

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

ELECTRON PARAMAGNETIC RESONANCE STUDIES
ON OXYGEN RELATED DEFECTS
IN MEMRISTIVE SYSTEM

BÜNYAMİN ÖZKAL
A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF PHYSICS

GEBZE

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2019

T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
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İLGİLİ KUSURLAR ÜZERİNDE
ELEKTRON PARAMANYETİK REZONANS
ÇALIŞMALARI

BÜNYAMİN ÖZKAL
YÜKSEK LİSANS TEZİ
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SUMMARY

In this thesis, the structural and optical properties of the thin TiO_2 thin films have been grown on the SiO_2 substrate by pulsed laser deposition (PLD) method are presented. In addition, Argon (Ar^+), Cobalt (Co^+) and Iron (Fe^+) ion implantation and annealing were performed on (100) and (001) crystal oriented single crystal TiO_2 samples for the formation and dynamics of oxygen defects.

Commercially purchased TiO_2 substrates with different crystal planes were implanted with Ar^+ , Co^+ and Fe^+ ions at the Kazan Physics Institute in Russia and annealing was performed. Prepared bulk single crystal samples were investigated for magnetic properties using Bruker EMX X-band (9.5 GHz) model ESR spectrometer. Local symmetries of paramagnetic ions are explained by the presence of oxygen defects. Production of TiO_2 thin films using KrF laser ($\lambda = 248 \text{ nm}$) based PLD system for the memristive circuit element, structural properties, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), x-ray reflection (XRR) at Gebze Technical University, and Cary Eclipse Fluorescence technique at Bahçeşehir University. In addition, the magnetization measurements of paramagnetic ion-doped samples were measured using vibrating sample magnetometer (VSM).

The presence of oxygen imperfections in the structure as a result of both ion grafting and heat treatment was observed and it was demonstrated that the samples prepared as thin films could exhibit memristive behavior.

Key words: EPR, Oxygen Defects, TiO_2 , Memristor.

ÖZET

Bu tez çalışmasında, darbeli lazer biriktirme (PLD) yöntemi ile SiO_2 alttaş üzerinde büyütülen memristif TiO_2 ince filmlerin yapısal ve optik özellikleri sunulmuştur. Ayrıca oksijen kusurların oluşturulması ve dinamiğinin araştırılması için (100) ve (001) kristal yönelimli tek kristal TiO_2 örnekler Argon (Ar^+), Kobalt (Co^+) ve Demir (Fe^+) iyonu aşılması ve tavlama işlemi yapılmış ve karakterize edilmiştir.

Ticari olarak satın alınan farklı kristal düzlemlere sahip TiO_2 alttaşlar Rusya Kazan Fizik Enstitüsü'nde Ar^+ , Co^+ ve Fe^+ iyonları ile aşınlanmış ve tavlama işlemi uygulanmıştır. Hazırlanan bulk tek kristal örnekler, Gebze Teknik Üniversitesi'nde Bruker EMX X-band (9.5 GHz) model ESR spektrometresi kullanılarak manyetik özellikleri araştırılmıştır. Paramanyetik iyonların yerel simetrisi oksijen kusurlarının varlığı ile açıklanmıştır. Memristör devre elemanı için KrF lazer ($\lambda = 248 \text{ nm}$) tabanlı PLD sistemi kullanarak TiO_2 ince filmler üretilip yapısal özellikleri, X-ışını fotoelektron spektroskopisi (XPS), X-ışını difraksiyonu (XRD), x-ışını yansıması (XRR), ve Bahçeşehir Üniversitesi'nde Cary Eclipse Flourescence tekniği kullanılarak aydınlatılmıştır. Ayrıca paramanyetik iyon katkılı örneklerin mıknatıslanma ölçümleri Titreşimli örnek manyetometresi (VSM) kullanılarak ölçülmüştür.

Gerek iyon aşılması gerekse ısıtma işlemi sonucu yapı içerisinde oksijen kusurlarının varlığı gözlemlenmiş ve ince film şeklinde hazırlanan örneklerin memristif davranış sergileyebilecekleri ortaya konulmuştur.

Anahtar kelimeler: EPR, Oksijen Kusurları, TiO_2 , Memristör.

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LIST of ABBREVIATIONS and ACRONYMS

<u>Abbreviations</u> <u>and Acronyms</u>	<u>Explanations</u>
$\text{\AA}$:	Angstrom
ϵ :	Dielectric Constant
$\emptyset_B$:	Magnetic Flux
μ_0 :	Magnetic permeability
θ :	Angle
Hz :	Hertz
w :	Doped Thickness
ΔE :	Difference of Energy
eV :	Electron Volt
μ_v :	Avarage ion mobility
g_e :	g-factor or Lande factor
$WL\alpha$:	Tungsten L-alpha peak
M :	Memristance
C :	Capasitance
I :	Current
S :	Spin angular momentum
L :	Angular Momentum
L :	Inductance
μ_e :	Magnetic Moment
μ_B :	Bohr Magnetron
λ :	Wavelength
ν :	Frequency
ϑ :	Velocity
E :	Electric Field
B :	Magnetic Field
H :	Magnetic Field
J :	Current Density
N :	Turn of wire

G	:	Gauss
Pa	:	Pascal
F	:	Farad
D	:	Switch Thickness
h	:	Planck Constant
V	:	Voltage
v_d	:	Drift velocity
ρ	:	Resistivity
R_{on}	:	Low Resistance State
R_{off}	:	High Resistance State
τ	:	Avarage Time
q	:	Charge
Q	:	Charge
A(t)	:	Amper
A	:	Area
AC	:	Alternative Current
ArTO	:	Argon implanted Titanium dioxide
BJT	:	Bipolar Juction Transistor
CCD	:	Currend Controlled device
CPS	:	Count Per Second
Co	:	Cobalt
C	:	Carbon
CW	:	Continuous Microwave
DC	:	Direct Current
CCD	:	Currend Controlled device
CPS	:	Count Per Second
EDS	:	Energy Dispersive X-ray Spectroscopy
EPR	:	Electron paramagnetic resonance
ESR	:	Electron spin resonance
Fe	:	Iron
FMR	:	Ferromagnetic Resonance
GHz	:	Giga Hertz
HP	:	Hewlett-Packcard

HV	:	High Vacuum
ILU-3	:	Ion accelerator
KrF	:	Krypton difluoride
kV	:	kilovolt
LV	:	Low Vacuum
MV	:	Medium Vacuum
0MW	:	Microwave
N ₂	:	Azode
NI	:	Nanotechnology Institute
nm	:	Nanometer
O	:	Oxygen
PL	:	Photoluminescence
PLD	:	Pulse laser deposition
PPMS	:	Physical Properties of Magnetic Materials Spectroscopy
Pt	:	Platinum
SEM	:	Scanning Electron Microscopy
Si	:	Silicon
SiO ₂	:	Silicon dioxide
T	:	Tesla
Ta	:	Tantalum
Ti	:	Titanium
TiO ₂	:	Titanium Dioxide
TiO _{2-x}	:	Titanium Dioxide with Oxygen vacancy
UHV	:	Ultra High Vacuum
UV	:	Ultraviolet
VCD	:	Voltage cotrolled device
VHV	:	Very High Vacuum
VSM	:	Wibration sample magnetometer
XHV	:	Extreme Hihg Vacuum
O	:	Oxygen
PL	:	Photoluminescence
PLD	:	Pulse laser deposition
PPMS	:	Physical Properties of Magnetic Materials Spectroscopy

XPS	:	X-Ray Photoelectron spectroscopy
XRD	:	X-ray Diffraction
XRR	:	X-ray Reflection

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1. INTRODUCTION

Titanium dioxide (TiO_2) is one of the most promising and intensively studied materials in the fields of biology, gas sensor, photocatalytic, dental, orthopedic and osteosynthesis applications due to its strong oxidizing power, high photostability, and redox selectivity [1, 2]. Transparent single crystals or thin films TiO_2 have been used for optical applications due to the high refractive index [3, 4]. Nowadays, the transport properties of TiO_2 thin films depend on the stoichiometry of oxygen and titanium play a crucial role in electronic chip technology [5].

Different forms of TiO_2 in different research fields have been used such as bulk crystal, thin film, powder and composite materials. The TiO_2 crystal exists in two major forms: rutile and anatase. Anatase is thermodynamically metastable and can be transformed irreversibly to rutile phase at high temperatures [6, 7]. Transition metal oxides are generally nonstoichiometric at atmospheric oxygen pressure and the oxygen vacancy is the most important defect in many metal oxides specifically in TiO_2 [8]. The oxygen vacancies in the material introduce an excess of electrons resulting in an increase of the electrical conductivity [9]. The oxygen vacancies act as electron donors, thus substoichiometric TiO_{2-x} is an n-type semiconductor.

Available information storage technology is increasingly up to reach physical upper limit due to the smallest bit size. Therefore, intensive studies on new storage technologies have been initiated. Nowadays, magnetic random-access memory, spin-transfer torque random access memory, ferroelectric random-access memory and redox-based resistive random-access memory of various technologies are promising in technological industry [10]. In order to be permanent in the storage market, a future technology must include the requirements of soundness, capabilities, excellent performance, high speed, low power consumption and low-cost. Comparison with other information storage technologies, storing information on each physical element to be 0 or 1 binary bit's system, the element called as memristive device theoretically offers almost unlimited information storage capacity on the same geometric bit size. Since the electrical resistance of these elements depends on the applied external electric field, and each resistance value of elements can represent different information. The memristor was originally introduced in 1971 by circuit theorist Leon Chua as a missing non-ohmic passive two terminal electrical component relating electric charge and

magnetic flux linkage [11]. Since that day, it has stuck in the mind as a theoretical idea until the first real device was discovered by Williams and his group at Hewlett-Packard Lab in 2008 [11]. In addition to the resistor, capacitor and inductor it was identified as the fourth passive circuit element. Since that recent discovery it has attracted increased attentions of the scientists. Normally, the concept of memristor can be envisioned as a metal-insulator-metal, (MIM), structure demonstrating reversible and non-volatile resistance-switching behavior [11]. It was seen that memristors have the potential to transform the market for nonvolatile memory and could lead to novel forms of computing [12]. The electrical resistance of a memristor is not constant and it depends on the history of current that had previously flowed through the device, i.e., its present resistance depends on how much electric charge has flowed in what direction through it in the past. The device remembers its history, that is, when the electric power supply is turned off, the memristor remembers its most recent resistance until it is turned on again. Using this fundamental circuit element memristor, new kinds of programmable amplifiers, adaptive filters, programmable oscillators, many other devices can be designed. The first discovered memristor by Williams and his team was produced as a Pt/TiO₂/Pt thin film-based sandwich structure. The first nano structured memristor device as formed *Electrode/TiO₂/Electrode* is shown in Figure 1.1 [11].

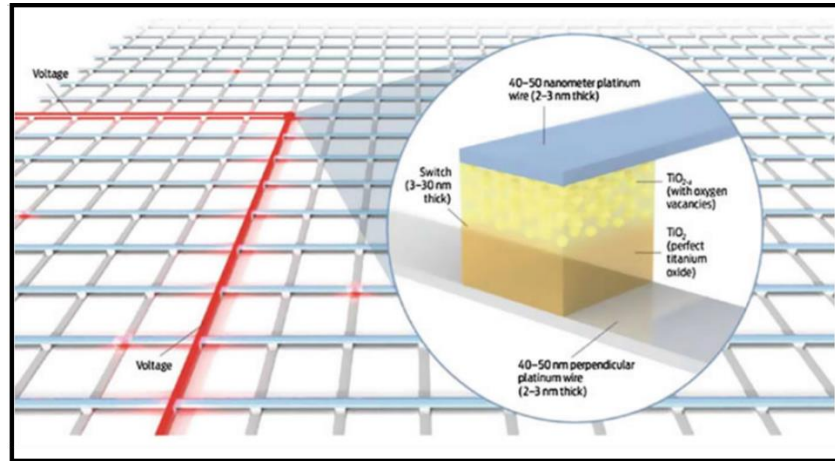


Figure 1.1: HP memristor.

The structure of TiO₂ thin film used in R.S Williams's nanoscale Pt/TiO₂/Pt device was explained with his ownwords as [13]: “Chemical structure of our devices was not what we thought. Chemically it was separated in two different layers. First layer is composed of perfect TiO₂ molecules which has stoichiometric ratio of oxide oxygen to titanium respected 2 to 1. But TiO₂ were formed that near the top Pt

electrode has less oxygen about (%2 to %3) than the other region. We called this layer that has oxygen vacancies as TiO_{2-x} (where x is about 0,005)". Easily it can be understood from this expression that a memristor device is formed by two electrically different layer. Absolutely TiO_2 is semiconductor but TiO_{2-x} is conductor because of their oxygen vacancies that are like electron donors, namely positive charge. Oxygen vacancies are able to be move up to down by applied voltage cause of electrical charge in TiO_2 material. Thereby, switching of these devices have been occurred.

In this study, single crystal TiO_2 thin films that included oxygen vacancies have been proposed by using pulsed laser deposition (PLD) method. Structural, optical and electronic properties of TiO_2 thin films grown on Si substrate are presented. The stoichiometry and the oxidation degree of films were analyzed by considered the Ti_{2p} and O_{1s} core energy levels with high resolution X-Ray Photoelectron spectroscopy (XPS). The structural characteristics of the films have been investigated by XRD and SEM. The optical absorption region of growth TiO_2 thin films were analyzed by Photoluminescence technique.

2. THEORETICAL

2.1 Active and passive elements

Active circuit elements such as Voltage controlled device (VCD), Current controlled device (CCD) can produce generating energy while passive circuit elements such as resistor, capacitor and inductor can not produce energy [11] . Bipolar junction transistor (BJT) can be shown voltage controlled device as an example.

2.2 Current and Resistance

According to Coulomb's law, when Electric field ($\vec{E}$) interacts an electric charge which has push or pull fields. Electrical force occurs on the electric charge [14]. This Force ($\vec{F}$) relation has been shown in the below.

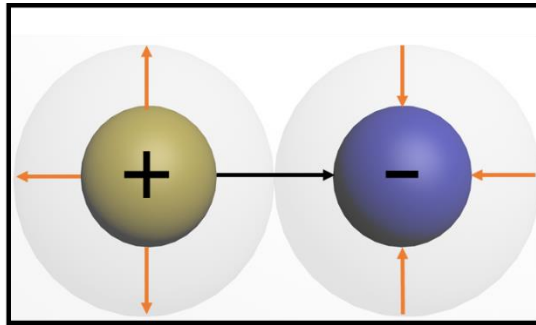


Figure 2.1: Interaction between two electric charges as schematically.

$$\vec{E} = \frac{1}{4\pi\epsilon_0 r^2} \hat{r} \quad (2.1)$$

$$\vec{F}_e = q\vec{E} = \frac{1}{4\pi\epsilon_0} \frac{qq}{r^2} \hat{r} \quad (2.2)$$

Electrical force causes motion of charge from one point to another point. This motion is called current (I). Electrons move in the opposite direction to the applied electric field due to electrons that have negative charge and each one leaves a hole

behind them, this hole is named as a positive charge which moves in the same direction to the applied electric field [14].

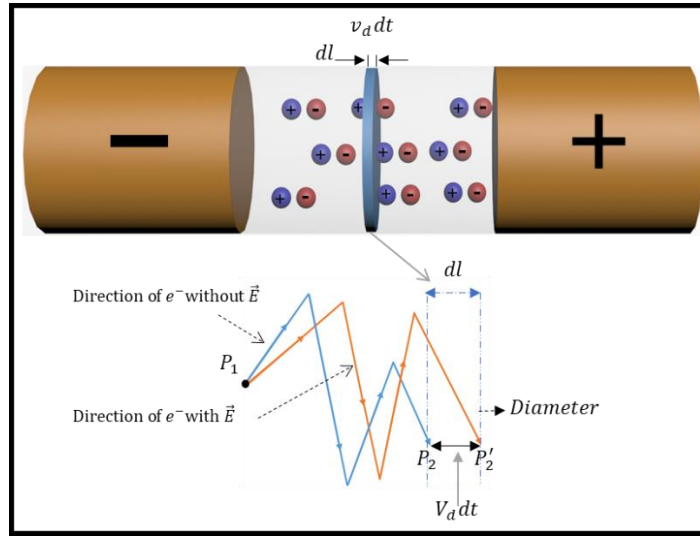


Figure 2.2: Direction of electron in a conductor which depends on Electric Field.

Electron moves haphazardly P_1 to P_2 without $\vec{E}$. When Electric field is applied that is like on the (figure 2.2) and this travelling more haphazard P_1 to P'_2 . There are way's difference between two points. This difference is called net displacement ($V_d dt$, drift velocity $\vec{v}_d$) which has been shown in Figure 2.2 [14].

$$v_d = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n} \quad (2.3)$$

$$dl = d(P'_2 - P_2) = v_d \cdot dt \quad (2.4)$$

Resistance is capability of enforce against electron flowing in conductors and semi-conductors materials. Current density ($\vec{j}$) depends on applied $\vec{E}$ as one of the physcial properties of conductor materials. There is temperature increases which is caused by charge collisions due to applied $\vec{E}$ in materials at the same time resistance increases which depends on temperature. But $\vec{j}$ is almost commensurate $\vec{E}$ at a given temperature. This condition is known as Ohm's laws which discovered by Georg Simon Ohm who is German physicist, 1826. According to law that the current (I) flowing is commensurate the applied voltage (V) and inversely commensurate the resistance (R) of the materials in electric circuits [14].

Ohm law is stated by this equation;

$$V = IR \quad (2.5)$$

And resistance depends on;

$$R = \rho \frac{L}{A} \quad (2.6)$$

Where ρ is the resistivity;

$$\rho = \frac{m_e}{ne^2\tau} \quad (2.7)$$

Where τ is the average time between collision of two electrons;

$$\tau = \frac{\lambda}{v} \quad (2.8)$$

$$\rho = \frac{m_e v}{ne^2 \lambda} \quad (2.9)$$

2.3 Capacitor and Inductor

Capacitor is a passive circuit element which is able to store energy in its electric field. Capacitance appertains the physical structure of the capacitor and its unit is stated as Farad (F) that is comes from physicist Michael Faraday [11].

In this equation, q is the charge, v is the potential and C is the capacitance.

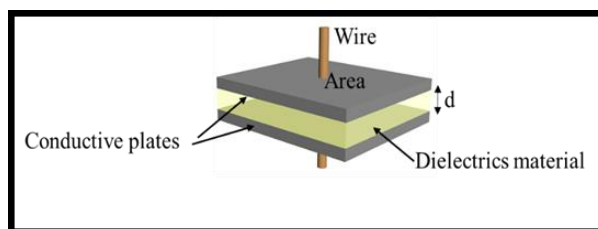


Figure 1.3: Schematic of inductor.

$$C = \frac{q}{v} \quad (2.10)$$

And C is stated,

$$C = \frac{\epsilon A}{d} \quad (2.11)$$

Inductor is a passive circuit element which is able to store energy in its magnetic field. Inductance appertains the physical structure of the inductor and it is stated L. Solenoid can be shown as an example for inductor [11].

