealed at 600°C.

Figure 4.4 shows the XRD patterns of MoS₂-EG-G sample annealed at 570°C. Here, we observed 2H-MoS₂ XRD peak at 14.6° with diffraction plane (002) (Barzegar, Irajizad, & Tiwari, 2019; Chang & Chen, 2011; Dam, Thakur, G, & Hussain, 2019; He, Fernandez, Primo, & Garcia, 2018). The peak observed around 26.3° belongs to the orthorhombic α -MoO₃. The main difference between the MoS₂-EG-G sample and the MoS₂-EG-Q is heat treatment temperature. Once we decreased the heat treatment temperature from 600°C to 570°C, the MoS₂ crystals occurred.

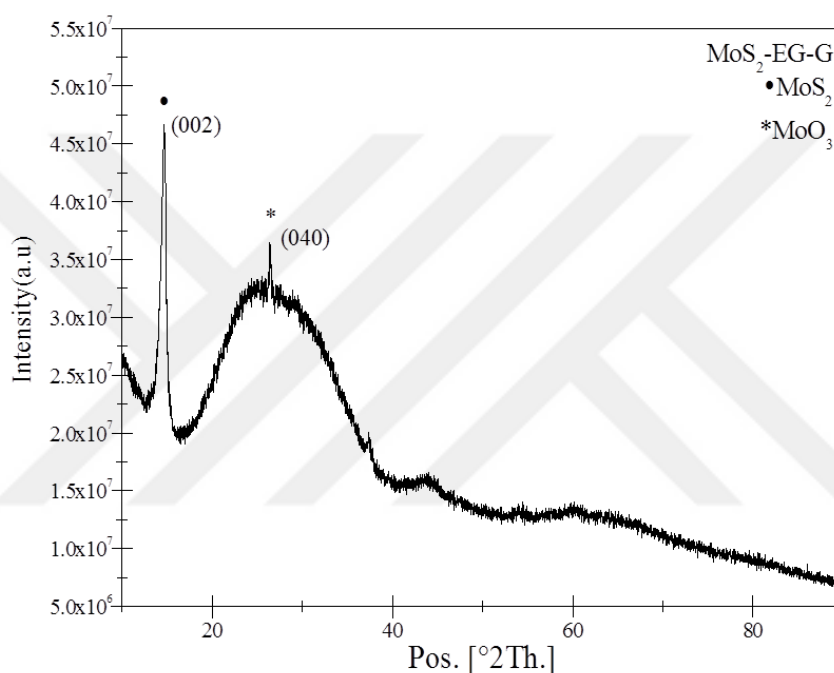


Figure 4.4. XRD result of MoS₂-EG-G sample annealed at 570°C.

The heat treatment temperature was even reduced below 570°C, 2H-MoS₂ crystals without MoO₃ peaks were created when it was annealed at 550°C. Figure 4.5 shows the main peak of 2H-MoS₂ observed at 14.4° with diffraction plane (002). The heat treatment temperature effect on the formation of single 2H-MoS₂ is clearly seen between Figure 4.4 and Figure 4.5.

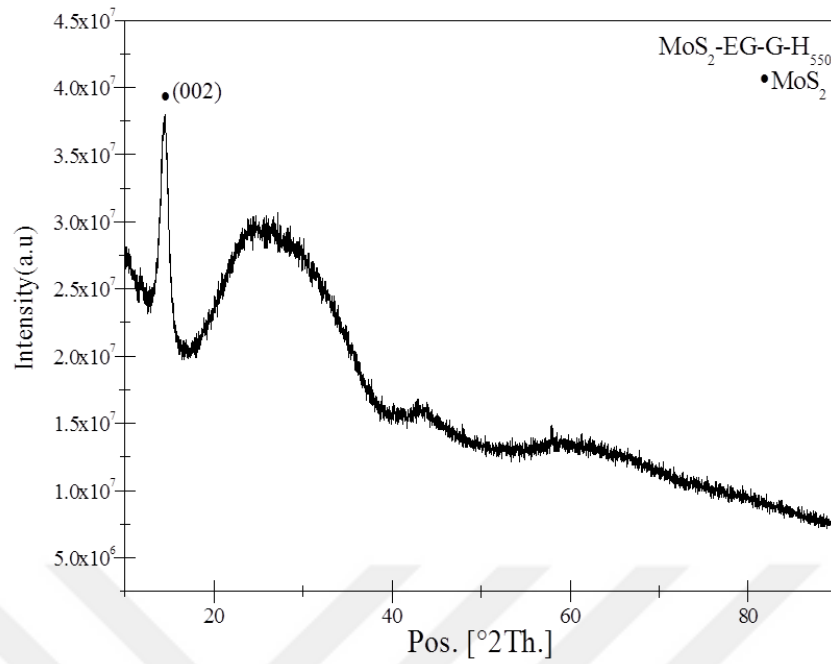


Figure 4.5. XRD pattern of MoS₂-EG-G sample annealed at 550°C.

The (002) diffraction plane for 2H-MoS₂ and (020) α -MoO₃ is quite similar but there is a slight difference in the diffraction angle value. The 2H-MoS₂ (002) peak stays at $\cong 14^\circ$ but (020) orthorhombic α -MoO₃ peak stays at $\cong 12$ - 13° . Red dashed-dot lines are added in Figure 4.6 to show these phase differences. According to Figure 4.6(c), the main peak of 2H-MoS₂ is vanished when the annealing temperature is reached to 600°C. The main peaks of orthorhombic α -MoO₃ are observed at 12.6° , 25.6° , 38.8° and 67.4° with diffraction planes (020), (040), (060) and (0100), respectively (H. Hu et al., 2015). These three main peaks of orthorhombic α -MoO₃ show that the H₆₀₀ heat treatment process is suitable to produce α -MoO₃ (H. Hu et al., 2015; Krishna et al., 2008).

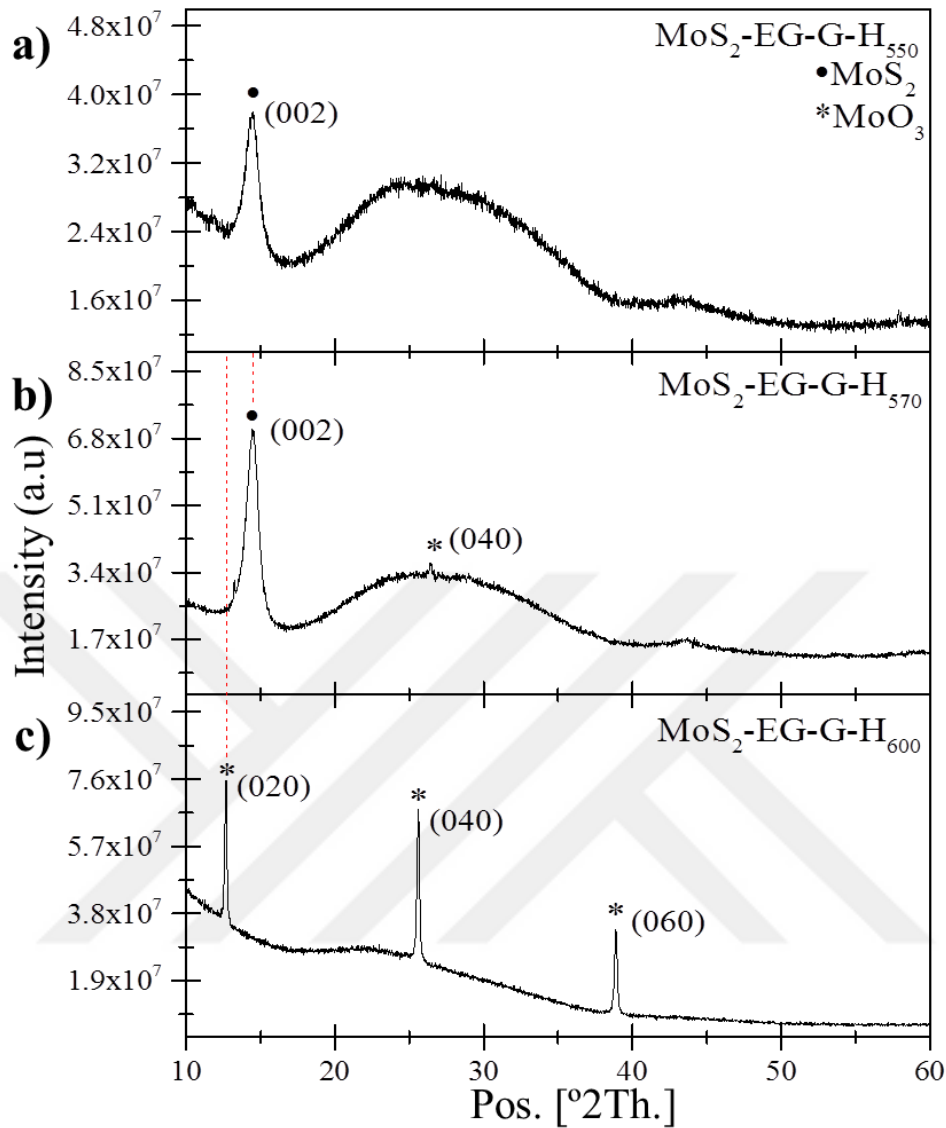


Figure 4.6. XRD patterns of a) $\text{MoS}_2\text{-EG-G-H}_{550}$ b) $\text{MoS}_2\text{-EG-G-H}_{570}$ and c) $\text{MoS}_2\text{-EG-G-H}_{600}$ samples.

From XRD results of three produced samples at different temperatures, 550 and 570°C heat treatment procedure temperatures are suitable for ensuring crystallinity of the films. The slight difference in peak intensity between these temperatures allows us to use 570°C heat treatment temperature as the main parameter.

4.1.2. Raman results of optimization samples

Raman measurements of optimization samples were carried out at 532 nm laser wavelength. According to Figure 4.7, there is no valid peak for MoS_2 in $\text{MoS}_2\text{-M-G}$ and $\text{MoS}_2\text{-M-Q}$ samples. Since we observed only MoO_3 phases for these samples in the XRD experiment, the Raman results shown in Figure 4.7 are expected.

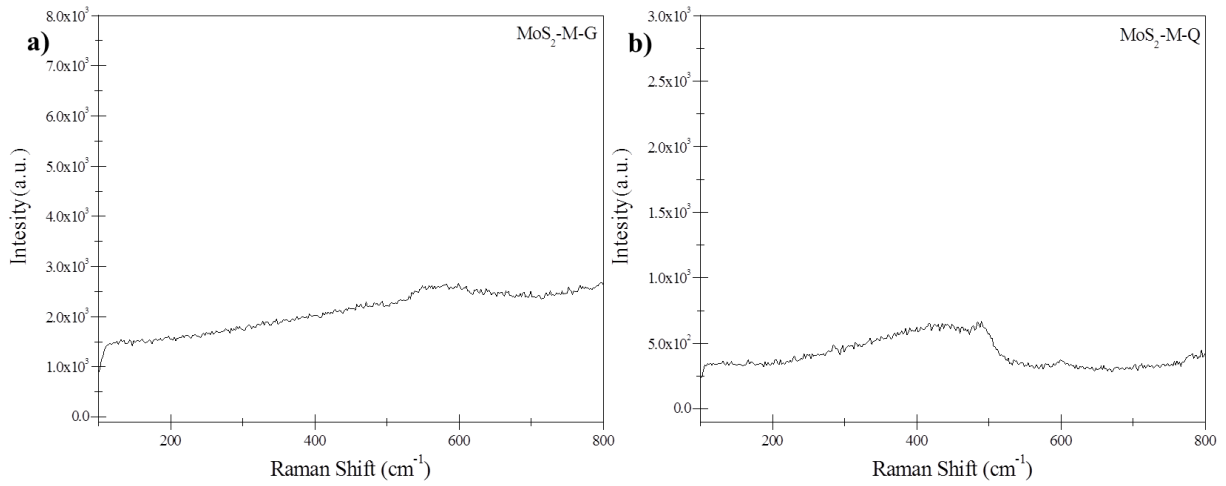


Figure 4.7. Raman patterns of a) MoS₂-M-G and b) MoS₂-M-Q samples.

Next, we performed the same Raman experiment on a MoS₂-EG-G-H₆₀₀ sample (Figure 4.8). As expected from the XRD data, we could not see any vibration modes of MoS₂ because of MoO₃ formation in this sample.

