

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

MAGNETIC PROPERTIES of $\text{Mn}_5\text{Ge}_3/\text{PZT}$
HETEROSTRUCTURES

CAN TANER
A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF PHYSICS

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THESIS SUPERVISOR
ASSOC. PROF. DR. LEYLA ÇOLAKEROL ARSLAN

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T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

Mn₅Ge₃/PZT HETERO YAPILARIN
MANYETİK ÖZELLİKLERİ

CAN TANER
YÜKSEK LİSANS TEZİ
FİZİK ANABİLİM DALI

DANIŞMANI
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GEBZE
2022

GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 27/01/2022 tarih ve 2022/05 sayılı kararıyla oluşturulan jüri tarafından 10/02/2022 tarihinde tez savunma sınavı yapılan Can TANER' in tez çalışması Fizik Anabilim Dalında YÜKSEK LİSANS tezi olarak kabul edilmiştir.

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27/01/2022 tarih ve 2022/05 sayılı kararı.

SUMMARY

The rapid approach of microelectronic technology reaches to limit values and potential spintronic technology for next generation magnetoelectronic devices have attracted attention. Controlling the ferromagnetic transition with the electric field provides benefits such as low power consumption and minimum instability, especially in semi-metallic ferromagnets, magnetoelectronic devices. In this thesis, the main obstacles encountered in the growth studies of Mn_5Ge_3 magnetic films on thin ($100\mu\text{m}$) Si(111) substrate are emphasized.

Mn_5Ge_3 thin film was investigated due to its high spin injection efficiency, high spin polarization and room temperature ferromagnetism. In this thesis, we combined ferroelectric lead zirconium titanate (PZT) ceramics and Mn_5Ge_3 film, which have been widely used recently, and examined the magnetization, anisotropy and coercive field control of Mn_5Ge_3 film as a result of applying voltage to PZT. In the first step of this thesis, the parameters for the solid phase epitaxy growth of single crystalline Ge on thin Si substrate ($100\mu\text{m}$) and the formation of Mn_5Ge_3 hexagonal crystal structure were determined. After the Mn_5Ge_3 structure was grown and confirmed by XRD and XPS methods, the magnetic characterization of the film was made and the results were compared with the results in the literature. While investigating the Mn_5Ge_3 structure, evaluations were made on the films with different thicknesses (5nm, 10nm, 15nm). Surface morphology was investigated by AFM and SEM methods. The magnetic properties of the films were investigated using PPMS and ESR. In the second step, the combination of Mn_5Ge_3 film with PZT piezoelectric structure with the help of an epoxy and the changes in the magnetic properties of the Mn_5Ge_3 film with magnetostrictive effect were investigated.

Key Words: Mn_5Ge_3 thin films, Multiferroic heterostructure, Thin Si (111), Voltage controlled magnetization.

ÖZET

Mikroelektronik teknolojisinin sınır değerlere hızlı yaklaşımı ve yeni nesil manyetoelektronik cihazlar için potansiyel spintronik teknolojisi dikkatleri üzerine çekmiştir. Elektrik alanı ile ferromanyetik geçişin kontrol edilmesi özellikle yarı metalik ferromanyetlerde, manyetoelektronik cihazlarda düşük güç tüketimi ve minimum kararsızlık gibi faydalar sağlar. Mn_5Ge_3 filmleri bu çalışmada Si teknolojisi ile uyumluluklarından dolayı magnetron püskürtme ve moleküler ışın epitaksi kullanılarak Si altlık üzerinde üretilmiştir. Bu tezde, ince ($100\ \mu m$) Si(111) alttaş üzerine Mn_5Ge_3 manyetik filmlerin büyüme çalışmalarında karşılaşılan başlıca engeller üzerinde durulmuştur.

Mn_5Ge_3 ince filmi yüksek spin enjeksiyon verimi, yüksek spin polarizasyonu ve oda sıcaklığındaki ferromanyetizma nedeniyle incelenmiştir. Tezde son zamanlarda yaygın olarak kullanılan ferroelektrik lead zirkonyum titanat (PZT) seramikleri ile Mn_5Ge_3 filmini birleştirdik ve PZT'ye voltaj uygulanması sonucu Mn_5Ge_3 filmin manyetizasyon, anizotropi ve zorlayıcı alanın kontrol edilmesini inceledik. Bu tezin ilk adımında, ince ($100\ \mu m$) Si(111) alttaş üzerinde tek kristalli Ge'nin katı faz epitaksi büyümesi ve Mn_5Ge_3 altıgen kristal yapısının oluşumu için parametreler belirlendi. Mn_5Ge_3 yapısı büyütülerek XRD ve XPS yöntemleriyle doğrulandıktan sonra filmin manyetik karakterizasyonu yapılmış ve sonuçlar literatürdeki sonuçlarla karşılaştırılmıştır. Mn_5Ge_3 yapısı incelenirken farklı kalınlıklarda (5nm, 10nm, 15nm) filmler üzerinde değerlendirmeler yapılmıştır. Yüzey morfolojisi AFM ve SEM yöntemleri ile araştırıldı. Filmlerin manyetik özellikleri PPMS ve ESR kullanılarak araştırıldı. İkinci aşamada, Mn_5Ge_3 filminin PZT piezoelektrik yapısı ile bir epoksi yardımıyla birleştirilmesi ve manyetostriktif etkiye sahip Mn_5Ge_3 filminin manyetik özelliklerindeki değişimler araştırılmıştır.

Anahtar Kelimeler: Mn_5Ge_3 ince filmleri, Multiferroik hetero yapılar, İnce Si (111), Voltaj kontrollü manyetizasyon.

ACKNOWLEDGEMENTS

I would like to express my gratitude and respect to my valuable advisor, Associate Professor Leyla ÇOLAKEROL ARSLAN, who contributed to my development with her ideas and suggestions at every stage of my research throughout my graduate education.

I would like to thank my very esteemed jury members Prof. Dr. Kemal ÖZDOĞAN and Assoc. Prof. Dr. Sinan KAZAN, who read my thesis and guided me with their valuable ideas.

I'd like to thank Dr. Erdem DEMİRCİ, Dr. Mustafa ÖZTÜRK, MSc.Eng Emrah ANİĞİ, Okan ÖZDEMİR, Mehmet Emre AKÖZ, and İlknur GÜNDÜZ who contributed to this study at laboratory studies. I am very grateful to all of you.

I'd like to convey my gratitude to Gebze Technical University for providing me with labs and resources.

Also, I'd like to thank TUBITAK for support with 118M193 TUBITAK Project.

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LIST of ABBREVIATIONS and ACRONYMS

<u>Abbreviations</u> <u>and Acronyms</u>	<u>Explanations</u>
$\text{\AA}$	: Angstrom
θ	: Angle
$^{\circ}\text{C}$	: Celsius Degree
K	: Kelvin
μ_0	: Permability of Free Space
μ_B	: Bohr Magnetron
Hz	: Hertz
eV	: Electron Volt
E	: Energy (Joule)
μ	: Permability
J	: Exchange Integral
S	: Spin Angular Momentum
φ	: Angle
r	: Vectoral Dictance
t_{2g}	: Conduction Band
e_g	: Free Electron
k_B	: Boltzman Constant
P	: Pressure (mbar)
d_n	: Number of Gass Molecules
d_t	: Time Changes
m	: Atomic Mass
π	: Pi Number
λ	: Wavelenght
c	: Speed of light
h	: Planck Constant,
γ	: Interlayer Energy
ν	: Frequency

E_B	: Binding Energy of Electron
E_K	: Binding Energy of Electron
$\emptyset$	: Work Function
emf	: Electromotive Force
ε	: Magnetic Flux
M	: Magnetization
g	: Spin Factor
T_c	: Currie Temperature
GHz	: Giga Hertz
mT	: Militesla
eO	: Oersted
C	: Carbon
Co	: Cobalt
Cr	: Crom
Fe	: Iron
Ge	: Germanium
Mn	: Mangesese
N	: Nitrogen
Ti	: Titanium
AES	: Auger Electron Spectroscopy
AFM	: Atomic Force Microscopy
CMOS	: Complementary Metal Oxide Semiconductor
DMS	: Diluted Magnetic Semiconductors
ESCA	: Electron Spectroscopy for Chemical Analysis
ESR	: Electron Spin Resonance
FC	: Cooling Under The Field
FMR	: Ferromanyetic Megnetic Resonance
HR-TEM	: High Resolution Transmission Electron Microscopy
LT-MBE	: Low Temperature Molecular Beam Epitaxy
MBE	: Molecular Beam Epitaxy
SEM	: Scanning Electron Microscopy
SPE	: Solid Phase Epitaxy
RCA	: Radio Co-operating of America

RHEED	: Reflection High Energy Electron Diffraction
RKKY	: Ruderman-Kittel-Kasuya-Yosida Interaction
PZT	: Lead Zirconate Titanate ($\text{Pb}[\text{Zr}_{(x)}\text{Ti}_{(1-x)}]\text{O}_3$)
UHV	: Ultra High Vacuum
VSM	: Vibrating Sample Magnetometer
XPS	: X-Ray Photoelectron Spectroscopy
ZFC	: Zero Field Cooling
PMN-PT	: $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$



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1. INTRODUCTION

The use of magnetic materials in today's technology is based on the control of magnetic properties without any change in the crystal structure of the material. For example; bits used in information storage technology refers to directions of magnetization which are controlled by applying external magnetic fields. Although these magnetization directions change, the magnetic anisotropy and magnetization value of the magnetic medium do not change. The charge properties of electrons are utilized because the controlling of magnetization is done as controlling of current in the data storage technology. Problems such as high power consumption, warming, slowness in information processing speed, the emergence of nanoscale quantum effects and the reduction of the size of technology elements used in this field are encountered as a result of the operation with current control. In spintronic technology, the spin property of the electron is used to overcome these problems. Spintronics relies on the control of fundamental electric charge in solid state devices as well as the spin of the electron. Therefore, electric field can alternatively be used to control the magnetic configuration of magnetic systems. One way to control magnetization by electric field is to develop hybrid ferroelectric / ferromagnetic devices. The magnetic properties of the ferromagnetic film grown on the ferroelectric substrate which has a magnetostrictive effect, are tried to be controlled by the mechanical stress caused by the voltage applied on the ferroelectric substrate.

Mn_5Ge_3 is a promising material as a ferromagnetic layer on Si substrate. Mn_5Ge_3 is very attractive both because it has a strong magnetization at room temperature and it is possible to control the magnetic properties of the Mn_5Ge_3 thin film by mechanical stress.

Within the scope of this thesis, first of all the effective parameters of the growth of Mn_5Ge_3 on thin (100 μm) Si (111) substrate were tried to be determined. Then, the most effective ferromagnetic structure was tried to be obtained by growing the Mn_5Ge_3 on Ge thin film with magnetron sputtering and MBE methods at three different thicknesses. Finally, how the magnetic properties of Mn_5Ge_3 changed after the shape change and its magnetostrictive properties were investigated.

2. Mn_5Ge_3 THEORETICAL REVIEW

2.1. Experimental Studies on GeMn

GeMn structures created by employing Ge as a semiconductor and Mn as a transition element have gained the most interest. The main reasons for this preference are that Ge and Mn separately have properties that are considered advantageous for spintronic technology.

Ge element stands out from other semiconductors with its high hole mobility of $1900 \text{ cm}^2/\text{V.s}$ at room temperature [1]. Furthermore, it has been shown that Ge is far more compatible with Si than other semiconductors, that they have the same amount of valence electrons, that their crystal structures are identical, and that their lattice constants differ by only 4.2 percent. Today's microelectronic technology should be easily incorporated into CMOS circuits in order for Ge based materials produced in the future to be quickly turned into relevant and usable spintronic devices. As a result of its compatibility with Si technology, Ge-based materials can be easily transferred to Si technology.

Mn, on the other hand, is frequently used as a transition element in DMS investigations involving various element groups. Mn is separated from other ferromagnetic elements due to the antiferromagnetic interaction between its neighboring ions [2,3]. The interaction between the magnetic moments of the Mn atoms becomes ferromagnetic due to the holes as the distance between them increases [4]. The element Mn was chosen because of the carrier-mediated ferromagnetism required to create an electrically controlled ferromagnetic system.

Park et al. aimed to empirically validate the theoretical results obtained from the mean field solution of the Zener model. In the years when scientists had not yet identified the above-mentioned properties. As a result of this approach, he noted that, aside from the III-V and II-VI groups, ferromagnetic order could be fixed in DMS structures like as Si, Ge, and C, and $\text{Mn}_x\text{Ge}_{1-x}$ films could be formed on Ge and GaAs(100) substrates [5]. Hole-mediated ferromagnetism detected depending on the distance between Mn atoms in GeMn and the existence of Curie temperature observed between 25 K and 116 K depending on Mn concentration have been brought to the literature.

In the same year, Cho detected the Curie temperature at 285 K in the GeMn, single crystal film formed by putting powder Mn and Ge in a capsule. Although the secondary phase was not discovered in this sample, which was generated with a Mn content of 6%, as research on the GeMn structure progressed. It became clear that these phases did exist in the system in the years to come [20]. This study was significant since it coincided with Park's work in the same year, demonstrating that the subject drew the attention of both groups at the same time. Many investigations have been carried out behind the introduction of the GeMn DMS structure to the literature, and this structure has become the most obviously developing and stunning topic of DMS studies, thanks to Park and Cho's leadership. The following is a summary of recent research aimed at improving the carrier-induced ferromagnetism exhibited in the GeMn structure and overcoming the challenges encountered during growth.

J. Zou et al. investigated the behavior of Mn atoms in $\text{Mn}_{0.04}\text{Ge}_{0.96}$ thin film growth studies using Si(100) substrate with MBE technique [6]. According to the results, it was understood that the Mn concentration on the surface was much higher due to the tendency of Mn atoms to diffuse the surface during the growth of the film. Mn clusters were formed on the surface depending on the thickness of the film and the temperature. As a result of these findings, Zeng et al. proposed the subsurfactant epitaxy method, in which they first enlarged 0.5 ML Mn on Ge at 150 K so that the Mn atoms were trapped in the lattice, and then used the tendency of Mn atoms located in the intermediate regions of the Ge lattice to rise to their advantage in the second step [7]. Thus, the formation of Mn clusters was prevented by the 20nm Ge layer they applied to the film, and ferromagnetism at 400 K Curie temperature was observed even at 0.25 percent Mn contribution rate.

In addition, the magnetic characteristics of GeMn systems, which haven't gotten much attention in recent years, have been studied primarily in terms of their structural features and formation methods. This memorization was broken by Kazakova and his friends. The group was fascinated by the spin dynamics and ferromagnetic properties of GeMn systems, leading to extensive ESR findings [8]. The resonance peaks and magnetization curves of GeMn thin films with a 4 percent Mn content in three distinct temperature ranges, which they determined as a consequence of the experiments they made with Mn. Farle, were then thoroughly studied. In the experimental results, besides paramagnetic signals between 4 – 60 K, spin wave resonance (SWR) peaks, which indicate the presence of spin states with long-range interacting, were detected.

They discovered that between 60 and 220 K, all ferromagnetic signals vanished and only paramagnetic signals remained, whereas the signals recorded between 220 and 300 K were from the Mn_5Ge_3 structure [9]. Because one of the major goals of this thesis is to demonstrate Mn_5Ge_3 structural compatibility with Si technology, all of the samples were made on a thin Si substrate. Although this condition has received little attention in the GeMn investigations, there are few outstanding works. Y. Wang's films were produced on a Si(100) substrate with a buffer Ge layer [10,11]. He found Mn clusters in his TEM analyses after covering the buffer layer with 85 nm thick GeMn. There were three transition temperatures reported in the magnetic measurements of the 4 percent Mn doped film: 250, 300, and 22 K. Magnetic studies of the 4 percent Mn doped film revealed three transition temperatures: 250, 300, and 22 K, as well as the presence of magnetic precipitates, particularly DMS, and the secondary phase Mn_5Ge_3 in the formed film. Following this research, Xiu proposed the superlattice technique, claiming that the magnetic MnGe structures created in the system can be regulated during development, that regular nanowires and nanodots can be grown, and that direct spin injection can be achieved with these nanostructures [12]. By layering 10-period Ge and MnGe layers over GaAs, the group was able to generate GeMn nanowires with the same crystal structure as the substrate. Despite the fact that the enlargements were carried out at a low temperature (70° C), the findings were identical to Wang's, and the creation of various metallic phases in the film could not be avoided. In the same year, Jain et al. used the LT-MBE system to explore the magnetic characteristics of self-formed nano-columns on Ge(100) and Ge(111) substrates at 100 and 150 degrees Celsius [13]. He demonstrated the ease of Mn_5Ge_3 formation on Ge(111), and the magneto crystal anisotropy is dominated by the shape anisotropy of the structures, while the nano-columns display cubic anisotropy in the (111) easy axis direction and perpendicular uniaxial anisotropy. As a result, Jain emphasized the relevance of not just the structures creation procedures, but also their magnetic characteristics and anisotropies for future spintronic devices.

Meanwhile, Wang conducted extensive HR-TEM studies on samples with Mn content ranging from 4% to 1%, which he produced on Si substrate at 70°C to refine his research and examine the formation of phases formed in the system. As a result, he observed that Mn precipitates began to form in the matrix even at low temperature and 1% Mn amount. He emphasized that the increase in temperature and concentration had the same triggering effect on precipitate formation in samples grown at low

temperature and at 3 percent Mn concentration, and in samples grown at 1 percent Mn and 150°C. Secondary phase and metallic aggregates formed in samples grown at low temperature and 3 percent Mn concentration and in samples grown at 1 percent Mn and 150°C. In the same years, Yin et al. demonstrated that secondary phase development may be prevented in MnGe films made by ion implantation method below 85°C, as an alternative to MBE systems, to prevent poor Mn dissolution rate and secondary phases. Yin modified the ion implantation process to operate at low temperatures and for a short time, which usually induces the formation of the secondary phase with the annealing step at high temperatures. It was discovered that after samples with 1.1 percent concentration were passed through a one-minute rapid thermal annealing (RTA) step at 300°C, matrix defects were reduced, the number of Mn atoms in the system increased, and precipitates were formed. However, he found that the $0.7 \mu_B/\text{Mn}$ value, which is significantly below the predicted value, declines further with annealing temperature and indicating that the Mn atoms in the matrix begin to separate, and the short-range interaction diminishes overall magnetization [14].

In DMS research, which started with the creation of IV-based GeMn systems, high resistivity and low conductivity values above Curie temperature were recorded in amorphous GeMn films. In addition, secondary phases were discovered as a result of electronic and magnetic analyzes due to the high Mn concentration used by L. Wang and D. Hou in their experiments. The fact that these results are not sufficient for spintronic device applications has led to a decrease in interest and studies on amorphous structures. The homogenous and ferromagnetic behavior seen by Yada et al. in their investigations when the Mn content was maintained low prompted other researchers to return to this field.

The results obtained with ion implantation led to the idea that samples created by the MBE method would have higher magnetic properties than those prepared by ion implantation. With this point of view, the increase in the crystal qualities, magnetic properties and Curie temperatures of GeMn films, even at high doping concentrations, as a result of the inclusion of Co, Mn, Fe and Cr in the MBE system, attracted Hou's attention. Hou explained that by implanting the samples grown by magnetron sputter method on Si(100) substrate with $2 \times 10^{-16} \text{ cm}^{-2}$ dose Co implantation, firstly secondary phase formation can be prevented, but Co atoms cause a decrease in saturation

magnetization since it disrupts the d-d exchange interaction between Mn atoms in the system [15].