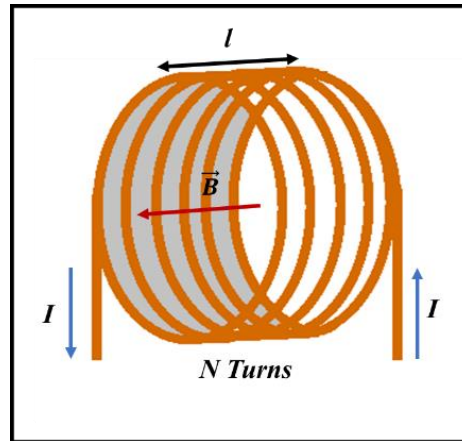


Figure 2.4: Inductance of solenoid.

$$\vec{B} = \frac{\mu_0 N I}{l} = \mu_0 n I \quad (2.12)$$

$$\phi_B = B A = \mu_0 n I \cdot (\pi R^2) \quad (2.13)$$

$$L = \frac{N \phi_B}{I} \quad (2.14)$$

2.4 Memristive System

There are two elements as active and passive circuit elements in electrical circuits. Three circuit elements were available until the theory of memristance was discovered. Memristance was described the relation between charge (Q), and magnetic flux (Φ) by L. Chua in 1971. As the forth passive circuit element memristor was named and memristor's name came from "memory-resistors" words are brought together owing to the properties of these circuits elements to remember the last resistance states. Chua's this foresight has been a highly promising development for artificial intelligence technology and memory devices in computer systems. Since beginning of theory which exhibited. Some science groups have studied and successful results have been recieved. Chua's missing forth circuit element that first physical device which is the same properties of the memristor was produced by Hewlett-Packard laboratory in 2008 [15]. Relation of four passive circuit elements have been shown in Figure 2.5 [11].

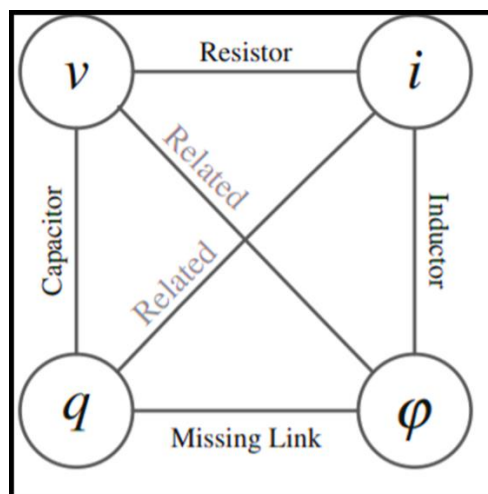


Figure 2.5: Relation of four passive circuit elements.

2.4.1 Memristance

Faraday induction laws gives minus voltage that equals derivation flux (ϕ) respect to time;

$$V(t) = -\frac{d\phi}{dt} \quad (2.15)$$

Current is equal.

$$I(t) = \frac{dq}{dt} \quad (2.16)$$

Memristive device principle of switch depends on moving of electrical charges. Thus, we can state (ϕ) as an f function that depends on electric charge (q).

$$\phi = f(q) \quad (2.17)$$

Then flux is derived by the respect to time;

$$V(t) = \frac{d\phi}{dt} = \frac{df(q)}{q} \frac{dq}{dt} = \frac{df(q)}{q} i(t) \quad (2.18)$$

Where

$$\frac{df(q)}{q} \quad (2.19)$$

It means memristance $M(q)$ and equation is stated [11];

$$V(t) = M(q)i(t) \quad (2.20)$$

2.4.2 HP Memristor Model

HP memristor has been made by TiO₂ thin film (3-30 nm) between two Pt plates that have 40-50 nm width and 2-3 nm thickness [11]. TiO₂ switch is consist of two chemically layers [11]. This switch is composed of perfect TiO₂ and TiO_{2-x} which have doped oxygen vacancies that are positive charges[11]. Hp memristor structure has been shown in Figure 2.6.

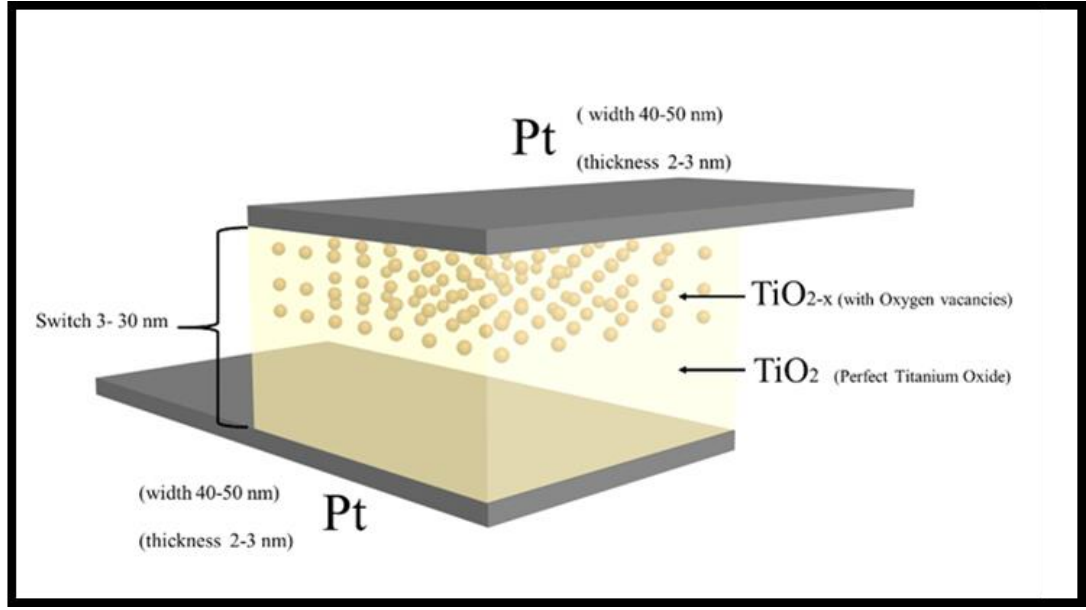


Figure 2.6: Schematic of HP memristor.

Where μ_v is the average ion mobility. Where w is stated as doped thickness. Where D is stated as switch thickness. Drifting of the doped section has been shown with the derivation of w respect to time at the applied voltage in Equation 2.21.

$$\frac{dw}{dt} = \frac{\mu_v R_{on}}{D} i(t) \quad (2.21)$$

Basic HP memristor equation state has been shown as Equation 2.22 at any time [11].

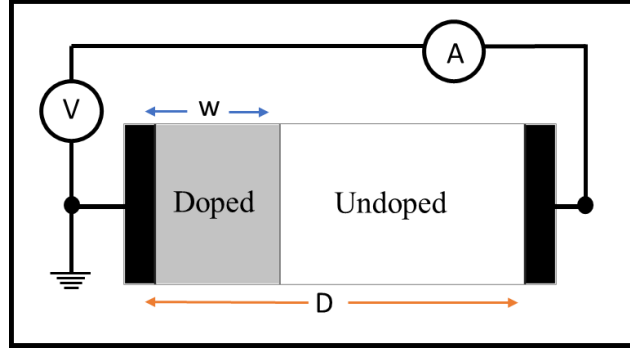


Figure 2.7: HP memristor relation.

$$M(t) = \left(R_{on} \frac{w(t)}{D} + R_{off} \left(1 - \frac{w(t)}{D} \right) \right) \quad (2.22)$$

When the positive voltage applied to memristor from perfect TiO_2 side, ions move from negative electrode to positive electrode and w thickness goes zero, $R_{on} \frac{w(t)}{D} = 0$. Memristor state becomes as R_{off} it means high resistance state [11]. The operation of memristor has been illuminated in Figure 2.8 and Equation 2.23.

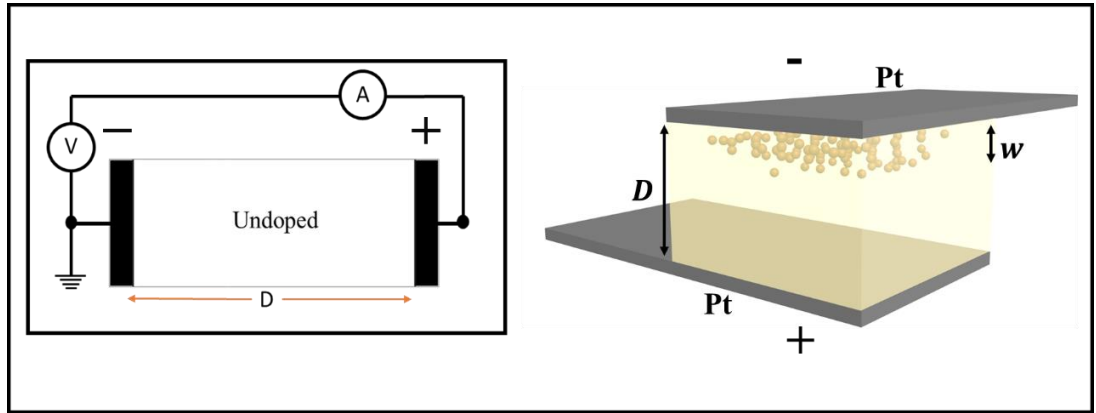


Figure 2.8: High resistance state of memristor.

$$M(t) = \left(R_{on} \frac{w(t)}{D} + R_{off} \left(1 - \frac{w(t)}{D} \right) \right) = R_{off} \quad (2.23)$$

When the positive voltage applied to memristor from perfect TiO_{2-x} side, ions move from negative electrode to positive electrode and w thickness is D . And $R_{on} \frac{w(t)}{D} = 1$ and $R_{off} \left(1 - \frac{w(t)}{D} \right) = 0$. Memristor state becomes as R_{on} , it means low

resistance state [11]. The operation of memristor has been illuminated in Figure 2.9 and Equation 2.24.

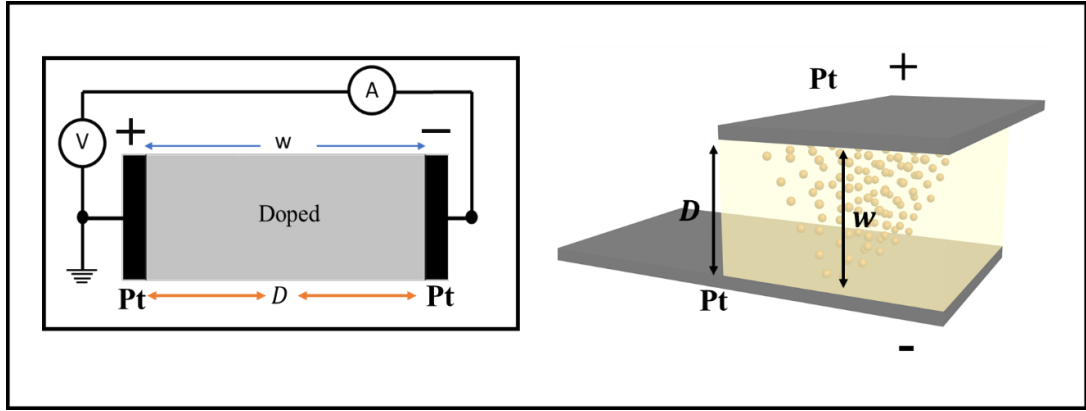


Figure 2.9: Low resistance state of memristor.

$$M(t) = \left(R_{on} \frac{w(t)}{D} + R_{off} \left(1 - \frac{w(t)}{D} \right) \right) = R_{on} \quad (2.24)$$

2.5 Physical Properties and Crystal Structure of TiO_2

Titanium dioxide films have excellent properties, high optical transmittance, high refractive index (anatase 2.49, rutile 2.903), good durability, non-toxic. TiO_2 has existed in different forms on the earth. In addition to amorphous TiO_2 , there are four crystal lattices. Structures are brookite (rhombohedral), anatase (tetragonal) and rutile (tetragonal). Also, there is cotunnite phase which has been synthesized at high pressure. In the technological side, anatase and rutile are more applicable. Crystalline structures of rutile and anatase have been shown in Figure 2.10 [16].

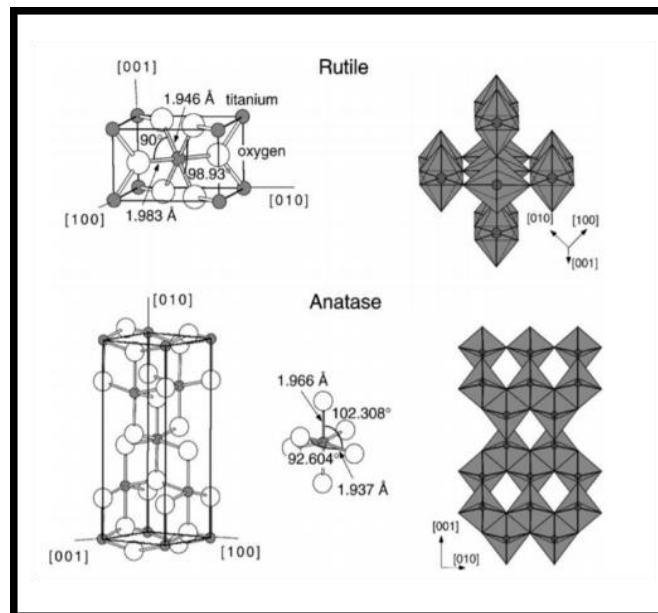


Figure 2.10: Lattice structure of Rutile and Anatase.

2.6 Oxygen Vacancy in TiO_2

Oxygen vacancies can be named as point defects, which are common in metal oxides, especially in TiO_2 [8]. The production of oxygen vacancies on TiO_2 leads to the formation of unpaired electrons and Ti^{3+} centers that could form donor levels in the structure of TiO_2 [8]. These vacancies provide ionic conduction in TiO_2 thin films. Oxygen vacancy is produced by various method. Such as they can be created during production or field cycling when bonds are weakened by the electric field, ion implantation, thermal treatment or during thin film growth [8].

1. EXPERIMENTAL TECHNIQUES

3.1 Sample Preparation And Measurements Techniques.

In this study, the PLD technique has been used for thin-film production. Magnetic measurements have been measured by EPR and VSM techniques. Surface morphology of samples has been photographed by Scanning electron microscopy (SEM). Crystal structure and thickness measurements of samples have executed by X-Ray diffraction (XRD) method. Optical properties have been measured by photoluminescence spectroscopy method.

3.2 Vacuum

The vacuum is the absence of any type of matter in an isolated system but this is applicatively unrealizable in experimental techniques. In another saying, the vacuum has the pressure of atmosphere dramatically less than the air atmosphere that is about 760 bar or 760 torr in a closed system determined by American Vacuum Society, 1958. The pressure is stated in millimeters of a column of mercury [17]. The conventional unit of pressure is millibar, abbreviation: bar. Torr is no longer used as a measurement unit [18].

Vacuum technique is applied to all processes and physical measurements under atmospheric pressure. Many industrial materials and electronic devices need a vacuum which range is about from 10^{-7} mbar to 10^{-17} mbar [17].

3.2.1 Natural Vacuum

Because of gases covering, there are no natural vacuum areas on the earth. But there is a lower vacuum in the respiratory tract of some animal and humans. We are able to make a vacuum about 400 mbar with using our mouth. Atmosphere pressure starts from sea level about 1013 mbar and decreases depending on height. This pressure is about 10^{-13} mbar at 10.000 km from away sea level [19].

3.2.2 Artificial Vacuum

Gases molecules move everywhere randomly on the earth. So there must be a system so as to making vacuum area. This system consists of a pump and an enclosed volume. Obtained vacuum by pumping takes different values according to the power of the used pump. The reached vacuum level is obtained from measuring system pressure. Artificial vacuum levels are classified as low (LV), medium (MV), high (HV), very high (VHV), ultra-high (UHV) and extreme high vacuum (XHV). These levels have been shown in Table 3.1 [19].

Tablo 3.1: Vacuum levels.

Vacuum Range	mbar	Pascal (Pa)	Density of Gas (Molecule/m³)
Low vacuum (LV)	1013-1	10^5 - $3,3 \cdot 10^3$	$2,5 \cdot 10^{25}$ - 10^{22}
Medium Vacuum (MV)	$1 \cdot 10^{-3}$	$3,3 \cdot 10^3$ - 10^{-1}	10^{22} - 10^{19}
High Vacuum (HV)	10^{-3} - 10^{-6}	10^{-1} - 10^{-4}	10^{19} - 10^{16}
Very High Vacuum (VHV)	10^{-6} - 10^{-9}	10^{-4} - 10^{-7}	10^{16} - 10^{13}
Ultra High Vacuum (UHV)	10^{-9} - 10^{-12}	10^{-7} - 10^{-10}	10^{13} - 10^{10}
Extereme High Vacuum (XHV)	$<10^{-12}$	$<10^{-10}$	$<10^{10}$

3.3 X-RAY AND X-RAY MEASUREMENTS TECHNIQUES

Charged particles have physical characteristics that we are able to observe in research. Electrons can be shown as examples which used to define element ratio, thickness, roughness, molecular structure and crystal structure of materials by X-ray measurement techniques in thin-film studies [20].

3.3.1 X-Ray Production

There are mechanisms used to produce x-ray. Such as X-ray tube, rotating anode tube, cyclotron accelerator, and synchrotron facility.

One of the mechanisms is the x-ray tube that produces x-ray from the property of the electron's acceleration as a basic example. There is a filament so as to produce x-ray on the structure of the x-ray tube. When filament is heated. Electrons leave from filament and they became free. Free electrons are accelerated by applied high voltage about 35 keV- 40 keV. They move from the cathode to hit anode and stop. X-rays are emitted in there by electrons that slowed down suddenly and this is called Rotating Anode Tube is like an X-ray tube mechanism but Rotating anode tube has a rotating anode. Structures of the X-Ray tube and Rotating anode tube has been shown in Figure 3.1 and Figure 3.2.

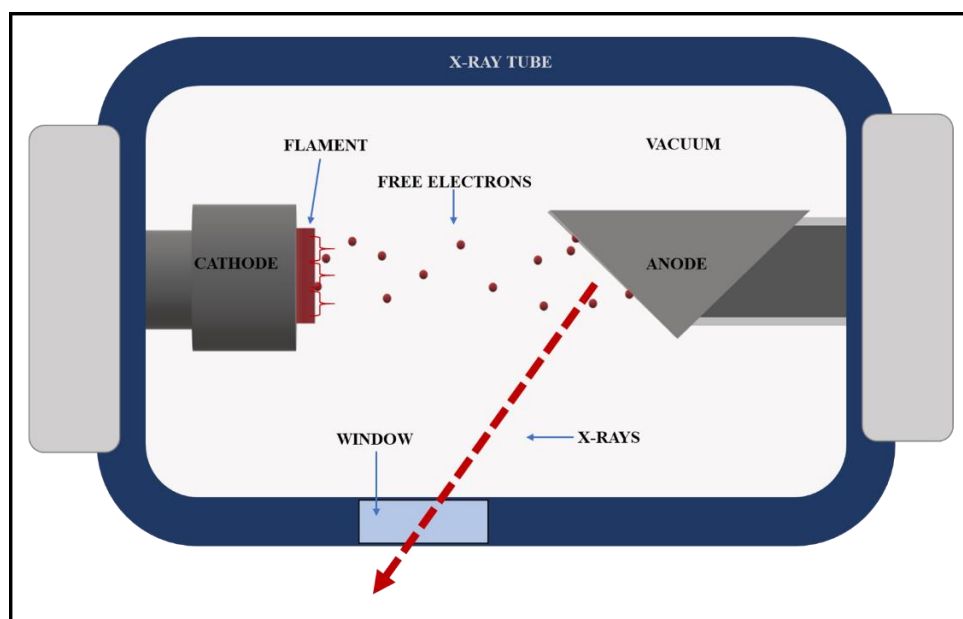


Figure 3.1: Schematic of X-ray tube.