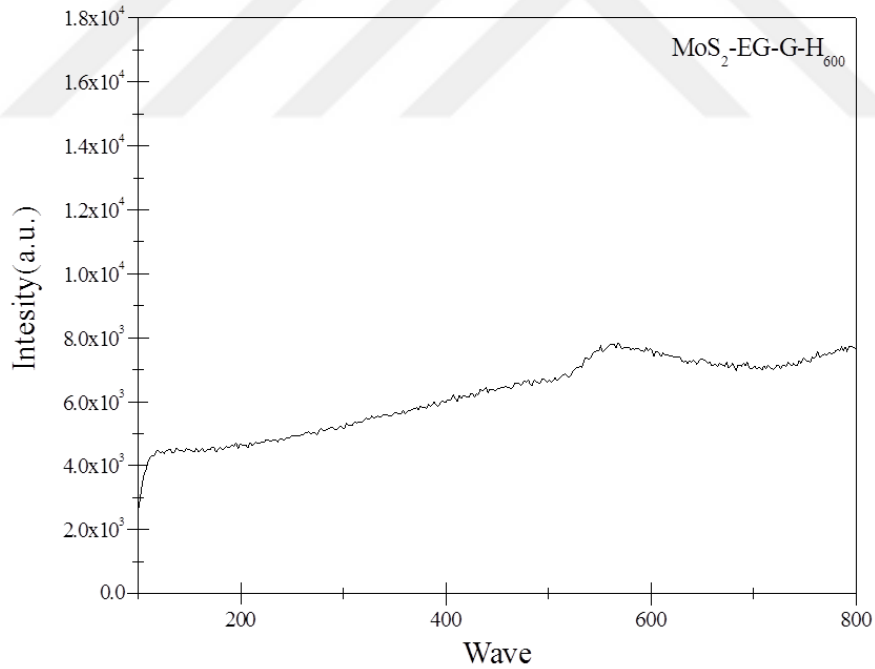


Figure 4.8. Raman spectrum of MoS₂-EG-G annealed at 600°C.

Figure 4.9 shows the Raman patterns of the MoS₂-EG-G sample annealed at 570°C. According to the spectrum, main vibrations modes of 2H MoS₂ E_{2g}^1 and A_{1g} are observed at 379.29 and 405.69 cm⁻¹, respectively. The difference between these peaks specifies the layer number of samples. The calculated value for this sample is 26.4 cm⁻¹ which is close to the

bulk value of MoS₂. Since the linear relation between the width of vibration modes of MoS₂ and the layer number, when the difference between these two peaks decreases, the layer number of MoS₂ is also decreases (Chen et al., 2016; Fu et al., 2017; Gołasa et al., 2013; Gong et al., 2017; J. He et al., 2018; Qian et al., 2019; Woods et al., 2016; Yu et al., 2013; Zhan et al., 2012).

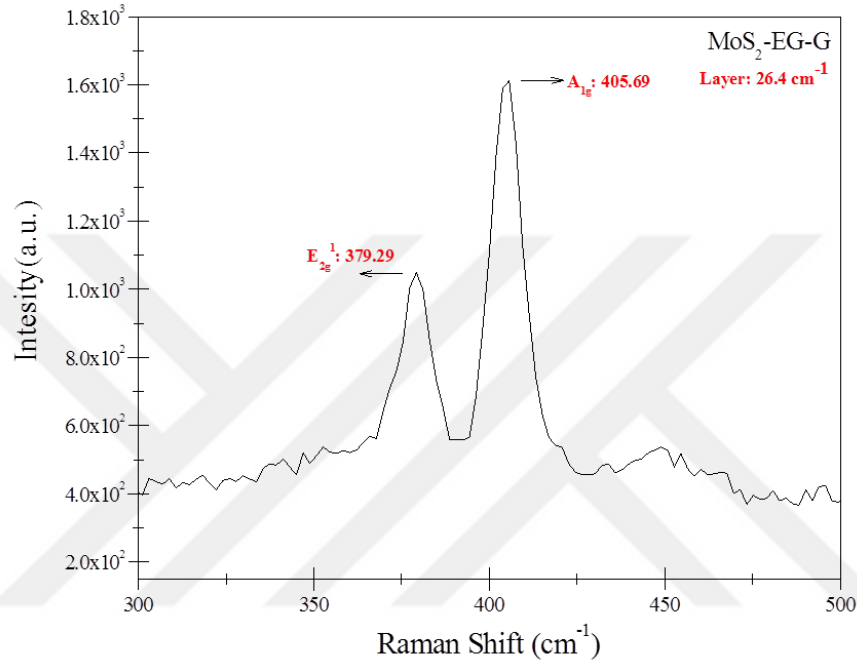


Figure 4.9. Raman pattern of MoS₂-EG-G (2.5 wt. ATTM) sample annealed at 570°C.

Next, we worked on the effect of ATTM concentration on the formation of MoS₂ film. Figure 4.10(a-c) shows the Raman spectrums of the samples MoS₂-EG1-G, MoS₂-EG2-G and MoS₂-EG3-G which have 1.25, 2.25 and 3.25% ATTM concentration, respectively. The only MoS₂-EG1-G sample having 1.25% wt. ATTM in EG has characteristic 2H MoS₂ vibration modes that stay at 382.77 cm⁻¹ and 408.83 cm⁻¹. The difference between these peaks is 26.06 cm⁻¹ which is less than the MoS₂-EG-G sample (26.40 cm⁻¹). These results mean that the layer number of MoS₂ can be slightly decreased by changing the weight percent of the precursor.

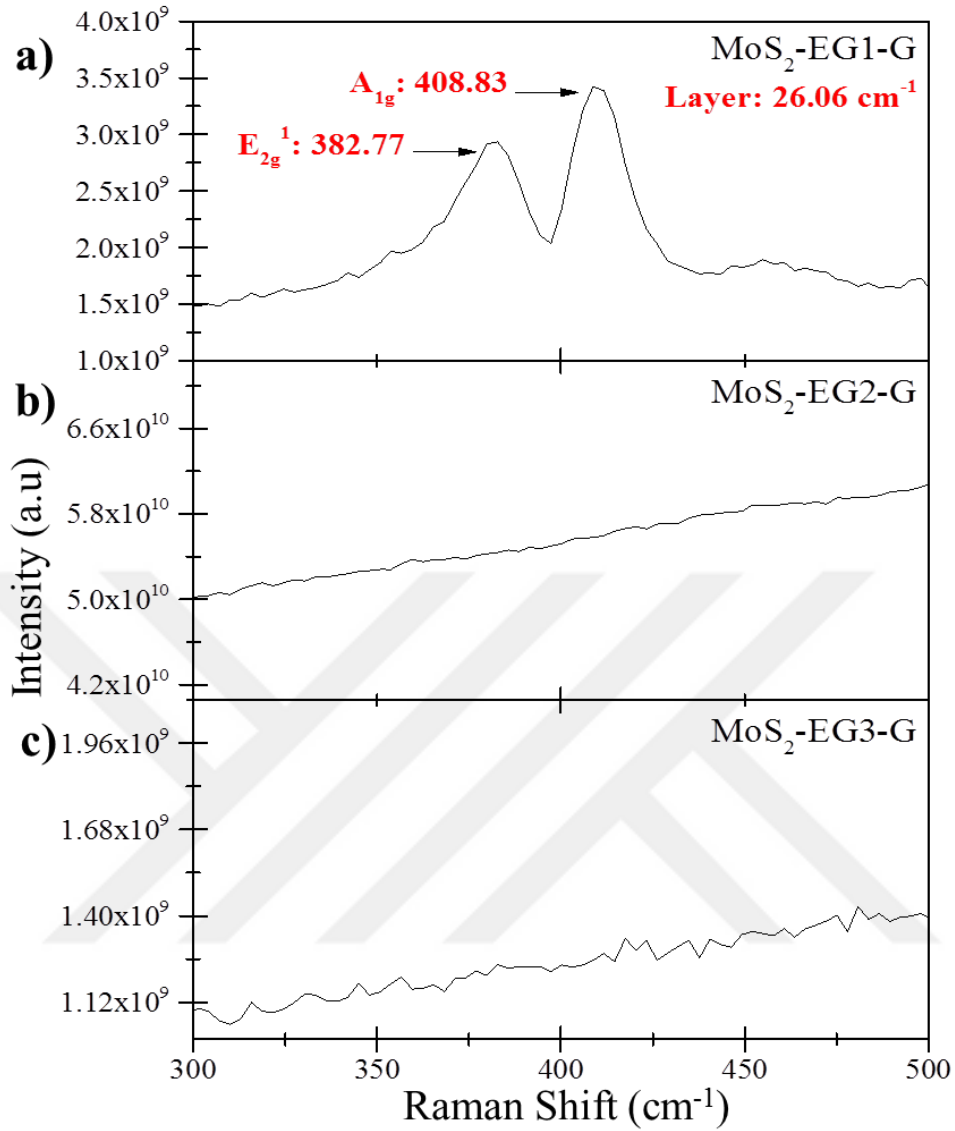


Figure 4.10. Raman spectrums of a) MoS₂-EG1-G, b) MoS₂-EG2-G and c) MoS₂-EG3-G samples annealed at 570°C.

We also produced a MoS₂ thin film called MoS₂-DMF3-G by using DMF solvent. In the Raman spectrum of MoS₂-DMF3-G (see Figure 4.11), characteristic vibration modes of 2H MoS₂ E_{2g}^1 and A_{1g} were observed at 382.8 and 408.8 cm⁻¹, respectively. The calculated difference between peaks is 26.0 cm⁻¹ which is slightly less than samples produced by using EG as solvent. Due to the better solution conditions, solubility properties, quick and easy chemical production and structural results, DMF solvent were chosen as solvent in the following processes.

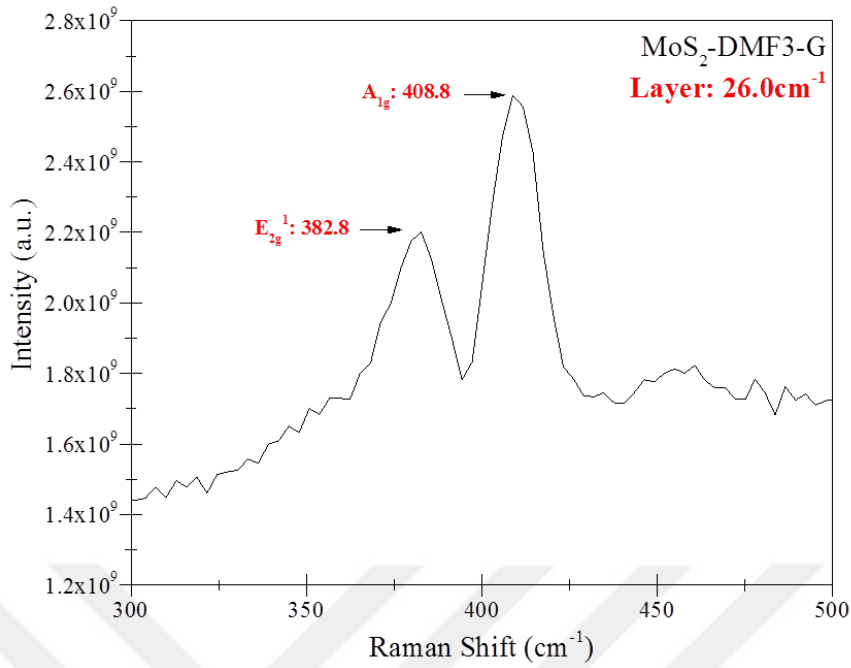


Figure 4.11. Raman spectrum of MoS₂-DMF3-G annealed at 570°C.

4.2. Structural and magnetic results of MoS₂-DMF samples

In this section, structural and magnetic characterization results of MoS₂ samples produced by using DMF as a solvent will be discussed. The structural properties of samples were investigated by using Raman spectroscopy and SEM characterization techniques.

4.2.1. Raman results of MoS₂-DMF samples

MoS₂ samples structural characterization results were investigated by performing Raman spectroscopy at 532 nm laser wavelengths. In this part, we prepared three sample solutions having 0.82%, 0.95% and 1.08% wt. ATTM concentration in DMF (see Table 3-7). As explained in Chapter 3, we coated these solutions on Si/SiO₂ substrate by using a spin-coating system. The grown samples are called MoS₂-DMF1-S, MoS₂-DMF2-S and. MoS₂-DMF3-S for 0.82%, 0.95% and 1.08% wt. ATTM concentration, respectively.

Figure 4.12(a-c) shows the Raman results of MoS₂-DMF1-S, MoS₂-DMF2-S and MoS₂-DMF3-S samples. In all samples, we observed characteristic Raman peaks of E_{2g}^1 and A_{1g} 2H-MoS₂. These characteristic peaks of E_{2g}^1 and A_{1g} 2H-MoS₂ were found as 383.0 cm⁻¹, 409.0 cm⁻¹; 383.1 cm⁻¹, 409.1 cm⁻¹; 383.0 cm⁻¹, 408.9 cm⁻¹ for MoS₂-DMF1-S, MoS₂-DMF2-S and. MoS₂-DMF3-S samples, respectively. The differences between these peaks are 26.0

cm^{-1} , 26.0 cm^{-1} and 25.9 cm^{-1} . Although all these values are close to each other, the MoS_2 -DMF3-S sample's peak intensities are lower than the other samples. The intensities of the peaks are close to each other, but the largest is the MoS_2 -DMF2-S sample when we compare it to the other samples. Therefore, we concluded that the optimum ATTm concentration is 0.95% in DMF solvent. In the next sample productions, this concentration was chosen.