S. Guchhait et al. also tried to explain the source of magnetism and the formation of secondary phases in Mn doped amorphous MnGe systems grown by UHV-CVD method on Si(100) substrate. They proved that as Mn concentration decreases, the Curie temperature and saturation magnetization drop [16]. They discovered that the structure was paramagnetic as a result of Mn implantation at concentrations below 6%. Measurement of the magnetic moment value expected to be $2.5 \mu_B / \text{cm}^3$ as $0.232 \mu_B / \text{cm}^3$ shows that only 10% of the Mn atoms added to the system are in ferromagnetic interaction with each other in the example where 6 percent Mn concentration and 170 K Curie temperature were observed and the best result was obtained. They also used the annealing procedure at 300°C to collaborate the results of prior experiments. The effect of annealing at 300°C was that the system began to transition to the crystalline phase and the volume of the magnetic phases began to decrease. However, there was no change in the Curie temperature of the system and there was a decrease in saturation magnetization. In addition, these data were completely crystalline as a result of the high temperature annealing procedure carried out in other studies, and gave results compatible with the analyzes obtained on films exhibiting paramagnetic behavior. The method utilized, the growth temperature, and the quantity of Mn doped influenced the formation mechanisms of GeMn systems, as can be seen from the investigations, which led to the studies being categorized under these areas. It is assumed that the problem of low dissolution rate of Mn atoms can be overcome by reducing the growth temperature, aiming to remove the system from the equilibrium state as much as possible. Depending on the change in growth temperature, it can be determined that Mn_5Ge_3 clusters and magnetic precipitates are formed above 180°C , nanostructures with high Curie temperatures at temperatures between $110 - 150^\circ \text{C}$, long structures and amorphous precipitates with dense Mn atoms below 80°C . Thanh et al., as a result of these comments, changed the amount of Mn between 1% and 14% in the samples grown on Ge(100) with MBE technique at 130°C , and examined the growth mechanism of GeMn films and examined the structures that emerged depending on the concentration at the most appropriate temperature [17]. They determined that as a result of the co-doping of Ge and Mn atoms, T_c increased from 80 K to 150 K at 1% to 2% Mn concentration and all the contribution came from the diluted matrix.

However, they proved that when the ratio is exceeded 2%, Mn-dense nano-structures begin to form and nano-structures between 5-6% turn into nano-columns with high T_c . When these concentrations were exceeded, the development of nano-columns was evident between 8% and 10%, but as the film thickness increased, Mn atoms began to dissociate towards the surface. It has been stated that the Mn concentration on the surface comes to around 62-63%, which is sufficient for the formation of the Mn_5Ge_3 phase, due to Mn atoms that begin to diffuse upwards, allowing Mn_5Ge_3 clusters to form, and nano-columns exhibit metastable behavior after this rate. When the film was doped with 12 – 14% Mn, they proved that mostly Mn_5Ge_3 clusters were present in the DMS structure. The researchers also noted that they could not obtain a homogeneous DMS structure even in films formed using the growth process with a 1 percent Mn concentration, and that the concentration of Mn atoms is an important variable in addition to the film thickness.

Although several organizations have examined the amplification of Mn-doped epitaxial Ge films on Ge(100) substrates for DMS research, there have been few studies on MnGe nanostructures and structures on quantum dots. Previous research has indicated that the system may have localized magnetic moments as a result of the hole constraint, and T_c will rise. The inclusion of Mn atoms into the stretch-induced Ge nanodots, however, requires extremely low temperatures. This problem in Mn doping to stress-induced nanodots, however, does not apply to spontaneously generated Ge nanodots. The ferromagnetism of Mn doped Ge nano-dots produced on Si(001) may be regulated by the electric field supplied to the entrance, as shown by X. Ma and C. Lou' [18]. Because they lowered the hole density and extended the interaction distance, $Mn_{0.02}Ge_{0.98}$ quantum dots, which Kassim et al. also grown on Si, generated more dilute structures than X. Ma and C. Lou. However, they discovered that 50% of the quantum dots generated were mixed with Si, and 30% of the total Mn content was precipitated in the Si substrate [19]. The magnetization of the structures doped with 2% Mn was substantially below the predicted value, notwithstanding the absence of a secondary phase. Thereupon, M. Özer et al. introduced a third magnification procedure and enlarged the sample at values close to the solubility limit. They maintained the growth temperature in the films between 95° C and 200° C, set the Ge deposition rate to 1.3 per minute, and the Mn ratio in the system to 0.25 percent. In this way, they proved that the formation of intermetallic phases was prevented in samples grown only at 95°C, and the crystal and magnetic properties of the film

increased qualitatively [20]. In the light of recent studies, the low solubility of Mn in the Ge structure, the defects that occur in the system, and the magnetic properties have always been among the problems that attract attention.

2.2. Literature Review on Mn_5Ge_3

Compounds containing Mn began to gain interest in the 90s owing to their tunable magnetic and magneto-optical characteristics. Among these, the Mn_5Ge_3 structure has become the focus of research because of its high Curie temperature. K. Morrii et al., for the first time, investigated the transformation of Mn/Ge layers deposited on glass into Mn_5Ge_3 phase depending on temperature and growth rate, using the ion beam scattering technique [21]. Along a further investigation, the group demonstrated that Mn_5Ge_3 possesses a hexagonal D8 crystal structure which is inclined to develop in the (001) c axis direction, independent of the element ratios. Furthermore, they noted that metallic phases developed in the system as Mn concentration increased, and the solubility of Mn atoms in Ge was low and depended on many factors [22] in the conductivity measurements.

On the other hand, Sürger et al. In order to increase the maximum temperature at which the Mn_5Ge_3 structure remains in the ferromagnetic phase, samples were grown on sapphire (Al_2O_3) substrate at different temperatures and carbon amounts [23]. They discovered that the Curie temperature T_c could be increased to 445 K in the $\text{Mn}_5\text{Ge}_3\text{C}_x$ ternary compound with $x=0.75$ grown on the substrate at 680 K. The XRD data obtained by the group in the analysis of the films showed the non-ferromagnetic Mn_5Si_3 structure outside the phase desired to be formed in the film. During this time, the majority of the experiments were focused on learning more about the structural characteristics of Mn_5Ge_3 [24,25]. Sürger et al., on the other hand, concentrated on the cause for magnetization in the Mn_5Ge_3 system and how it could be enhanced, and their investigations drove the literature. Due to experimental conditions from about 15 years ago, contaminations, and unknowns in the growth parameters, only a single crystal Mn_5Ge_3 thin film could not be formed that was free of non-magnetic metallic secondary phases. However these studies on glass and Al_2O_3 have been an important infrastructure for future research.

In the following years, scientists have been looking for new materials for spintronic applications due to unsolved challenges. As a consequence of this anticipation, Mn_5Ge_3 has emerged as the most promising choice for spintronic applications, according to its electrical, magnetic, and structural properties that are compatible with Si technology.

For the first time, Zeng et al. proposed that Mn_5Ge_3 structures may be employed for spin injection in spintronic next generation devices in 2003. By developing this ferromagnetic structure on Ge, they hoped to generate metal/semiconductor interfaces that could be easily transferred to semiconductor Si technology (111). As a consequence, they developed Mn_5Ge_3 epitaxially on the Ge (111) surface using solid phase epitaxy (SPE) approach [26]. However, in those years, comprehension of the significance of the group's achievements was not at the desired level.

Theoretical research to corroborate the experimental findings and get more precise information about the structure began in 2004. In their FLAPW calculations for the Mn_5Ge_3 structure, Freeman et al. discovered that there are two Mn types in the system, positioned at separate places in the lattice and with differing magnetic moments [27]. Furthermore, computations have showed that the total magnetic moment of the Mn1 and Mn2 atoms that make up the Mn_5Ge_3 structure is $2.6 \mu_B$ per unit cell, and that the structure has metallic character, owing to Mn - Mn interactions at the Fermi level [28]. The most important conclusion to be drawn from these theoretical calculations is that the system's largest spin polarization is attained along the hexagonal 'c' axis, making this plane the most ideal for spin injection.

After the compatibility of the Mn_5Ge_3 structure created using the MBE technology with the Ge(111) plane was understood, and investigations began to rise afterwards. Several groups began to consider this ferromagnetic phase as a strong candidate for application in spintronic devices and due to its compatibility with Si. Structural properties were heavily emphasized in theoretical and experimental studies. Moreover, the electronic structure of Mn_5Ge_3 was investigated using XAS and XMCD techniques, as well as the configurations and magnetic moments of Mn atoms in the Mn_5Ge_3 structure [29,30].

Following this stage, researches focused on systems that might be converted to semiconductor technology. Second phases, which are seen as defects in the process of forming a promising Ge-based diluted magnetic semiconductor for spintronic applications, have suddenly started to attract attention. Due to previous DMS research,

it was known that high growth temperatures and Mn concentrations allowed the development of metallic phases such as Mn_5Ge_3 in $\text{Mn}_x\text{Ge}_{1-x}/\text{Ge}(001)$ films, allowing the process to advance quickly. The fact that there are numerous studies on the growth of Mn_5Ge_3 on $\text{Ge}(100)$. In addition, they wanted to see the advantages that the Mn_5Ge_3 phase, which they created in a controlled manner inside the DMS structure, would provide to the films in their experiments.

Berbezier et al. [31] conducted the initial research, which was focused at bringing together the $\text{Mn}_x\text{Ge}_{1-x}$ and Mn_5Ge_3 structures. The creation circumstances and architectures of micro-sized Mn_5Ge_3 clusters embedded in Ge crystal were examined in this work. According to the findings, Mn_5Ge_3 nanostructures began to develop in $\text{Mn}_x\text{Ge}_{1-x}/\text{Ge}$ films when the growth temperature was above 85°C and $x = 0.01$ was surpassed. They further confirmed that Mn_5Ge_3 clusters developed predominantly towards the surface using TEM analysis, because Mn atoms tend to dissolve towards the film's surface during growth. Afterwards, several groups have conducted comparable experimental experiments to better understand the size fluctuations, magnetic characteristics, and crystal orientations of Mn_5Ge_3 clusters developing harmoniously in a diluted single crystal MnGe matrix.

However, in the following years, the focus shifted away from studying the magnetic and structural effects of Mn_5Ge_3 formations in DMS. Using p-type $\text{Ge}(001)$ substrate, the groups explored the formation, axial orientation, crystal structure, and dispersion of the Mn_5Ge_3 structure seen in the diluted GeMn matrix. The goal was to raise the Curie temperature by interacting GeMn films diluted with Mn, which have a Curie temperature of roughly 116 K, with Mn_5Ge_3 clusters produced in the same matrix [32]. The collected results clearly shown that these films are inadequate to accomplish high-efficiency spin injection between ferromagnetic metal/semiconductor at desirable temperatures. As a result, the researchers used the ferromagnetic compound Mn_5Ge_3 to transport the spin polarized current straight into the semiconductor in their experiments. The goal is to transmit polarized spins directly into the Ge semiconductor by developing high-quality films, which have epitaxial orientations of Mn_5Ge_3 (001)/Ge (111) based on earlier research. Many investigations have been conducted in order to avoid the system of defects created at the film-substrate interface and the Mn segregation process. Thanh et al. used a solid phase epitaxy approach to grow a 10 nm Mn_5Ge_3 layer on $\text{Ge}(111)$ surface under UHV conditions in 2008 [33]. The creation of this film has been thoroughly investigated

using a variety of experimental approaches [34]. As a consequence of TEM and diffraction analyses, it has been shown that the Mn_5Ge_3 unit cell has a $\sqrt{3} \times \sqrt{3}$ structure, which is the Ge(111) unit cell's 30° rotated state. Despite the 3.7 percent difference in lattice characteristics, it was understood that the structure's unit cells' harmony permitted Mn_5Ge_3 to be the dominant single crystal phase developing on Ge (111). The researchers modified the growth procedures subsequently and generated Mn_5Ge_3 films of various thicknesses by sending Mn and Ge atoms together on the substrate, rather than focusing on structural changes during growth. The Curie temperature could be increased up to 340 K when the thickness of the structure was increased and transformed into a stack when the saturation magnetization and coercive field of Mn_5Ge_3 films varying from 5 to 180 nm were studied [35]. Padova et al. next used the solid phase epitaxy approach to grow 3.3 nm Mn_5Ge_3 films on which a 14 nm Ge layer was placed in order to see if the information gathered from the previous studies would be valid for thin films. They stated the complete overlap of the $\text{Mn}_5\text{Ge}_3(030)$ and Ge(220) planes in their investigation, however there is compressive stress in the 'c' plane owing to the mismatch in the lattice parameters [36]. They found a Curie temperature of 325 K for such a thin magnetic layer, which is similar to prior research. At ambient temperature, the magnetic moment value per Mn_5Ge_3 unit cell was $2.7 \mu_B$, while at 13 K, it was around $7 \mu_B$. While some groups continue to investigate the magnetic and structural properties of Mn_5Ge_3 under various conditions, Than et al., one of the pioneers of these studies, began looking for solutions to the properties of the Mn_5Ge_3 structure that need to be developed in order to adapt it to today's technology. Following the success of their papers in the same year, they refocused their research on Mn_5Ge_3 .

Mn_5Ge_3 must be able to protect its features up to 700°C in order to be used in CMOS technology. When subjected to heat treatment at 650°C , however, Thanh found that saturation and permanent magnetization of the Mn_5Ge_3 structure drop dramatically, and Mn atoms segregate from inside the Mn_5Ge_3 structure, generating the $\text{Mn}_{11}\text{Ge}_8$ antiferromagnetic structure [37]. $\text{Mn}_{11}\text{Ge}_8$ is the most stable phase with the highest chance of production among Mn-Ge compounds, as discovered in the initial studies. As a result, following the growth, heating the film at a high temperature leads the system to stabilize, causing the crystal structure of Mn_5Ge_3 to change to $\text{Mn}_{11}\text{Ge}_8$. Tahlan et al. recommended covering the film surface with 4 ML carbon to keep the Mn_5Ge_3 structure stable even at high temperatures and avoid Mn atom

segregation towards the film surface [38]. As a consequence, the carbon atoms in the Mn_5Ge_3 structure were moved to the intermediate areas, and the Curie temperature was raised to 430 °C, yielding the $\text{Mn}_5\text{Ge}_3\text{C}_x$ structure. Unlike Mn_5Ge_3 , this structure retained magnetic characteristics after annealing at 850°C. Low atomic radius impurities such as boron, nitrogen, and carbon are included in the lattice by settling in the intermediate areas rather than being replaced by atoms, which prevents long-range diffusion in the film. As a result of ensuing fixed domain structures, the Mn_5Ge_3 phase has been shown to be more stable. During annealing, the carbon layer also operated as a diffusion barrier, preventing precipitate formation on the surface or in the Ge matrix as a result of Mn atom segregation.

The Mn_5Ge_3 structure has been demonstrated to be a viable magnetic material for injecting spin into future generation electronic devices as a consequence of knowledge acquired over the previous ten years. Structures can be grown epitaxially in single-crystal quality on Ge at the necessary thickness and that can boost the Curie temperature to high levels by adding carbon.

As previously stated, the investigations have shown the true potential of the Mn_5Ge_3 structure in general and have opened the way for further research by scientists for specific uses. In the search for materials with uniaxial orthogonal magnetism that will form the infrastructure of the next generation information storage technology, the problem of not adapting Co-based compounds such as CoPt to semiconductor technology has emerged. With its discovered features, Mn_5Ge_3 has made it the apparent best candidate for this type of information storage technology. As a result, current research has focused on investigating the magnetic characteristics of Mn_5Ge_3 and making it appropriate for information-storage applications.

In their initial investigation on the magnetic characteristics of the Mn_5Ge_3 structure, Spiesser et al. claimed that there is a critical thickness of roughly 10 nm that causes changes in the system's easy axis [39]. To further examine this variation, the thickness of the produced Mn_5Ge_3 films was prepared in a wide range between 4 and 200 nm. As a result, they were able to investigate the anisotropies of the films, the easy axis deflection thickness, and the domain shapes in more depth. They discovered that in samples with a thickness of less than 10 nm, the magnetostatic energy forces the magnetization to stay in the sample plane due to the single-domain structure. Whereas above 10 nm thickness, the magnetocrystalline energy increases and the system tends toward vertical magnetization due to the multi-domain structure. The outcomes of the

group's theoretical and experimental analyses were nearly identical. As a result, it has been established that the change from parallel to perpendicular magnetization takes place in the 10-25 nm region. The Mn_5Ge_3 structure transition thickness to perpendicular magnetization is one-quarter that of its nearest rival Co, and its domain size is substantially lower, highlighting the structure's strong application potential in Si-Ge-based electronics and information storage devices once again.

The most effective spin injection between FM/SC surfaces is the key need of the current generation spintronic devices, according to Wang et al. Using the single crystal Mn_5Ge_3 structure as a source-drain, they demonstrated spin injection into strongly indoped Ge nanowires [40]. They found that Ge nanowire spintronic devices constructed with Mn_5Ge_3 /Ge/ Mn_5Ge_3 structure can be easily transferred to today's standard CMOS technology, based on spin diffusion length and spin lifetime measurements.

2.3. Source of Ferromagnetism

Spins or magnetic moments within a material can communicate with each other thanks to electron interactions. Depending on the magnetic phases in the system, this results in the production of a short or long distance magnetic order. The dipole dipole interaction is the most basic electron exchange interaction. The interaction energies of the two magnetic dipoles (μ_1 and μ_2) depending on their position (r) relative to each other, is in the form.

$$E = \frac{\mu_0}{4\pi r^3} \left[\vec{\mu}_1 \cdot \vec{\mu}_2 - \frac{3}{r^2} (\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r}) \right] \quad (2.1)$$

This energy is determined by the alignment and separation of the magnetic moments with regard to each other, as shown in the formula. This equation, which gives very powerful results in calculating the energy between two bar magnets in microscopic dimensions, gives the result $E = 10^{-23}$ Joules = 1K when set to atomic dimensions, namely $\mu_1 = \mu_B$ and $r = 1\text{\AA}$. In other words, the equation can't account for the ferromagnetism found on the atomic scale at ambient temperature. An electrostatic interaction is a change in energy caused by an exchange contact that is proportional to the distance between charges of the same sign. An electrostatic interaction is a change in energy caused by an exchange contact that is proportional to the distance between

charges of the same sign. Quantum mechanics has helped us understand the definition and real source of this interaction. The fact that electrons are particles that follow the Pauli exclusion principle explains the observed charge exchange interaction. According to the Pauli exclusion principle, two fermions with the same spin cannot be in the same place at the same time. The requirement of the electrons, which are fermions, to follow this rule has resulted in a change in electrostatic energy as a result of the difference in spin orientations based on the distance of the electrons relative to each other. According to the Heisenberg model, if two atoms i and j have spin angular momentum S_i and S_j , respectively, the exchange energy E between them is provided by the following formula (2.2).

$$E = -2JS_iS_j = -2JS_iS_j\cos\varphi \quad (2.2)$$

The exchange integral is J , and the angle (φ) between the spins is. If J is positive, E is the smallest when the spins are parallel ($\cos\varphi = 1$) and the greatest when they are antiparallel ($\cos\varphi = -1$). When J is negative, the lowest energy state is when the spins are antiparallel ($\cos\varphi = -1$), and the highest energy state is when the spins are parallel ($\cos\varphi = 1$). When considering the preceding equation, keep in mind that ferromagnetism is caused by the parallel orientation of nearby atoms' spin moments, and that in this process, as in all others, the system will choose the lowest energy state. In light of these findings, it is evident that the exchange integral must have a positive value in order for ferromagnetism to develop.

Long-range exchange interactions between local spin moments occur when atoms of non-magnetic semiconductors and magnetic elements are partly replaced for different reasons. The magnetic characteristics of the host semiconductor are entirely changed as a result of the indirect exchange interactions that generate this. The section continues with detailed explanations of direct and indirect exchange interactions under two primary areas.

2.3.1. Direct Exchange Interaction

The direct exchange mechanism happens when the wavefunctions of two moments are sufficiently near that they overlap. Because it offers short distance

contact, this mechanism demonstrates rapidly decreasing magnetism when the ions are isolated from each other. When atoms are very close to each other, the Coulomb interaction is minimal and electrons can move between each other's nuclei. The probability of electrons being in the same place at the same time increases as a result of this. The Pauli exclusion principle, on the other hand, stipulates that the spins of two electrons that are so near and identical must have opposing orientation.

As can be understood from the explanations above, if the distance between electrons and neighboring atoms is short in systems that interact directly, they align their spins antiparallel to each other, following the Pauli exclusion principle, since they spend most of their time on neighboring atoms. The electron-electron repulsion force is minimized when the atoms are separated by a sufficient distance. Because there is no rule constraining the electrons, the spins in the system are aligned parallel to each other. Figure 2.1 shows the spin orientations that differ depending on the electron locations in the direct contact system.