Rotating anode tube schematic has been shown in Figure 3.2 [21].

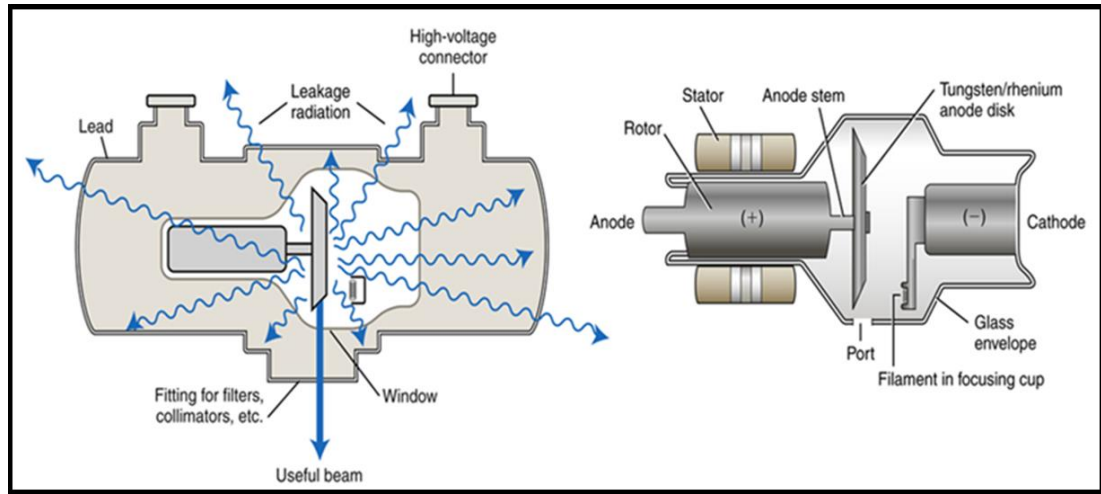


Figure 3.2: Rotating anode tube.

The cyclotron is a circular accelerator invented by Ernest Lawrence in 1929. Today, used in Nuclear power plant. Protons are accelerated by a mechanism under square wave electric field and uniform magnetic field so as to x-ray production in a cyclotron. Cyclotron has two “D” shapes Cavite that charges are accelerated as circular in there. Electric field forces to accelerate charges in the straight direction. Magnetic Field forces charge circular direction. X-rays are obtained by this motion.

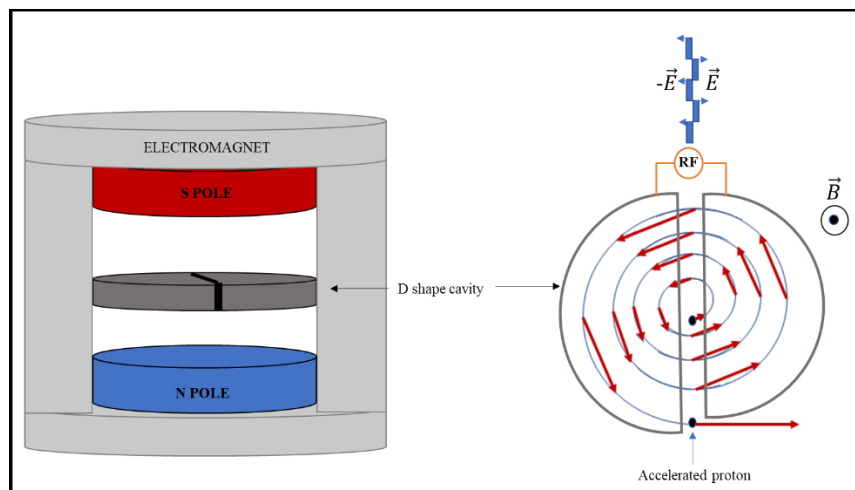


Figure 3.3: Cyclotron's x-ray production uses accelerated proton.

Synchrotrons are known as large accelerators. They produce high intensity and x-ray. Construction of synchrotron includes four main sections. These are linear accelerator (Linac), booster synchrotron, storage ring and beamlines with end stations. Linac is the first section where electrons are free and accelerated under 200kV-250kV

owing to its construction that includes electron gun than for the injection booster synchrotron. Booster synchrotron is the second section and first-long-circular accelerator where electrons are accelerated about 6 GeV so as to inject storage ring. The storage ring is the biggest circular ring where accelerated electrons that close to light speed move circular direction under very low pressure [22].

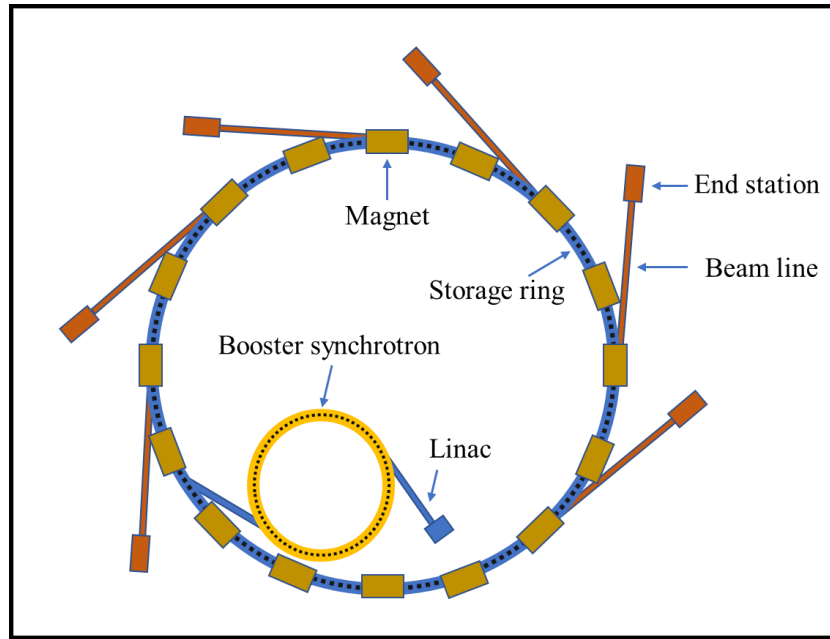


Figure 3.4: Structure of synchrotron.

This ring has various magnets which are focusing magnets, bending magnets and undulators (insertion devices). Focusing magnets force electrons for they move in the their ideal direction. Bending magnets bend electrons into their orbit. X-rays are emitted as result of this motion. Bending magnet have been shown in Figure 3.5 [22].

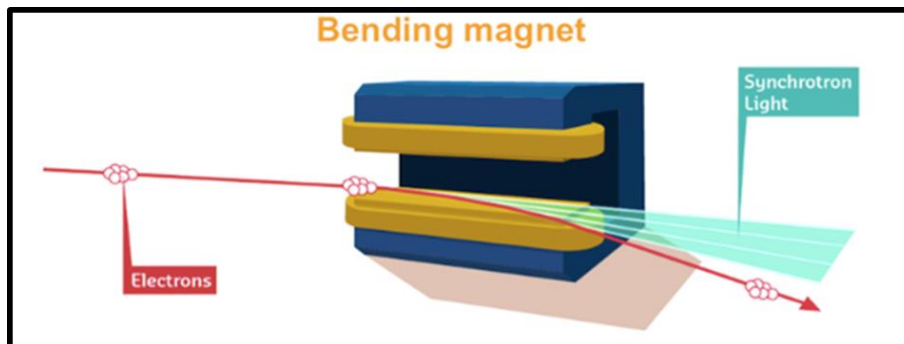


Figure 3.5: The motion of the electron beam in the bending magnet and emitted x-rays.

Undulators are constructed by array magnets. These magnets force electrons. They oscillate then x-rays are emitted by the oscillated electrons. Working principle of undulator has been shown in Figure 3.6 [22].

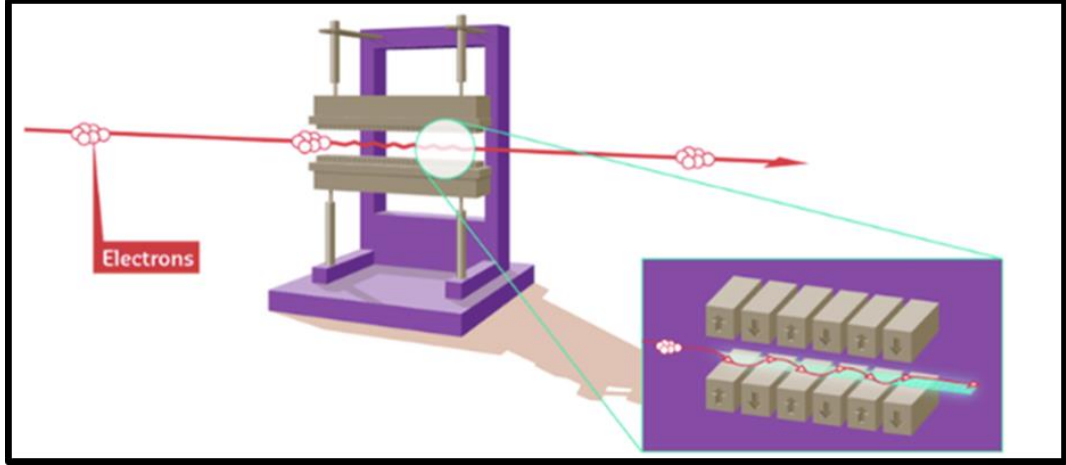


Figure 3.6: Undulator's working mechanism and x-ray production.

As the Final, produced x-rays are sent for the specific experiment by beamlines from storage ring to experiments hall or and station.

3.3.2 X-Ray Diffraction

X-ray diffraction (XRD) method is used to define the molecular structure and crystal structure of materials. According to Von Laue, if the crystal is constructed by atoms which aligned regularly and have scattering center's behavior, x-ray's wavelengths approximate two atomic distance about (1-2 Å) in crystal. X-ray diffraction is possible. In 1912, William Henry Bragg and William Lawrence Bragg formulated x-ray diffraction simpler than Von Laue as mathematical [20, 23].

XRD can be understood as basically by the Bragg equation.

$$n\lambda = 2 d \sin \theta \quad (3.1)$$

In the equation, n is an integer, λ is expressed as the characteristic wavelength, d is the interplanar distance between rows of aligned atoms and the θ is the angle of the X-ray beam according to planes [24].

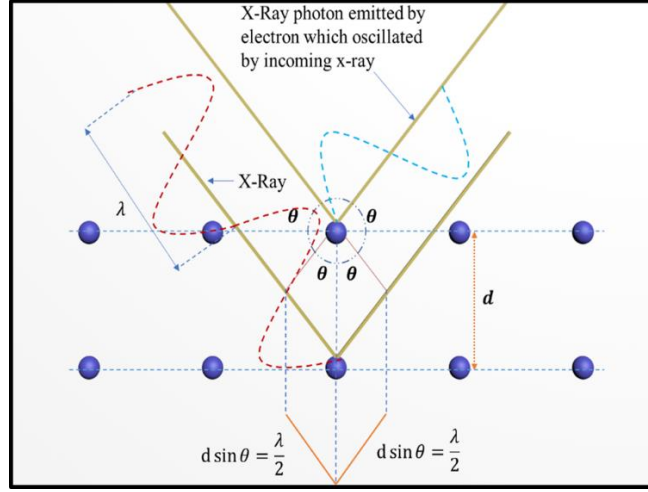


Figure 3.7: Schematic of Bragg's law.

$$d \sin \theta + d \sin \theta = \frac{\lambda}{2} + \frac{\lambda}{2} \quad (3.2)$$

$$2 d \sin \theta = \frac{2\lambda}{2} \quad (3.3)$$

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

If electromagnetic waves interact with material, there can be four results. They are Coherent scattering, Compton effect, Photoelectric effect, Pair production, and Photodisintegration.

Therefore, when x-rays are sent on the material that has a perfect crystal structure. There is an interaction between x-ray and electrons of atoms of the crystal and electrons are oscillated and emit radiation everywhere. Then some radiation waves that emitted by oscillated electrons ignore each other and some of them which have the same direction and same phases produce constructive interference. This interference is detected by various x-ray counter.

A sample is placed with an angle of θ between moving x-ray source and moving detector. Photons are sent from x-ray source. X-ray source and Detector move equal angle in reverse circular direction and scattered x-rays are detected by x-ray counter which has been placed according to the angle that is 2θ of x-ray photon direction that comes from the x-ray source [25].

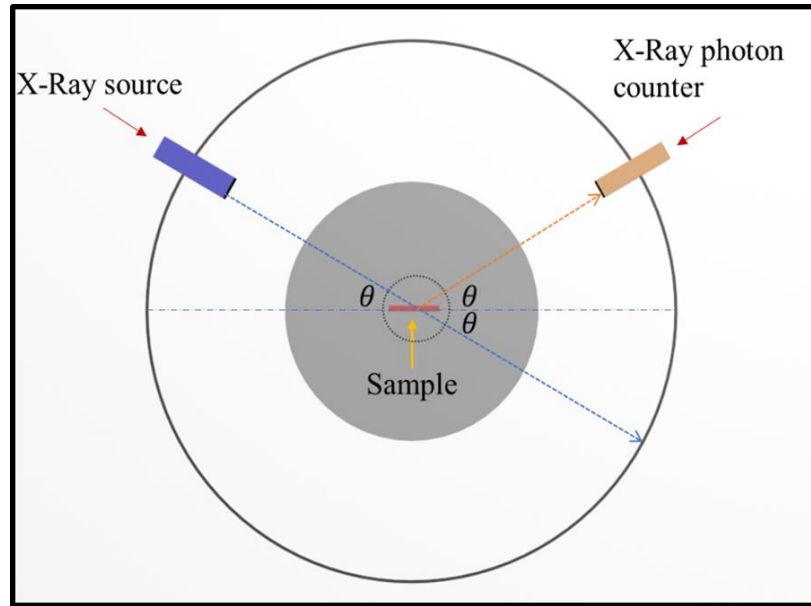


Figure 3.8: Schematic of the XRD mechanism.

3.3.3 X-Ray Reflectivity

The density of the Electron, layer thickness and roughness of interlayers and surface can detect with x-ray reflectivity method that is non-destructive measurement technique and can detect between 5 Å – 400 nm layers thickness and 0-20 Å roughness by using x-ray on a single layer and multilayer thin films. An XRR example has been shown in Figure 3.9 [26].

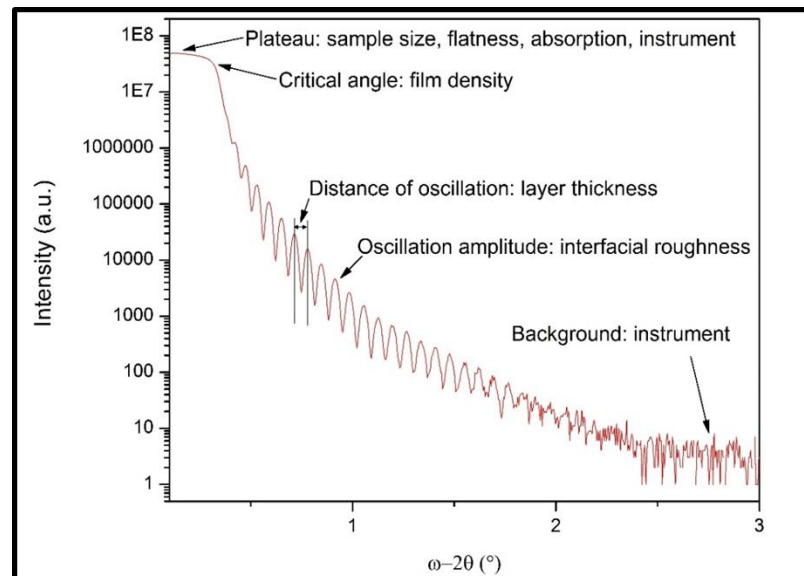


Figure 3.9: information of the x-ray reflectivity.

3.3.4 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface analysis measurement technique for the materials. XPS has photon source, a sample holder, electron optics, analyzer, detector and operation under vacuum that is about minimum 10^{-9} mbar.

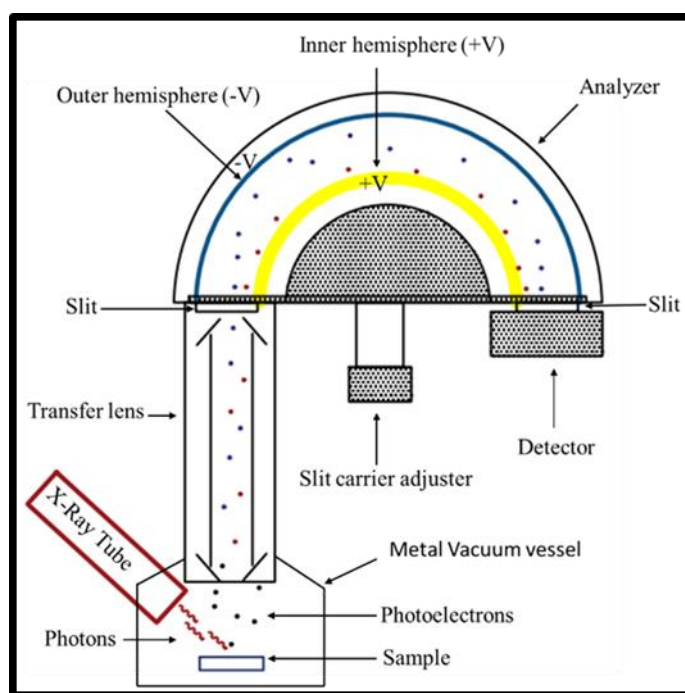


Figure 3.10: Schematic of XPS.

Photoelectrons are occurred by applied x-ray photon. When x-ray photon hit any an electron of the atom. An electron can escape its shell and this condition is called as obtaining of the photoelectron. Heinrich Hertz who observed it As the first (1887). Albert Einstein who explained it as the first (1905). Another case, an electron can reach a place of the removed electron from atom and x-ray is emitted. This x-ray photon can hit an electron of the shell of the outermost and can be removed from the atom. That electron is called Auger electron which discovered by Lise Meitner (1922) and Pierre Victor Auger (1925). There is also emission of Fluorescence (Characteristic x-rays) that are produced by high level's electrons which reach the place of the removed electron from the atom.