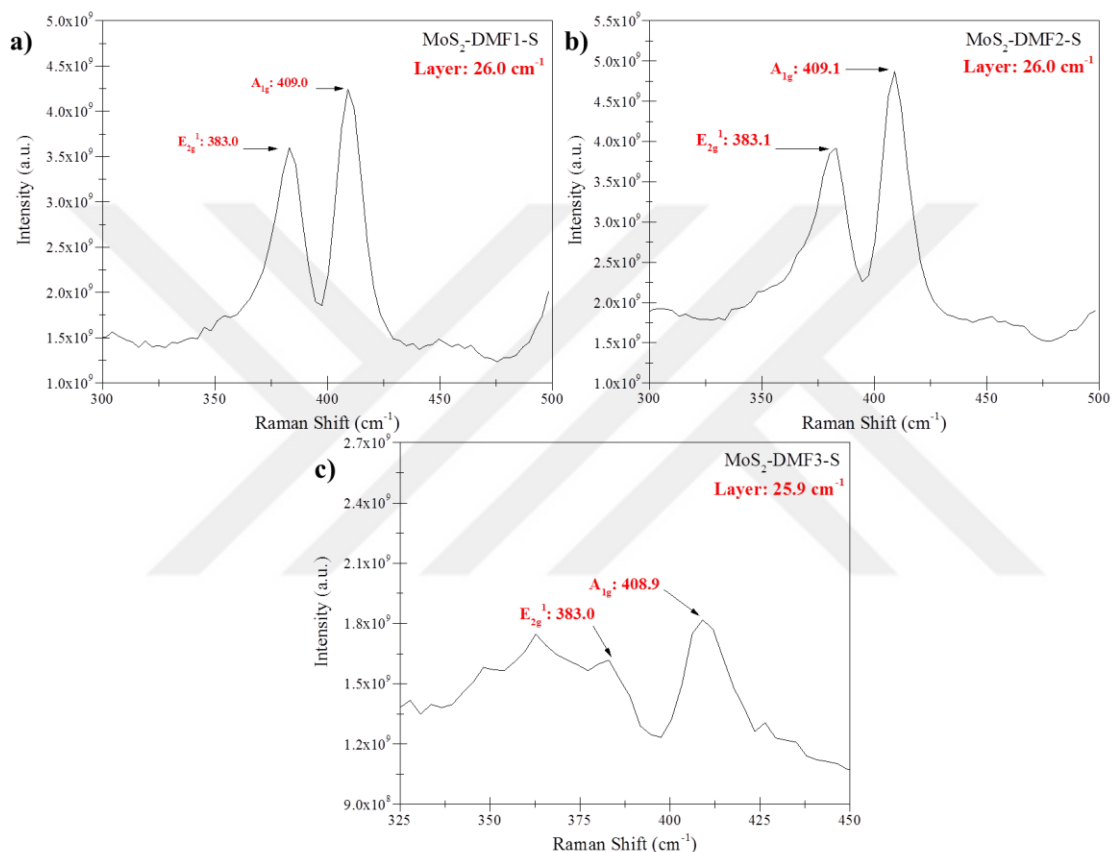


Figure 4.12. Raman spectroscopy of a) MoS_2 -DMF1-S, b) MoS_2 -DMF2-S, c) MoS_2 -DMF3-S samples.

4.2.2. SEM images of MoS_2 -DMF2-S sample

The morphological properties of the produced MoS_2 -DMF2-S sample has been investigated by performing a scanning electron microscope (SEM) imaging experiment. The SEM images give information about film surface's morphology, grains size/shape and their distributions. SEM images of MoS_2 -DMF2-S sample having 0.95% ATTm were taken at 3kX, 10kX and 26 kX magnifications as shown in Figure 4.13(a-c), respectively. According to the SEM images, the MoS_2 structure formed as a back-to-back triangle shape structure. The MoS_2

grains are uniformly distributed through the substrate. In Figure 4.13(b-c), the size of each back-to-back triangle shape is shown. Figure 4.14 shows the grain size distribution histogram. The average grain size was found as $2.20\ \mu\text{m}$ by selecting all grains in the figure.

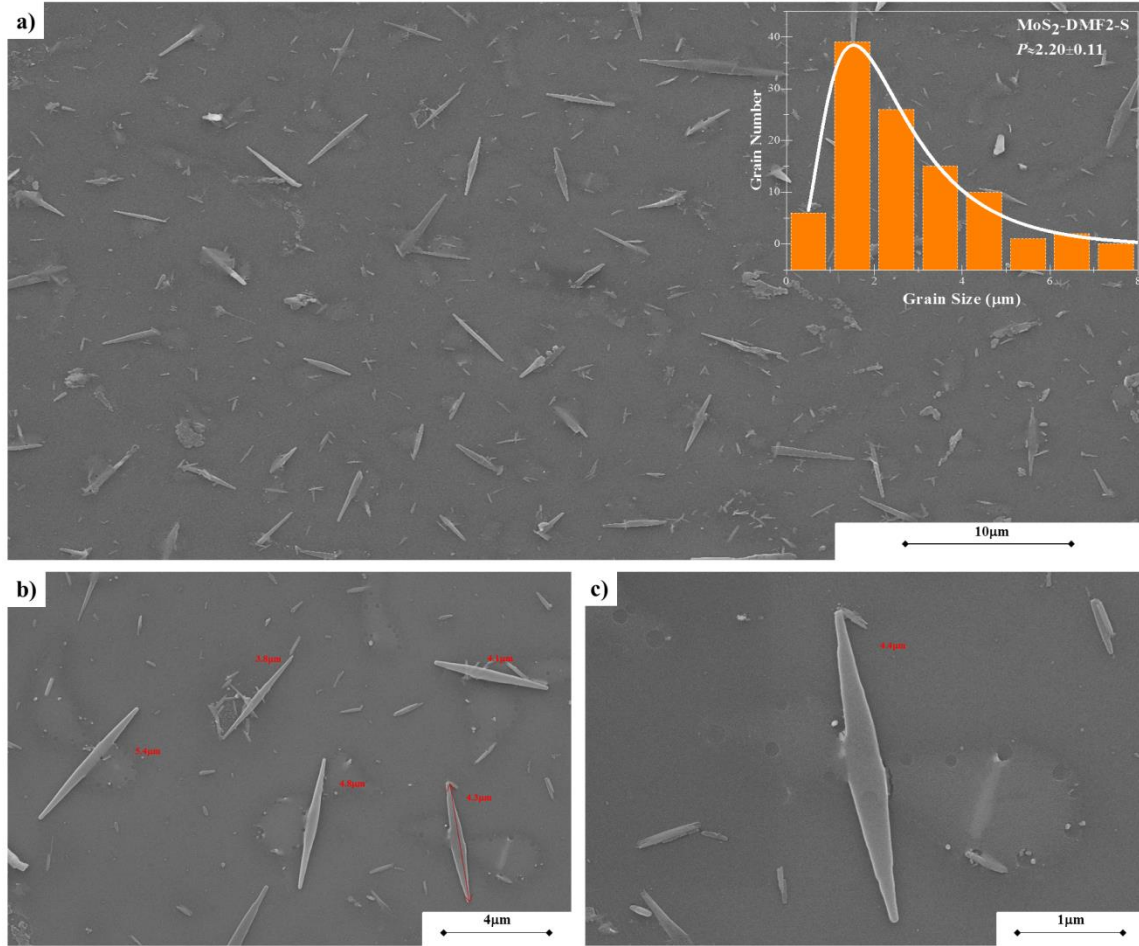


Figure 4.13. SEM images of MoS₂-DMF2-S sample a) 3kX, b) 10kX and 26kX magnifications.

Normally, the shape of the MoS₂ nanoflakes at surfaces forms as an equilateral triangle (Chhowalla et al., 2013). For our sample, it is seen that MoS₂ triangles become integrated producing back-to-back triangle shapes with long lateral length. The reason for this situation might be the heat treatment process or other unknown mechanism.

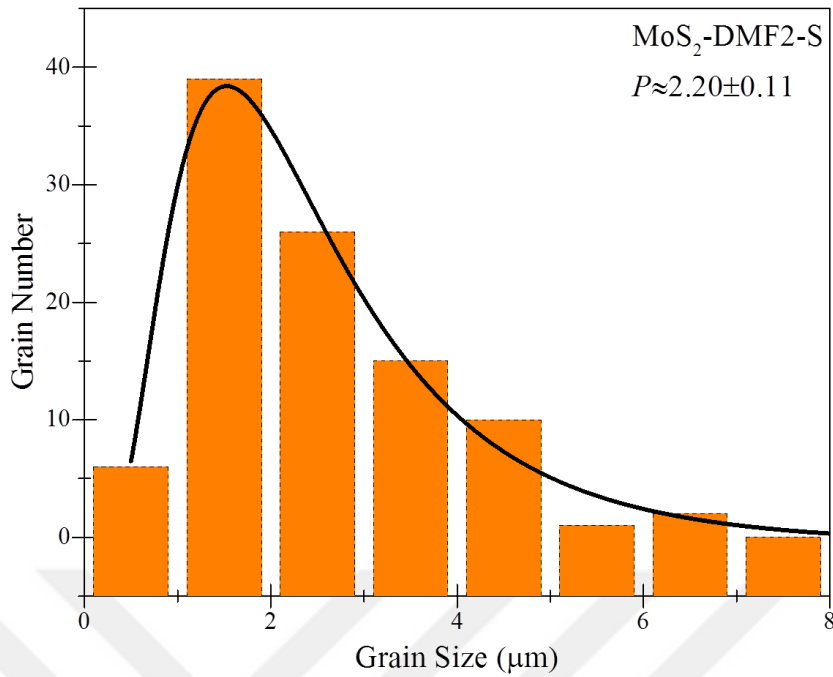


Figure 4.14. Grain size distribution of MoS₂-DMF2-S sample

4.2.3. Magnetic properties of MoS₂-DMF sample

The magnetic properties of the MoS₂-DMF sample were investigated by performing temperature and magnetic field dependence magnetization measurements using a vibrating sample magnetometer (VSM). The temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization were carried out under 500 Oe applied magnetic field by sweeping temperature between 5 and 300 K. In the ZFC magnetization measurement, the sample was cooled from room temperature to 5 K under zero field and after stabilization of temperature, moment data of the sample was recorded by heating the sample under a magnetic field of 500 Oe. In the FC mode, a magnetic field of 500 Oe was applied to the sample, then the sample was cooled down from room temperature to 5 K and moment data of the sample was recorded by heating the sample under the field.

Although the magnetic behavior of MoS₂ material is still a mystery, it is seen from the literature that ferromagnetism can be observed in MoS₂ produced in nanoparticle form (Tongay et al., 2012). Since our samples are in thin film form, there is no direct a work on the magnetism. Because the moment value of MoS₂ thin film is extremely small, the collecting moment data has significant noise signals in the VSM measurement. Figure 4.15 shows the temperature dependence of magnetic moment of MoS₂-DMF2-S sample. The interesting point is the ZFC and FC curves magnitude changes by the temperature. The ZFC data increase

gradually with increasing temperature up to ~247 K and then, it decreases with the increasing temperature. Finally, ZFC and FC moment values become equal at room temperature. This abnormal situation in ZFC and FC curves could be explained by following relation (Deng-Lu Hou, 2002);

$$M_{ZFC}(T) = M_{FC}(T)k \frac{H_a}{H_c} \quad (3)$$

where M_{ZFC} is magnetization in ZFC, M_{FC} is magnetization in FC, H_a is applied field, H_c is coercive field and k is a constant. If H_a is less than H_c , M_{ZFC} will be less than M_{FC} . If H_a is equal to H_c , then $M_{ZFC} = M_{FC}$. When H_a is more than H_c , then M_{ZFC} becomes more than M_{FC} . At $T_N = T_B$ which are Neel and Blocking temperatures, respectively, the M_{ZFC} is equal to M_{FC} . In between T_N and T_B , H_a is more than H_c to make ZFC more than FC that implies a ferrimagnetic behavior. In our experiments, we used 500 Oe as an applied field that might be larger than the H_c value for our sample based on the Eq.(3). In addition, the peak in moment versus temperature curve in ZFC measurement (~247 K) can be called a blocking temperature for MoS₂.