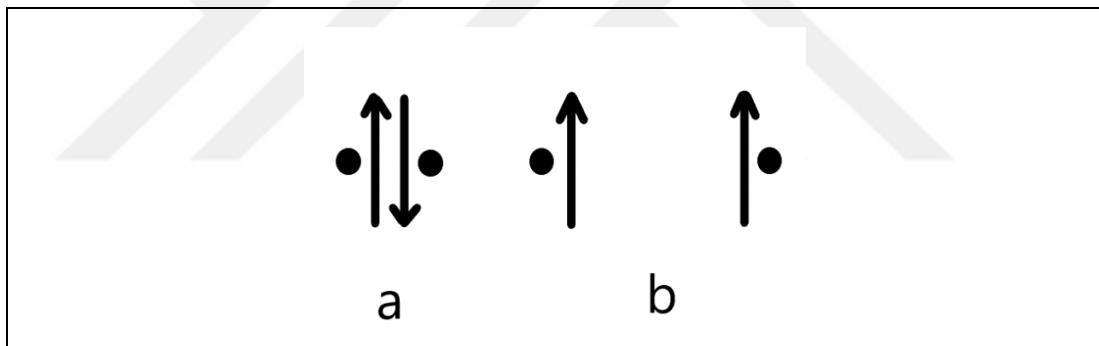


Figure 2. 1: Spin system figure The order in which electrons spin as a result of direct interaction when the distance between atoms is a) small and b) large.

The Bethe-Slater curve, shown in Figure 2.2, illustrates Heisenberg's direct exchange contact between nearby localized electrons. This curve, which shows the dependence of the exchange integral on the ratio of the mean diameter of the electron cloud and the distance between the atoms, has been very useful in explaining the change in magnetic order and Curie temperature, especially in Mn compounds. The distance between two nearby atoms is represented by r_a , while the orbital radius of the 3d electrons is represented by r_{3d} [41].

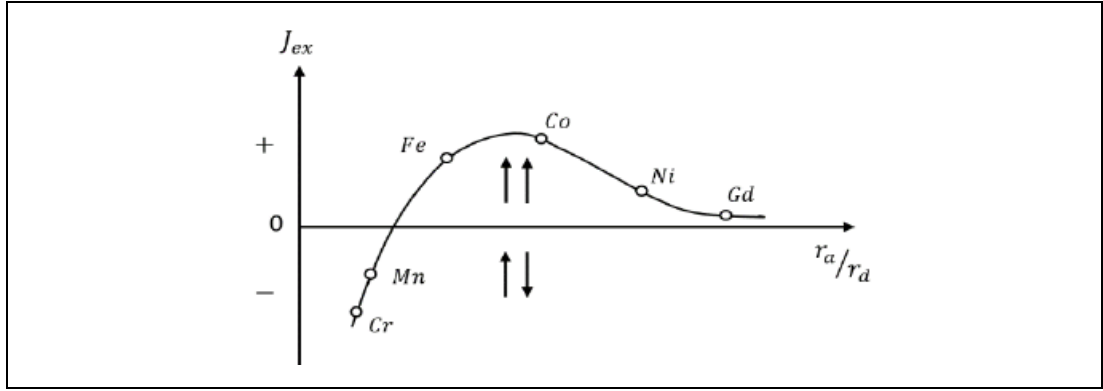


Figure 2. 2: Bethe Slater curve expressing the situations where the exchange integral is positive or negative depending on the distance between atoms and orbital radii.

As can be observed, the exchange integrals of Fe, Co, and Ni are ferromagnetic because exchange integrals of these materials are positive, but the exchange integrals of Mn and Cr are antiferromagnetic since they are negative. Direct interaction could only explain the magnetic properties exhibited by the two nearest neighbor magnetic atoms when the electronic wave functions directly overlap or are far apart.

2.3.2. Indirect Exchange Interaction

Indirect exchange mechanisms have been postulated and developed to explain the magnetism seen in semiconductors doped with transition metals and rare earth elements. The main ones are RKKY, pair-exchange and super-exchange interactions.

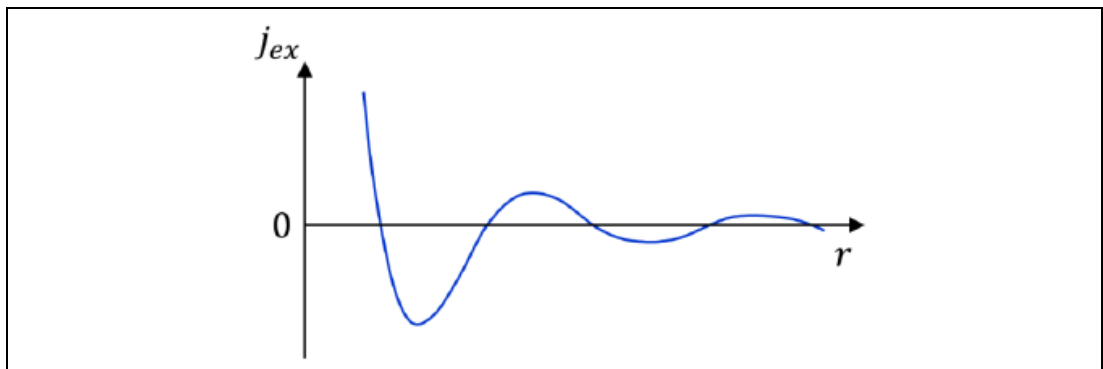


Figure 2. 2: Exchange interactiona graph according to the distance between atoms and RKKY interaction mechanism.

2.3.3. RKKY Carrier Mediated Exchange

RKKY is an indirect exchange interaction discovered by Ruderman, Kittel, Kasuya, and Yosida. The Coulomb exchange that takes place across the band electrons in this structure achieves the coupling of the magnetic moments, which are partially separated by huge distances [42,43]. This idea was developed to explain how ferromagnetism develops in metals and systems with high free electron concentrations. Because there is little or no chance of nearby electrons' wave functions intersecting in metals, contact occurs through an intermediate. It is the conduction electrons that provide this interaction in metals. According to the fluctuation of the spacing between the ions, the RKKY exchange coefficient j travels from positive to negative, as illustrated in Figure 2.4, with a damped oscillation movement [44]. As a result, the magnetic interaction becomes either ferromagnetic or antiferromagnetic depending on the spacing between the ion pairs.

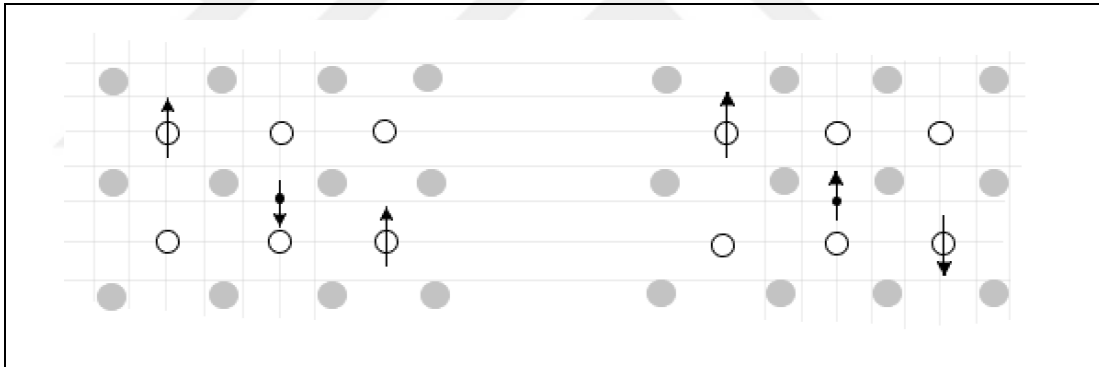


Figure 2. 3: RKKY interaction, in the system, the hollow circles with the arrows attached represent the magnetic atoms, and the black circle represents the electron.

2.3.4. Binary Exchange Mechanism

Clarence Zener proposed the double exchange interaction, which is a spin-dependent interaction process between magnetic ions in DMS structures [45,46]. When electrons pass from one ion to another, this process refers to the coupling between ions with different charge states. Hasegawa et al. proposed that the electron of the d orbital jumps from one ion to another through the p orbitals of surrounding anions for the $Mn^{+2} Mn^{+3}$ ion pair. In subsequent studies, it has been shown in many

DMS mechanisms, especially ZnO, that $\text{Mn}^{+2} - \text{Mn}^{+3}$ ions cause double exchange when they are together [47].

The $\text{Mn}^{+3} \text{Mn}^{+4}$ condition, which is depicted schematically in Figure 2.5, is discussed in depth for a better understanding of the bilateral exchange interaction. Mn ions can exist in several oxidation states in Mn-containing molecules. Mn^{+3} and Mn^{+4} are just two of these valence states. Only in the presence of equal spins can the e_g electrons in Mn^{+3} ions shift to the nearby place when these two states coexist in the system. The absence of electrons in the e_g shell of adjacent Mn^{+4} does not prevent the transition from taking place. But the presence of strong single center interaction between the three electrons in t_{2g} and the e_g electron of the Mn^{+4} structure will want to keep the spins of all electrons in line. Therefore, it is not appropriate in terms of energy for the e_g electron of Mn^{+3} to pass to the neighboring ion, whose t_{2g} spin orientation is anti-parallel to e_g . It is obvious from this that, while surrounding ions' spins must align for ferromagnetic order, the spin order in both acceptor and donor ions must be maintained [48].

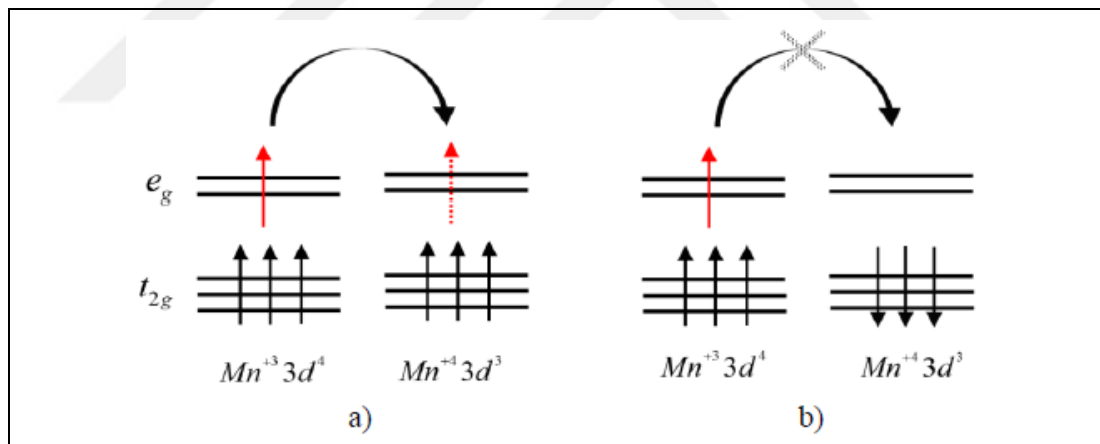


Figure 2. 4: $\text{Mn}^{+3} \text{Mn}^{+4}$ ion interaction for magnetism figure The double-exchange interaction between Mn^{+3} and Mn^{+4} ions produces ferromagnetic order. a) The electron is expected to pass to the nearby ions in their ferromagnetic orientation, whereas b) the electron is not expected to flow to the neighboring ions in their antiferromagnetic orientation.

2.3.5. Super Exchange Mechanism

The correlation between the spins of the two ions is owing to the valence p band and the exchange interaction between each of the two ions according to their spins,

unlike the spin-spin (d-d) interaction between magnetic ions. The super-exchange mechanism, whose transition diagram is given in Figure 2.6, shows the interaction of the nearest neighbor transition metals via the shared anion. After the antiferromagnetism found in many transition metal combinations could not be explained by the direct exchange mechanism, Kramers proposed it in 1934 and Anderson developed it in 1950 [49,50]. It results in the bouncing of carriers between the fully occupied p orbitals of anions and the d orbitals of cation magnetic transition metals.

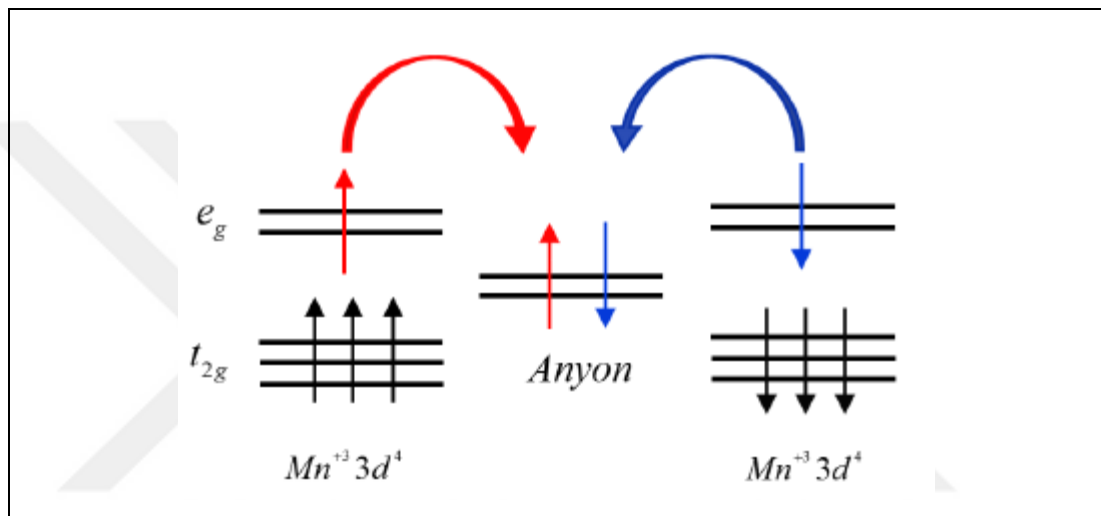


Figure 2. 5: Super exchange interaction The order formed by the super-exchange interaction between Mn^{+3} ions.

Because transition metal cations and big anions are separated by a significant distance, direct contact is impossible. In such a case, the probability of a direct transition between the d orbitals is very low. The anion, which interacts directly with the nearest transition element neighbor and is shared amongst the d orbitals, is responsible for realizing this coupling. Because the electrons of two nearby atoms will be put in the same p level, the Pauli exclusion principle will act as a limiting factor, causing the spins to be oriented in opposing directions. Thus, the p orbital of the anion with opposite spins and the d orbitals of the cations exhibit antiferromagnetic interaction. The main difference between this process and the binary exchange interaction is that the electrons between the transition metals do not migrate. While electrons in the double-exchange process are thought to wander and switch between

ions, electrons in the super-exchange interaction do not travel and instead correlate the spins of the transition metal with s(p) d hybridization.

2.3.6. Spin Glass

This structure, called after a combination of the terms "glass" and "spin," is made up of magnetic ions that are hard like glass and stable, but do not have a regular microscopic size distribution like crystals. The fixing of randomly ordered magnetic moments as a result of mixed interactions contending for diverse causes inside the system is characterized as the behavior of spin glasses [51].

The key components that contribute to the formation of this glassy behavior observed inside the material are tension and disorder. Figure 2.7 shows a schematic representation of Ising spins interacting antiferromagnetically in a triangular lattice in order to better comprehend these formations. When two-spin systems have opposing orientation, they obtain the lowest energy state. In a closed system, however, the spin will not be able to attain equilibrium since it will not be able to complete all interactions in accordance with the limits imposed by other spins. The lowest energy state of two-spin systems is achieved when they show opposite orientation. In a closed system with three spins, the antiparallel alignment of the two spins produces dispute about the orientation of the third spin. Completing the three bonds at the same time will not allow you to achieve the equilibrium state. Due to conflicting magnetic interactions within the system, this phenomenon, which we term strain in general, may be described as a scenario in which an optimal configuration for the orientation of the spins cannot be obtained. The stress effect alone is not sufficient for the formation of spin glass behavior in systems. It's also required to correct irregularities in the spins induced by a variety of factors, including chemical bonding, lattice geometry, and topological features. These materials' magnetic moments freeze in random places at low temperatures, destroying the long-distance order between them. In this way, there is no thermodynamic equilibrium state in the collection of irregular spins. However, since the variables causing the disorder do not cause time-dependent differences in the system below the freezing temperature, the situation we call suppressed randomness occurs.

It was first observed at low temperature in diluted magnetic semiconductor materials by two groups consisting of De Nobel-Du Chantenier and Zimmermann-Hoare [52,53]. The groups encountered two unexpected results in their observations. Independent of the Mn concentration, a linear expression was found in the heat capacitances of the materials they studied. The peak position in the magnetic saturation curve was seen in Cannella et al. investigations with the identical materials, depending on the temperature [54]. This temperature was later determined to be the spin glass freezing point, which is the temperature at which the magnetic moments are frozen in their uneven equilibrium orientations without any long-range interaction. After that, spin glass behavior was found in compounds like ZnMnTe, CdMnTe, and CdMnSe in II-VI DMSs at low Mn concentrations. The spin freezing values of GaMnN and Te-doped GaMnAs systems in III-V systems examined were 4.5 K and 30 K, respectively, as a result of advancements in DMS systems. In C. Jarger et al. $\text{Mn}_x\text{Ge}_{1-x}$ systems, spin glass behavior was found at 12 K and 15 K for $x = 0.03$ and $x = 0.2$, respectively, in III-IV systems [55]. This freezing state observed at low temperatures is explained by the blocking transition of interacting superparamagnetic GeMn nanoclusters at freezing temperature.

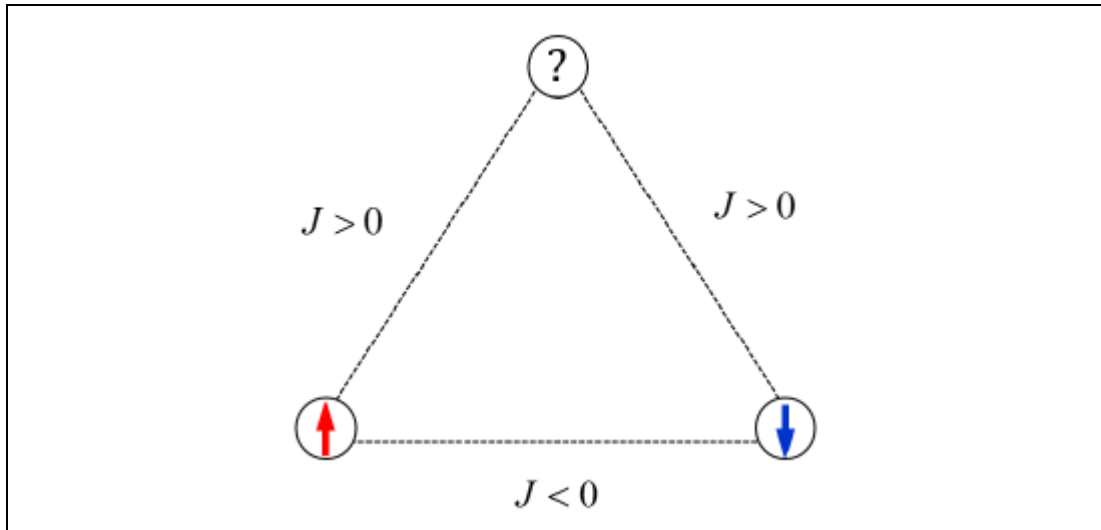


Figure 2. 6: Schematic representation of compression, which is one of the active behaviors in the formation of the spin-glass structure.

3. EXPERIMENTAL TECHNIQUES

3.1. Molecular Beam Epitaxy (MBE)

Molecular Beam Epitaxy is a great method for pure growth of thin films shown in Figure 3.1. In this technique materials were heated and to obtain a pure atomic beam for coating of thin films on substrate. Because of that this method is generally used for obtaining high quality crystal thin films.

Four main crystal growth characteristics are observed in the MBE system. First of that, atoms or molecules hit on the substrate surface and hold on the surface. Secondly, the attached molecules or atoms dissociate on the surface and spread to the surface. Thirdly atoms combine with crystal pattern of substrate surface or crystal pattern of grown film. The lastly unstable atoms or molecules dissociated thermally.

The MBE technique, which has been used to produce semiconductor films in the rapidly growing electronics industry since the 1980s has been one of the widely used techniques in the production of insulating, metal and superconducting epitaxial films.

The working principle of the MBE growth technique is that the atoms or molecules formed by heating solid source materials are directed to the heated or unheated substrate in a high vacuum environment and deposited in the same crystal structure on the surface of the substrate.



Figure 3. 1: Molecular beam epitaxy (MBE).