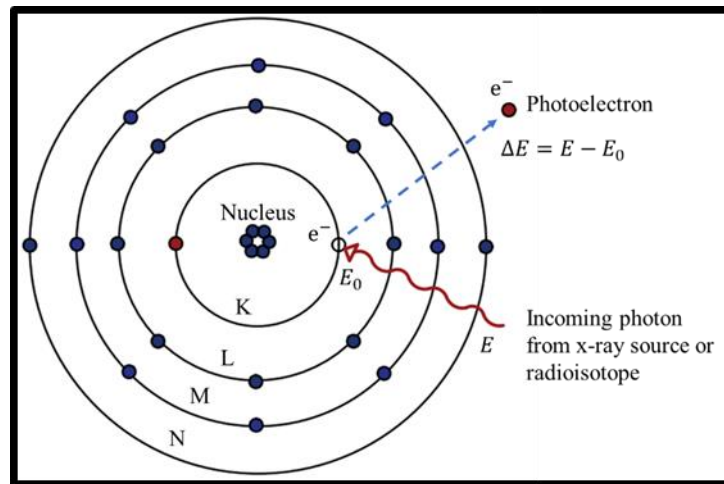


Figure 3.11: Occurring of the photoelectron.

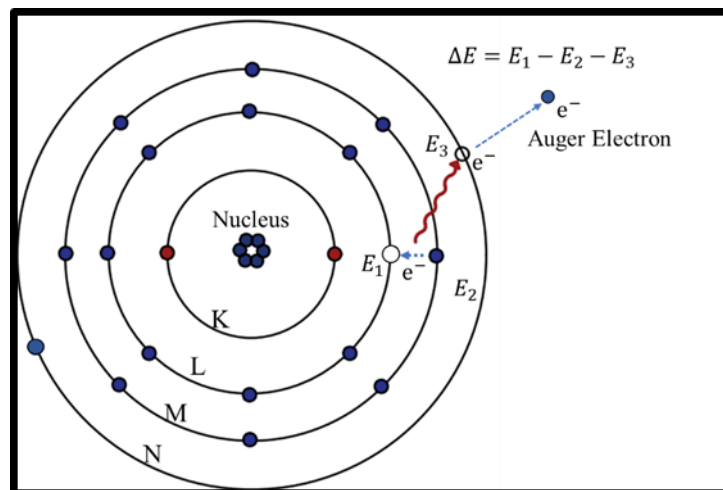


Figure 3.12: Occurring of Auger electron.

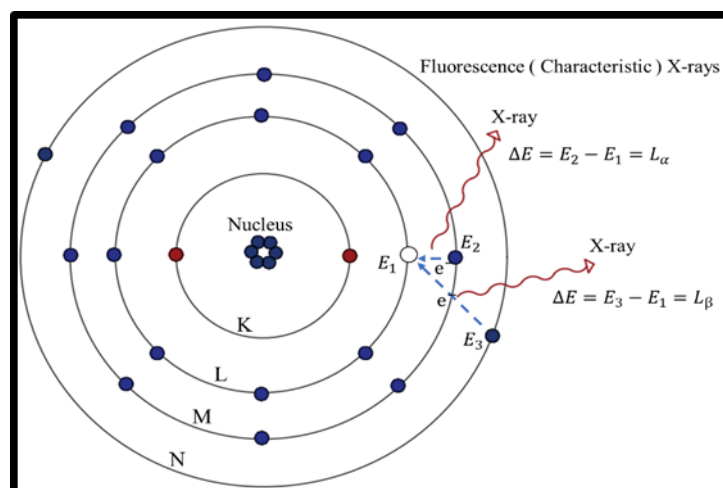


Figure 3.13: Emitting Fluorescence mechanism.

In this method, Photoelectrons are emitted cause of x-rays that are sent to sample from the x-ray source. They are focused before coming to the analyzer by transfer lens

on the XRD mechanism. Focused photoelectrons pass into hemisphere analyzer and they are forced to circular motion to be passed into x-ray counter by two electrodes that are positive potential and negative potential. Their binding energies (eV), kinetic energies (eV) and counting of photoelectron per second (CPS) are saved by a computer which has XPS software. Each element has specific photoelectron emission, so easy to understand peaks on the graphic.

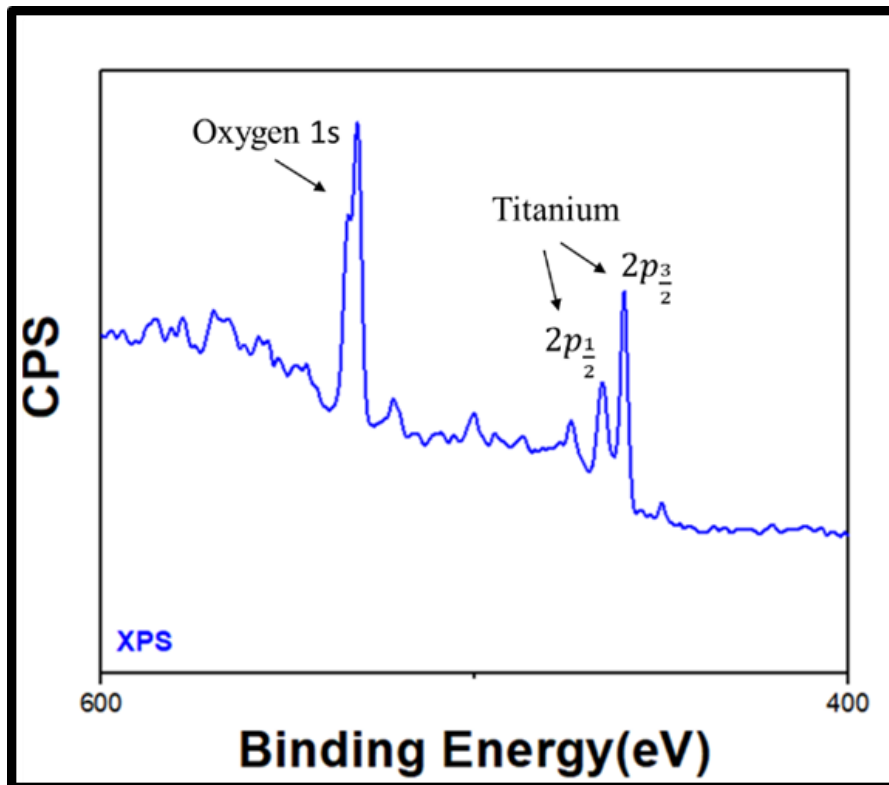


Figure 3.14: An example of XPS data TiO_2 film on software.

3.4 Photoluminescence Spectroscopy

When Electrons come from an excited state to ground state. They emit fluorescence and this condition called photoluminescence. Ground state atom is which have electrons that rather occupy the lowest state. The excited state is electrons of an atom that temporarily occupies higher energy state greater than the ground state [27].

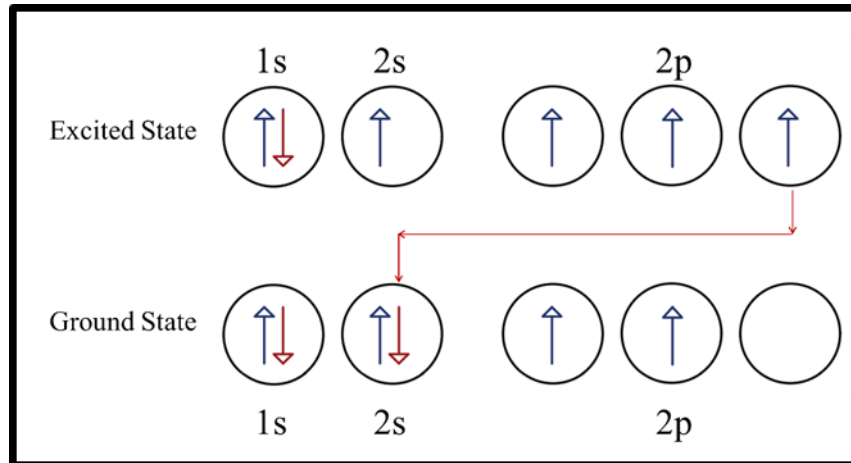


Figure 3.15: An example excited state of Carbon atom.

When atoms are excited. There are two states. These are Singlet state and Triplet state. If electron that is in excited state which has parallel spin direction according to its ground state spin direction, this is called singlet state. Other condition, If electron that is in excited state which has anti-parallel spin direction according to its ground state spin direction, this is called triplet state. Excited state is triplet state that is shown figure of the Carbon atom, in Figure 3.16.

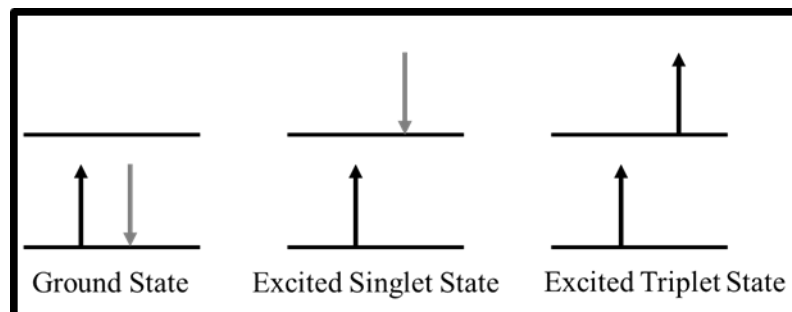


Figure 3.16: States of an atom has been shown as schematic.

Especially, the optical properties of luminescent semiconductor materials are inspected by photoluminescence (PL) spectroscopy. As state in data of PL. Kind of

impurities, bandgap, ion vacancy and impurity activation energy can be known from the graphic.

Semiconductors include valance band, forbidden band and conduction band. Electrons of the ground state are in the valence band of the semiconductor. Electrons can not pass from valence band to conduction band without any force due to there is a band gap that electrons have to surpass between valence and conduction band.

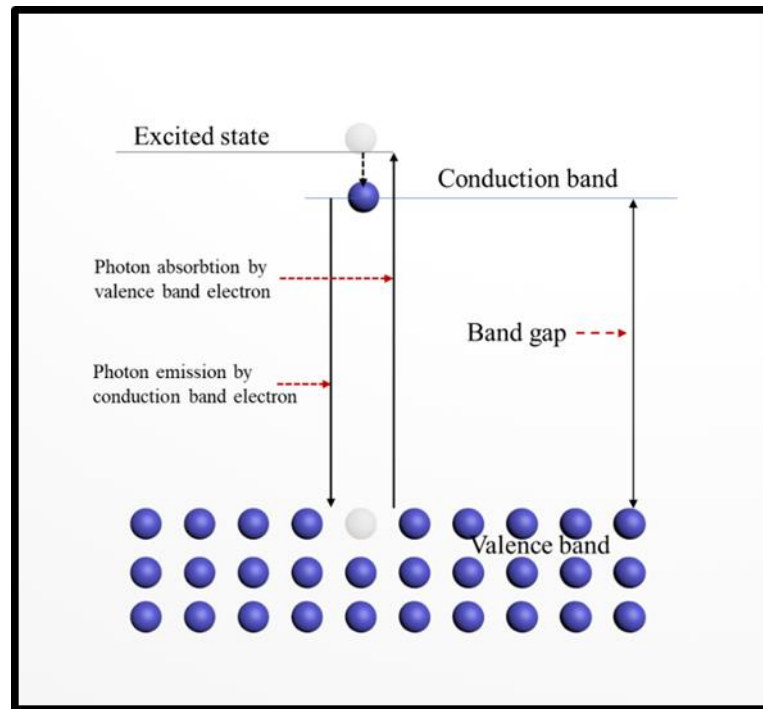


Figure 3.17: Principle of photoluminescence spectroscopy.

When electron of valence band absorbs energy from a photon that has energy greater than bandgap energy, the electron is excited state before it surpasses from valance band to conduction band, after than it comes back to valence band from conduction in a short span of time and it emits photon energy equal to bandgap energy. There is no radiation emission, while electron passes from an excited state to the conduction band. Type of element is able to be identified from the emitted photon in this process. Block diagram of PL spectroscopymeter has been shon in Figure 3.18.

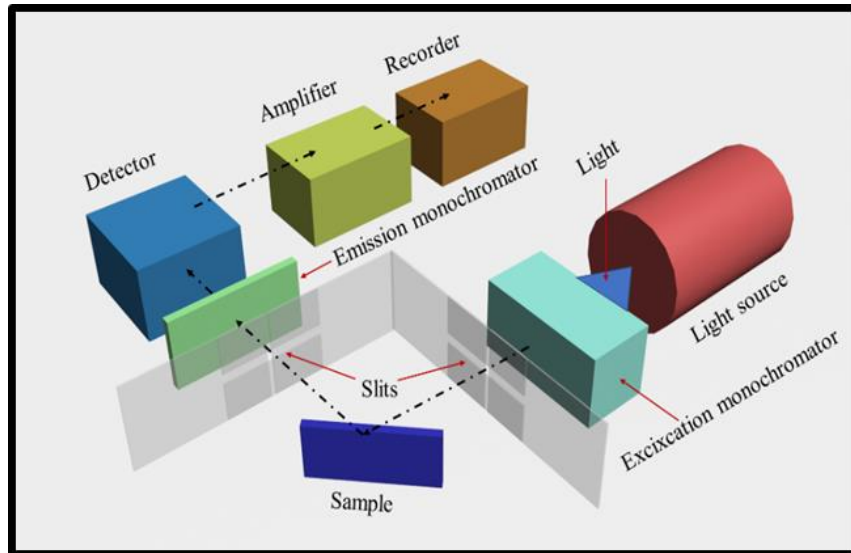


Figure 3.18: Block diagram of PL spectrometer.

3.5 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a method that is able to observe of the surface of the sample at nanoscale, energy dispersive x-ray spectroscopy (EDS) and detects the thickness of growth sample from cross-section view. There are some effects that are the cause of the inelastic and elastic collision. These effects are secondary electrons, backscattered electrons, and characteristic x-rays. When a sample is exposed to brighten with an electron beam which is called primary electrons, it emits a secondary electron from its surface. Secondary electrons are produced by the interaction between the electron beam and sample. When a primary electron hits electrons of atoms of the sample as inelastic collision, electrons of an atom is ejected from their place and these electrons are called secondary electron, they have lower energy than backscattered electrons and information of topography of specimen surface is observed with detected secondary electrons. When the direction of primary electrons is changed by target atoms, these scattered electrons are called backscattered electrons that are the density of the element is able to be detected. There is also emission of Characteristic x-rays that are produced by high level's electrons which reach a place of the removed electron by primary electrons from an atom of the specimen, type of elements are detected from these x-rays emissions. Characteristic x-ray mechanism has been shown in Figure 3.13 and mechanism of the secondary electron and the backscattered electron has been shown in the below [28].

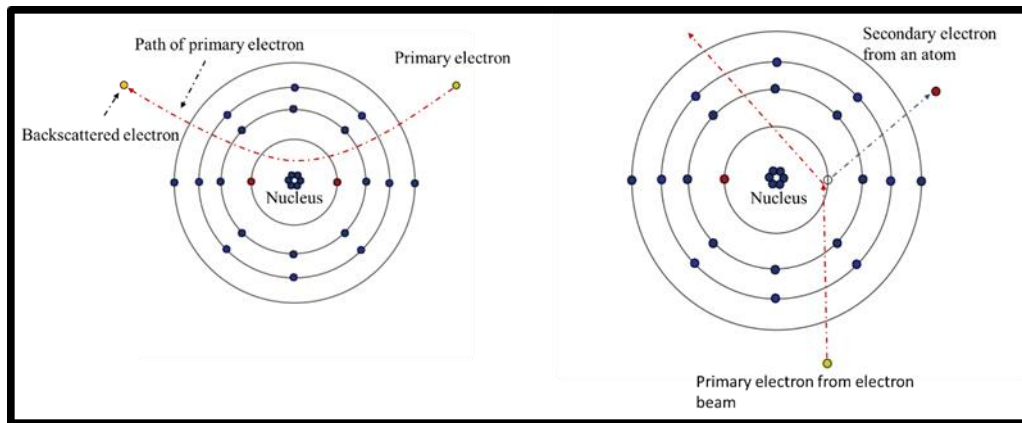


Figure 3.19: Schematic of backscattered electron and secondary electron.

Structure of SEM includes electron gun where primary electrons are produced, electromagnet lenses where electron beams are condensed, sample holder, x-ray counter and electron detectors so as to operate.

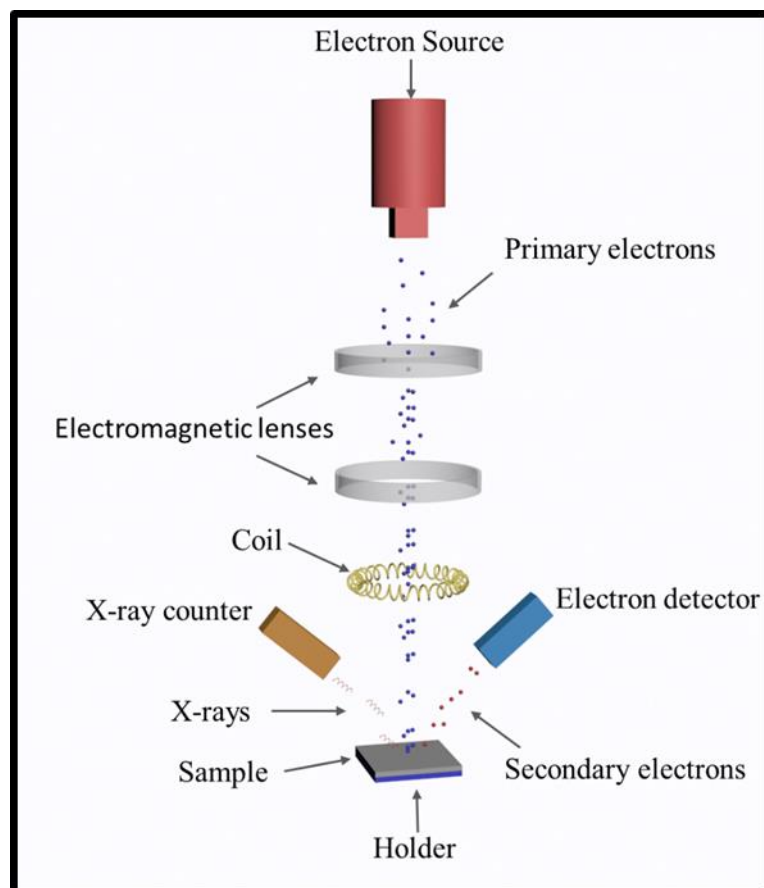


Figure 3.20: Schematic of Scanning electron microscopy.