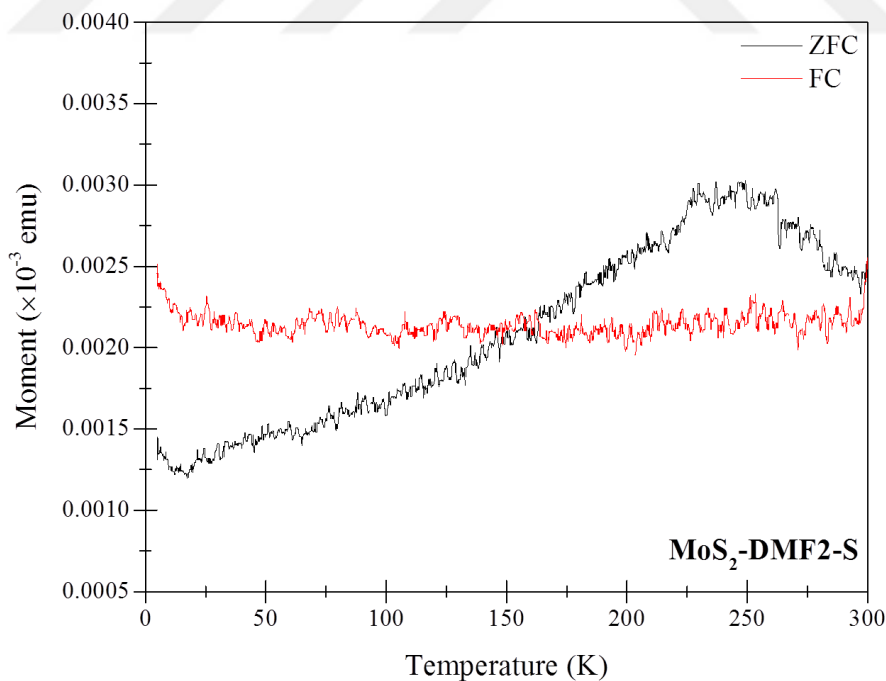


Figure 4.15. Temperature dependence of magnetic moment of MoS₂-DMF2-S sample.

Next, we performed the magnetic hysteresis (M - H) measurements by sweeping the applied field at low (5 K) and room temperature (300 K). For low temperature measurement, the

sample was cooled without applying a magnetic field. Then, a magnetic field is applied to the samples by continuous increment. The moment values of samples were not normalized by the size (volume) because the film surface was not covered with MoS₂ layers as observed in SEM images.

According to the magnetic hysteresis curves of the MoS₂-DMF2-S sample (Figure 4.16(a)), the film shows a ferro/ferri-magnetic behavior at 5 K. This behavior is consistent with the M - T results of the sample. Since the magnetic signal is not strong as bulk materials, the data analysis of this sample is not performed deeply. M_s and H_c values of the film were found as 0.014 emu and 279 Oe, respectively. On the other hand, the MoS₂-DMF2-S sample shows diamagnetic characteristics at 300 K. The diamagnetism might come from the substrate. The film's own magnetic moments are extremely small as shown in Figure 4.16(b). The sources of magnetic interaction in MoS₂ are caused by the discontinuity of the crystals of material on the surface of the sample. According to the SEM images of undoped sample, crystallization of material is low and there is a certain discontinuity of crystals. In accordance with the literature, this kind of discontinuities leads to formation of ferromagnetic ordering (Sanikop & Sudakar, 2019; Tongay et al., 2012). The edges which are the discontinuity of crystals show different magnetic ground state from the continuous part of the material (C. Ataca, 2011; Hai Li, 2012; Yafei Li, 2008). In this sample MoS₂-DMF2-S, the separate crystals might cause the ferromagnetic signals in magnetic measurements.

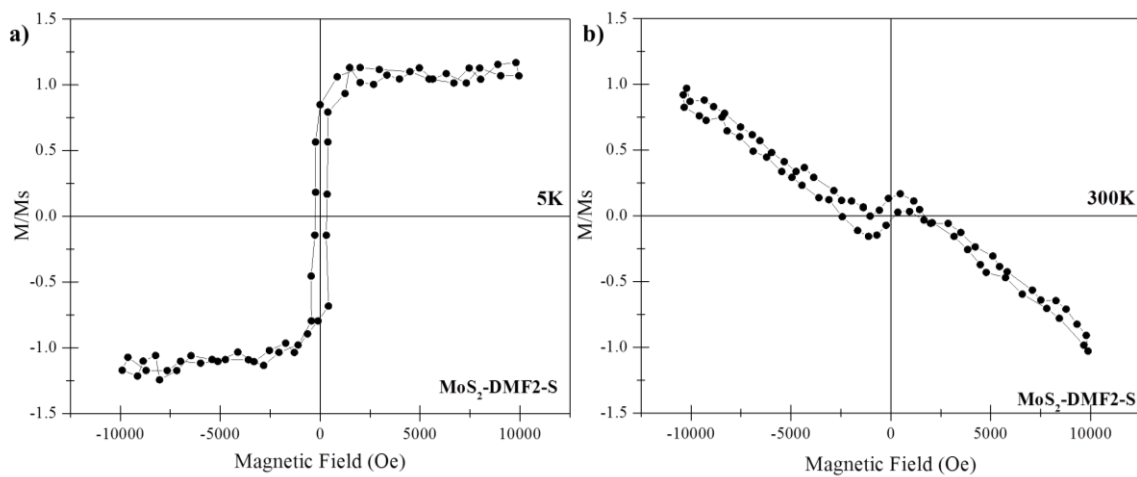


Figure 4.16. Magnetic hysteresis curve of MoS₂-DMF2-S sample measured at a) 5K and b) 300 K.

4.3. Structural and magnetic results of Fe-doped MoS₂ samples

The optimized MoS₂ sample is further studied by Fe-doping. Here, various Fe concentrations (0.5, 0.75 and 1.0 % wt.) were doped in MoS₂. The produced samples' structural and magnetic properties are discussed in this section. As we explained in detail in Chapter 3 (Table 3-8), the films are called as Fe_{0.50}:MoS₂-S, Fe_{0.75}:MoS₂-S and Fe_{1.00}:MoS₂-S and for 0.50%, 0.75% and 1.00% and Fe concentrations, respectively. The structural properties of samples were investigated by using Raman spectroscopy and SEM characterization techniques. The magnetic properties were studied by using the VSM system.

4.3.1. Raman results of Fe-doped MoS₂ samples

The Raman spectroscopy measurements of Fe-doped MoS₂ samples were carried out at 532 nm laser wavelength. Figure 4.17(a-c) shows the Raman spectrum results of produced Fe_{0.50}:MoS₂-S, Fe_{0.75}:MoS₂-S and Fe_{1.00}:MoS₂-S samples, respectively. The characteristic Raman peaks E_{2g}^1 and A_{1g} of 2H-MoS₂ are shifted and their intensities decrease significantly when Fe atoms are added to the main structure. In addition to characteristic MoS₂ peaks, we observed various Raman peaks in the spectroscopy. These peaks are tabulated in Table 4.1.

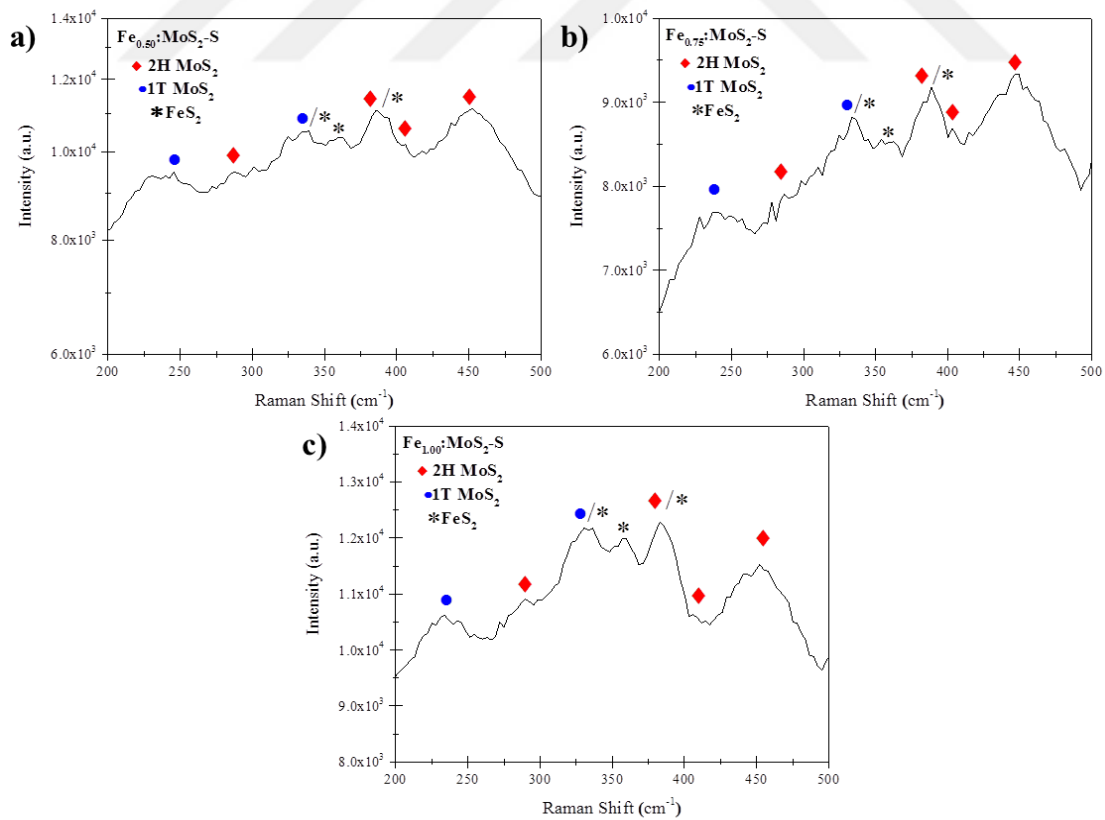


Figure 4.17. Raman spectroscopy results of a) Fe_{0.50}:MoS₂-S, b) Fe_{0.75}:MoS₂-S, c) Fe_{1.00}:MoS₂-S.

Table 4.1. The table of Raman peaks of Fe-doped samples.

Raman Peaks	Sample Codes		
	Fe _{0.50} :MoS ₂ -S	Fe _{0.75} :MoS ₂ -S	Fe _{1.00} :MoS ₂ -S
1T MoS ₂ (J ₂)	239.7	237.3	232.7
1T MoS ₂ (J ₃)	336.9	333.1	335.5
2H MoS ₂ (E_{2g}^1)	385.4	388.6	383.3
2H MoS ₂ (A_{1g})	405.2	404.2	405.5
2H MoS ₂	286.7/452.3	285.4/448.5	289.2/452.3
FeS ₂	336.9/359.4/385.4	333.1/358.1/382.9	335.5/359.0/383.3

According to the Raman data, 1T MoS₂ is formed in all Fe doped samples. The peaks are observed at 239.7, 237.3 and 232.7 cm⁻¹ for samples having 0.50%, 0.75%, and 1.00% wt. Fe, belong to the 1T MoS₂ (J₂) structure, respectively. The vibration modes observed around ~285 cm⁻¹ belong to the 2H MoS₂ (Zhao et al., 2017).

The peaks observed at 336.9/333.1/335.5 cm⁻¹ might be either 1T MoS₂ (J₃) or FeS₂ E_g vibration modes (T. Hu, Li, & Dong, 2013; Kao et al., 2018; Xia, Yang, Ma, Tao, & Gao, 2017; Zhao et al., 2017). On the other hand, $T_g(1)$ vibration mode of FeS₂ was observed around ~358 cm⁻¹ (Blanchard et al., 2009). The transition of the 2H-1T phase is formed by the displacement of S atoms from the unit cell to pyramidal position which decreases the energy barrier of the 2H-1T phase transition. Moreover, production of the 1T phase is ensured by the S atoms vacancies due to acting as nucleation formation site for 1T phase formation. For Fe-doped samples, the discontinuity in the S-Mo-S structure might occur by bonding S atoms with Fe. Thus, the lack of the S atoms leads to formation of 1T phase in Raman results of Fe-doped samples (Gan et al., 2018).

The peaks observed at 385.4, 382.9 and 383.3 cm⁻¹ for 0.50%, 0.75% and 1.00% doped samples belong to either 2H MoS₂ (E_{2g}^1) or FeS₂ $T_g(2)$. There are two possibilities of these peaks which are either MoS₂ or FeS₂. FeS₂ peaks might be obscured because of the shadowing effect of MoS₂ (Blanchard et al., 2009; Lee et al., 2012; Xia et al., 2017; Yuan, Luan, & Tu, 2012; Zhao et al., 2017).

The one of two main characteristic vibration modes of 2H MoS₂ (A_{1g}) were observed at 405.2, 404.2 and 405.5 cm⁻¹ for sample having 0.50%, 0.75%, and 1.00% wt., respectively (Lee et al., 2012; Xia et al., 2017; Yuan et al., 2012; Zhao et al., 2017). The other peak of 2H

MoS₂ was observed at 452.3, 448.5 and 452.3 cm⁻¹ for samples having 0.50%, 0.75%, and 1.00% wt. Fe due to the combinational band between LA(M) and (*A_{2u}*) modes, respectively (Hong Li et al., 2012; Zhao et al., 2017).