Two types of growth methods, namely homoepitaxy and heteroepitaxy, can be performed with the MBE technique. In homoepitaxial growth, since the growth material and the substrate are the same material, there is no roughness in the thin film during the transition from the substrate to the film, and the substrate lattice and the film lattice are identical. However, in heteroepitaxial growth, the growth becomes much more complicated because the film and substrate are different materials. The differences between substrate and the overgrown film lattice parameters cause the discrepancy in the interface layer. The discrepancies will result in the relaxation of the growth of the film through the defects formed in the transition zone between the layers and its growth in its own crystallographic order. The growth mechanism changes depending on the surface compatibility between the film and the substrate as shown in Figure 3.2

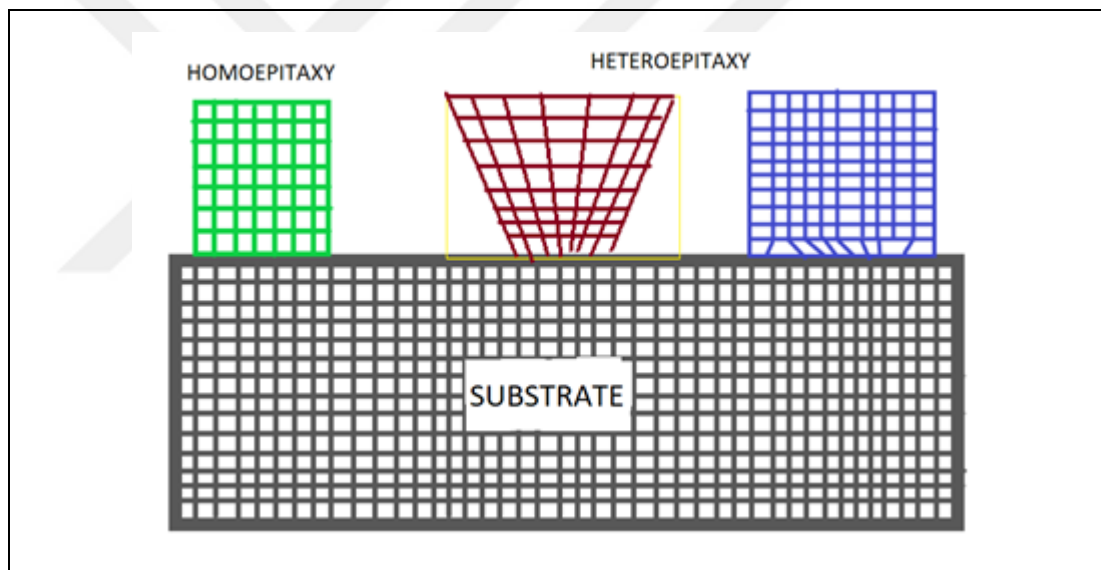


Figure 3. 2: Amplification of homoepitaxy and heteroepitaxy in a strained, relaxed system, respectively.

The MBE system includes several key components. These are ultra high vacuum, electron beam evaporator, effusion cells, sample holder, sample holder heater and manipulator and vacuum chamber.

3.1.1. Vacuum

The pressure of the MBE system is the most important factor for the film growth process. The pressure value is reduced to the ultra-high vacuum level of 1×10^{-10} mbar. In this way, the crystal quality of the film can be obtained with high purity. The ratio of residual gas molecules hitting the sample surface depending on the pressure is calculated with the formula (3.1).

$$\frac{dn}{dt} = \frac{P}{\sqrt{2m\pi kT}} \quad (3.1)$$

P denotes the pressure of the boiler in mbar, m for the atomic mass of the residual gases, k_B for the Boltzman constant, and T for the substrate temperature in Kelvin. In clean systems, the concentration of impurities must be one part per million or less than 1×10^{-6} mbar of pressure. In UHV systems, the required pressure is reached with a three-stage pumping system. The pressure is reduced to 1×10^{-10} mbar values by using mechanical, turbo molecular and ion pumps, respectively, according to the pressure values they work at.

The mechanical pump is the most basic pump used in UHV systems and the pump with the highest pressure value. It is used in the first stage of pumping and usually to bring the pressure of the opened system to the order of 1×10^{-3} mbar. It doesn't work at values below this pressure. In our system, oil-free mechanical pumps, the working principle of which are shown in Figure 3.3 are used [64].

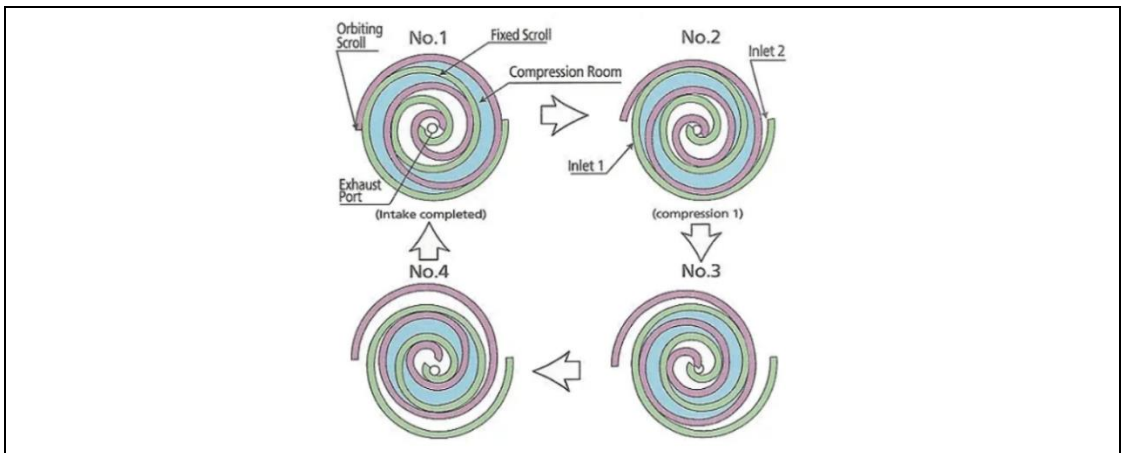


Figure 3. 3: Mechanical pump working diagram.

The mechanism in mechanical pumps consists of 4 steps, as seen in the figure, the air taken in from the inlet is trapped and compressed, and then thrown out.

High vacuum pressures below 1×10^{-3} Torr are descended with a turbo molecular pump. By using the mechanical and turbomolecular pump to support each other, the system pressure can be reduced from the air environment to the high vacuum level of 1×10^{-9} Torr. Turbomolecular pumps consist of rotating and fixed sharp blades stacked in successive layers. As seen in the Figure 3.4 [65], the movable blades transfer the momentum and mechanical energy they gain with their rotation speed of 20,000 rpm to the gas molecules in the system. The inlet part of the turbomolecular pump refers to the vacuum chamber and the outlet part refers to the connection part with the mechanical pump.

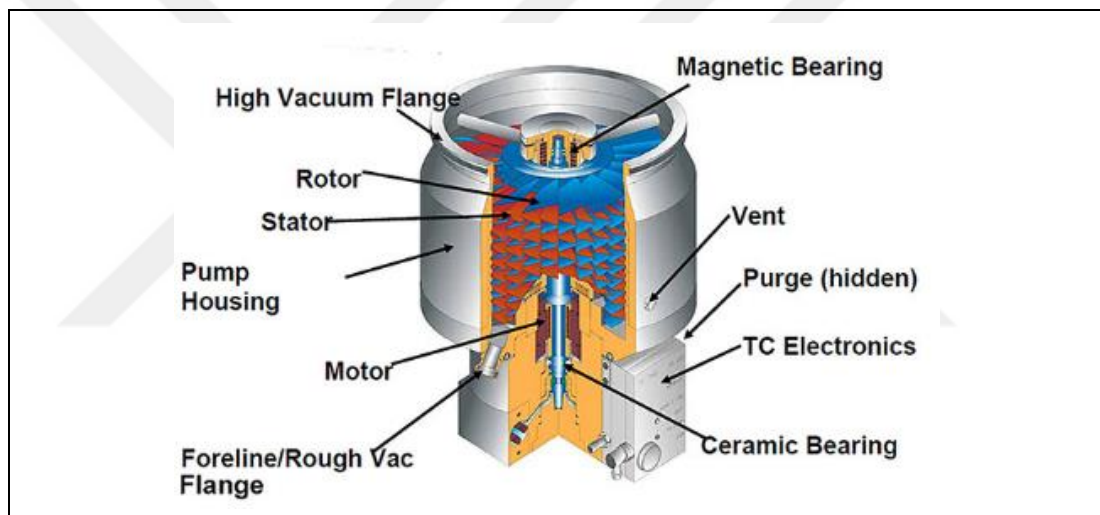


Figure 3. 4: Turbomolecular pump.

With the momentum they gain, the gas molecules move down the gas transfer gaps and collide on the fixed leaves on the lower floor.

There are two more types of pumps used in the system to reach the UHV pressure. These are ion and titanium sublimation pumps. After the pressure of the vacuum chamber is reached to 1×10^{-9} Torr, UHV levels with the mechanical and turbo pump, the ion pump can be activated and can reduce the pressure of the system down to 1×10^{-11} Torr. Ion pumps, as can be clearly seen in Figure 3.5 [66], are a mechanism formed by placing the structure consisting of stainless short cylinders (anode) sandwiched between two metal plates (cathode) into a high magnetic field arranged

parallel to the axis of the cylinders. Electrons accelerated under the magnetic field collide with gas atoms and ionize them. Ionized positively charged molecules are accelerated towards the Ti surface. Since the gas molecules trapped in this way will remain attached to the surface indefinitely, the ion pump does not need another booster pump at the gas outlet. However, since the cathode surfaces in the ion pump reach saturation over time, the titanium coating on the surface must be renewed periodically. Otherwise, the surface will not be able to hold more gas molecules and the pressure of the vacuum chamber will not be reduced by the ion pump. The sublimation of the Ti source, on which high current is passed, and the coating of the cathode walls with a clean Ti film is carried out with a turbo sublimation pump. Thus, by trapping the surface gas molecules, it is reactivated to form bonds.

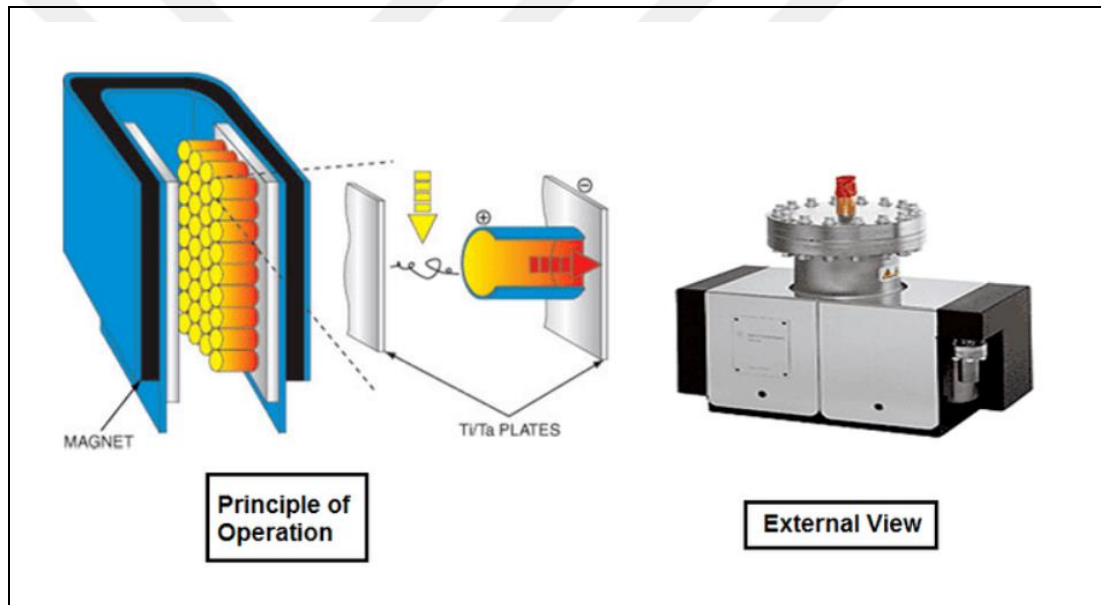


Figure 3. 5: Ion pump.

3.1.2. Manipulator

The task of the manipulator is to keep the sample placed in the vacuum chamber during the operations to be performed here, and to transfer the sample to other vacuum chambers by moving on the x , y , z axes according to the need. In addition to the x , y , z motion axes of the MBE system used throughout the thesis, the manipulator rotates 360° on azimuthal and polar coordinates, that is, its inner and outer axes, providing convenience especially in Rheed analyzes and transfer operations. With the tungsten

filament under the sample holder where the sample is placed in the manipulator, temperatures of approximately 1000° C can be reached on the sample. Temperature control is provided simultaneously from euroterm brand digital units, for example, by means of the heat meter right next to it. In addition, the temperature measurements of the samples in the vacuum chamber were made with the help of vacuum windows from the outside with a pyrometer.

3.1.3. Evaporators

In its simplest form, evaporators provide the high purity materials placed in the crucible to be evaporated with various heating apparatuses and sent to the substrate surface in the form of atomic and molecular beams. Due to the low pressure in the vacuum chamber, the average free paths of the evaporating atoms and molecules are very long. This means that the high-purity material will not interact with any residual gas during evaporation or when it is sent to the sample for storage. Therefore, this phenomenon, which we call steam, is perceived as a beam created by the atoms of the element that has been evaporated, and the name of the magnification system is molecular beam epitaxy.

Atomic rays of 99.999% purity Si, Ge, Mn elements used in this study were produced with single filament and dual filament effusion cells. Effusion cells have a small opening in order to maintain the UHV conditions in the chamber and to make the equilibrium vapor pressure in the effusion cell equal to the vapor pressure of the material. Effusion cells have a small opening in order to maintain the UHV conditions inside the chamber and to make the equilibrium vapor pressure in the effusion cell equal to the vapor pressure of the material. The source material is first placed in a crucible made of Pyrolytic Boron Nitride (pBN) to be evaporated. pBN is one of the crucible materials frequently used in effusion cells because it is resistant to temperatures above 1300° C and it releases gas from this temperature limit. The pBN crucible, one of the components of the effusion cell, is shown in Figure 3.6. The heating of the effusion cells is provided by Mo filaments. In addition, it can be adjusted and controlled automatically in the cell with the euroterm brand heat meter connected to this heating mechanism.

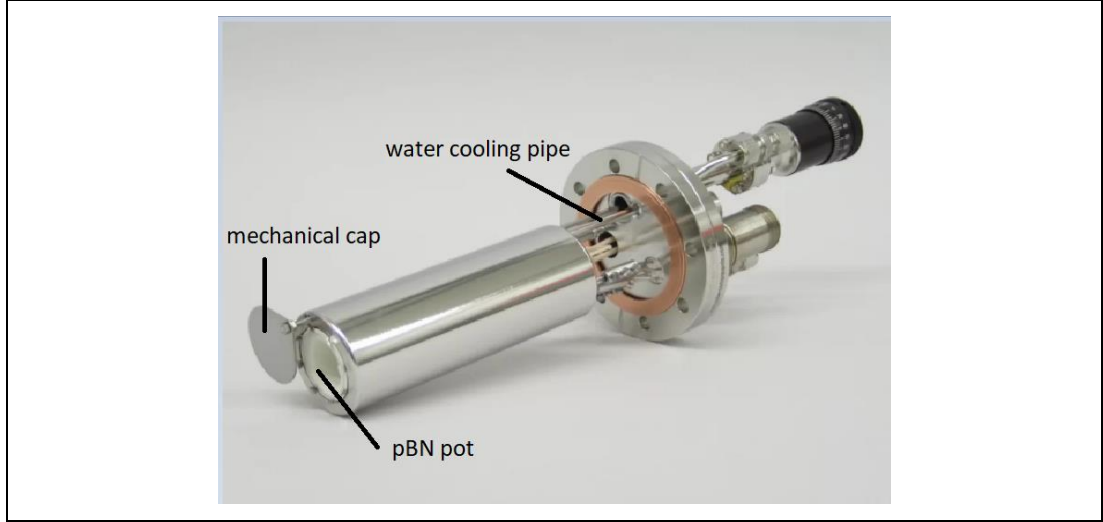


Figure 3. 6: Effusion cell.

The most basic elements of MBE systems, vacuum pumps and effusion cells, have been described in detail above. With the combination of high purity environment free from unwanted gases provided by UHV conditions and effusion cells and the ability to make coatings in the most precise dimensions possible, magnification models have emerged, which we call epitaxial, where every step of material storage is carried out under atomic scale control.

Based on the thermodynamic characteristics of the energy between the substrate and interfaces in epitaxial growths, three major growth models have been developed: Frank-van der Merwe, Vollmer Weber, and Stransk-Krastanov.

$$\gamma_{\text{substrate}} \geq \gamma_{\text{film}} + \gamma_{\text{interface}}$$

$$\gamma_{\text{substrate}} < \gamma_{\text{film}} + \gamma_{\text{interface}} \quad (3.2)$$

$$\gamma_{\text{overlayer}} > \gamma_{\text{substrate}}$$

Homo and heteroepitaxial growth on a single crystal is particularly dependent on the force between the atoms and the surface. To clearly explain the transition between growth modes, as expressed in the formula in (3.2), the surface energy of the substrate is greater than the sum of the surface energy of the film and the interface energy between the film and the substrate, which means that Frank-Van der Merwe

type growth occurs because the atoms bond more strongly with the substrate than with each other. As a second step, Volmer-Weber type growth occurs because the surface energy of the substrate is less than the sum of the surface energy of the film and the interface energy between the film and the substrate. In this case, the absorbed atoms make a weaker bond with the substrate than they do with each other. This causes their concentration on the surface to be low, due to their rapid evaporation from the surface. The third phase, Stranski-Krastanov type growth, is produced by a shift in the balance of forces, which is generally generated by tension between the deposited layer and the substrate. This is created by low concentration atoms on the surface coming together.

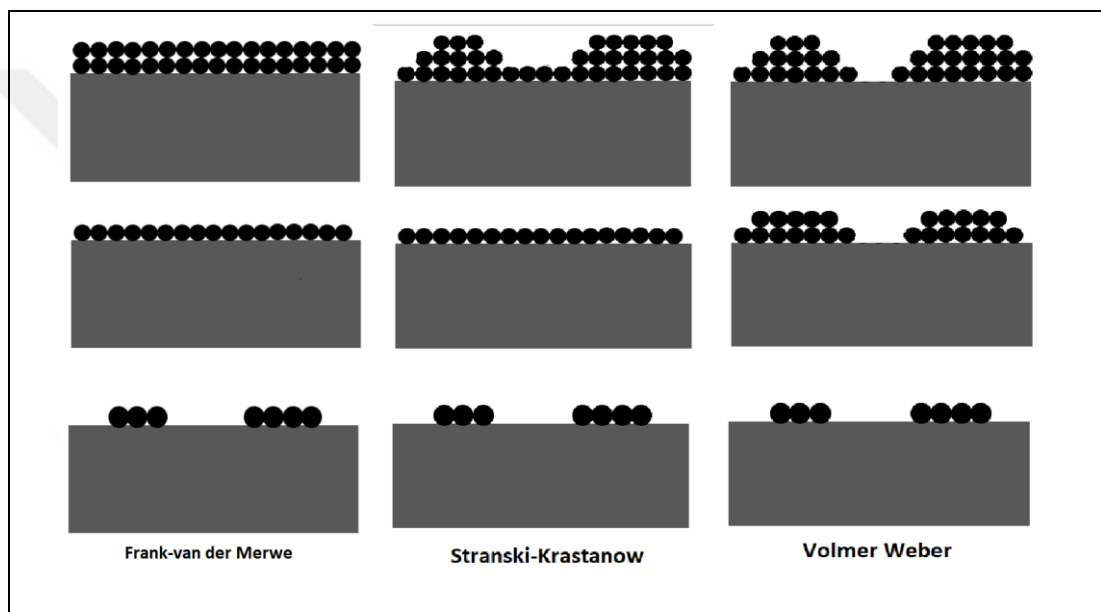


Figure 3. 7: Growth modes of thin films.

3.2. X-Ray Diffraction (XRD)

X ray corresponds to the wavelength of the X-ray spectrum between $0.1 \text{ \AA}$ and $10 \text{ \AA}$. They are electromagnetic waves that are categorized based on their X-ray energies as low-energy (soft) in the range of 120 eV to 1 keV and high-energy (hard) in the range of $1-120 \text{ keV}$. X-rays have extremely high energy due to their short wavelengths. Therefore, they have much higher penetration compared to Ultraviolet, visible light, Infrared or radio waves. The conversion between energy, frequency and

wavelength is provided by the De Broglie equation, where h Planck's constant, c speed of light, λ wavelength of propagation, and ν frequency, respectively.

$$E = h\nu = \frac{hc}{\lambda} \quad (3.3)$$

The atoms in the crystals are arranged in the form of repeating planes and show a three-dimensional periodic arrangement (Figure 3.8). When X-rays interact with crystals, they pass completely through the crystal, are absorbed by the crystal, or are scattered or reflected after striking the crystal.