3.6 Electron Spin Resonance Spectroscopy

Electron resonance spectroscopy (ESR) is one measurement technique that uses electromagnets so as to the interaction between unpaired electron spin and magnetic field. Elements that have unpaired electrons, defects of single crystals, radicals, dosimetric, archaeological and geological studies are able to be investigated with ESR. Sample is exposed to constant continuous microwave (CW) about X-Band 9,8 (GHz) and magnetic field as Gauss(G) or Tesla (T) between from 0 T, G – 16000 G, 1.6 T. Direction of unpaired spins of electrons bear applied magnetic field direction then they reach resonance and interact with applied CW. Signal of CW which is an electromagnetic wave that has electric field and the magnetic field is changed because of electrons that have magnetic moments with resonance and absorption occurs from this interaction. This absorption is the difference of energy (ΔE) between two energy state. States have been shown in Figure 3.21 [29].

$$\Delta E = h\nu \quad (3.5)$$

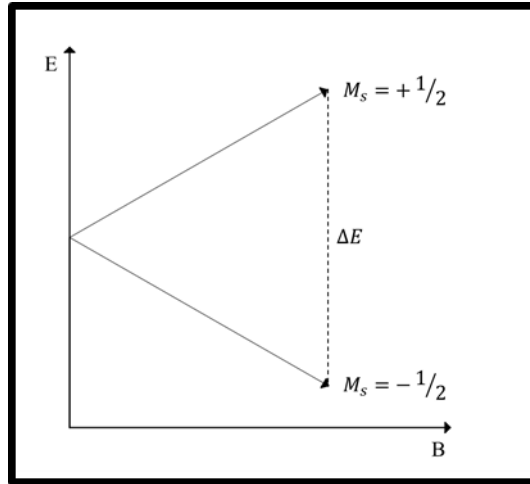


Figure 3.21: Energy state in magnetic field.

In the magnetic field, an energy state of an electron can be expressed by;

$$E = g_e \mu_B B_0 M_s = \pm \frac{1}{2} g \mu_B B_0 \quad (3.6)$$

This equation, $g_e = 2.0023$ the electron g-factor or Landé-factor. B_0 , magnetic field. M_s , spin.

μ_B is the Bohr magneton;

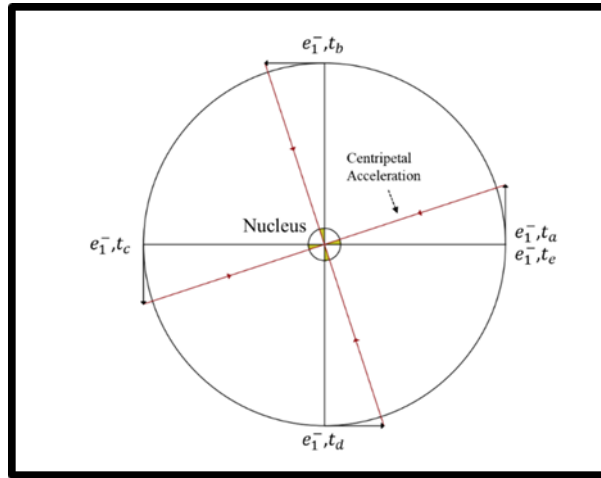


Figure 3.22: Electron motion in orbit of nucleus.

$$I = \frac{e^-}{T} = - \frac{ev}{2\pi r} \quad (3.7)$$

I is the current, v is the velocity of the e^- , T is the period of motion of the e^- in circular path.

$$I = \frac{e^-}{T} = - \frac{ev}{2\pi r} = - \frac{em_e r v}{2\pi m_e r^2} = - \frac{eL}{2\pi m_e r^2} \quad (3.8)$$

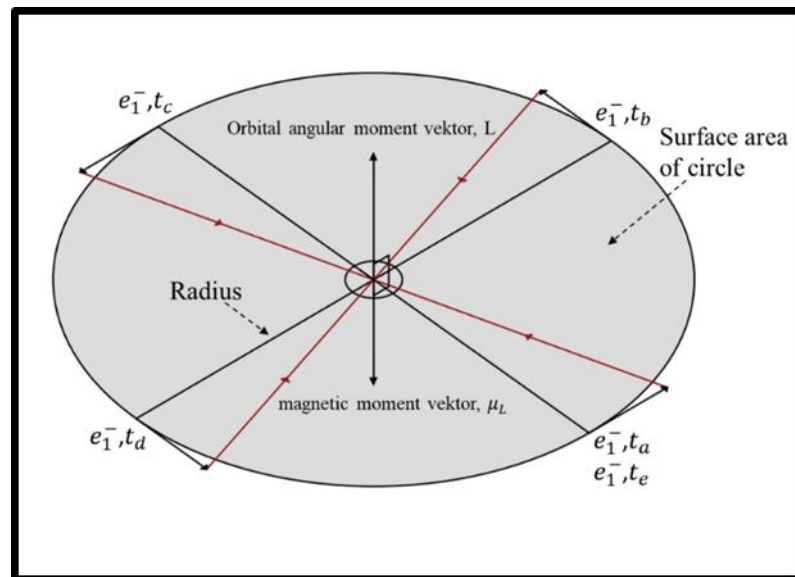


Figure 3.23: Schematic of orbital angular and magnetic moment.

$$\mu_e = IA = -\frac{eL}{2\pi m_e r^2} \pi r^2 = -\frac{eL}{2m_e} \quad (3.9)$$

$$L = \sqrt{l(l+1)}\hbar \quad (3.10)$$

$$\mu_e = -\frac{e\sqrt{l(l+1)}\hbar}{2m_e} \quad (3.11)$$

The z-component of the magnetic moment is given by;

$$\mu_z = -m_l \mu_B \quad (3.12)$$

Unit magnetic moment called as “Bohr magneton, μ_B ”;

$$\mu_B = \frac{e\hbar}{2m_e} = 9.27 * 10^{-24} \text{ JT}^{-1} \quad (3.13)$$

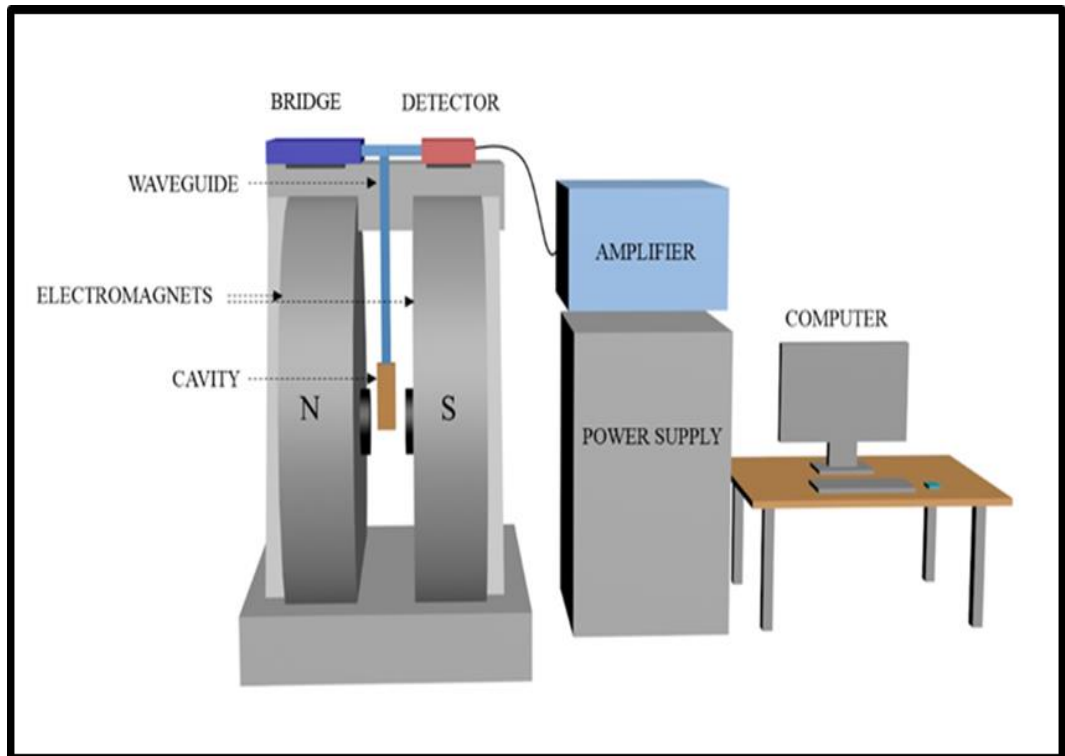


Figure 3.24: Schematic of Electron spin resonance spectrometer.

Block diagram of microwave has been shown in Figure 3.25 [30].

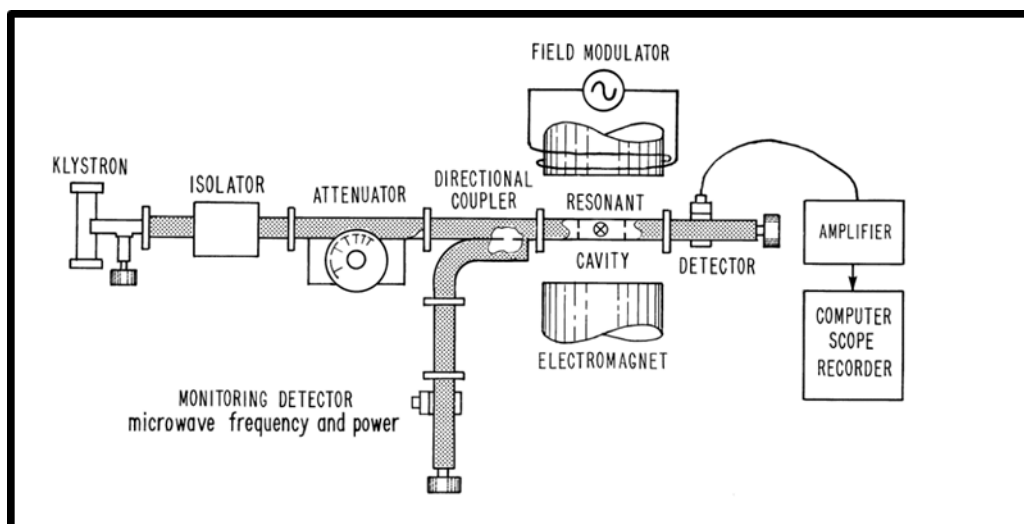


Figure 3.25: Block diagram of microwave.

Continuous microwaves are supplied as fixed frequency by a microwave bridge. A wave guide transmits microwaves from the bridge to sample cavity is a device that is able to subject sample with microwave energy, also this energy can be tuned and sent back to the detector in the bridge. Two magnets mechanism produces a uniform magnetic field with DC power supply so as to direct the same way spins of electrons for interaction between MW and spins of the electron. MW is absorbed by the sample then signal of absorbed MW reaches detector. An electrical signal which is equal coming MW occurs in there. The signal obtained is amplified by amplifier and modulator and it is shown as the first derivative of an absorption line of the spectrum by the computer. Derivation of the absorption signal has been shown in Figure 3.26 [29].

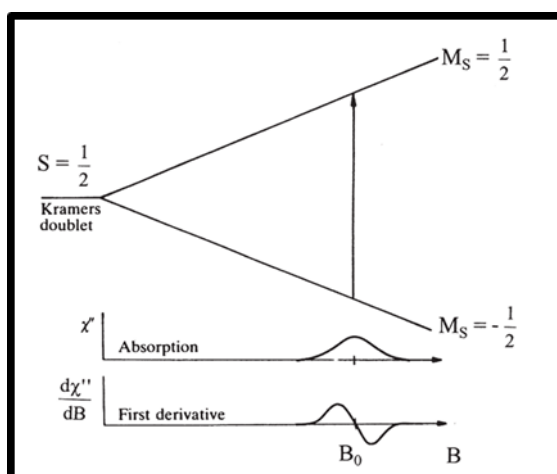


Figure 3.26: Derivation of absorption signal.

4.EXPERIMENTS and RESULTS

TiO₂ thin films have been grown using the PLD technique on Glass, SiO₂ (100) and SiO₂ (111) substrate materials. Thin films have been characterized with using XPS, XRD, XRR, PL and EPR measurement techniques in Nanotechnology Institute ESR laboratory at Gebze Technical University.

4.1 Argon (Ar⁺) Implemented TiO₂

Argon (Ar⁺) has been implanted TiO₂ (100) crystal so as to obtain oxygen vacancies to be characterization at Kazan Institute of Physics.

Crystal TiO₂ has 3.05 eV band gap at its rutile phase. Oxygen defects change significantly optical and conducting properties of TiO₂. Crystals of TiO₂ that have natural paramagnetic defects whihc have been bombarded with using high energytic Ar ions. Defects has occured from surface to depth of 40 nm. After implantation, Doped TiO₂ samples has been heated in order to adjust center of color. Parameters of implantation of samples has been given Table 4.1.

Table 4.1: Parameters of implantation of Ar⁺.

Sample No	Paramaters
ArTO-1h	Dose rate = 1.5×10^{17} CurrentDensity= $8 \mu\text{A}/\text{cm}^2$ Tempreture = 630 °C 40 keV Ar ⁺
ArTO-5h	Dose rate = 1.5×10^{17} CurrentDensity= $9 \mu\text{A}/\text{cm}^2$ Tempreture = 620 °C 30 keV energytic Ar ⁺

Implanted TiO₂ samples kept their opacity but their colors changed. The sample has been shown in Figure 4.1.

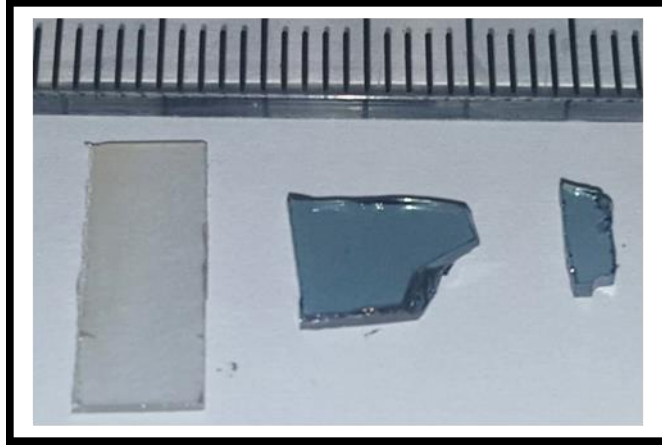


Figure 4.1: Changing of color of TiO₂, after Ar⁺ implantation.

In Figure 4.2, UV spectroscopy results of pure crystal of TiO₂ and implanted TiO₂ samples are seen. According to absorption graphic, border of the wavelength of Pure TiO₂ is equal 410 nm. This value is near value given by literature (406.8 nm, $E = \frac{hc}{\lambda}$, $E = 3.05$ eV). Calculation of band gap value is impossible because of the range of scanning. But results of Ar⁺ ion implantation shows there is changing of band gap value due to defects energy levels. It means there is shift of 5nm, it means decreasing of bandgap energy that is 60 meV.

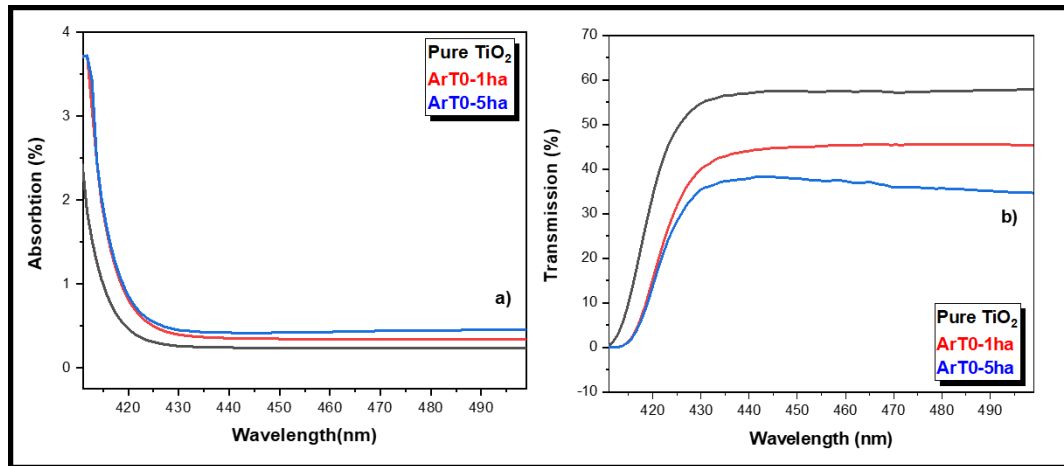


Figure 4.2: UV spectrums of Ar⁺ implanted TiO₂ a) Absorbtion b) Transmission.

Characterization of Structural of samples have been investigated as “Out of plane” and “in-plane” by using XRD.

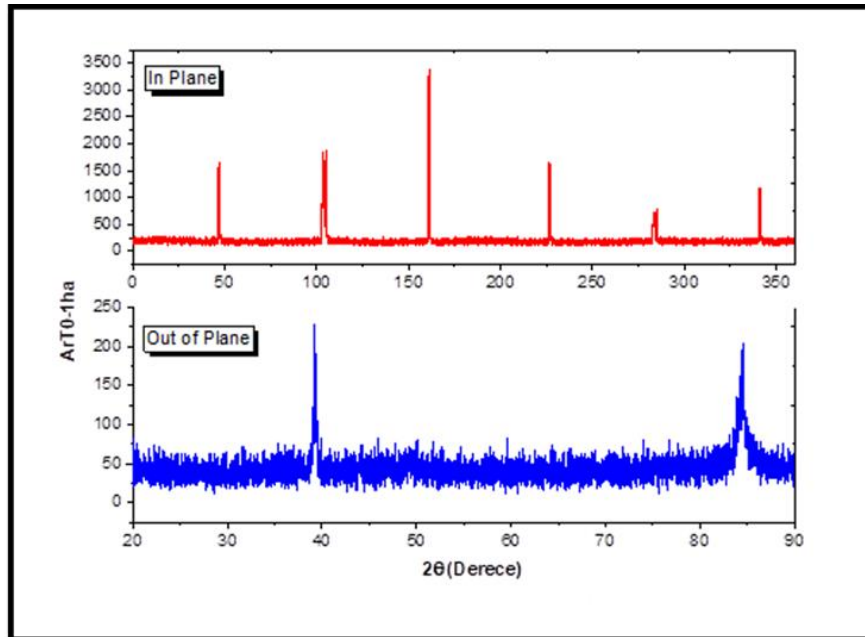


Figure 4.3: XRD results of Ar⁺ implanted TiO₂ along 1 hour. In-plane graphic shows crystal symmetry. Out-of-plane graphic shows distance of lattice and layers.

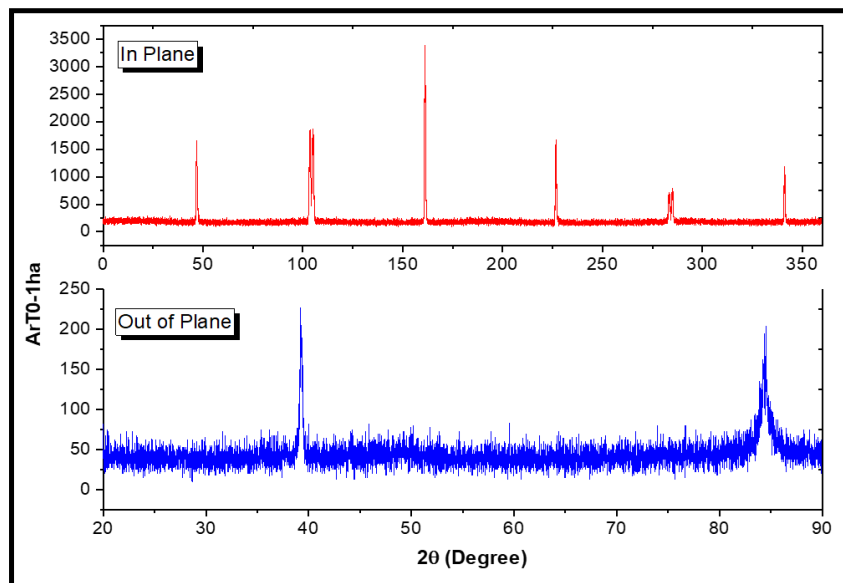


Figure 4.4: XRD results of Ar⁺ implanted TiO₂ along 5 hours. In-plane graphic shows crystal symmetry. Out-of-plane graphic shows the distance of lattice and layers.