In conclusion, the peaks observed around ~331, ~358 and ~380 cm⁻¹ for all samples might belong to either MoS₂ or FeS₂ vibration modes (Blanchard et al., 2009). The closeness of the peaks to vibration modes of 2H MoS₂ makes it difficult to reach an accurate conclusion. According to the result, the reason of the resulting lack of S atoms and 1T formation in structure might be caused by formation of FeS₂ structure. According to this approximation, Raman peaks of FeS₂ shows that Fe atoms take place in the MoS₂ structure by bonding with S atoms.

4.3.2. SEM images of Fe-doped MoS₂ samples

SEM images of 0.50% Fe doped (Fe_{0.50}:MoS₂-S) sample were taken at 50 and 100 kX magnifications as shown in Figure 4.18(a-b). According to the image, the back-to-back triangle grain shape of MoS₂ becomes worse when Fe is added to the main structure. Although there are still MoS₂ grains formed as back-to-back triangle shapes, their distribution is not as good as pure one. The grain size distribution was determined from the SEM image and shown in Figure 4.18(c). The average grain size is found as 0.36 μm. Here, we just considered grain's length as a grain size. In Figure 4.18(b), some nanoclusters having average 73.9 nm are formed in Fe_{0.50}:MoS₂-S sample.

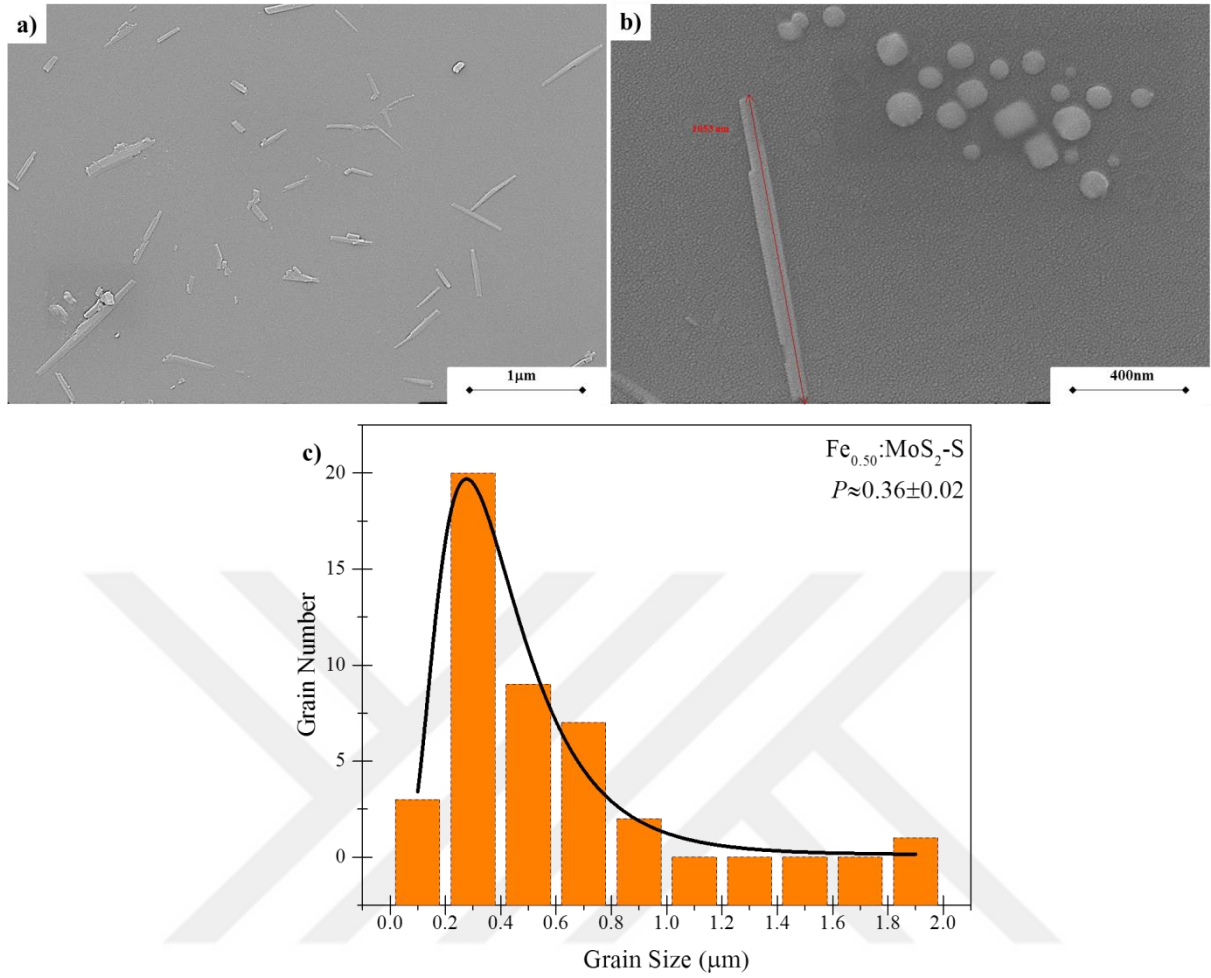


Figure 4.18. SEM images of 0.50% Fe-doped MoS₂ sample at a) 50 kX, b) 100 kX magnifications, c) grain size distribution of Fe_{0.50}:MoS₂-S sample.

SEM images of 0.75 % Fe doped MoS₂ sample were taken at various magnifications as shown in Figure 4.19(a-c). The MoS₂ grains are formed as nanorods and distributed randomly on the substrate as seen from the figures. The average size of the nanorods is calculated by selecting all grains in the SEM image. Figure 4.19(d) shows the grain size distribution. The average length and width of these nanorods are found as 2.38 μm and 110 nm, respectively. In addition to MoS₂ grains on the surface of substrate, the nanoparticles line up on the MoS₂ nanorods in a straight path as seen in Figure 4.19(c).

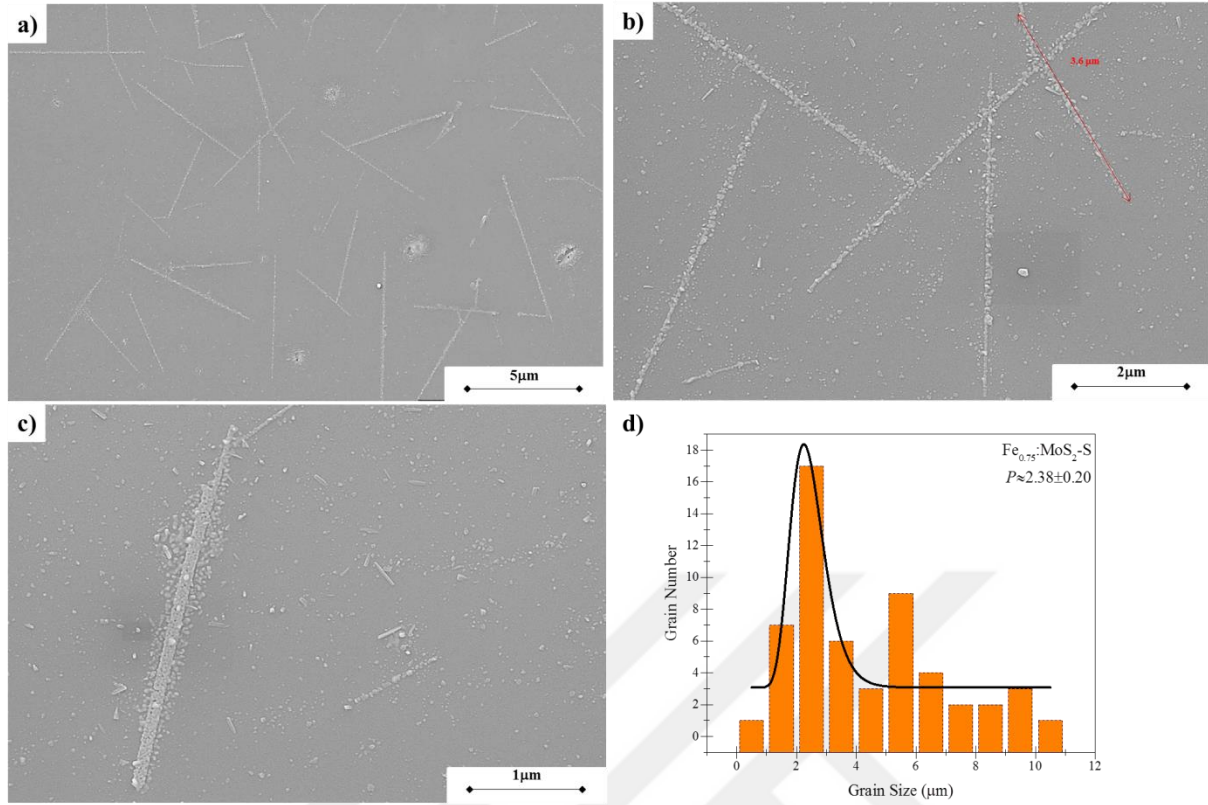


Figure 4.19. SEM images of 0.75% Fe-doped MoS₂ sample at a) 10 kX, b) 40 kX, c) 46 kX magnifications, d) grain size distribution of Fe_{0.75}:MoS₂-S sample.

SEM images of 1.00 % Fe doped sample were taken at 20 and 80 kX magnifications as shown in Figure 4.20(a-b). It is seen that there is the forming of vertically grown nanowalls. According to the image, the nanowalls enclose an area with small nanoparticles, where the average particle size of these particles is 57 nm which is shown in Figure 4.20(c).

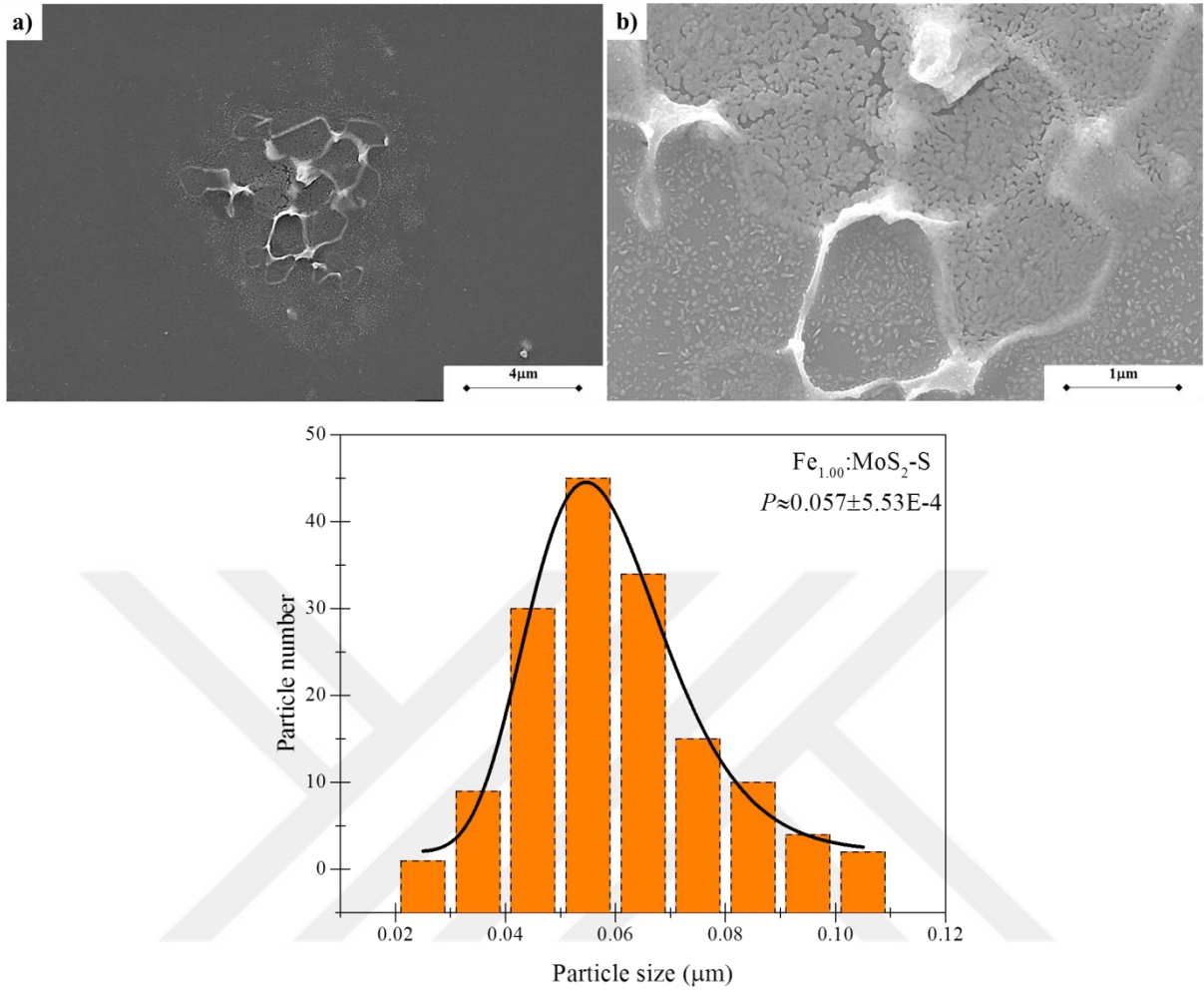


Figure 4.20. SEM images of 1.00% Fe-doped MoS₂ sample at a) 20 kX, b) 80 kX magnifications, c) particle size distribution.