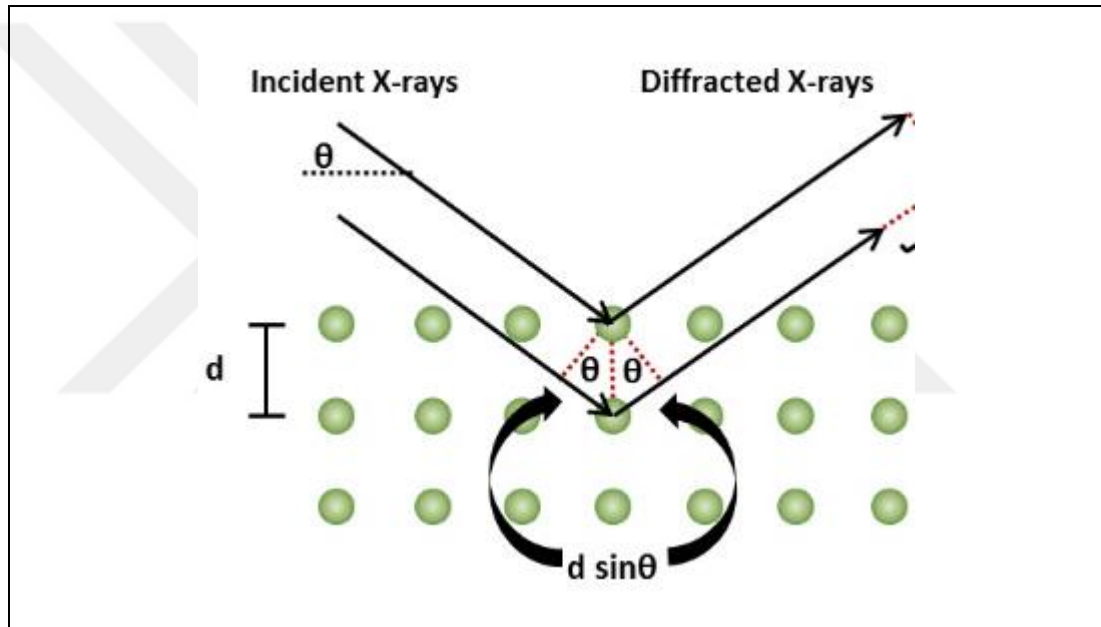


Figure 3. 8: X-ray diffraction schema.

$$n\lambda = 2d\sin\theta \quad (3.4)$$

Depending on these interaction types, we can perform different applications such as the distance between the atomic planes in the crystal, the determination of the defects of the crystal size and the tensions in the thin film with the x-ray diffraction technique. When a beam of X-rays radiates an atom, electrons around the atom begin to vibrate at the frequency of the X-ray. When radiation with a wavelength λ similar to atomic spacings is dispersed in a specular form (mirror-like reflection) by the atoms

of a crystalline system, constructive interference occurs. The waves are dispersed from lattice planes separated by the distance d between successive layers of atoms in a crystalline solid. As can be observed from the equation when θ is the angle between the incident and scattered wave, d is the distance between the planes, and λ is the wavelength of the incident light.

3.3. X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique based on the photoelectric effect that can identify the elements present in a material (elemental composition) or on its surface, as well as their chemical states, and the overall electronic structure and density of the electronic states in the material. XPS is a useful measuring method since it displays not only what components are there, but also what other elements they are bound to. When combined with ion-beam etching, the process may be employed in line profiling of the elemental composition over the surface or in depth profiling. It's frequently used to investigate chemical reactions in materials in their raw condition or after cleavage, scraping, heat, reactive gases or solutions, ultraviolet radiation, or ion implantation. XPS is a type of photoemission spectroscopy that involves irradiating a material with an X-ray beam to get electron population spectra.

Measurements of kinetic energy and the quantity of expelled electrons are used to infer chemical states. Although ambient-pressure XPS, in which materials are evaluated at pressures of a few tens of millibar, is currently under development, it needs high vacuum (residual gas pressure $p \sim 10^{-6}$ Pa) or ultra-high vacuum ($p < 10^{-7}$ Pa).

The energy of the photon transmitted from the X-ray source to the sample is transferred to the electron attached to the nucleus during XPS measurements. The energy of the photon sent to the sample in the vacuum environment is transferred to the nucleus of the electron. If the binding energy is higher than the binding energy and the electron has a high enough energy, for example, to overcome the work function, the electron leaves the material. A hemispherical analyzer measures the kinetic energy of the electron exiting the sample (HSA). Figure 3.9 shows the HSA utilized for XPS analyses throughout the thesis. The binding energies of electrons are calculated by

substituting the measured and known values in the Einstein equation given in equation 3.5. Thus, it is determined which elements are present in the system. In addition, by determining the chemical shifts in the bonding energies of the orbitals of the elements with the effect of the atomic environment in XPS measurements, a state analysis of the valence of the element can be made.

$$E_B = h\nu - E_K - \phi \quad (3.5)$$

The binding energy of the ejected electron E_B can be calculated from equation 3.5, where E_k is the kinetic energy of the ejected electron, $h\nu$ is the energy of the emitted X-ray, ϕ the extra energy required to transport the electron from the sample to the analyzer, that is, the work function.

In addition, since the mean free path of the electron is not very long due to the scattering and absorption events occurring in the solid, XPS can receive data from a few nanometers from the sample surface. Therefore, the XPS technique is a useful technique for thin-film samples and requires UHV to allow the electron removed from the sample to go to the analyzer without losing energy.

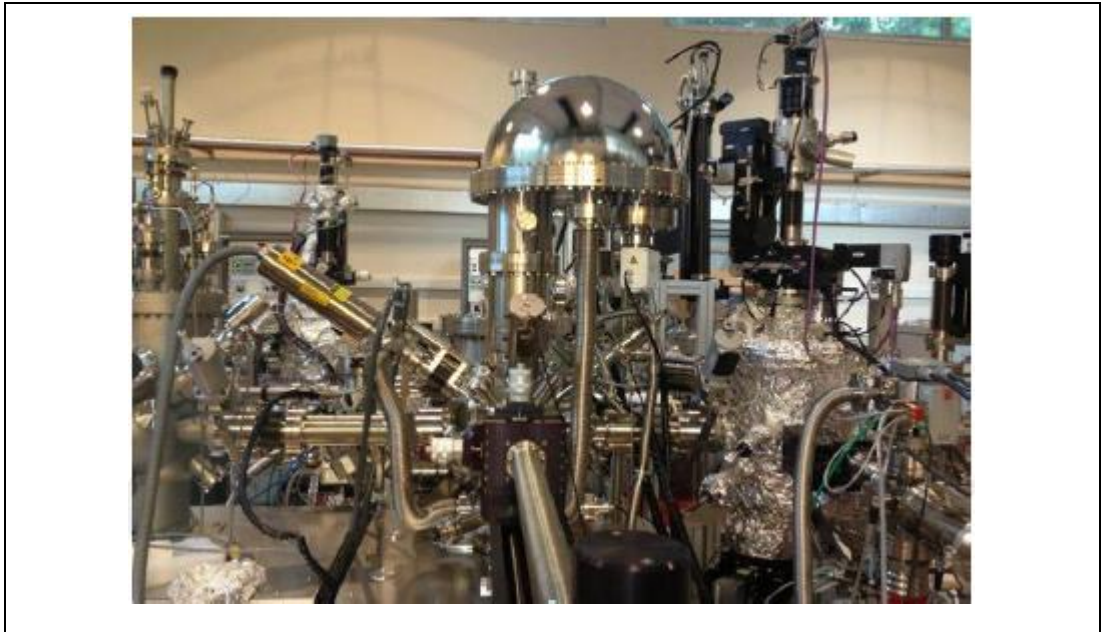


Figure 3. 9: XPS system.

3.4. Reflection High Energy Electron Diffraction (RHEED)

RHEED (reflection high-energy electron diffraction) is a surface analysis technique that has gained popularity due to its compatibility with methods of vapor deposition and epitaxial thin film development in ultra-high vacuum, allowing thin film formation and analysis to be done concurrently. An electron gun, a phosphor screen, and a clean surface for the sample to evaluate are all that is required for the implementation. The tightly collimated electron beam's normal energy range is 8 to 20 keV, while energies as high as 100 keV have been employed in rare situations. Due to the interaction between electrons and atoms, RHEED is most sensitive to the structure in the first few atomic planes of a crystal lattice, which only enables a minimal penetration depth of incoming electrons. The electron beam is targeted at the sample's surface at a very low incidence angle, which has a significant impact on the diffraction patterns that arise. RHEED patterns are often utilized to extract information regarding atomic arrangement periodicity, surface flatness, grain or domain size of surface structures, epitaxial relationship between the formed film and the substrate, thin film growth style, and the number of atomic layers developed. Figure 3.10 depicts the RHEED equipment. Deflection coils can vary the incidence angle of the electron beam, and θ_g should be less than a few degrees. The RHEED pattern is generally average in a macroscopic region due to the grazing incidence.

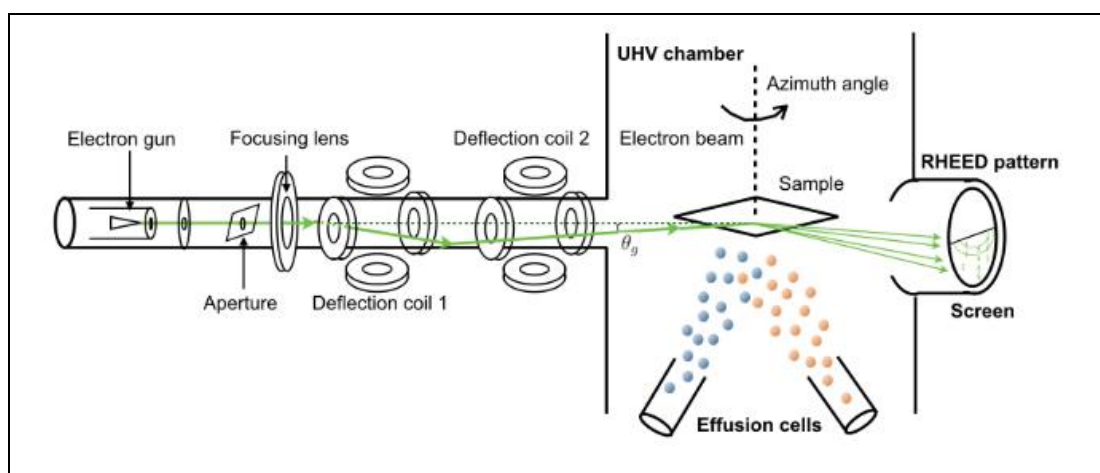


Figure 3. 10: RHEED system.

The Ewald construction creates the relationship between the reciprocal space and the geometrical elements of a RHEED pattern by combining energy and momentum conservation. The presence of constructive interference is the basis for the diffraction condition. When elastic scattering is taken into account, the wavevector (k) for incident (g) and diffracted (f) waves has the same magnitude. The incident and diffracted waves' parallel components must vary by a factor of 2 times the reciprocal lattice constant ($1/a$)

$$k \cos\theta_g - k \cos\theta_f = \frac{2\pi n}{a} \quad (3.6)$$

The endpoints of the diffracted wavevectors describe a sphere of radius k , which is known as the Ewald sphere, due to elastic scattering. The center of the sphere is the common origin for all diffracted waves under the elastic scattering theory. The reciprocal lattice is the intersection of two sets of planes rotated by 90 degrees to one other, which is a set of rods, in a square lattice of equidistant atoms. When both elastic scattering and diffraction conditions are met, the RHEED pattern develops from the reciprocal space intersection of the Ewald sphere and the rods, resulting in diffraction spots. As a result, in the instance of RHEED, the diffraction spots are always on concentric circles. The spots can be elongated into streaks depending on the incident angle of the electron beam and the crystal domain size at the surface of the sample. Depending on the incidence angle of the electron beam and the crystal domain size at the sample's surface, the spots can lengthen into streaks. Because the coordination of atoms at the surface is not the same as in the bulk, the atoms at the surface can undergo rearrangements in order to minimize the surface energy, this process is called surface reconstruction. The periodicity at the surface may differ from that of the bulk crystal depending on the method of reconstruction. Because RHEED patterns only provide information on a few layers of the surface, two-dimensional lattices must be defined, which may differ from full three-dimensional lattices. The periodicity at the surface may differ from that of the bulk crystal, depending on the type of re-construction. A two-dimensional lattice can be represented by the vector, where n_1 and n_2 are integers and a_1 and a_2 are the surface lattice's unit mesh vectors.

$$\overrightarrow{R_n} = n_1 \overrightarrow{a_1} + n_2 \overrightarrow{a_2} \quad (3.7)$$

A reciprocal vector can be defined as $B_m = m_1 a_1^* + m_2 a_2^*$, which is similar to the situation of three-dimensional lattices.

$$\begin{aligned} a_1^* &= 2\pi \frac{a_1 \times n}{a_2 \times n} \\ a_2^* &= 2\pi \frac{a_1 \times n}{a_2 \cdot (a_1 \times n)} \end{aligned} \quad (3.8)$$

The vector n represents the unit vector normal to the sample's surface. The reconstructed surface's base vectors b_1 and b_2 may be written as a function of the fundamental basis vectors a_1 and a_2 in the following way:

$$\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} n_{11} & n_{12} \\ n_{21} & n_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \quad (3.9)$$

As a result, a transformation matrix connects the rebuilt surface lattice with the bulk structure. Wood's notation can also be used to designate the rebuilt surface, for example, 2×1 structure of Si (001). Fundamental spots, which appear in the 0th and 1st Laue zones and are generally bright, are caused by scattering not only from the topmost atomic layer but also from multiple atomic layers in the bulk area. The superlattice dots, which correspond to the rebuilt surface, are found between the basic points. Similar to polycrystals, the surfaces may not be completely smooth or contain domains of varying sizes. As a result, the RHEED patterns are altered from their ideal state, revealing the nature of the surface flaws. Because the width of the reciprocal rod is inversely proportional to the domain's average size, crisp patterns with dots represent high domain sizes, but extended streak patterns reflect lower domain sizes. Surface steps result in modulated patterns. Inclining streaks emerge from vicinal surfaces. The presence of transmission dots in the RHEED pattern, as seen in Figure 3.11, generally indicates a three-dimensional growth mode in MBE.

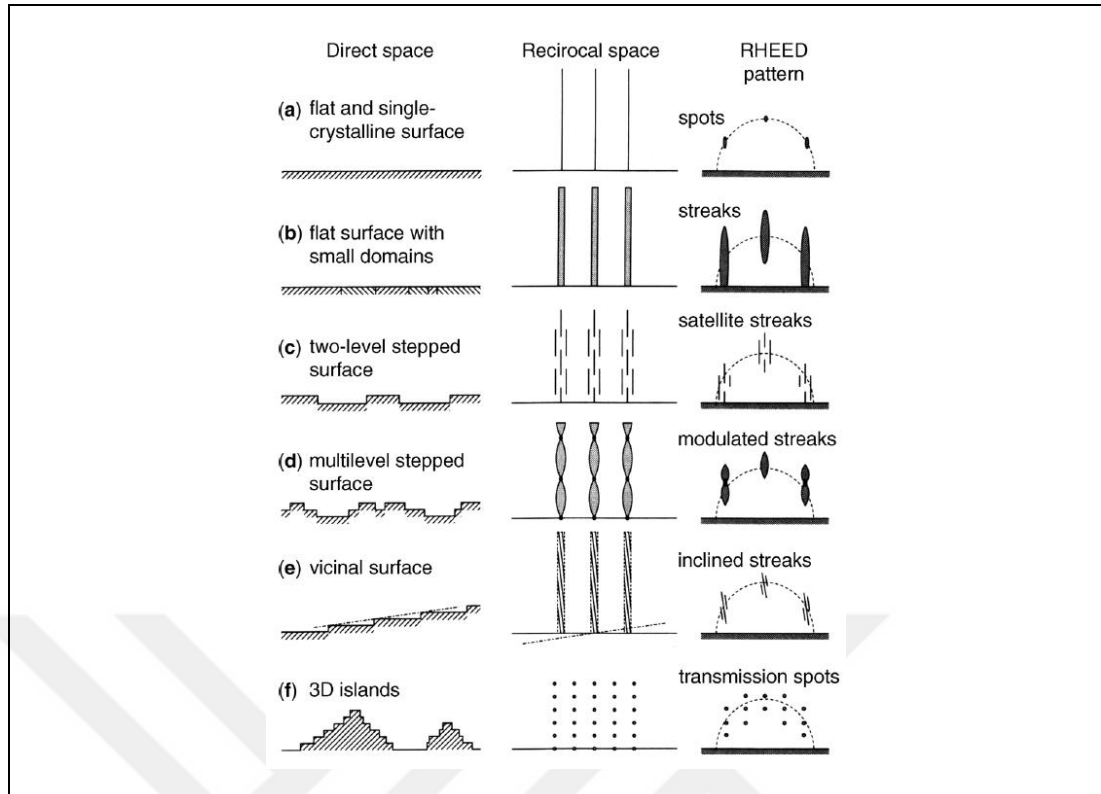


Figure 3. 11: RHEED designs and schematics of several types of realistic surfaces in real-space morphology and reciprocal space.

3.5. Vibrating Sample Magnetometer (VSM)

Vibrating sample magnetometer (VSM), which is a device that basically works according to Faraday's law of induction, is used to investigate the magnetic properties of materials. According to Faraday's law of induction, the change in magnetic flux in a closed circuit creates an induction electromotive force (*emf*) in the circuit. The expression for electromagnetic induction can be explained by the magnetic flux change being equal to the induced *emf*.

Faraday's law is based on the *emf* produced by the magnetic flux change. By varying the amount of magnetic field traveling through the loop, Faraday discovered that an *emf* and current can be induced. He also discovered that the "magnetic field quantity" might be represented as magnetic field lines going through the loop. To understand Faraday's law, let's observe a simple experiment with the Figure 3.12.

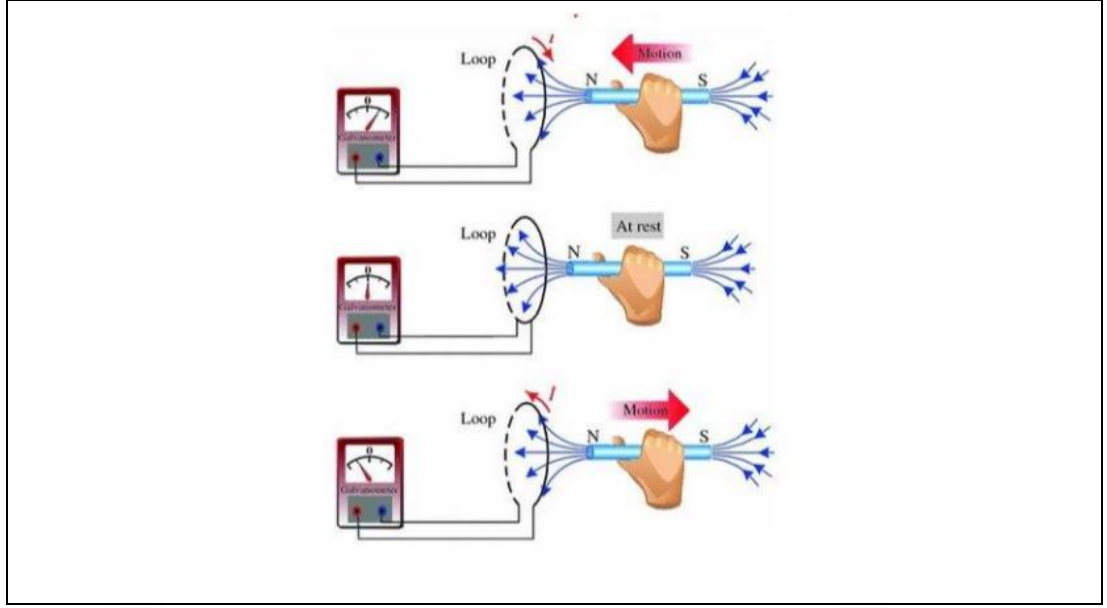


Figure 3. 12: Faraday's law.