4.2 Cobalt (Co⁺) Implanted Crystal of TiO₂

In this study, Cobalt (Co⁺) ions have been implanted to TiO₂ (100) and TiO₂ (111) single crystals. Parameters of implantation have been given Table 4.2.

Table 4.2. Parameters of Co⁺ implantation to TiO₂ crystals.

Ions	Co ⁺
Dose	1.50x10 ¹⁷ Ion/cm ²
Ion current density	8 μ A/cm ²
Ion energy	40keV

This process has been executed with using ILU-3 ion accelerator at Kazan Institute of Physics. Then implantation, the sample has been heated for along 1 hour at 950 °C and atmospheric pressure. Afterward, the magnetic properties of Co⁺ implanted TiO₂ have been measured by Vibrating Sample Magnetometer (VSM) and Ferromagnetic Resonance (FMR) technique at room temperature.

The magnetic properties of Co⁺ implanted TiO₂ (100) and TiO₂ crystals have been investigated from 11 K to 300 K with using Quantum Design PPMS VSM that is able to produce 9T magnetic field (Vibrating Sample Magnetometry) in PPMS Laboratory of Department of Physics at Gebze Technical University. Hysteresis curves have been measured to examine how the applied magnetic field changes the magnetization of samples. Measurements have been shown in Figure 4.5 and Figure 4.6.

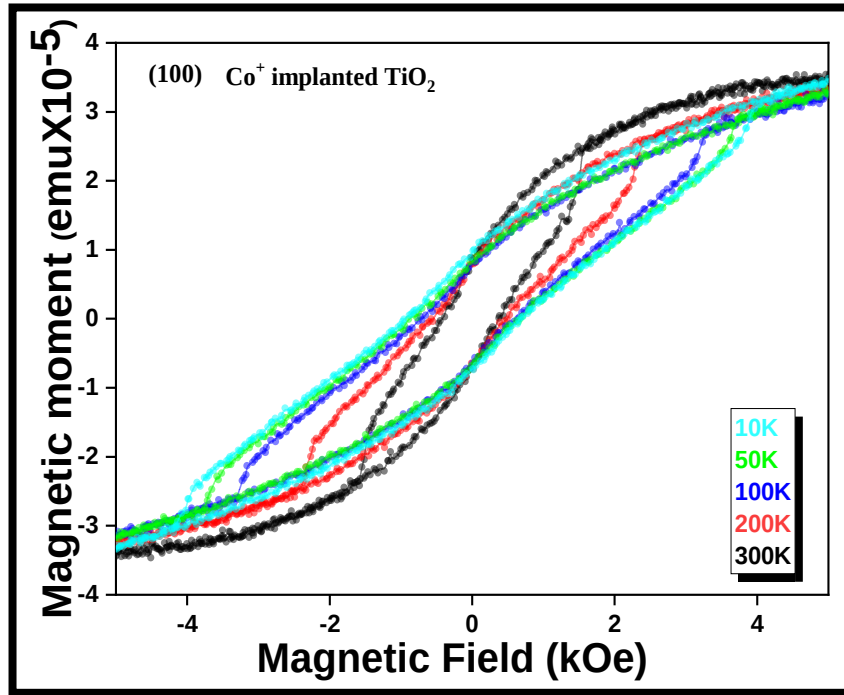


Figure 4.5: Obtained hysteresis curves of various temperature of Co⁺ implanted TiO₂ (100) on VSM measurements.

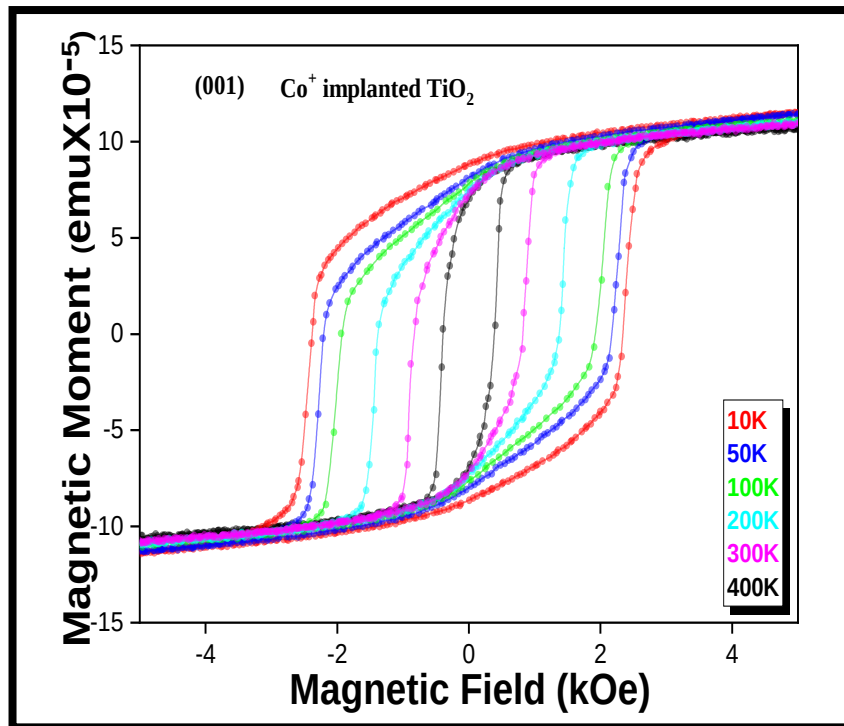


Figure 4.6: Obtained hysteresis curves of various temperature of Co⁺ implanted TiO₂ (001) on VSM measurements.

Figure 4.6 shows that both saturation magnetization and coercive field of Co⁺ implanted TiO₂ (100) less than Co⁺ implanted TiO₂ (001). M-H curve has been determined the cause of occurred nano particles due to near-surface Co ions that their

strict dipoles or exchange-bias attraction each other rather than intrinsic magnetism and result of this, more curved hysteresis has been evaluated. Observed hysteresis curves of Co^+ implanted TiO_2 (001) has been more like a square shape at measurements of different temperatures. In this sample, Occurring the higher the ferromagnetic magnetization and the anisotropy show that increase density of defects and intensity of exchange bias attraction as a result of implantation.

FMR measurements of heated samples have been actualized at different temperatures with using Bruker EMX X-band (9.7 GHz) EPR spectrometer in Department of Physics at Gebze Technical University. Results of measurements have been obtained at 0 – 16000 G and which rotated as both “in-plane geometry” and “out of plane geometry”.

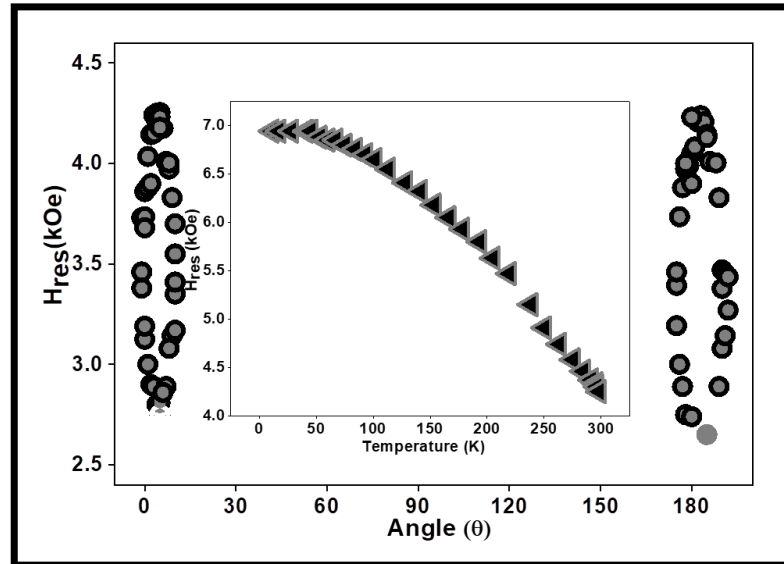


Figure 4.7: In-plane angular dependences of the FMR resonance fields of Co^+ implanted (100)-oriented TiO_2 sample.

In Figure 4.7, results of FMR measurements show that Co^+ implanted samples have ferromagnetic behavior rather than paramagnetic behavior. Results are significantly led to that ferromagnetic behavior is like semiconductor behavior cause of oxygen defects. The reason of Ferromagnetism is stated that depends on Co ions that placed some part metal cobalt nanoparticles and another part Ti indirect attraction exchange bias with on oxygen defects cause from implantation of 3d ion. There is no the same result that exchange bias attraction from the annealed sample that its removed oxygen defects.

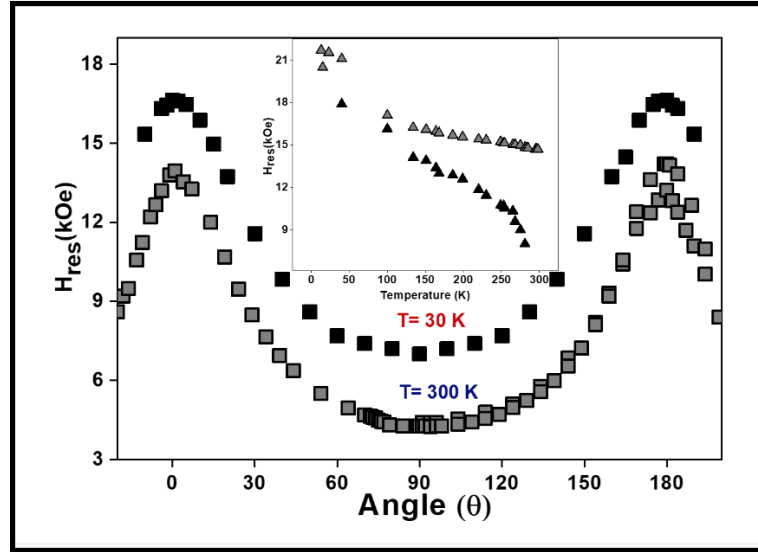


Figure 4.8: Out-of-plane angular dependences of the FMR resonance fields of Co^+ implanted (100)-oriented TiO_2 sample.

Figure 4.8 shows FMR measurements of both room temperature and low temperatures. Results demonstrate shape anisotropy and effective magnetization on the sample.

Also, the same processes that are about oxygen defects have been carried out for Co^+ implanted TiO_2 (001). Dynamics of oxygen defects depend on crystal directions significantly from the point of the property of memristor. According to results, the intensity of exchange bias attraction is different for two crystal directions.

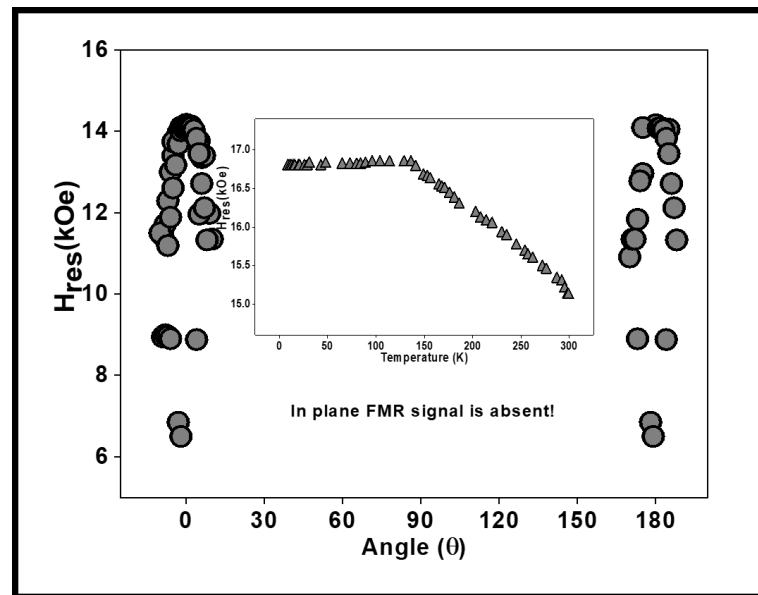


Figure 4.9: Out of plane angular dependences of the FMR resonance fields of Co^+ implanted (001)-oriented TiO_2 sample.

Experimental and simulation of the out-of-plane FMR resonance fields of Co^+ implanted (001)-oriented TiO_2 and Co^+ implanted (100)-oriented TiO_2 sample have been shown in Figure 4.10 and Figure 4.11.

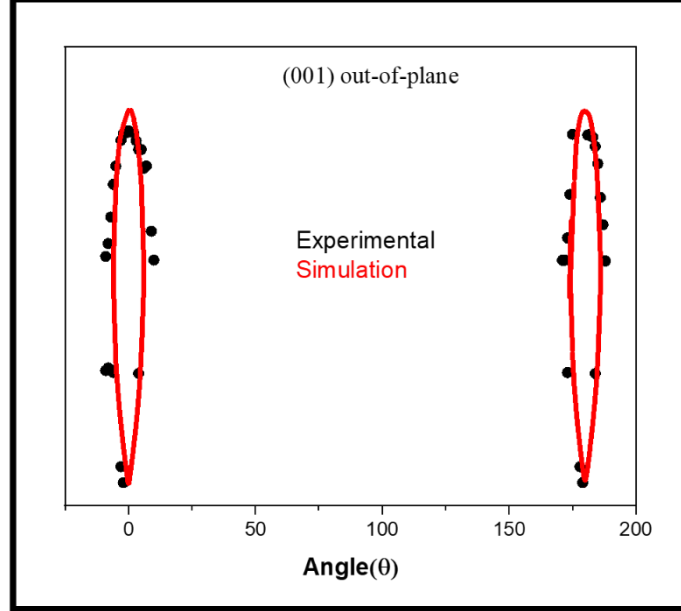


Figure 4.10: Experimental and simulation of the out-of-plane FMR resonance fields of Co^+ implanted (001)-oriented TiO_2 sample.

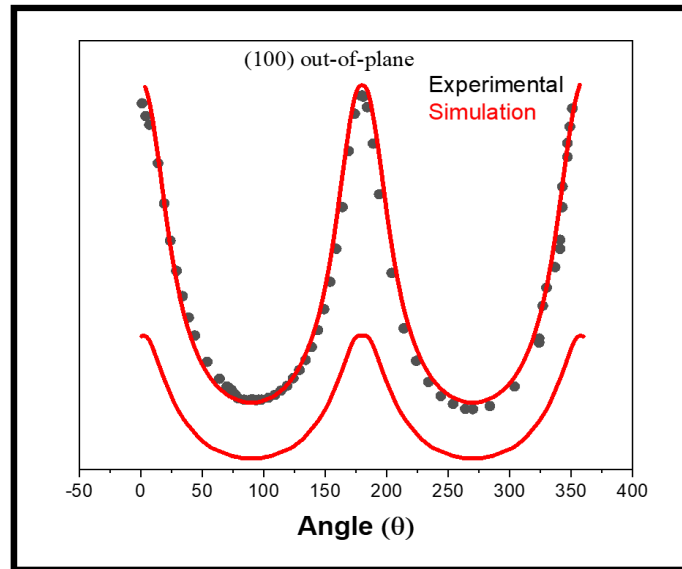


Figure 4.11: Experimental and simulation of the out-of-plane FMR resonance fields of Co^+ implanted (100)-oriented TiO_2 sample.

Experimental and simulation of the in-plane FMR resonance fields of Co^+ implanted (100)-oriented TiO_2 sample has been shown in Figure 4.12.

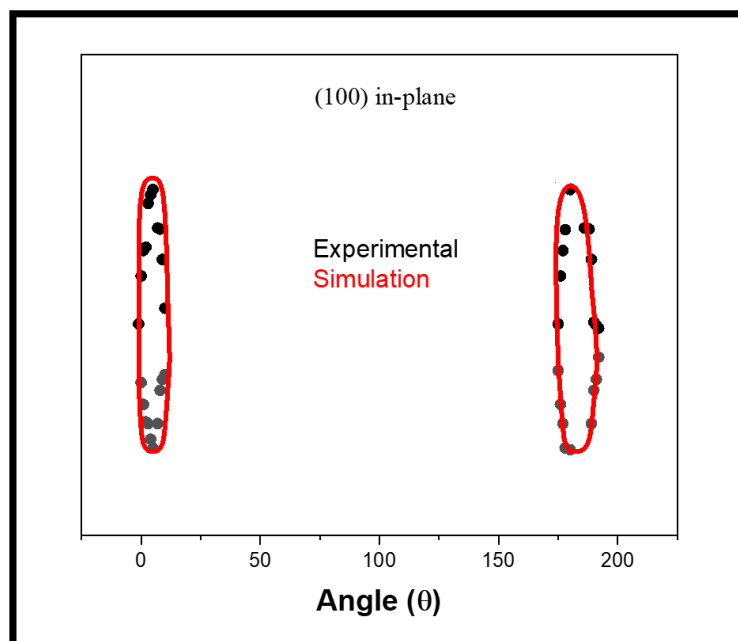


Figure 4.12: Experimental and simulation of the in-plane FMR resonance fields of Co^+ implanted (100)-oriented TiO_2 sample.

4.3 Fe⁺ Implanted TiO₂

In this study, Iron (Fe⁺) ions have been implanted to TiO₂ (100) and TiO₂ (111) single crystals. Parameters of implantation have been given Table 4.3.

Tablo 4.3: parameters of Fe⁺ implantation to TiO₂ (100) and TiO₂ (001)

Ions	Fe ⁺
Dose	1.50x10 ¹⁷ Ion/cm ²
Ion current density	8 μ A/cm ²
Ion energy	40keV

This process has been executed with using ILU-3 ion accelerator at Kazan Institute of Physics. Then implantation, the sample has been annealed for along 1 hour at 950°C and atmospheric condition. Also ~60 nm TiO₂ polycrystals have been growth by magnetron sputtering method on glass substrates and these samples annealed in the air for 8 hours at 250°C. TiO₂ polycrystalline samples have been implanted to be like TiO₂ single-crystalline samples.

Magnetic properties annealed and non-annealed single-crystalline samples and polycrystalline samples magnetic properties have been measured by Electron paramagnetic resonance (EPR) and Ferromagnetic Resonance (FMR) technique at room temperature by using a model of Bruker EMX X-band (9.5 GHz) ESR spectroscopy in Department of Physics at Gebze Technical University. Measurements have been executed at room temperature a static magnetic field that is from 0 to 22kOe.

Also, the magnetization of Fe⁺ implanted TiO₂ (100) and TiO₂ (001) have been measured with using Quantum Design PPMS VSM that is able to produce 9T magnetic field (Vibrating Sample Magnetometry) in PPMS Laboratory of Department of Physics at Gebze Technical University. Measurements have been executed between 10 K and 400 K.