4.3.3. Temperature dependence of magnetization results of Fe-doped MoS₂ samples

The magnetic properties of pure and Fe-doped MoS₂ were investigated by performing temperature and magnetic field dependence magnetization measurements. Same measurement procedures were used to measure the moment value of Fe-doped MoS₂ samples as we applied to the undoped MoS₂ sample. See details in Section 4.2.3.

According to Figure 4.21(b), the sample having %0.75 Fe concentration shows the magnetic transition temperature at 95.5 K. The addition of the Fe atoms at %0.75 concentration value shows the clear transition from ferromagnetic to paramagnetic. The contribution of the Fe atoms to ferromagnetic ordering is seen from the image. The difference between M-T graphs of pure and Fe-doped MoS₂ samples can be noticed with this sample. Considering transition

temperature of the pure and %0.75 Fe-doped, transition temperature decreases with the adding of Fe atoms into the structure.

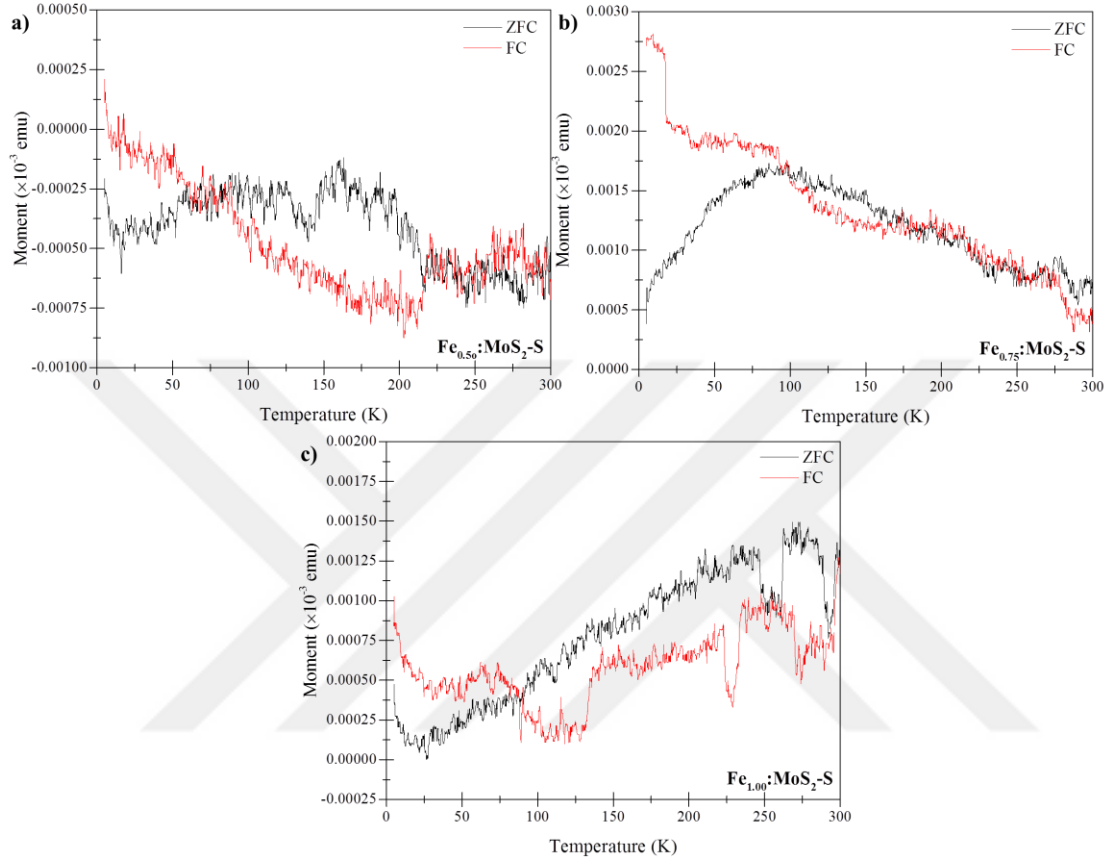


Figure 4.21. Temperature dependence of magnetic moment of samples a) $\text{Fe}_{0.50}:\text{MoS}_2\text{-S}$, b) $\text{Fe}_{0.75}:\text{MoS}_2\text{-S}$ and c) $\text{Fe}_{1.00}:\text{MoS}_2\text{-S}$.

The temperature dependence of magnetic moment of %0.50 and %1.00 Fe-doped samples are shown in Figure 4.21(a-c). Because the data of the measurements are lauded, the estimation of the transition temperature is quite impossible. This complicated data can be resulted from the sample structure. Considering the SEM images of the 0.50% and 1.00% Fe-doped samples, the structure of material did not form as we foresee. This failure in the crystallization and the forming of the structure might cause the magnetic measurements of the sample. The accurate prediction of the transition temperature cannot be made for these three samples.

4.3.4. Magnetic hysteresis curves of Fe-doped MoS₂ samples

Figure 4.22 shows the magnetic hysteresis curves of samples. According to the figure, the sample 'Fe_{0.75}:MoS₂-S' shows ferromagnetic ordering with very a small coercive field value at 5K. The existence of ferromagnetic characteristics at 5K consistent with the *M-T* graphs of sample. The *M_s* value of the sample increased to 0.018 emu with the adding of the Fe atoms. The *H_c* value of sample was found as 140 Oe which point to a decrease compared to pure sample (279 Oe).



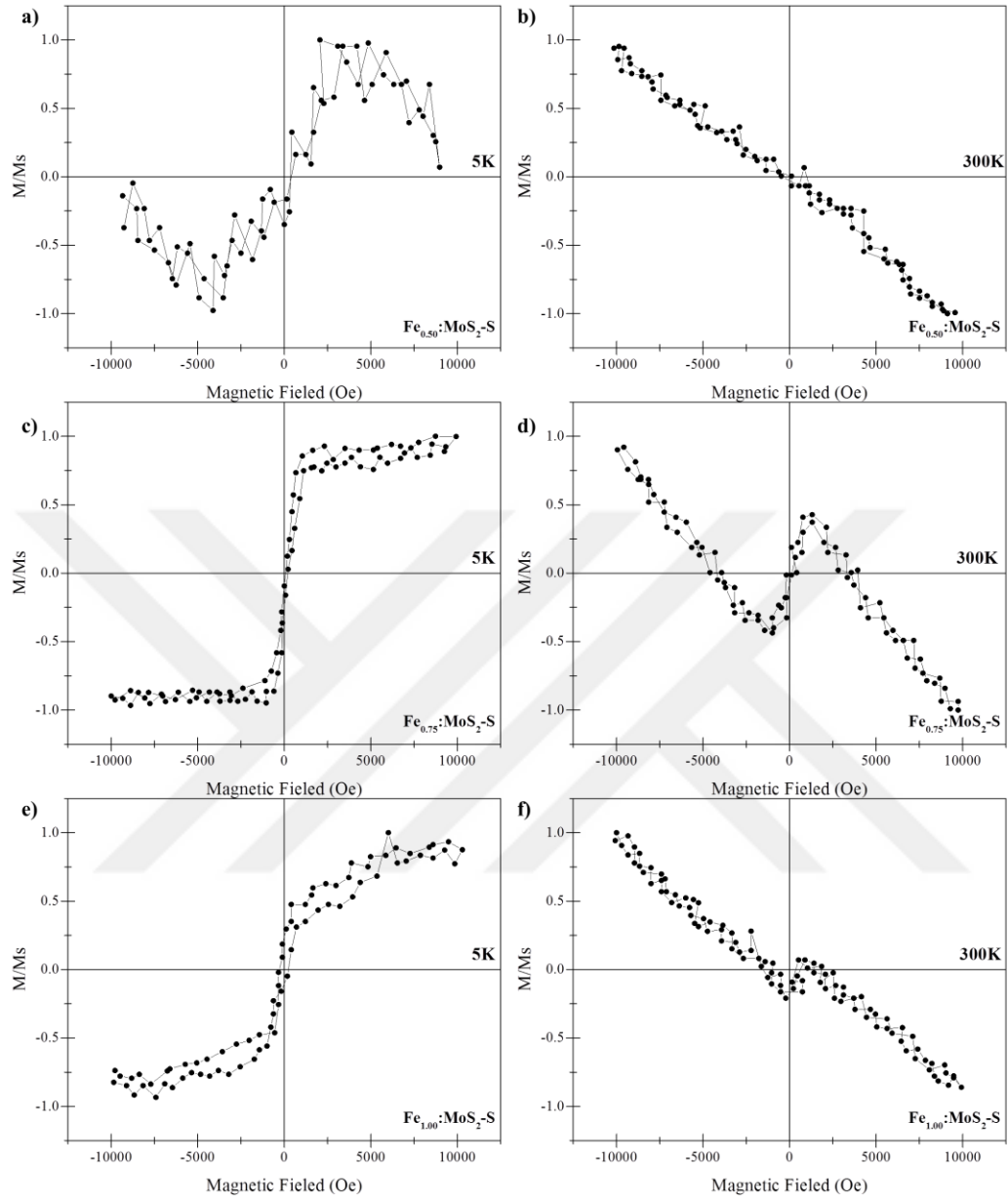


Figure 4.22. Hysteresis curves samples a,b) hysteresis curves of %0.50 Fe doped sample, c,d) hysteresis curves of %0.75 Fe doped sample and e,f) hysteresis curves of %1.00 Fe doped sample.

According to Figure 4.22, the hysteresis curves of three samples are quite simple. At room temperature, all samples, except %0.75 Fe-doped sample, show diamagnetic characteristics. Since the film is not fully covered on the substrate, the magnetic signals are extremely low. There are only slightly different M_s and H_c values for samples at 5K which can be seen in Table 4-2.

Table 4.2. Magnetic properties of pure and Fe-doped samples.

Sample	Fe concentration (%)	M_s (emu)	H_c (Oe)
MoS ₂ -DMF2-S	0.00	0.014	279
Fe _{0.50} :MoS ₂ -S	0.50	0.007	375
Fe _{0.75} :MoS ₂ -S	0.75	0.018	140
Fe _{1.00} :MoS ₂ -S	1.00	0.011	267

According to the Table 4-2, the M_s value increases but H_c decreases with the increasing Fe concentration considering pure (MoS₂-DMF2-S) and %0.75 Fe-doped (Fe_{0.75}:MoS₂-S) samples. As a result, the introducing of Fe atoms into the MoS₂ structure affects the magnetic properties as we predict. The diamagnetic characteristic of pure MoS₂ films is changed by the Fe atoms to small ferromagnetic ordering. Because of the bad magnetic data of the %0.50 and %1.00 Fe-doped samples, we cannot make accurate comments on characteristics and properties of doped samples.

4.4. Structural and magnetic results of Cu-doped MoS₂ samples

In this section, various Cu concentrations (0.50, 0.75 and 1.00% wt.) were doped in MoS₂ and the produced samples' structural and magnetic properties were discussed in detail. As we explained the details in Chapter 3 (Table 3-9), the films are called Cu_{0.50}:MoS₂-S, Cu_{0.75}:MoS₂-S and Cu_{1.00}:MoS₂-S for 0.50%, 0.75% and 1.00% and Cu concentrations, respectively. The structural properties of samples were investigated by using Raman spectroscopy and SEM characterization techniques. The magnetic properties were studied by using the VSM system.

4.4.1. Raman results of Cu-doped MoS₂ samples

The Raman spectroscopy measurements of Cu-doped MoS₂ samples were carried out at 532 nm laser wavelength. Raman results of Cu doped samples are shown in Figure 4.23.