Consider the wire loop attached to a galvanometer as shown in Figure 3.12. The needle of the galvanometer deviates to the right when a magnet is brought closer to the ring. If the magnet is removed from the wire ring, the pointer will deflect in the opposite direction. It has been observed that the needle of the galvanometer does not deviate in any way when the magnet is motionless with respect to the ring. In the same way, if the ring is moved in the direction approaching or moving away from the magnet, which is held at rest, the needle will deviate again. As it can be understood from here, there is a relationship between the current and the changing magnetic field. Although there is no battery in the circuit, a current is observed in the circuit. Such a current is called induced current because it is produced by induced *emf*. This induced *emf* is directly proportional to the time derivative of magnetic flux through the circuit.

$$\varepsilon = - \left(\frac{d\phi_B}{dt} \right) \quad (3.10)$$

Where $\phi_B = \int B \cdot dA$ is the magnetic flux through the circuit. We write the total *emf* in the circuit, with the surface area A and the number of turns N, as follows;

$$\varepsilon = - N \left(\frac{d\phi_B}{dt} \right) \quad (3.11)$$

When a magnetic material is placed inside a current-carrying coil, the magnetic flux is related to the magnetization of the material. If we substitute $\Delta B = \mu_0 M$ in equation 3.11, we get, μ_0 is the permeability of the free space.

$$\varepsilon . dt = - N . A . \mu_0 . M \quad (3.12)$$

The VSM system is a measurement technique that gives information about the magnetic properties of the samples. In VSM, a sinusoidal motion with a frequency of ν is made on the sample and an induced voltage with the same frequency of ν is obtained in the coils. The main parts that make up the VSM are shown in Figure 3.13.

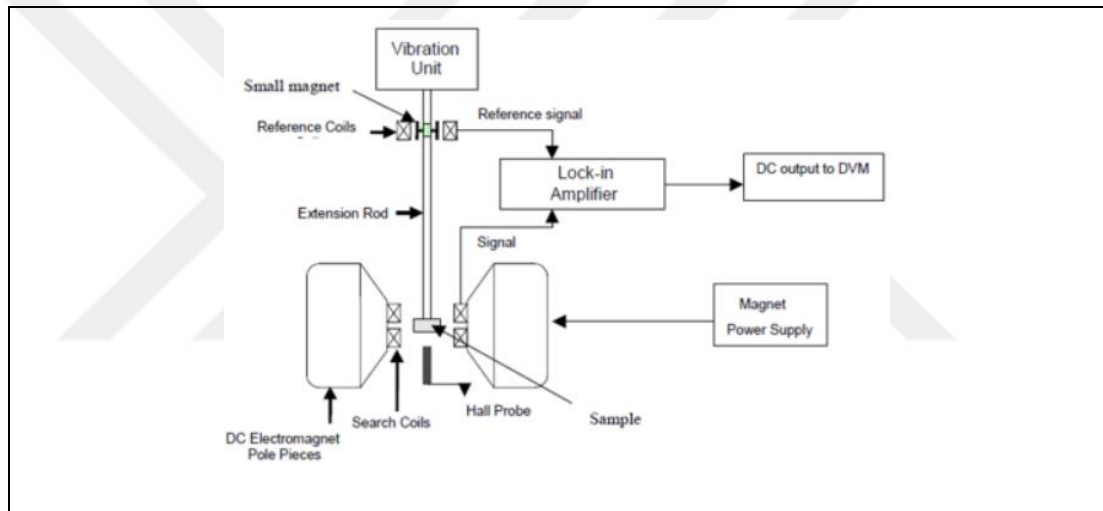


Figure 3. 13: VSM system.

Vibrating sample magnetometer system components:

- *Water cooled electromagnet and power supply:* It is used to generate a constant magnetic field to magnetize the sample.
- *Sample vibrator and sample holder:* The sample holder is placed at the end of the vibrating apparatus and suspended between two pieces of superconducting magnets (thereby obtaining a homogeneous magnetic field), where it is vibrated at a certain frequency value. The sample can be rotated in the desired x , y and z positions under a constant magnetic field. In order to obtain a clean data, the environment of the sample is under vacuum.

- *Sensor coils:* While the sample is vibrating, alternative current is generated in these coils at the same frequency. The resulting signal contains information about the magnetization of the material.
- *Amplifier:* The amplifier amplifies the signal acquired by the coils. The intensity of the output signal is directly proportional to the magnetic moment of the sample, the vibration amplitude and the frequency ν .
- *Liquid helium tank:* Allows to control the temperature of the environment. It is also used to cool the coils. The liquid helium tank is protected by a vacuum jacket. Because liquid helium can evaporate very quickly at a temperature of 273K. Thus helium loss is minimized.

3.6. Elektron Spin Resonance

Electron spin resonance (ESR), also known as electron paramagnetic resonance, is a technique that studies chemical compounds with one or more unpaired electrons, such as organic and inorganic radicals. ESR spectroscopy includes the microwave region of the electromagnetic spectrum and its resonance frequency is in the range of GHz.

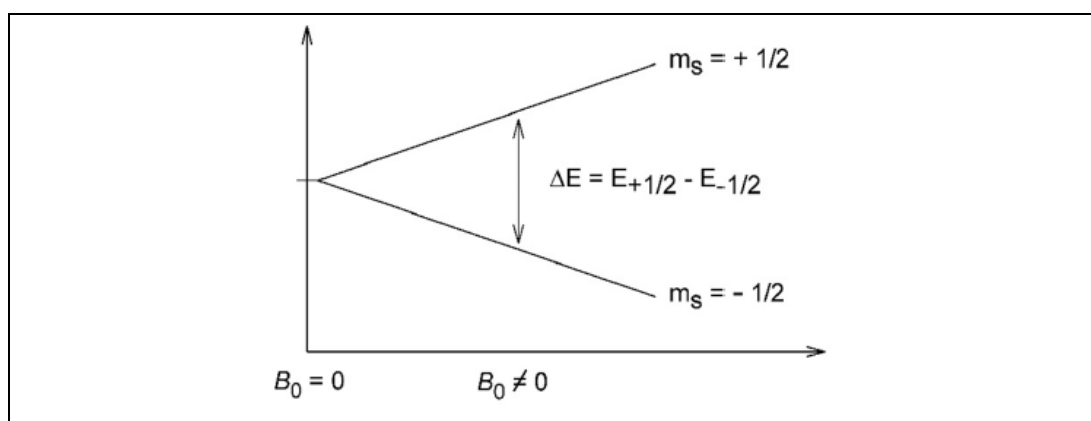


Figure 3. 14: Energy differences between spin states.

When a solid molecule has paramagnetism as a result of having unpaired electrons, an external magnetic field and electromagnetic energy can be applied to switch between spin states. The interaction between the spin of the electron and the external magnetic field depends on the magnetic moment of this spins. Applying a

magnetic field creates a magnetic potential energy proportional to the applied magnetic field (Zeeman effect), which splits the spin states. Radio frequency radiation is absorbed by the electron, resulting in a transition from one spin state to another. The energy difference between these two spin states is written as in the formula 3.13

$$\Delta E = \mu_b \cdot g \cdot B_0 \quad (3.13)$$

where μ_b is the bohr magneton, g is the spin factor, and B_0 is the flux density of the applied magnetic field. For absorption to occur, the electromagnetic wave sent must have as much energy as this energy difference.

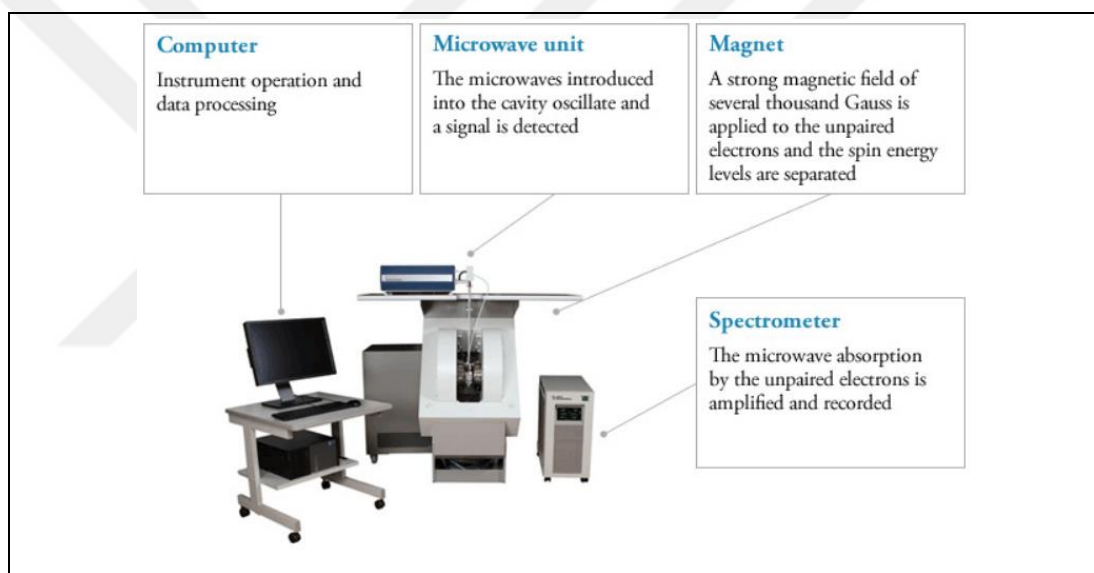


Figure 3. 15: ESR system.

Electron spin resonance system components:

- *Microwave source:* It measures and controls the intensity and frequency of the microwave beam. The system consists of a total of five parts: klystron, automatic frequency control, isolator, wave meter and attenuator.
- *Cavity:* It is the part where the sample is held. It has components that allow directing and controlling the microwave beam.

- *Magnet*: The electromagnet consists of a pair of coils wound on ferromagnetic materials to produce a uniform and stable static magnetic field.
- *Detector*: The microwave energy absorbed by the sample is detected and observed as a spectrum after some electronic processing.

3.7. Solid Phase Epitaxy (SPE)

The solid phase epitaxy (SPE) process involves using thermal heating to crystallize an amorphous layer grown on a single crystal, in Figure 3.16 [67]. The atoms that are in disorder in the amorphous layer are restructured layer by layer in the order of the single crystal structure with the effect of annealing. Temperature, pressure, crystal orientation, and order, as well as the concentration of additives, are the major factors influencing SPE growth kinetics. Although SPE seems to be a simple growth technique, it includes at least as complex steps as other amplification techniques. Depending on parameters such as pressure, growth rate, annealing temperature and time, many processes such as roughness in the amorphous-crystalline transition region, formation of defects and diffusion of impurities in the system are tried to be controlled.

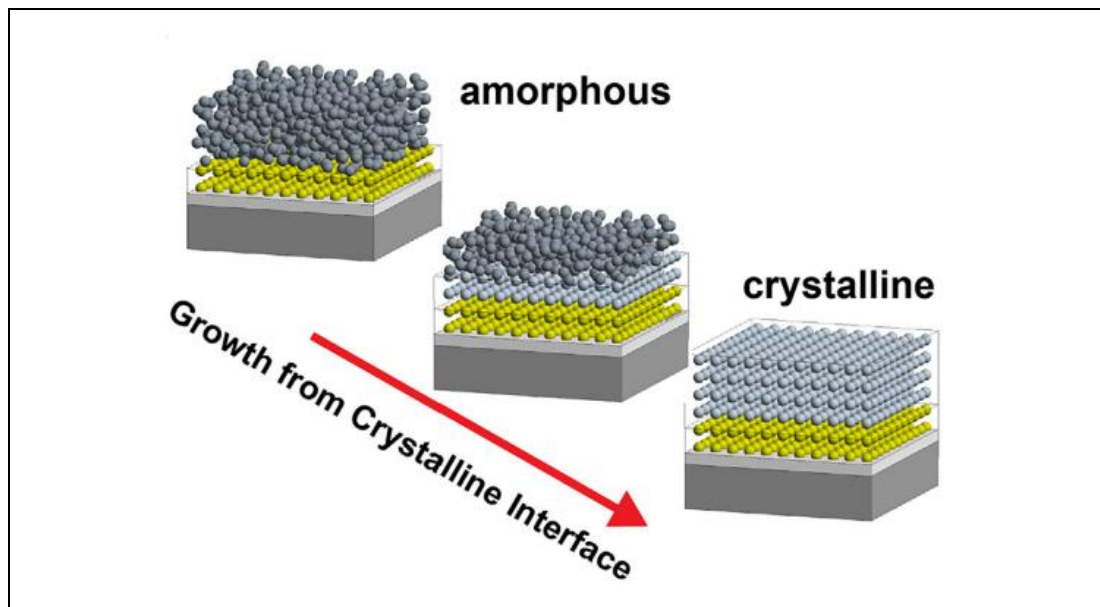


Figure 3. 16: Solid phase epitaxy crystallization process.

SPE technique has been playing an important role in the device production stages for many years, especially due to its contributions to the elimination of damages and amorphous regions in the crystalline arrangement due to various reasons such as the activation of additives and ion implantation. Compared to other techniques, since the process is carried out at low temperatures, its application area is also quite wide. It works with a variety of materials and manufacturing stages, including high-K dielectrics and metal gates. Due to all these features, SPE technique is used for the development of more functional new materials with unique properties due to the negativities encountered as a result of size reduction studies in semiconductor technology and plays an important role in the advancement of research. For these reasons, within the scope of the thesis studies, Mn_5Ge_3 films produced to support spintronic technology were grown by SPE technique.

4. EXPERIMENTAL RESULTS

4.1. Substrate Cleaning Procedure

Si (111) with a thickness of 100 micrometers prior to the cleaning procedure is cut in the form of 1 cm² squares. Substrate cleaning is a parameter that may affect the whole growth process as well as the magnetic properties of the grown samples. In this respect, the sample cleaning is important, before loading the sample into vacuum chamber. The cleaning process that differs according to the substrate can be carried out in several different ways. Although the general lines are the same, each group uses different cleaning prescriptions depending on their system.

The RCA (Radio Corporation of America) method is the most commonly used substrate cleaning procedure. RCA method is an appropriate method to use prior to high temperature operations in semiconductor technology. Werner Kern invented the basic procedure in 1965 while working at RCA. The RCA method involves first of all removal of the organic contaminants, next step removal of the thin oxide layer and finally removal of ionic contamination processes. The RCA method applied within the scope of this thesis involves primarily vibrating the sample in ultrasonic bath for a 5 minutes acetone, 10 minutes methanol and 10 minutes IPA consecutively. After removal of surface of organic contaminants, sample was dried with nitrogen and hold in 40% hydrofluoric acid solution diluted with diawater for 90 seconds. After the complation of chemical cleaning steps, samples were immersed in deionized water, dried with nitrogen gas and transferred to the vacuum chamber immediately. After placing in the vacuum chamber, the samples were heated up to 700 °C for several hours and were purified from surface impurities such as oxygen and carbon. The success of this cleaning procedure, which took approximately 6 hours, was checked by Auger Electron Spectroscopy (AES) and LEED techniques in the analysis chamber.

As can be seen from the LEED image in Figure 4.1 taken after the heat treatment, the 7x7 Si(111) pattern can be clearly observed. The LEED image was taken with an energy of 60 eV.

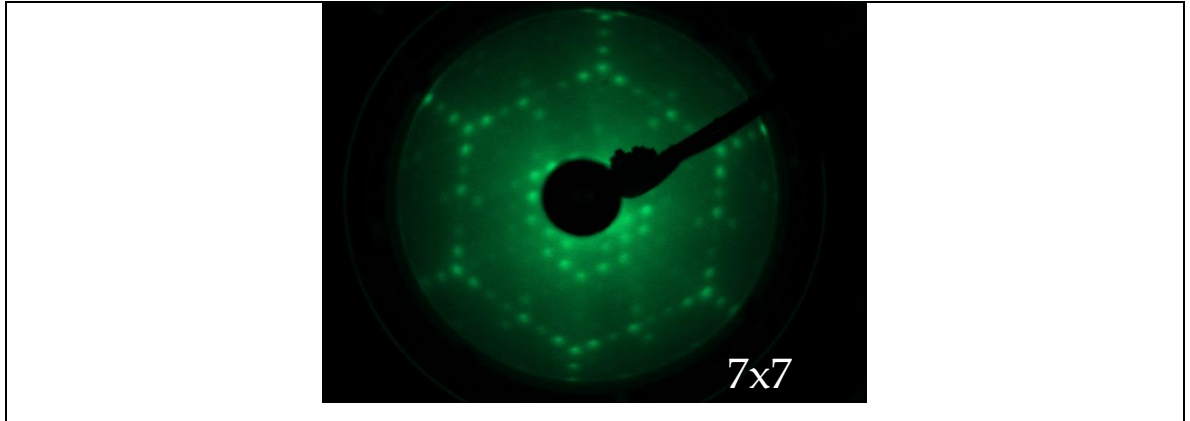


Figure 4.1: Si (111) 7x7 reconstruction.

This showed that the cleaning process was successful, the surface free of contaminants at atomic level and the pattern could be observed clearly. If the atoms settled on the lattice points are not bright and clear, the surface needs to be cleaned again.

It is understood by the AES image that the surface is completely free of contaminants. After the cleaning procedure of the samples in each set was completed, AES was applied and the presence of pollution and oxygen on the surface was checked. Figure 4.2 shows the AES spectrum of the Si(111) substrate taken after annealing in vacuum. As can be seen from the figure, no oxygen and carbon peaks were observed on the surface. Finally it is understood that a clean surface free of oxygen and carbon atoms is obtained in AES analysis, the samples are ready for growth.

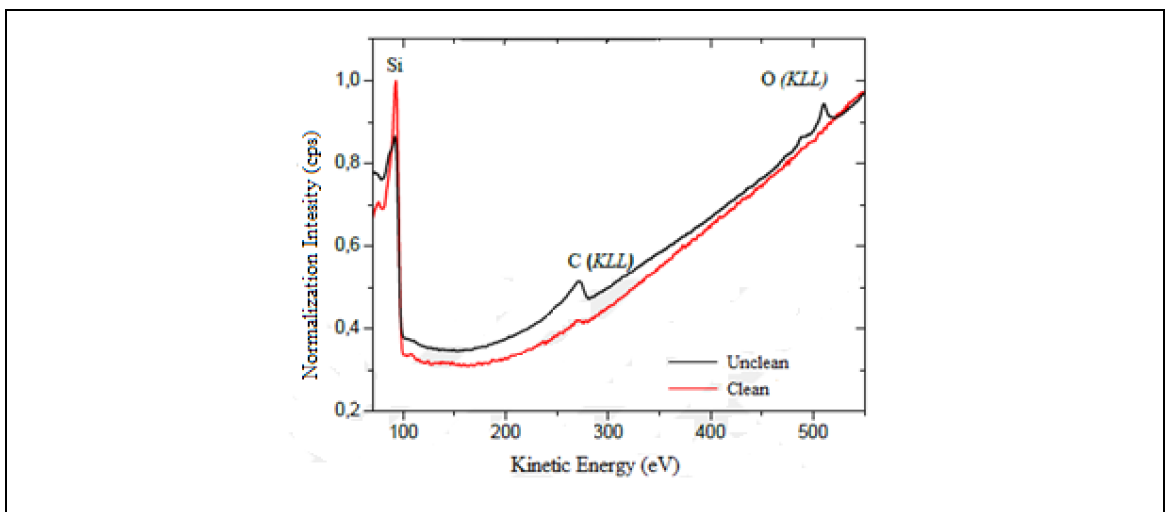


Figure 4. 2: AES spectra of the samples before and after cleaning by annealing.

4.2. Sample Growth Prosedure

Mn_5Ge_3 (002) thin films were grown on thin Si(111) substrates by rapid thermal annealing method. Since very thin (100 μm) Si substrates were obtained commercially, no film thinning method was applied. In the thesis, two different growth methods has used to manufacture the samples: Magnetron Sputtering and Molecular Beam Epitaxy. Firstly, silicon substrates were cut into 1 cm^2 pieces and passed through cleaning steps performed exsitu and insitu the vacuum before going to the film growing process in the vacuum chamber. After cleaning processes, the surface cleanliness was checked with LEED and AES. Then, it's moved to Magnetron Sputter chamber. By magnetron sputtering technique, germanium is grown on Si substrates. With magnetron sputtering technique, germanium grown on semiconductor Si substrate at 385° C degree under a partial pressure. While the basic pressure was about 2×10^{-8} mbar before germanium growth, the pressure level increased to 5×10^{-3} mbar due to the argon gas used during the growth process. 40W DC power was applied for the germanium target to be grown. The 150 nm thick germanium was grown with the sputter technique.