4.3.1 VSM measurements

Hysteresis curves of Fe^+ implanted TiO_2 (100) and TiO_2 (001) rutile single-crystalline and polycrystalline have been measured with VSM method between 10 K and 400 K and how changes samples behaviors that depend on temperature have been shown. Hysteresis curves of easy and hard axis have been accepted in the same class with depending on results of in-plane FMR measurements. Magnetic hysteresis curves of samples have been shown in Figure 4.14 and Figure 4.15.

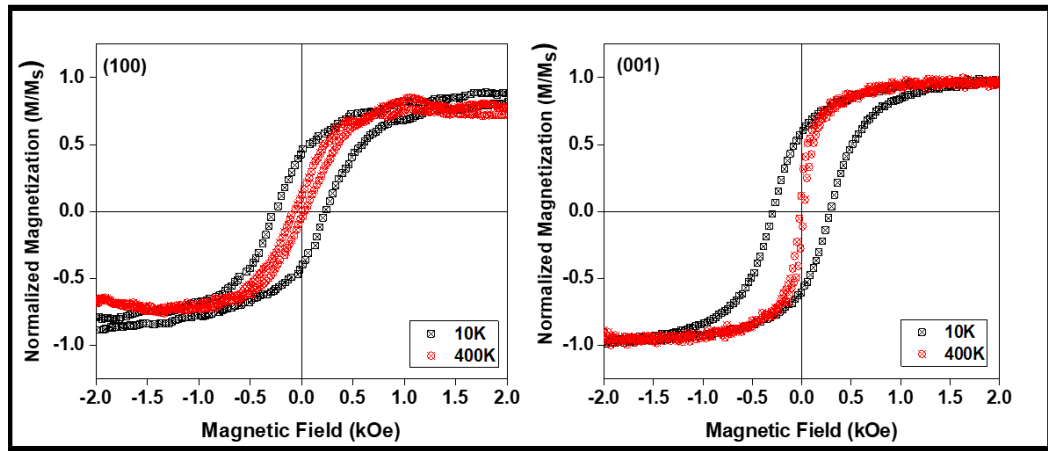


Figure 4.13: Hysteresis curves without paramagnetic effects of Fe^+ implanted TiO_2 (100) and TiO_2 (001) at 10 K – 400 K.

In Figure 4.13, both saturation magnetization and coercive field of Fe^+ implanted TiO_2 (100) are seen less than Fe^+ implanted TiO_2 (001). There is an extrinsic phase from close dipoles or exchange bias attractions rather than a magnetism that shape and temperature behaviors of M-H curves cause of placed diluted magnetic ions (intrinsic phase) in the lattice. Results of implantation of the plane of (001) show hysteresis curves have more square shapes. This condition, nanoparticles growing directions of (100) TiO_2 and (001) TiO_2 are different. Also, There is asymmetry that has been observed from the result of implantation TiO_2 (100). Especially at low temperatures, asymmetry has been referred existing antiferromagnetic layer has been referred at around Ferromagnetic nanoparticles

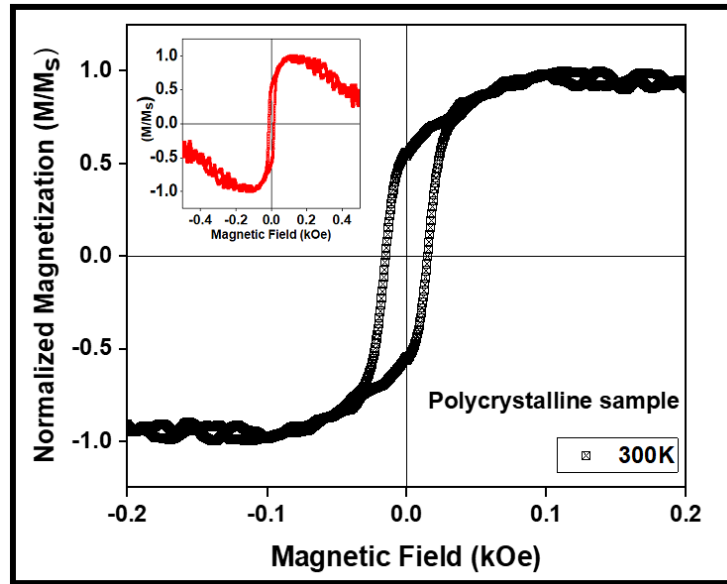


Figure 4.14: Hysteresis curve of Fe^+ implanted polycrystalline TiO_2 at 300 K without diamagnetic effect. Red colored graphic shows diamagnetic phase contribution and hysteresis curve of sample that is at large range magnetic field.

Hysteresis curve of polycrystalline TiO_2 has been shown in Figure 4.14. Magnetization measurements of this sample have been executed with using rotating inductive magnetometer. The diamagnetic contribution comes from the glass substrate. Obtained hysteresis curves at room temperature is a little wider than hysteresis curve of single-crystalline at the same temperature. That is to say, Room temperature coercive field is bigger. The general shape of hysteresis exhibits expectable behavior in polycrystalline samples. In this sample, observing ferromagnetism hysteresis curve is considered that cause from occurring constructed layer by nanoparticles.

4.3.2 EPR and FMR measurements of annealed samples

After samples (100) and (001) TiO_2 rutile single crystal planes were inoculated with Fe^{+3} ions at room temperature, some of the samples were annealed at the atmospheric temperature at 950°C for 1 hour. EPR spectra of implanted and annealed (100) and (001) TiO_2 rutile single crystals have been recorded at each angle value by rotating at room temperature and for example in the 0 - 360° angle range using the X-band ESR spectrometer. (100) for TiO_2 rutile single crystal; The measurements were carried out in two rotational planes: in-plane and out-of-plane. Angle-dependent spectra of (001) TiO_2 rutile single crystal (001) in in-plane geometry and (100) in out-of-plane geometry have been recorded. Figure 4.15 and Figure 4.15 show the EPR spectra for both single crystals recorded at different angles in the in-plane and out-of-plane geometry.

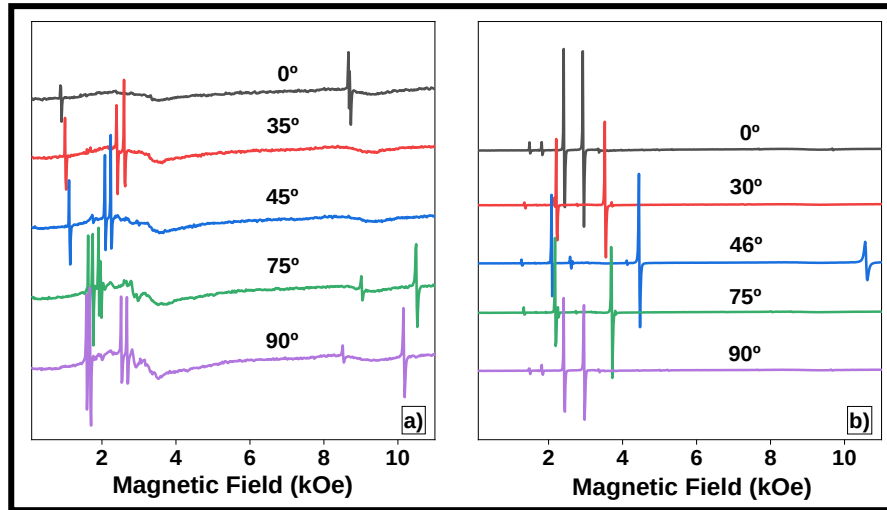


Figure 4.15: EPR spectrums of Fe^{+3} implanted (100) TiO_2 single-crystalline a) in-plane b) out of plane.

In Figure 4.15, when the EPR spectra of TiO_2 single crystals (100) and (001) have been examined, no ferromagnetic behavior was observed at room temperature in TiO_2 rutile crystals inoculated with Fe^{+3} ions. It is seen that the EPR spectra showing high anisotropy at room temperature are multiple peaks of trivalent dilute paramagnetic iron (Fe^{+3}) ($L = 0, S = \frac{5}{2}$) ions. Observation of Fe^{+3} EPR signal with angular dependence in iron-implanted samples annealed at high temperatures (950°C)

shows that annealing process causes the grafted iron to penetrate into the whole crystal from the rutile surface, causing the Ti^{+4} positions in the lattice to snap into place [31].

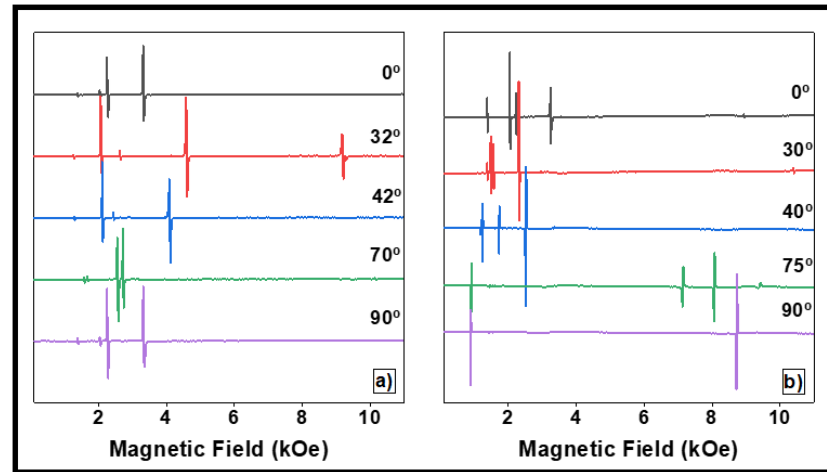


Figure 4.16: EPR spectrums of Fe^+ implanted (001) TiO_2 single-crystalline a) in-plane b) out of plane.

4.3.3 EPR and FMR measurements of non-annealed samples

(100) and (001) TiO_2 rutile monocrystalline planes have been implanted with Fe^+ ions at room temperature. EPR measurements of non-annealed single crystallines and polycrystalline samples have been shown in Figure 4.18.

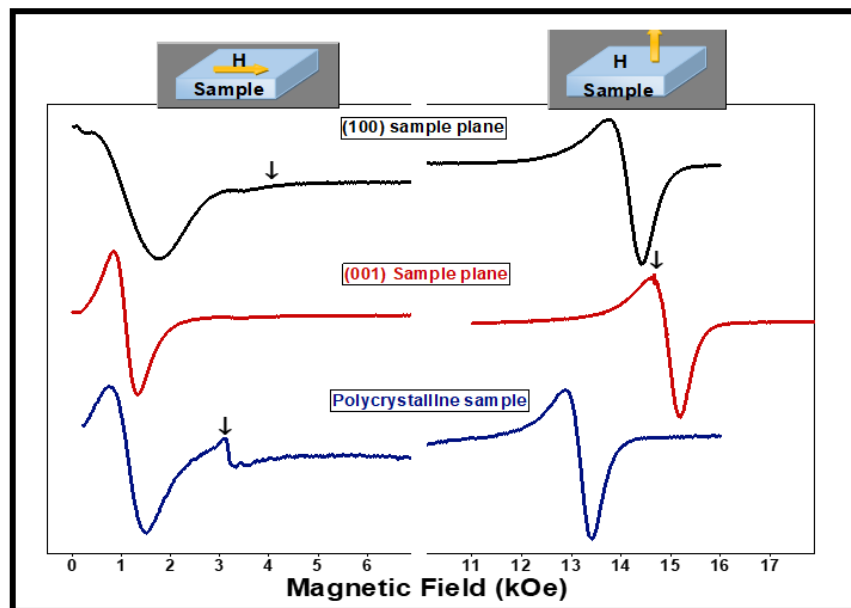


Figure 4.17: ESR spectra of Fe^+ implanted (001) TiO_2 , (001) TiO_2 single-crystalline and polycrystalline at room temperature.

Figure 4.17 shows the wide and intense ferromagnetic resonance signal with angular dependence as well as narrow and sharp ESR peaks in single crystal and polycrystalline samples planar (100) and (001) implanted with Fe^+ ion. The reason of ferromagnetism as a result of vaccination can be explained by two different models. First; intrinsic magnetism, that is, the formation of magnetic oxide material that is observed as a result of indirect exchange interaction of trapped electrons trapped on free electrons or oxygen defects by settling Fe ions on Ti sites. As the second; extrinsic ferromagnetism, which is known as iron atoms clustering to form metal (metal-oxide) nanoparticles and In addition, nanoparticles are released as a result of magnetic dipole-dipole interaction with each other. Although both phases have high magnetization and anisotropy in theory, in many experimental studies, high anisotropy and magnetization values are seen as signs of extrinsic phase.

Similar studies have demonstrated the presence of magnetic anisotropy in single-crystal TiO_2 materials inoculated with cobalt (Co), iron (Fe) and nickel (Ni) ions [31-35]. In most cases, the aggregation of these metal ions has been shown as the cause of the in-plane magnetic anisotropy of implanted TiO_2 with these transition elements (3d ions) [34-36]. In-plane magnetic anisotropy results from the consistent growth of nanostructures consistent with the crystal structure of the rutile matrix. Mössbauer spectroscopy (CEMS) measurements of Fe implanted TiO_2 rutile samples at room temperature has been shown that most of the iron in the implanted samples (about 70%) has been in the α -iron phase [37]. Thus, the ferromagnetism observed in the rutile TiO_2 crystal can be said to be caused by iron ion implantation at a high dose rate.

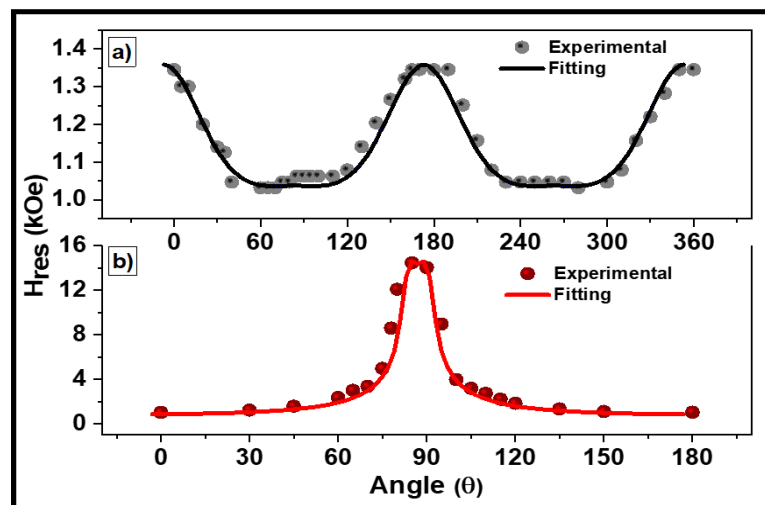


Figure 4.18: Resonance field that depends on angle and fit curves of ESR spectra of Fe^+ implanted (001) TiO_2 single-crystalline.

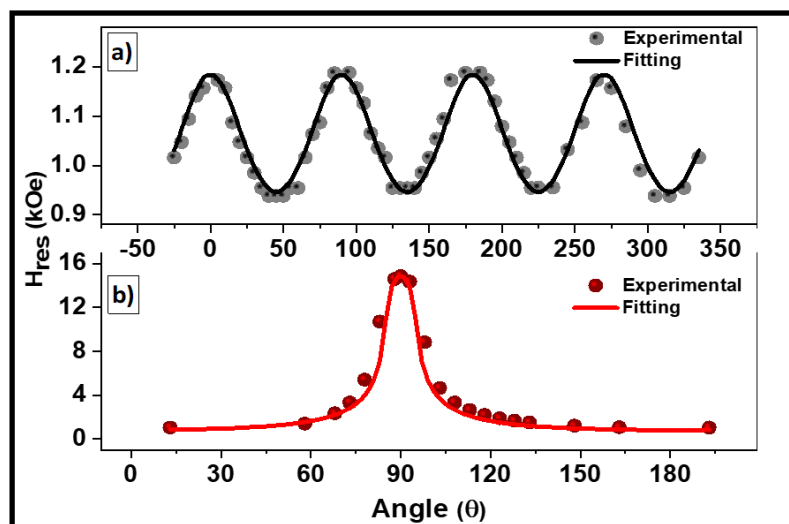


Figure 4.19: Resonance field that depends on angle and fit curves of ESR spectrums of Fe^+ implanted (001) TiO_2 single-crystalline.

Figure 4.18 and Figure 4.19 show the angular dependence and fit curves of the resonance fields of the ESR spectra of Fe implanted (100) and (001) plane TiO_2 single crystal samples recorded in in-plane and out-of-plane geometry. When the angular dependence of the resonance fields is examined, it is seen that four-fold magnetocrystalline anisotropy is formed in TiO_2 single crystal in (001) in-plane geometry. High anisotropy was observed for two samples in out-of-plane geometry.

4.4 Production of TiO₂ Thin films with using Pulsed Laser Deposition (PLD) and Characterization.

In this study, PLD system that has KrF ($\lambda = 248$ nm) Laser has been used so as to thin film growth in Nanotechnology Institute at Gebze Technical University. System has been shown figure 4.19. Also turbo molecular pump and mechanical pump have been used for vacuum ambient that is about from $\sim 10^{-8}$ mbar to $\sim 10^{-4}$ mbar at growth chamber. PLD system has been shown in Figure 4.20.

4.4.1 Pulsed Laser Deposition

The term meaning of PLD is pulsed laser deposition. This method is physical steam atomic layer deposition in nano-scale, executed in vacuum [38]. The technique has been used to fabricate quality thin films of materials for more than a decade. A high-energy laser pulse is used in order to melt, evaporate and ionize materials from a target in this technique. Abrasion causes highly glowing plasma plume that moves very fast away from the target surface and saved on a properly placed substrate upon which it concentrates and the thin film grows.

The evaporated material, containing neutrals, ions, electrons, etc., is known as a laser-produced plasma plume and expands that moves very fast away from the target surface. Film growth shows up on a substrate upon which some of the plume material re-concentrate. In fact, however, the condition is not so straightforward, with a lot of factors affecting the properties of the film, such as laser streaming, background gas pressure, and substrate temperature. These factors allow the film properties to be manipulated slightly, to comply with individual applications. However, optimization can be essential a significant amount of time and effort [39]. PLD's system has been shown as schematically in Figure 4.21.