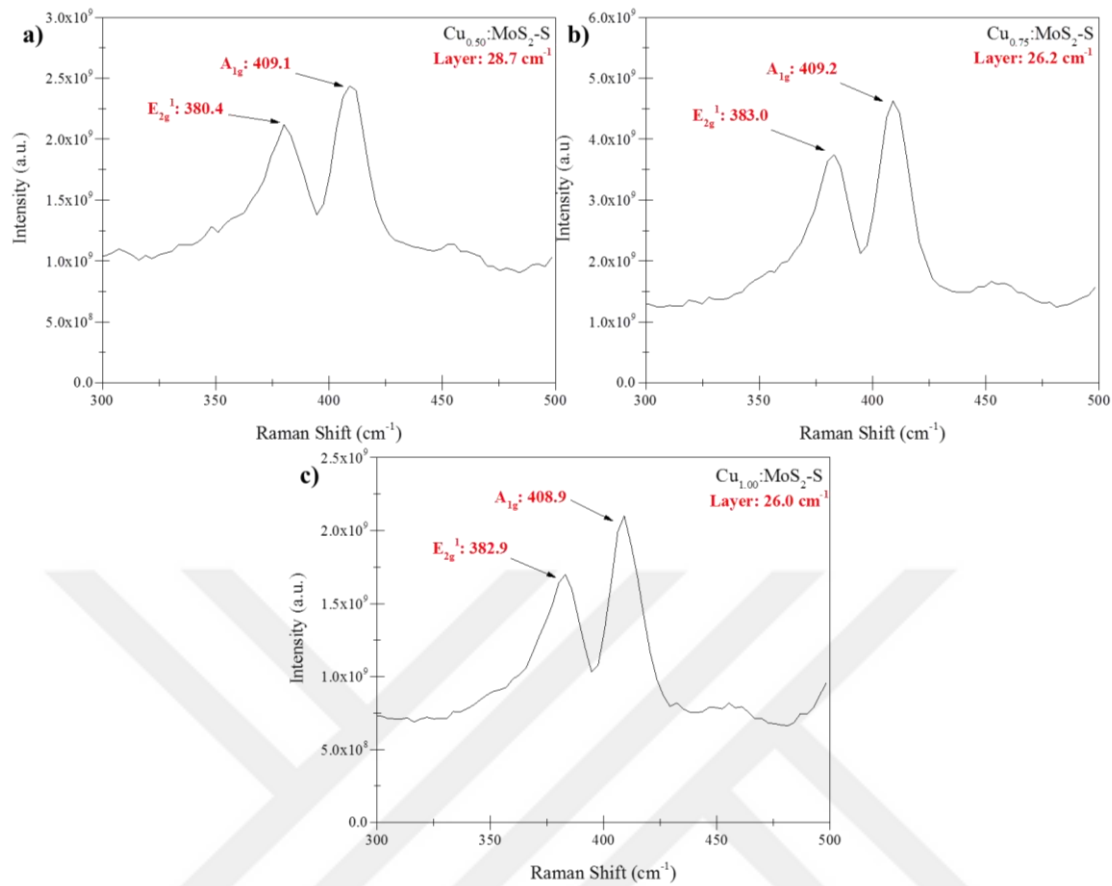


Figure 4.23. Raman spectroscopy results of a) $\text{Cu}_{0.50}:\text{MoS}_2\text{-S}$, b) $\text{Cu}_{0.75}:\text{MoS}_2\text{-S}$, c) $\text{Cu}_{1.00}:\text{MoS}_2\text{-S}$.

According to the Raman results of samples, two characteristic peaks of MoS_2 were observed at 380.4 and 409.1 cm^{-1} , 383.0 and 409.2 cm^{-1} , 382.9 and 408.9 cm^{-1} for samples 0.5, 0.75 and 1% Cu-doped samples, respectively. The differences between peaks were calculated as 28.7 , 26.2 and 26.0 cm^{-1} which correspond to the bulk value of MoS_2 . The results showed that all samples grown on Si/SiO_2 substrates as bulk form.

4.4.2. SEM images of Cu-doped MoS_2 samples

SEM images of 0.50% Cu doped ($\text{Cu}_{0.50}:\text{MoS}_2\text{-S}$) sample were taken at 50 and 100 kX magnifications as shown in Figure 4.24, respectively. According to Figure 4.24(a), the film structure appears as smooth and there are some lamellar structures on it. The amount of nanorod structure of Cu-doped samples is less than pure and Fe-doped sample (see Figure 4.18). The smooth structure can be observed at Figure 4.24. SEM images and Raman results of 0.50% Cu-doped MoS_2 sample show that the film stacked as bulk.

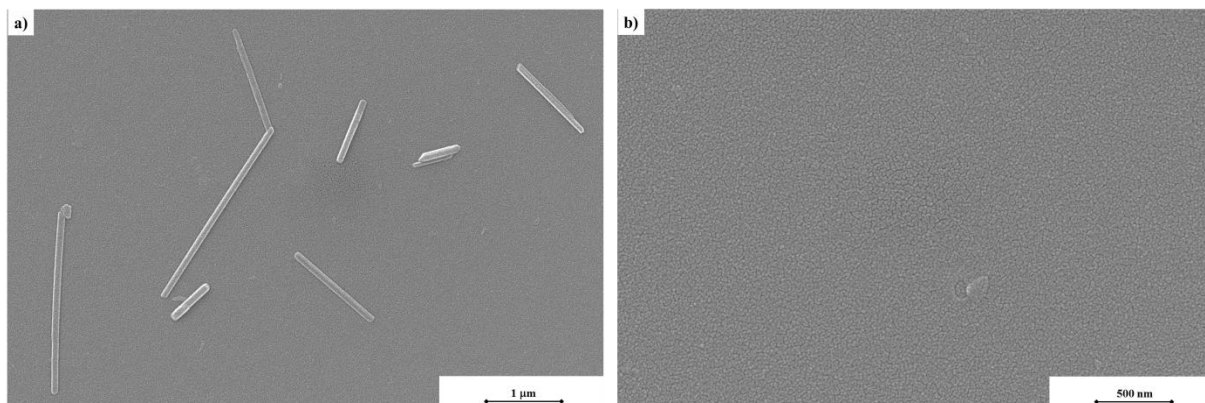


Figure 4.24. SEM images of 0.50% Cu-doped MoS₂ sample at a) 50 kX, b) 100 kX magnifications.

SEM images of 0.75% Cu doped (Cu_{0.75}:MoS₂-S) sample were taken at 50, 100 and 200 kX magnifications as shown in Figure 4.25. According to the SEM image of 0.75% Cu-doped MoS₂ sample, the smooth structure can be observed in all images. The rod-shape grains in the film's structure are more obvious than the 0.50% Cu doped sample. The stacking event of the layer of the films can be observed in Figure 4.25. The cavity on the film surface demonstrates the formation of the layered structure. The Raman results of the sample support this deduction of bulky structure of film as well (see Figure 4.23).

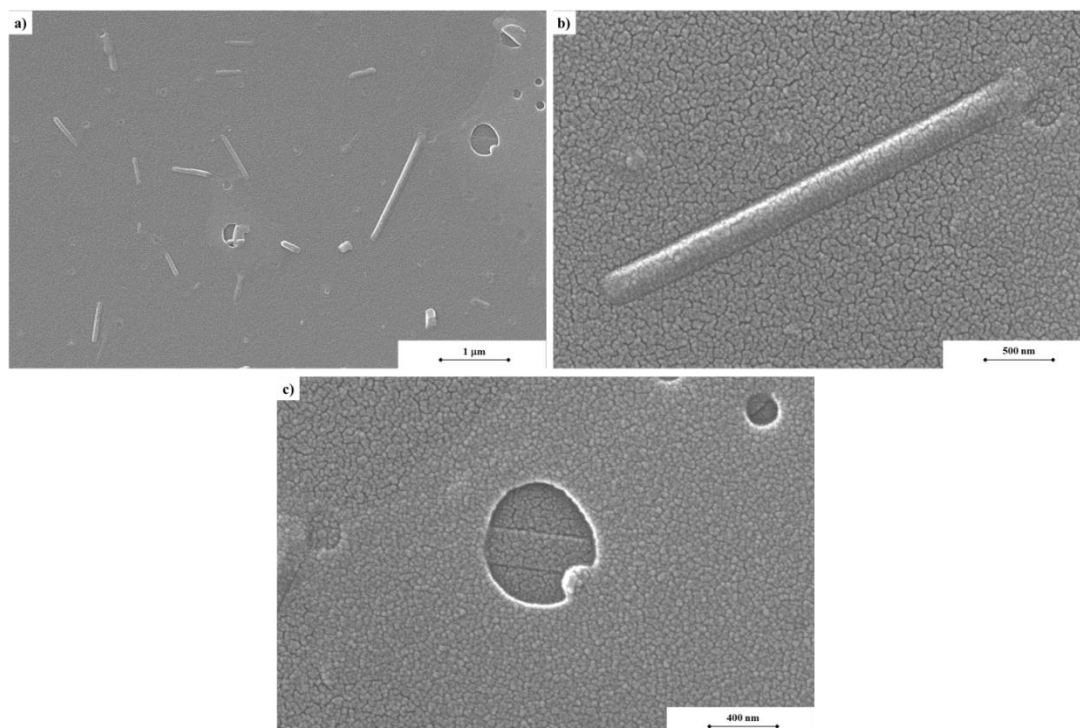


Figure 4.25. SEM images of 0.75% Cu-doped MoS₂ sample at a) 50 kX, b) 100 kX and c) 200 kX magnifications.

SEM images of 1.00 % Cu doped MoS_2 sample were taken at various magnifications as shown in Figure 4.26. According to the results, the film's surface is the same as the other Cu-doped samples. In conclusion, all Cu-doped thin film samples grow as bulk with a small portion of nanorod structure.

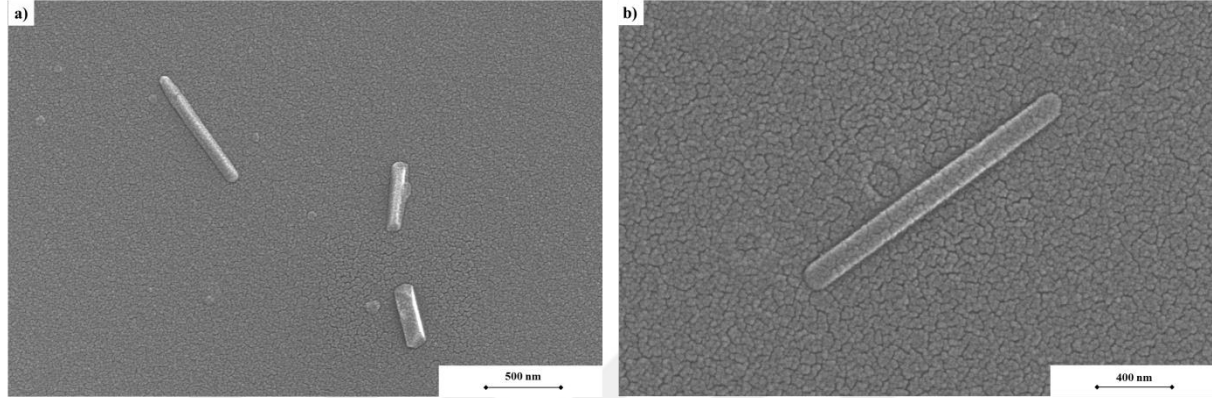


Figure 4.26. SEM images of 1.00% Cu-doped MoS_2 sample at a) 50 kX and b) 100 kX magnifications.

4.4.3. Temperature dependence of magnetization results of Cu-doped MoS_2 samples

The magnetic properties of Cu-doped samples were first investigated by performing temperature dependence magnetization measurements (M - T). The parameters of the characterization method are the same for pure and Fe-doped samples that we applied (see details in Section 4.2.3). Figure 4.27(a-c) shows the M - T curves of $\text{Cu}_{0.50}:\text{MoS}_2\text{-S}$, $\text{Cu}_{0.75}:\text{MoS}_2\text{-S}$ and $\text{Cu}_{1.00}:\text{MoS}_2\text{-S}$ samples, respectively. Due to the lack of magnetic source itself in the structure, the moment data of samples has noise and there is no trend in the temperature range that we worked here. In addition, there is no magnetic transition temperature for all samples. The reason for this might result from the bulky structure of the MoS_2 films dominating the magnetic characteristic of the samples. Unlike the Fe-doped samples, Cu-doped samples have a more stacked structure when we compare the SEM images (see section 4.4.2). The continuity of the Cu doped film structure might result in the formation of diamagnetic nature of MoS_2 which is characterized by the trigonal prismatic local coordination of Mo^{4+} ions in which the two $4d$ electrons are antiparallel and net magnetic moments is zero (Cai et al., 2015; Lei, Zhan, Tang, Zhang, & Wang, 2018).