After the Ge coating, the sample is taken to the MBE chamber and kept ready for the solid phase epitaxy process. Solid phase epitaxy process is the most important step of the whole sample preparation process, but it is the most difficult one. Because, reaching the desired temperature and time and cooling the sample back after a certain annealing period must be done very carefully. Ge coated film was taken to the MBE vacuum chamber after it was cooled slowly in order to obtain better crystallization. The germanium-coated samples taken into the MBE vacuum chamber were coated at room temperature with Mn layers of different thicknesses at 5 nm, 10 nm and 15 nm. The reason for growing it at different thicknesses is to observe the effect of thickness on Mn_5Ge_3 formation. While the samples were coating, the Mn effusion cell temperature was kept at 850° C. This temperature is the temperature required for Mn to sublimate to form vapor phase.

The time the sample reaches the annealing temperature and the cooling time are the most important factors affecting the whole film structure and whether the film will be in the Mn_5Ge_3 phase. If the sample temperature is increased rapidly, the Mn atoms in the structure tend to form metallic bonds with each other rather than bond with Ge atoms. Thus, the $\text{Mn}_{11}\text{Ge}_5$ structure is observed due to the rapid clustering of Mn atoms

rather than being in the Mn_5Ge_3 structure. In order to avoid this, the temperatures of the samples were gradually brought to the annealing temperature, proportional to their thickness, in the range of 12-15 minutes. The samples, which were annealed for 20 minutes at 320°C degree, were gradually reduced in temperature in a short period of 1-2 minutes. During the 20 minutes, Mn atoms diffuse into the Ge film and bond with Ge atoms. The reason for its rapid cooling is to facilitate its crystallization by preserving the Mn_5Ge_3 phase. After the samples, cooled down to room temperature, The preparation of the samples was finished by plating 10 nm gold to protect the Mn_5Ge_3 film against oxidation.

4.3. Structural Characterization of Mn_5Ge_3

The 150 nm thick single crystalline Ge layer, was successfully grown on Si substrate. Crystallinity was confirmed by the presence of XRD peak at 27.35° in Figure 4.3. The formation of a single crystal Ge(111) grown on Si(111) substrate is very important and required for the formation of the Mn_5Ge_3 phase. The RHEED pattern of the film formed after the Ge film is grown is shown in Figure 4.3 (a). Two-dimensional growth occurred due to the 4.2% lattice mismatch between Ge and Si. Although there is a striped pattern due to the Ge thin film formed at the underneath layer, a dotted RHEED pattern was observed due to the growing Ge islands near the surface region. In this way, dotted and lined structures are usually seen in heteroepitaxial layered structures with lattice mismatch, and this growth mode is known as the Stranski–Krastanov mode.

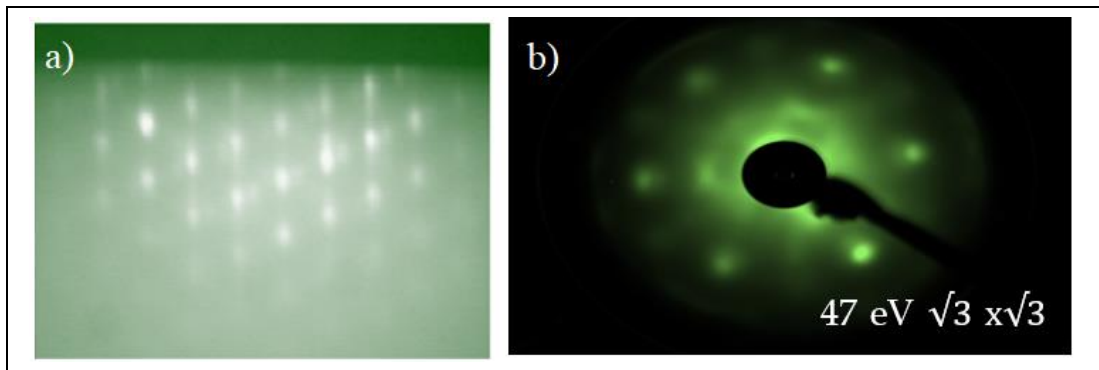


Figure 4. 3: (a) RHEED pattern of the Ge layer grown on a clean Si(111) ultrathin film. (b) LEED pattern of Mn_5Ge_3 layer formed on Ge at 47 eV.

The metallic Mn film, which was grown on 150nm Ge(111) crystal in MBE system under 8×10^{-9} mbar pressure, was annealed for 20 minutes by rising to 320°C in 10 minutes. It was observed that $\text{Mn}_{11}\text{Ge}_8$ structure appeared in the structure when the time was shortened, the temperature value of 320°C was reached in less than 10 minutes or the process was performed for more than 20 minutes. This result shows that Mn atoms tend to form metallic structure by bonding with each other instead of Ge atoms in the structure. As a result of solid phase epitaxy process, Mn atoms diffuse into Ge crystal and form Mn_5Ge_3 structure. The $\text{Mn}_5\text{Ge}_3(002)$ diffraction peak was observed at 37.5° as shown in Figure 4.4. It has been noticed that the best result among the selected 5nm, 10nm, 15nm Mn thicknesses is obtained from the 15nm thick Mn layer. This result shows that the Mn_5Ge_3 film was grown as a single crystal. In addition, as the film thickness increases, the peak width of Mn_5Ge_3 narrows and the peak intensity increases. Although they have the same Ge thickness, increasing Mn thickness causes an increase in film quality. Furthermore, AFM images were taken to investigate the surface morphology of the grown samples which are heteroepitaxially growth on Si surface.

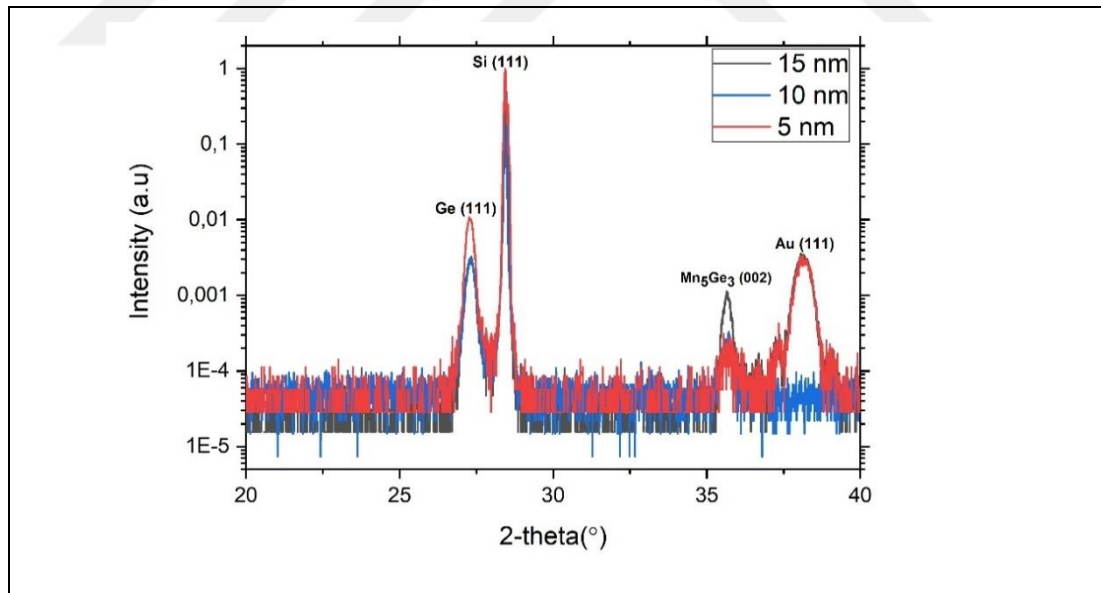


Figure 4. 4: XRD analysis of Mn_5Ge_3 film grown on 100 μm thick Si(111).

The AFM image of 15nm thick Mn_5Ge_3 layer grown on ultra-thin Si(111) is given in Figure 4.5. In this sample, there is an anisotropy and periodic pattern formation resulting from the target orientation and single angle grown in the sputter

system. Anisotropy of the surface support the magnetocrystalline anisotropy. The measured surface roughness of this sample is around 2.58 nm.

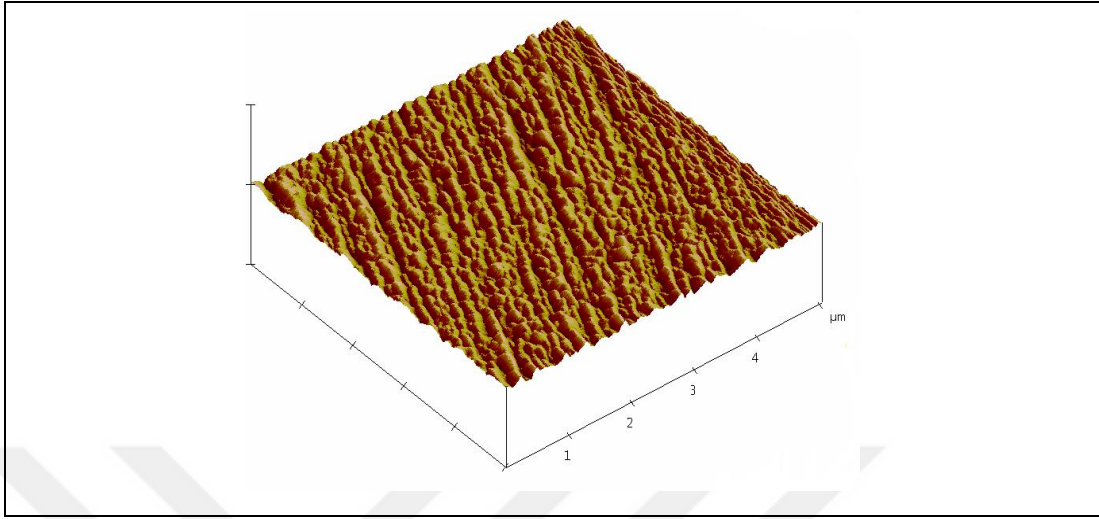


Figure 4.5: AFM image of Mn₅Ge₃/Si(111) film.

The fact that the surface roughness is so small shows us that the Mn₅Ge₃ layer grows as a thin film and there is no aggregation on the surface. SEM images were also taken to understand the surface structure of the grown samples. The SEM image of the Mn₅Ge₃ layer grown on ultra-thin Si(111) is given in Figure 4.6. The surface of the samples is quite smooth.

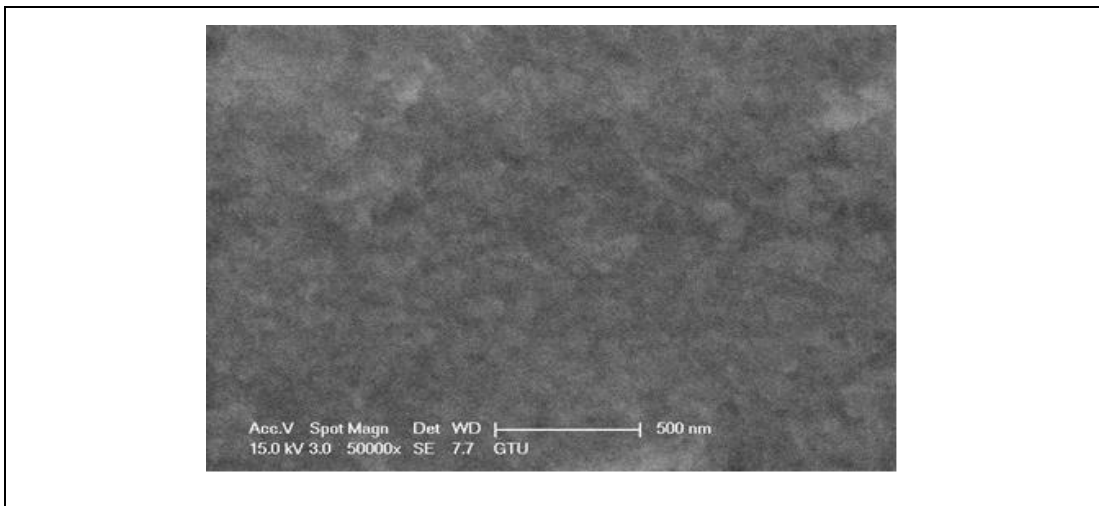


Figure 4. 6: SEM image of Mn₅Ge₃/Si(111) film.

4.4. Electronic Characterization of Mn_5Ge_3 Films

In order to examine the electronic structure of the grown samples, XPS measurements were carried out without wasting any time after the film was formed. First of all, the Mn and Ge 2p regions of the sample were scanned and the Mn and Ge concentrations in the film were determined from the areas under corresponding peaks. Mn densities were determined as 46.88%, 47.08% and 48.33% for the 5, 10 and 15 nm thick layers, respectively Figure 4.7. As the film thickness increases, Mn ratio also increases slightly. This increase is related to the thickness of the Mn_5Ge_3 film and it is seen that the Mn atoms are uniformly distributed in Ge and form the Mn_5Ge_3 structure. These values are slightly lower than the calculated Mn ratio of Mn_5Ge_3 film, which is 62.5%. However, as it can be understood from both LEED and RHEED results and SEM images, there are Mn_5Ge_3 islands near the film surface and the electrons leaking from the intermediate regions between the islets increase the Ge ratio as they scatter from the Ge layer and reach the spectrometer. The lower Mn ratio can also be associated with low annealing temperature, as well as by the different structural properties of the Ge layer.

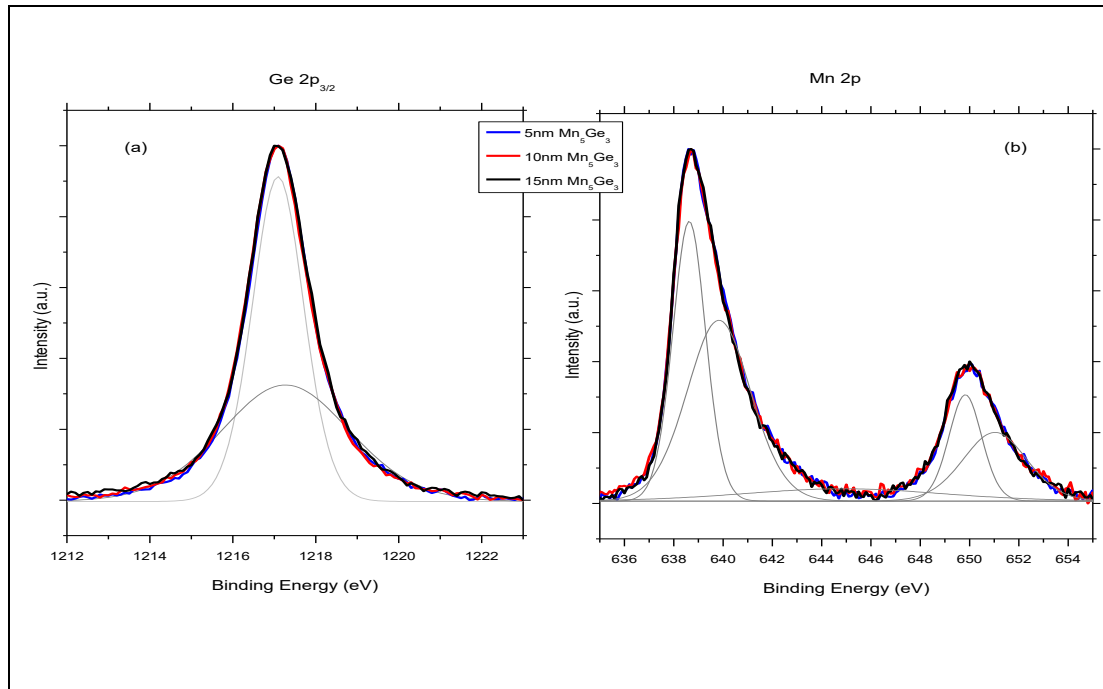


Figure 4. 7: Fitted XPS spectrum of (a) Ge 2p_{3/2} and (b) Mn 2p of 5, 10 and 15 nm thick Mn_5Ge_3 film grown on Si(111).

The Mn 2p_{3/2} and Ge 2p_{3/2} spectra of the Mn₅Ge₃ layers of different thicknesses taken from the sample grown on Si(111) are shown in Figure 4.7, respectively. Regardless of the film thickness, the spectra within both regions are the same, indicating that the electronic structures of Mn and Ge atoms in Mn₅Ge₃ are the same. For this reason, if the thickness of the Ge layer is kept the same, the properties of the formed Mn₅Ge₃ layer do not change. The spectra were tailored to each peak Voigt functions after Shirley background subtraction using CasaXPS. Consistent with previous work, the Ge 2p spectrum was fitted with Ge 2p_{3/2} and Ge 2p_{1/2} pairs, with spin-orbit separation of 31 eV and a branching ratio of 1:0.5 [56]. It is seen that the Ge-2p peak, in addition to the main peak originating from the Ge-Mn bond and centered at 1217.08 eV, forms a bond with a binding energy of 1217.27 eV originating from the subsurface layer [57]. The Mn 2p_{3/2} spectrum is similar to that of Mn metal and is divided into two peaks as shown in Figure 4.7 (a). The main peak with a binding energy of 638.6 eV originates from the Mn₅Ge₃ film [36]. The second peak with a binding energy of 639.75 eV is satellite component associated with the multiple structure of p core holes [58]. The absence of a third peak at the higher binding energy indicates that Mn atoms are not found in different Mn configurations [59,56].

4.5. Magnetic Characterization of Mn₅Ge₃ Films

In order to analyze the magnetic properties of Mn₅Ge₃ thin films, firstly the M-T and M-H data of the samples were taken with the PPMS system, and then the ESR spectra were taken to obtain information about the magnetic components of the film.

The temperature dependent magnetization curves of Mn₅Ge₃ thin film measured under 1000 Oe field is presented in Figure 4.8(a). The Curie temperature at which the transitions from paramagnetic to ferromagnetic phase occurs, is around 300K. Considering that the magnetic moment does not change momentarily at any temperature value outside this temperature, and also considering the XRD and XPS results. It can be easily said that secondary phases do not exist in this sample. In the literature, it is seen that precipitations with different Curie temperatures can occur due to the formation of different phases such as Mn₁₁Ge₈ or Mn₅Ge₃ in such structures [60]. However, we found no evidence of the presence of these secondary phases.

In order to obtain detailed information about low temperature magnetizations and coercive fields of Mn_5Ge_3 thin film, M-H curves were taken between 10-350 K at 50 K intervals. The samples were placed in the PPMS system with the applied magnetic field parallel to the surface of the samples. In the obtained hysteresis curves, there are also diamagnetic and paramagnetic contributions from the Si substrate.

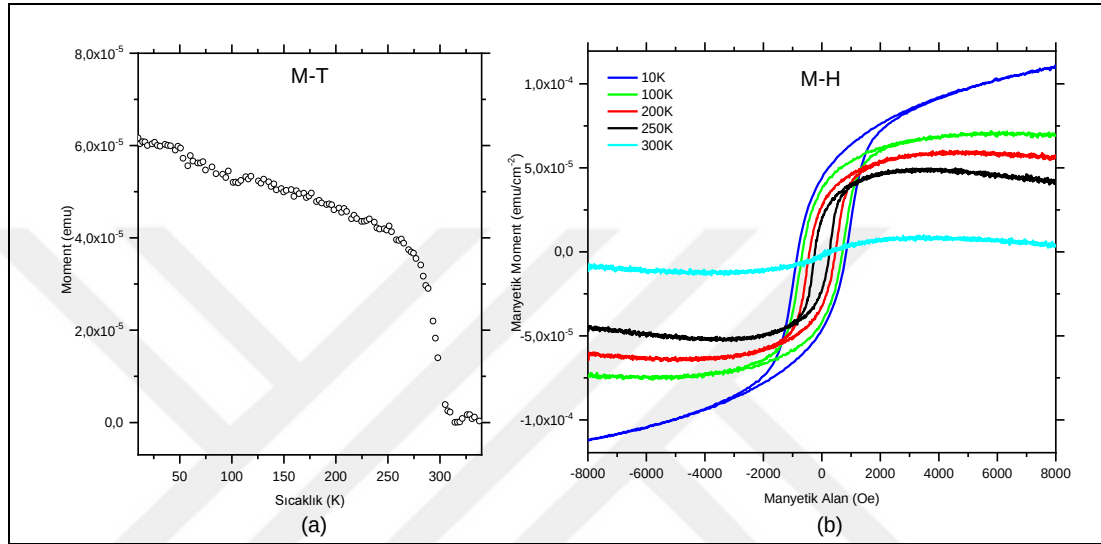


Figure 4. 8: $\text{Mn}_5\text{Ge}_3/\text{Si}(111)$ film (a) magnetization change with temperature (b) M-H hysteresis curves at different temperatures.