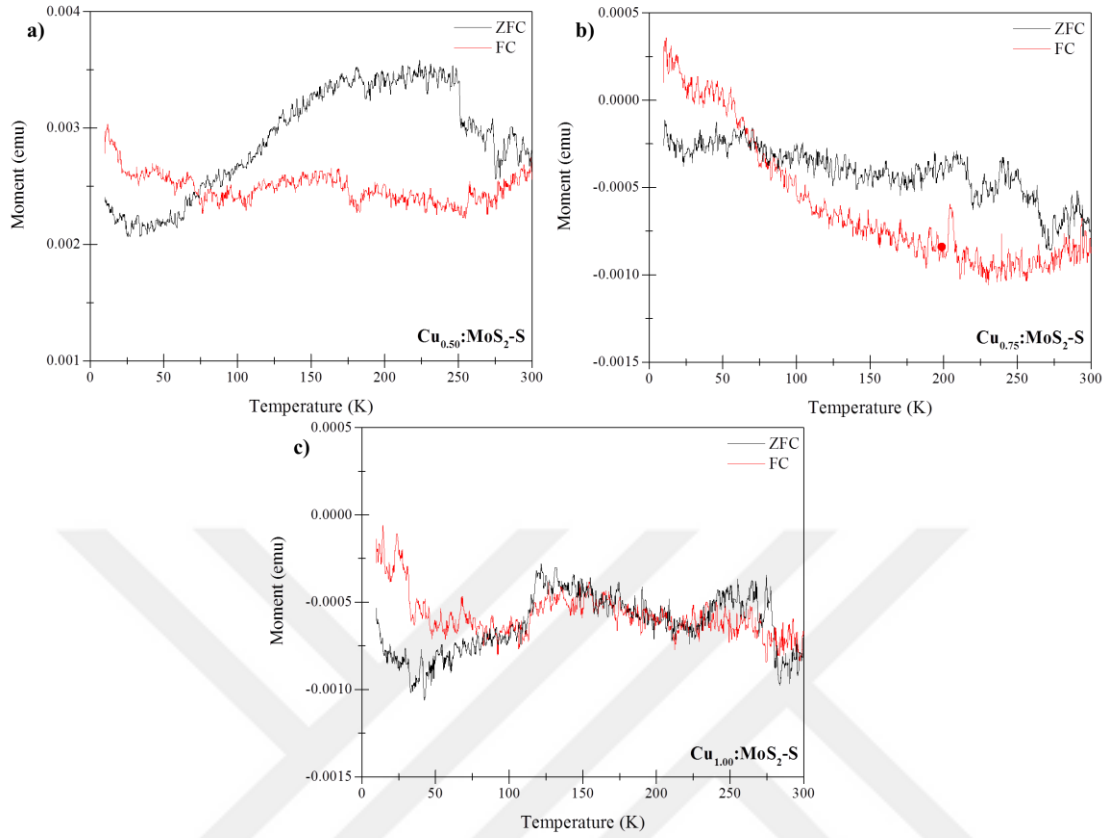


Figure 4.27. Temperature dependence of magnetic moment of samples a) $\text{Cu}_{0.50}:\text{MoS}_2\text{-S}$, b) $\text{Cu}_{0.75}:\text{MoS}_2\text{-S}$ and c) $\text{Cu}_{1.00}:\text{MoS}_2\text{-S}$.

4.4.4. Magnetic hysteresis curves of Cu-doped MoS_2 samples

Figure 4.28(a-f) shows the magnetic hysteresis (M - H) curves of Cu-doped samples at low and room temperatures. The moment data were normalized by each samples' saturation magnetization value. According to the figures, there is a weak ferromagnetic ordering under the low magnetic field region for all Cu-doped samples. However, the diamagnetic nature becomes dominant when the applied field is increased. Thus, the magnetic characteristics of the films are dominated by the diamagnetic order which can be observed for pure MoS_2 with a smooth and continuous film structure. As can be seen in SEM images of samples, the film structure is continuous and the intensity of the nanorods and discontinuities is low compared to undoped and Fe-doped samples. Thus, the bulky and uniform structure of the films results in the paired electrons in $4d$ orbital, which dominates the diamagnetic characteristics (Cai et al., 2015; Lei et al., 2018).

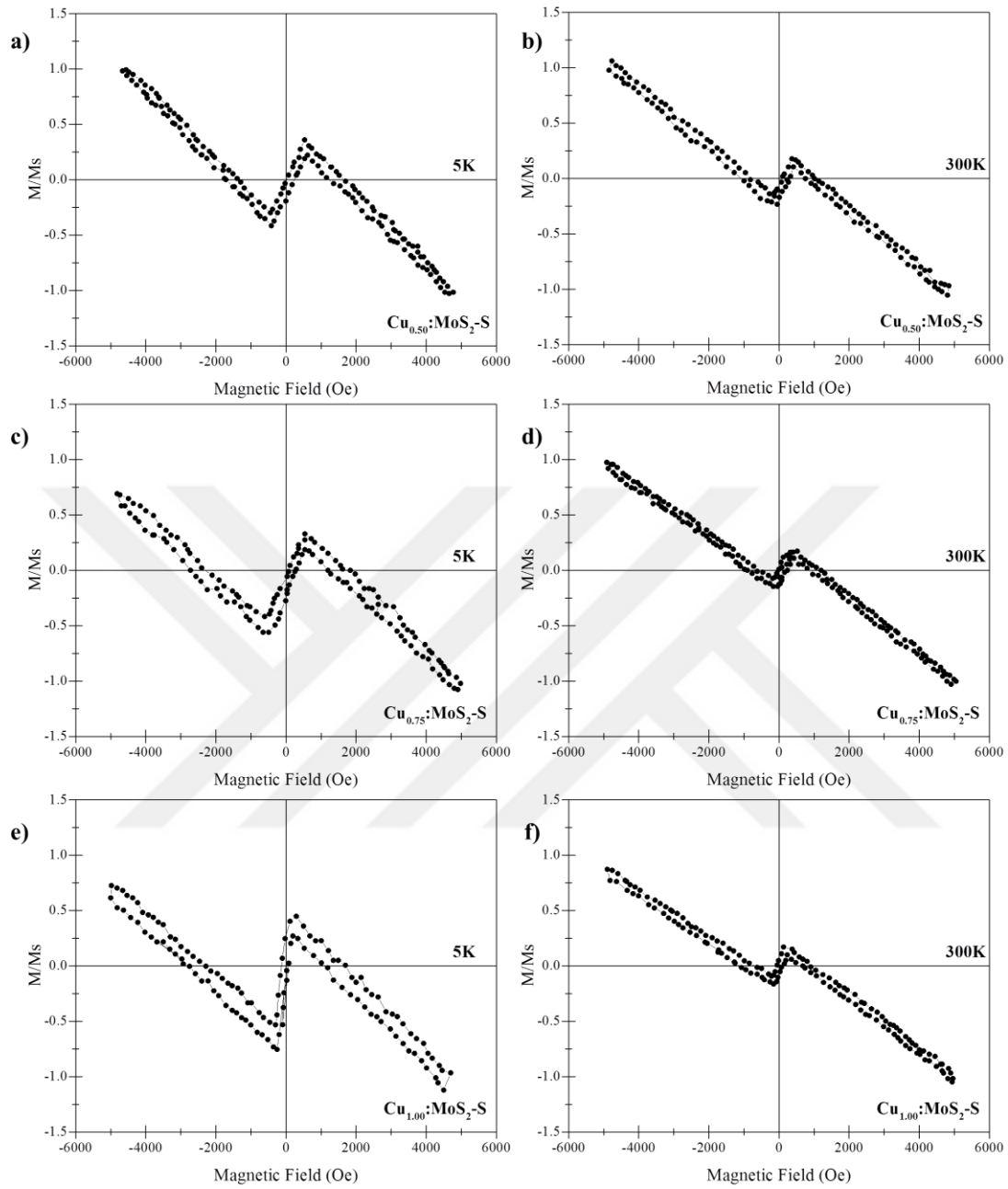


Figure 4.28. Hysteresis curves samples a,b) of %0.50 Cu doped sample at 5 and 300 K, c,d) of %0.75 Cu doped sample at 5 and 300 K and e,f) of %1.00 Cu doped sample at 5 and 300 K, respectively.

5. CONCLUSIONS

In the scope of the thesis, structural and magnetic properties of pure Cu and Fe-doped Cu_xMoS_2 and Fe_xMoS_2 (x : 0.50, 0.75 and 1.00%) thin films were synthesized by a using spin-coating method followed by a decomposition process. First, pure MoS_2 thin films were manufactured and then the effects of adding Fe and Cu atoms into the MoS_2 structure were investigated.

All samples were produced by using chemical processes. The chemical solutions were coated on the various substrates by using a spin-coating method. In the next step, the decomposition process is applied to all samples. The crystallization of films was ensured by applying heat treatment at various temperatures under N_2 flow.

After manufactured samples, XRD, SEM, Raman and VSM characterization techniques were used to investigate produced sample's structural and magnetic properties. XRD technique was used to determine the crystal structure of the samples; SEM method was used to investigate surface morphology and determine the particle size distributions. Raman technique was used to determine characteristic vibration modes of material and specify the layer number of films. In order to determine magnetic transition temperatures, $M(T)$ measurements were made in FC and ZFC process under 500 Oe magnetic field. Magnetic hysteresis measurements were carried out at 5 and 300 K in order to determine saturation magnetization, remenant magnetization and coercive field values.

In the first productions, solvent materials, coating, cleaning and heat treatment parameters were optimized. After optimization processes, pure MoS_2 and Fe-doped MoS_2 thin films were fabricated. According to the Raman results of samples, pure MoS_2 samples with %0.95 wt. ATTM concentration showed characteristic peaks E_{2g}^1 and A_{1g} at 383.1 and 409.1 cm^{-1} . The difference between these peaks is found as 26.0 cm^{-1} which determines the layer number of films. According to this value, the layer number of MoS_2 is close to the bulk value. The characteristic peaks of the MoS_2 are observed in both Fe-doped and Cu-doped samples. After producing pure samples, Fe and Cu-doped MoS_2 were manufactured with the same parameters in terms of solvent type, cleaning, coating and heat treatment.

Raman spectra of Fe-doped MoS₂ samples show that FeS₂ structure is formed. These results lead to the conclusion of bonding information between Fe and S atoms. According to the SEM images of pure MoS₂ sample with %0.95 wt. ATTM concentration, the MoS₂ crystals formed as a back-to-back triangle. When Fe atoms are added to MoS₂ the structure, the shape of crystals differ to nanorods across to sample' surface with an average distribution of 4.88 μm . SEM images of the Cu-doped samples show that film formed as smooth and continuous. The stacked structure of the film is observed for the samples by cavities in the film structure.

FC and ZFC measurements indicate that the magnetization transition temperature decreases when Fe atoms are introduced to the structure. The magnetization transition temperatures are 247.6 and 95.5 K for pure (%0.95 wt. ATTM) and %0.75 Fe-doped MoS₂. According to the magnetic hysteresis curves measured at 5 K, the magnetic ordering of pure and %0.75 Fe-doped samples show ferro/ferri-magnetic signals. At room temperature, all samples, except %0.75 Fe-doped sample, show diamagnetic characteristics. Since the film is not fully covered on the substrate, the magnetic signals are extremely low. Thus, a deep magnetic analysis could not be performed for these samples. But, in general, magnetic hysteresis curves of samples show that the M_s increases, but H_c values increase when Fe atoms (0.75%) are introduced to the main structure. The M_s and H_c values are 0.014 emu and 279 Oe for pure MoS₂, 0.018 emu and 140 Oe for %0.75 Fe-doped samples, respectively.

FC and ZFC measurements of the Cu-doped films indicate that there is no magnetic transition temperature for the films. According to the magnetic hysteresis curves of the Cu-doped films, the magnetic characteristic of the films is dominated by the diamagnetic response. The continuous film structure and stacking of the layers cause the canceling of the magnetic moments of the system. As a result, the ferromagnetic ordering of the Fe-doped samples is caused by the zig-zag edges, discontinuity of film and the impurities, while the diamagnetic ordering of the Cu-doped samples is caused by the continuous film structure and the increasing bulk layers.

6. RECOMMENDATIONS

In this study, structural and magnetic properties of pure, Cu and Fe-doped $\text{Cu/Fe}_x\text{:MoS}_2$ (x : 0.50, 0.75 and 1.00) thin film materials were investigated. Crystallizations of films were ensured by decomposing of the ATTM precursor at 570°C under N_2 flow. The magnetization transition temperatures were found as 247.6 and 95.5 K for pure (%0.95 wt ATTM) and %0.75 Fe-doped MoS_2 . Magnetic hysteresis curves show that the magnetic ordering of pure and %0.75 Fe-doped samples are ferro/ferri-magnetic at 5K. For Fe-doped samples, all samples except %0.75 Fe-doped, show diamagnetic characteristics at 300K. The M_s value increases while the H_c values decreases when Fe atom are added to structure (%0.75) which are 0.014 emu and 279 Oe for pure MoS_2 , 0.018 emu and 140 Oe for %0.75 Fe-doped samples, respectively. For Cu-doped materials, the diamagnetic behavior is observed. Considering all these parameters, reasons and the gains from the thesis studies, the works that can be envisaged in the near future are listed below.

- The crystallite formation of produced samples can be increased by using a more stable coating method and heat-treatment setup system. For example, MoS_2 thin films can be produced properly by using PVD and CVD compact systems.
- To carry detailed research, film smoothness can be and topology can be investigated by atomic force microscope (AFM) technique.
- To receive strong magnetic signals from samples, magnetic properties of the sample surface can be investigated by using a more sensitive magnetic properties measurement system.

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