For this reason, while the sample does not seem to reach saturation at 10 K where the paramagnetic contribution is quite high, an opposite effect is observed in room temperature measurements where the diamagnetic contribution suppresses the paramagnetic contribution. In Figure 4.8 (b), magnetization curves of Mn_5Ge_3 thin film taken at various temperatures are compared. As can be noticed, the coercive field of the sample starts to increase approximately just below the Curie temperature and reaches 850 Oe at 10K. Remanent magnetization is also quite high in these samples. The ratio of remanent magnetization to saturation magnetization at 10K is 0.53.

Electron spin resonance measurements were taken to analyze the magnetic properties of Mn_5Ge_3 thin films. First of all, the magnetic properties of the grown thin film and the anisotropy change according to the orientation of the applied field with respect to the sample plane were examined using the ESR system. Then the changes in the magnetic behavior of film were observed by epoxy bonding the Mn_5Ge_3 film on the PZT layer and applying electric field to the PZT dielectric layer. Initially, the

measurements were made at room temperature, but a time shift was observed in the spectra obtained. As can be seen in Figure 4.9, periodic shifts were detected in the sequentially measured spectra based on time without making any changes on the sample or measurement system when the DC magnetic field was parallel to the sample plane and perpendicular to the sample plane. In the examinations, it was understood that the water cooling system, which cools the ESR system and the magnet, periodically activates at certain intervals and causes the temperature of the system to fluctuate approximately 4°C. Since the Curie temperature of the Mn_5Ge_3 film is at 300K and the magnetocaloric effects of these films are high, it has been observed that the magnetic susceptibility of the Mn_5Ge_3 film is quite high at this temperature and the magnetic anisotropy changes greatly with temperature [61, 62]. For this reason, the sample was cooled using a liquid nitrogen system and measurements were made after the sample temperature was fixed at 0°C.

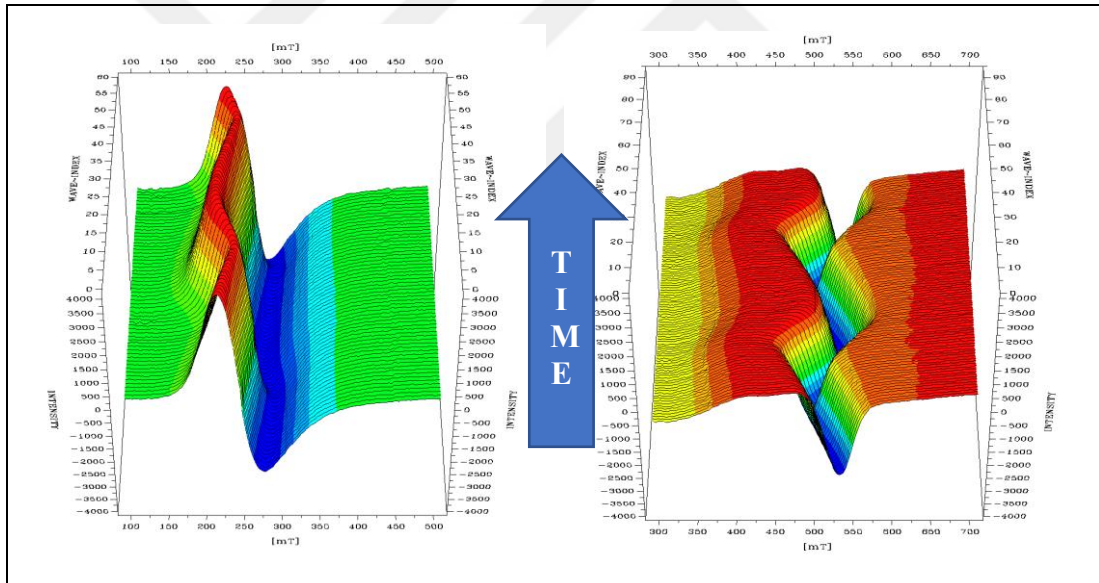


Figure 4. 9: Time dependent variation of the magnetic field (a) parallel to the sample plane (b) perpendicular to the sample plane of the Mn_5Ge_3 film.

The same anisotropy effect was observed from Mn_5Ge_3 films of different thicknesses, but changes were observed in the intensity of the ESR spectrum obtained depending on the thickness of the sample. Since this method gives more information about the orientation of the magnetization, not the total magnetization, unlike PPMS, and the magnetization orientation is independent of the sample thickness, therefore the results of the medium-thick sample are shown. In fact, it is possible to obtain

information about magnetization, but it is not possible to obtain reliable results when microwave absorbing substrates such as PZT is used. As mentioned above, the smaller the dielectric material, the higher the signal. The variation of the position of the ESR signal obtained from the 10 nm thick Mn_5Ge_3 thin film depending on the angle is shown in Figure 4.10.

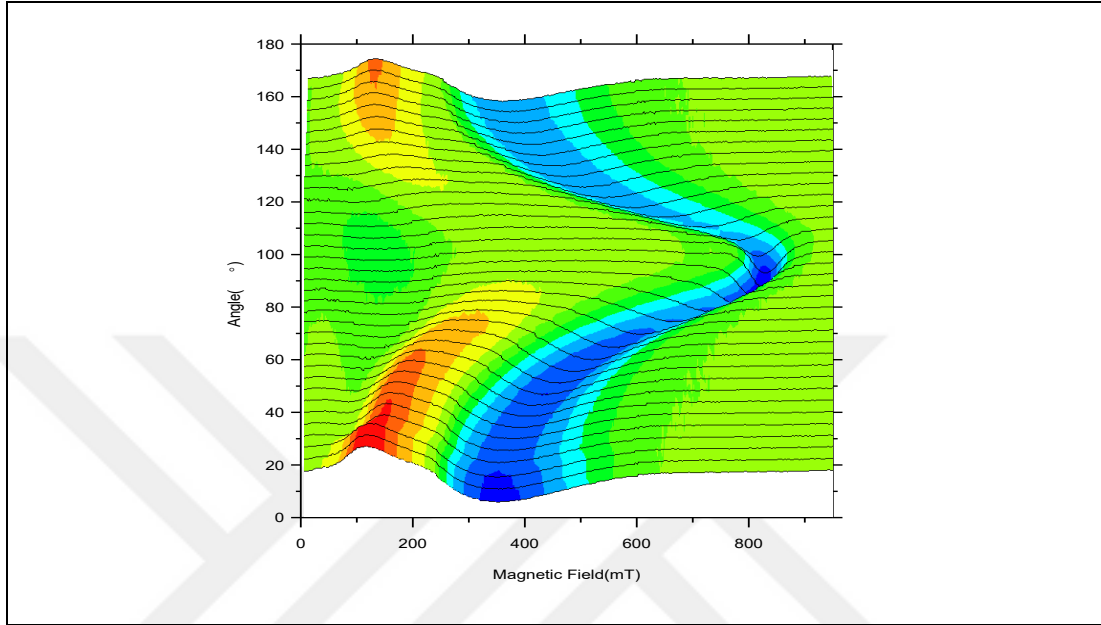


Figure 4. 10: 3D ESR image of $\text{Mn}_5\text{Ge}_3/\text{Si}(111)$ film showing the change in direction of magnetic field at 0°C .

In this sample, the substrate did not have any absorbing effect and the spectrum obtained is quite strong. The angular change seen here is fully consistent with both the anisotropy changes of Mn_5Ge_3 thin films grown on Ge and Si previously [59, 63]. The graph showing the change with the polar rotation angle is given in Figure 4.11.

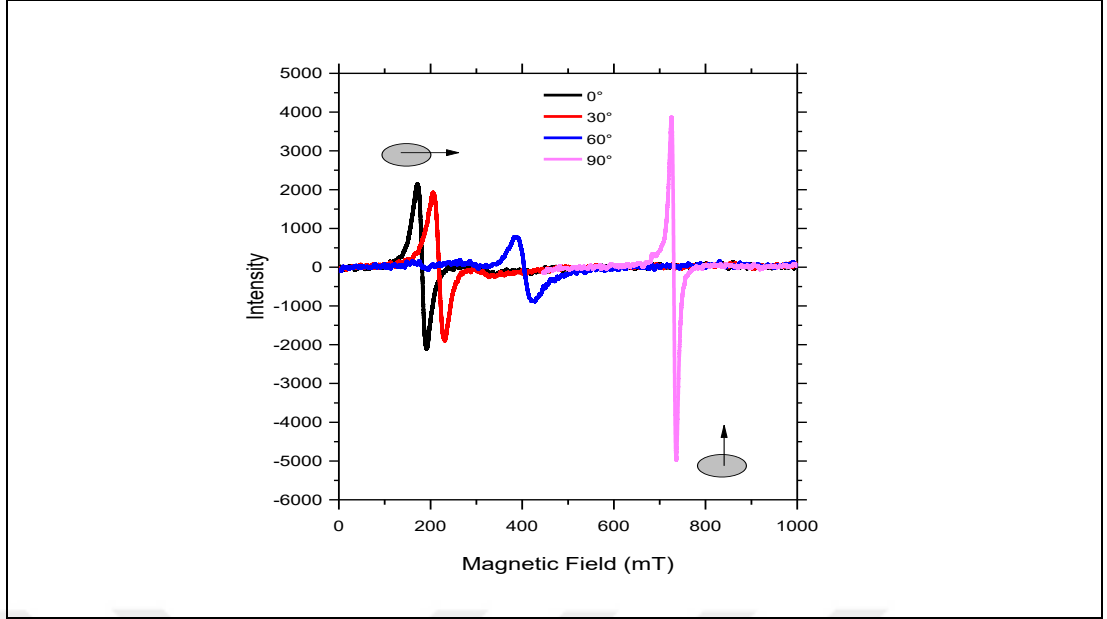


Figure 4. 11: Angle dependent FMR spectra of $\text{Mn}_5\text{Ge}_3/\text{Si}(111)$ film.

It is clearly seen in the figure that when the magnetic field is parallel to the plane of the film (0°), the signal level is low and the peak width of the spectrum to peak is 21mT. However, while the orientation of the sample magnetic field is rotated outward from the film plane, the peak first widens and shrinks, and when it approaches the right angle, it quickly narrows again and becomes sharpest. When it reaches exactly 90° , e.i. when the magnetic field is applied outward from the sample plane, the signal width decreases to 9mT. The reason for this is the sharp uniaxial magnetic anisotropy seen in the sample. The shape anisotropy causes this effect for very thin magnetic layers.

4.6. Magnetic Characterization of $\text{Mn}_5\text{Ge}_3/\text{PZT}$ Heterostructure

After examining the magnetic properties of the Mn_5Ge_3 film, depending on the angle and temperature, a very thin layer of epoxy was applied to the surface of the film and adhered to both side copper-coated PZT. In order for the epoxy to harden, it was kept at 80°C for one hour and cooled. After the sample has cooled, it is placed in a quartz tube designed for magnetic measurements under applied electric field. Afterwards, the sample was placed on the gold layer with the help of silver paste and then attached with a second cable from the top, a mechanism that would create voltage induced tension on PZT hwas prepared. A similar setup has been designed for the

PPMS system. Figure 4.13(a) shows the (FerroMagnetic Resonance) FMR spectra taken by applying tension to the $\text{Mn}_5\text{Ge}_3/\text{PZT}$ layered structure.

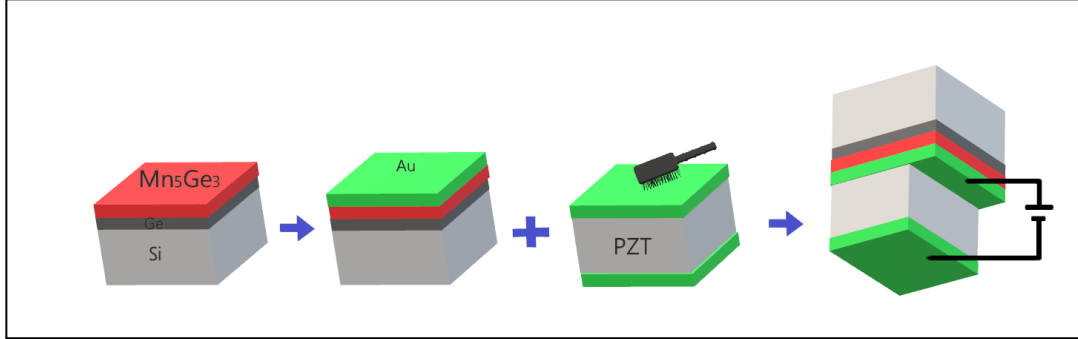


Figure 4.12: Film adhered with epoxy on PZT.

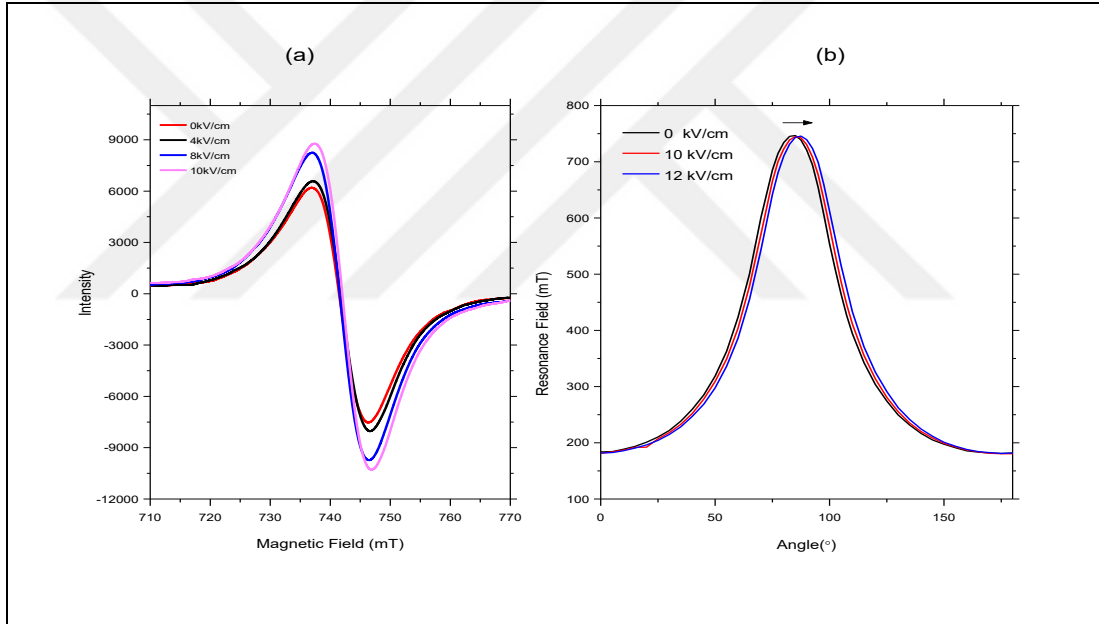


Figure 4. 13: (a) FMR spectrum (b) angle dependent resonance fields of the $\text{Mn}_5\text{Ge}_3/\text{PZT}$ layered structure under various stresses.

These spectra were recorded at 0°C with the sample plane in the position perpendicular to the applied field. Using an external high-voltage device, a maximum voltage of 700V was applied to the 0.5 mm thick PZT layer coated with copper on both sides. With the applied voltage increase, there was a slight increase in the intensity of the observed FMR spectrum and the spectrum shifted about 3mT. The fact that this value is quite small indicates that the magnetoelectric interaction between them is weak. The increase in the signal level shows that there is an increase in the total number

of moments oriented in the same direction with the magnetic field in the magnetic film. The interactions of the magnetic domains in the film increased slightly depending on the applied voltage and the total magnetic moment of the system increased. It should also be noted that when tension is applied to the PZT, a tension occurs in the film plane of the PZT layer. Since it will cause changes in the in-plane orientation of the sample, the change in this direction is expected to be small. The angle-dependent FMR spectrum recorded by applying different voltage values is given in Figure 4.13. Although the angular change trend was generally the same with the application of the field, little deviation occurred at the angle at which it reached the highest resonance value. This shows that the application of voltage to the lower PZT layer causes a slight change in the magnetic anisotropy of the upper magnetic film. On the other hand, different results were observed depending on the angle of the orientation of the atoms in the plane of the sample with the ferroelectric layer below.

Figure 4.14 shows the FMR spectra of Mn_5Ge_3 films epoxy bonded on PZT of different orientations under various stresses. Unlike the trend of change observed above, the signal level decreased with the increase of applied voltage. The reason for this is that the interaction of the PZT with the magnetic orientation of the film varies depending on the direction, and this should be considered when combining the two structures.

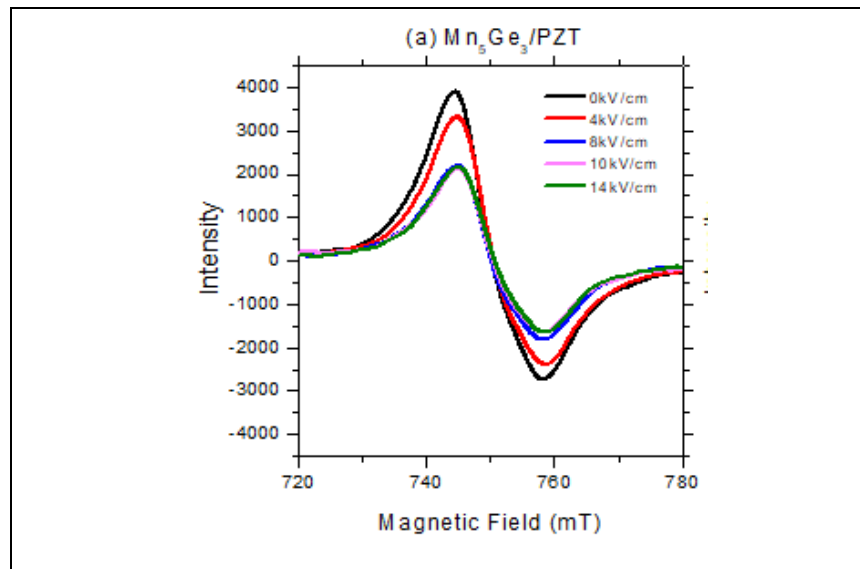


Figure 4. 14: FMR spectroscopies of layered structures formed by $\text{Mn}_5\text{Ge}_3/\text{PZT}$.

5. CONCLUSION

The physical parameters necessary for the formation of this structure were tried to be determined by trying to form Mn_5Ge_3 structure on thin ($100\ \mu\text{m}$) Si (111) substrate. The RCA method was chosen for the cleaning of the thin Si (111) substrate, and after this method, the substrates were annealed at 700°C and to remove carbon and oxygen contaminants from the surface. A clean substrate surface is great importance for Ge crystal formation and the desired Mn_5Ge_3 ferromagnetic structure. In the first step, Ge thin film was grown on thin Si (111) substrate by sputter deposition, and the growth parameters required for single crystal formation were optimized. It was determined that the most efficient parameters for the formation of single crystal Ge were 385°C temperature and $150\ \text{nm}$ thickness. In the next step, the Mn thin film was grown in the MBE system at room temperature. In order for Mn atoms to diffuse into the Ge structure and form the Mn_5Ge_3 structure, the parameters for the successful completion of the solid phase epitaxy process were determined. The parameters required for the Mn atoms to recrystallize to form Mn_5Ge_3 phase were recorded as heat treatment for 20 minutes at a 320°C . The growth structure of the Ge crystal was examined by RHEED and it was observed to form a Stranski-Krastanov growth mode. It was observed that Mn_5Ge_3 structure was successfully obtained with the XRD results. The film surface is smooth as obtained from AMF images. The electronic structure of the Mn_5Ge_3 structure was confirmed by XPS analysis method and evaluated by comparing it with the literature. Before combining the film with PZT, magnetic characterization measurements were made and Currie temperature, magnetic behavior, analysis of the easy and hard axis according to the crystal structure of the film were determined by PPMS and ESR methods. Then, Mn_5Ge_3 film was bonded with a PZT substrate with epoxy. FMR spectroscopy method was used to investigate the manipulation of magnetic properties of Mn_5Ge_3 with the strain induced in PZT with the applied voltage.

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