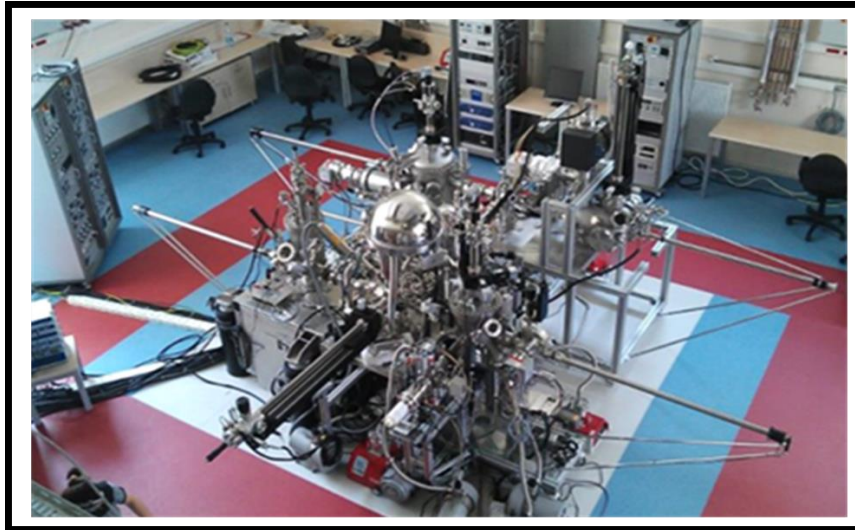


Figure 4.20: PLD system in Nanotechnology Institute at Gebze Technical University

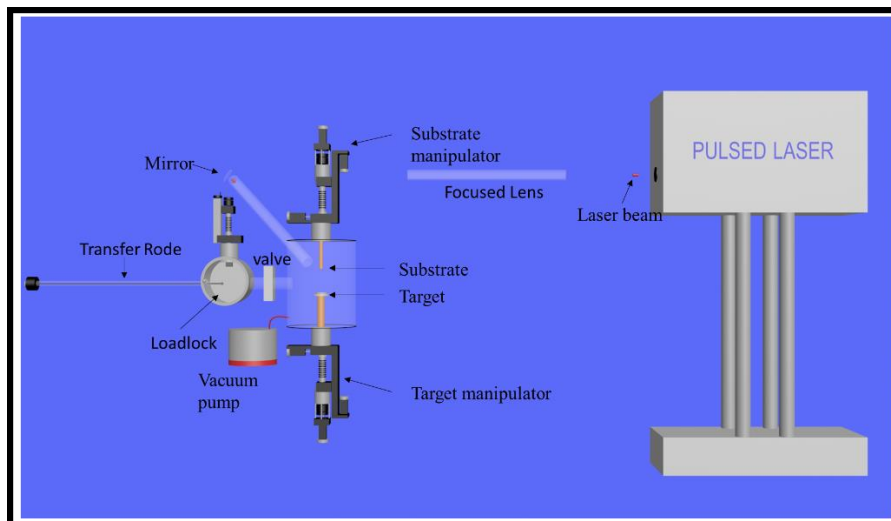


Figure 4.21: Schematic of PLD.

There are three steps so as to high quality thin film growth. Steps contain preparing the substrate, transferring to the manipulator and thin films growth.

4.4.2 Cleaning Process

Holder Substrate and target holders must be cleaned well. The cleaning process includes two sections. First procedure, One of them is the chemical process. Acid or alcohol are used in this operation. If holders are being used for the first time. It should be cleaned with acid. If they are not being used for the first time. They only should be cleaned with alcohol and dried with N_2 , this process is the second procedure. Another process of thermal treatment. This operation is at vacuum and approximately 600 °C about an hour which is required for holders that cleaned with acid. After the cleaning process, they can be used for thin-film production.

4.4.3 To place substrates and target to the holder and sending PLD manipulator.

Cleaned Substrates and target are placed on a molybdenum holder with using tantalum wire so as to hold them for production. The process has been shown in Figure 4.22.

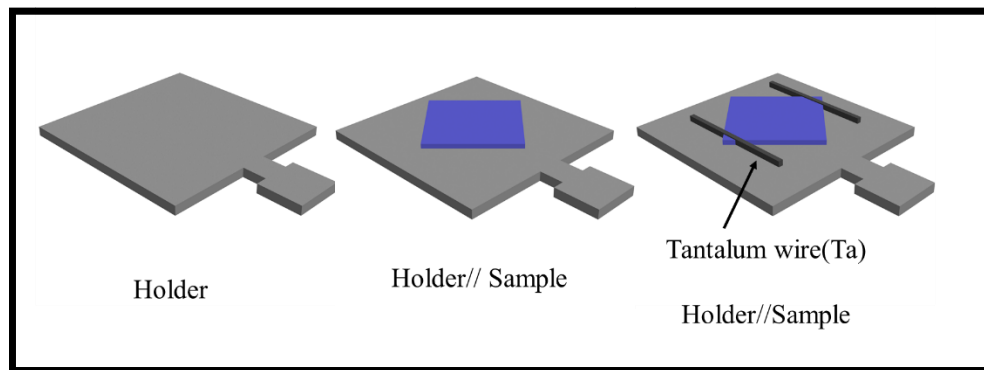


Figure 4.22: To place of substrate or target to holder.

Firstly prepared substrate and target is placed to PLD loadlock then they are sent computer controlled manipulators which are in PLD vacuum chamber with a rod that is able to be opened and closed. They are balanced to thin film production positions by using computer.

4.4.4 Thin Film Production with Pulsed Laser

Basic PLD process in this study, various laser beams are produced by KrF gas-based High -Powered Laser generator. Beams pass through the first lens and they focused.

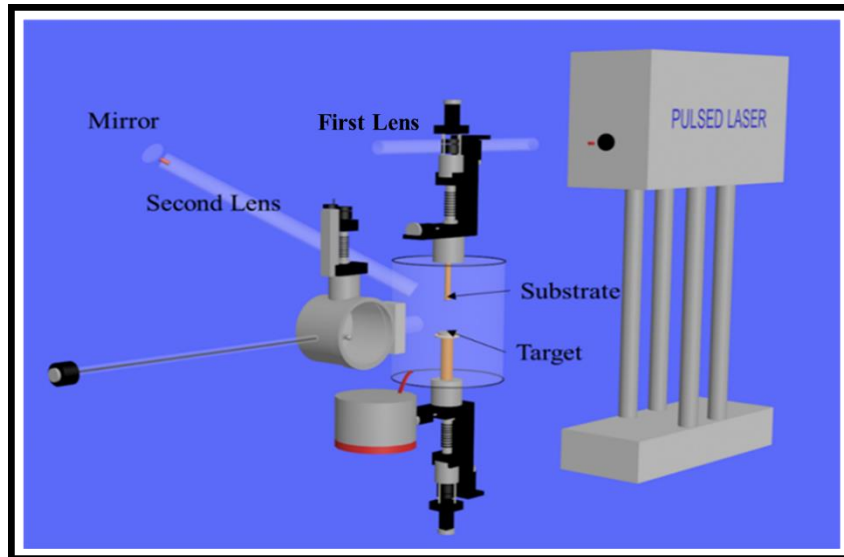


Figure 4.23: Schematic of laser beam direction in PLD system.

Then they hit the mirror and rotated 45° before the second lens. They are focused again by the second lens and sent to the target(left) and materials plumes leave from target and saved on substrate(right). The processes have been shown in Figure 4.25.

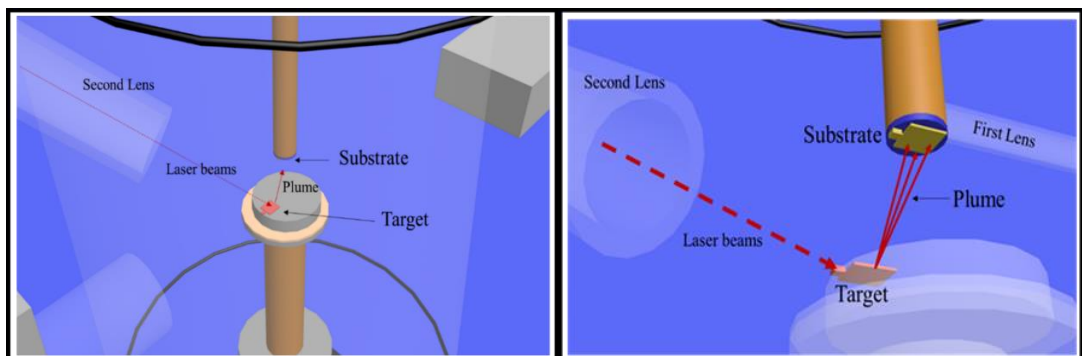


Figure 4.24: Attraction between laser beam and target materials in PLD system.

4.4.3.1 PLD Sample: XPS results of (100) SiO₂/TiO₂

XPS measurements of samples have been executed by XPS spectroscopy meter in Nanotechnology Institute at Gebze Technical University.

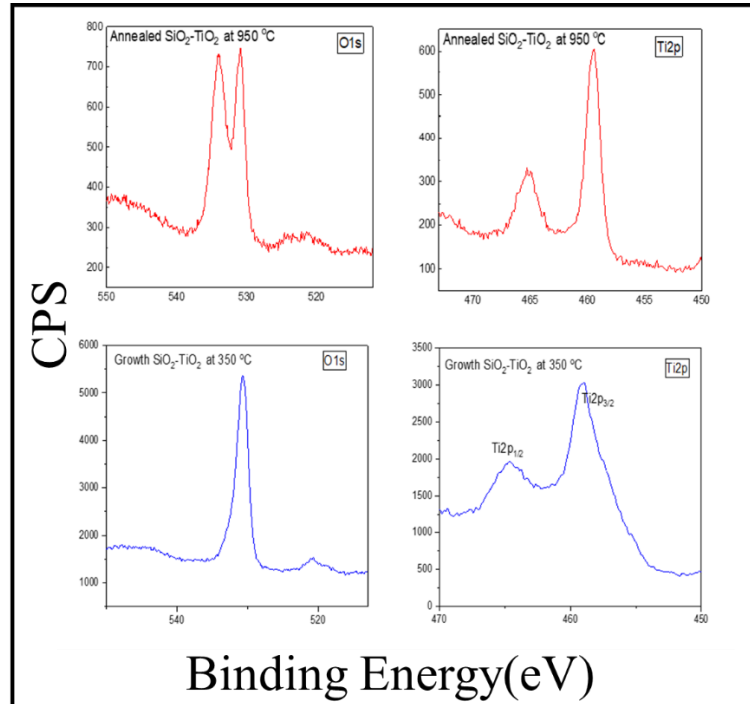


Figure 4.25: XPS measurements of TiO₂ (annealed at 950 °C) and TiO₂ (Growth at 350 °C)

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material [40]. Addition to the survey scan of growth films, narrow scan (or high resolution XPS spectra) belong to the Ti, O and C elements were examined. All experimental results are shown in Figure 4.25. In all spectra, peak at around 284 eV was observed (not presented in Figure 4.25 corresponding to the carbon impurities arising from the chemical etching of samples with some carbon based chemicals. We used this peak for the calibration of XPS spectra in survey scan. The Ti 2p_{1/2} and Ti 2p_{3/2} spin-orbital splitting photoelectrons for all samples are located at binding energies of about 465 eV and 460 eV, respectively, as can be seen in Figure 4.25. These data are in good agreement with literature. The spin orbit splitting energy for the as-grown sample at 350 C is about 5.61 eV and for the thermally annealed at 950 C is about 5.71 eV. Also

the below figure shows the O 1s core level spectra of pure and thermally annealed TiO₂ thin films. The peak at about 530 eV for all samples is due to O₂⁻ ion in the TiO₂ lattice. In all spectra at higher binding energy a shoulder and additional peak was observed and they can be attributed to the surface hydroxyl groups of water molecules on the surface of films. All experimental data have been analyzed with the CASAXPS software. The peaks for Ti elements are fitted three independent Gaussian peaks due to the Ti⁺⁴, Ti⁺³ and metallic Ti. These extra ions have been attributed to the surface defects due to the oxygen deficiency at surface which are consistent with the PL measurements.

4.4.3.2 PLD Sample: XRD and XRR results of (100) SiO₂/TiO₂

XRD and XRR measurements of samples have been executed by Rigaku XRD device in Nanotechnology Institute at Gebze Technical University.

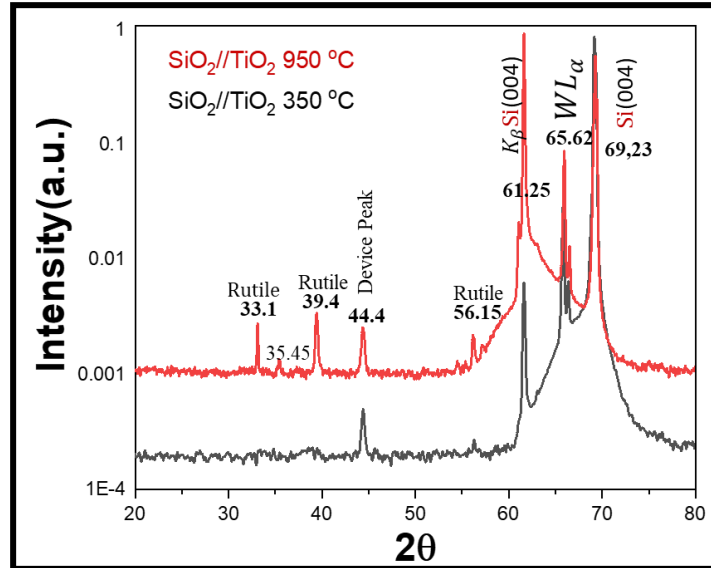


Figure 4.26: XRD measurements of TiO₂ (annealed at 950 °C) and TiO₂ (growth at 350 °C)

According to the result of XRD in Figure 4.26, rutile peaks have been detected at annealed 950 °C. The Peak can be stated as device peak at 44.4 degrees. The WL_{α} that peak comes from tungsten filament at 65.62 degrees. Rutile peak has not been detected at TiO₂ 350 °C except 56.15 degrees.

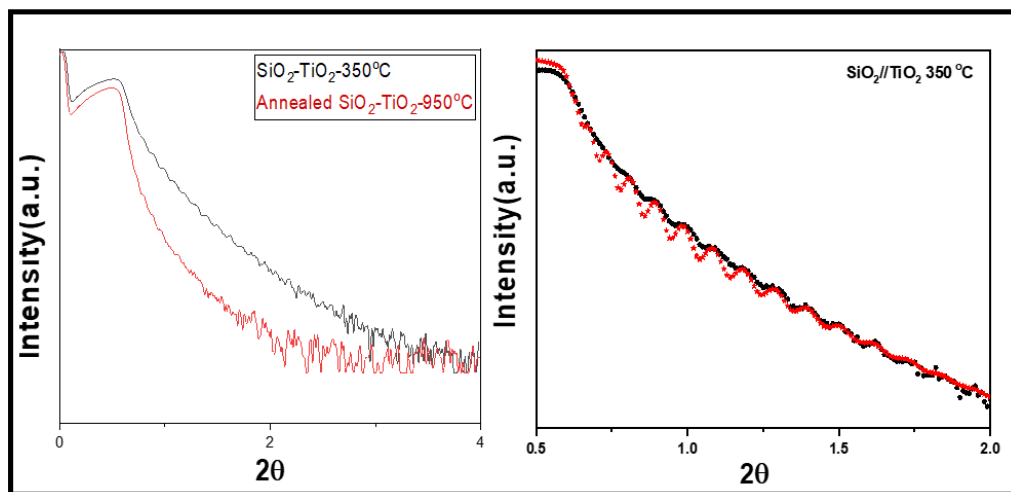


Figure 4.27: a) XRR measurements of TiO₂ (annealed at 950 °C) and TiO₂ (Growth at 350 °C), b) XRR Fit of growth TiO₂ at 350°C.

According to the result of XRR in Figure 4.27, The sample thickness has been determined as 74 nm. In this graphic, red line refers to fit data and black line refers to measurement data.

4.4.3.2 PLD Sample: Photoluminescence results of (100) SiO₂/TiO₂

Optical measurements of samples have been measured by Cary Eclipse Fluorescence Spectrophotometer at Bahçeşehir University.

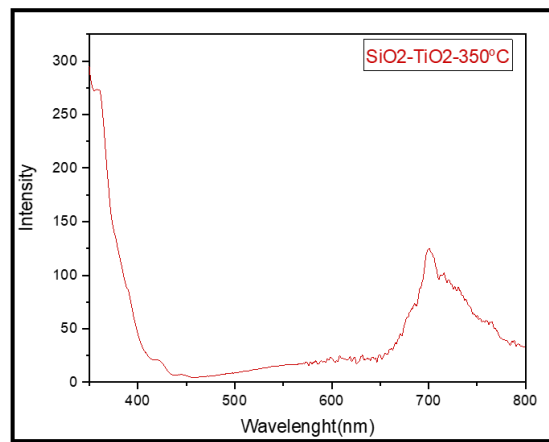


Figure 4.28: Photoluminescence of TiO₂ (Growth at 350 °C)

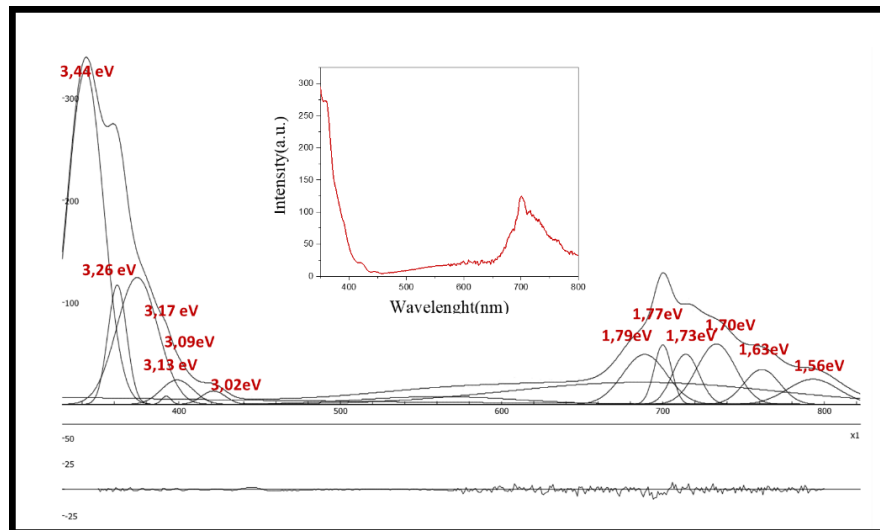


Figure 4.29: Fit of photoluminescence of TiO₂ growth at 350 °C.

According to result of fit in Figure 4.29, Oxygen vacancy energy levels are exist from 3,17 eV to 3,02 eV and 1,79 eV – 1,56 eV in TiO₂ anatase phase (Bandgap 3,2 eV).

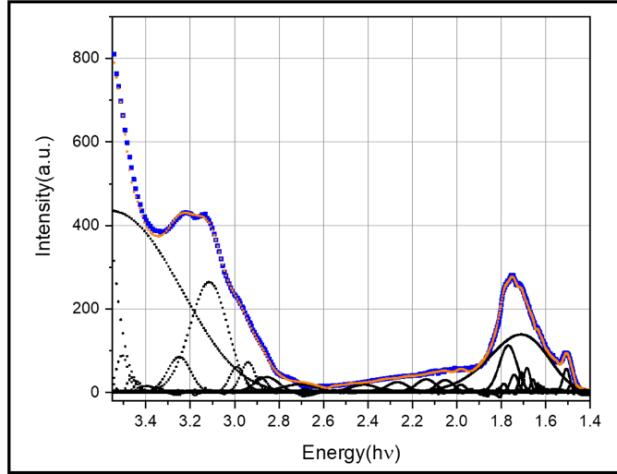


Figure 4.30: Fit of photoluminescence of TiO₂ growth at 350 °C respect to Energy.

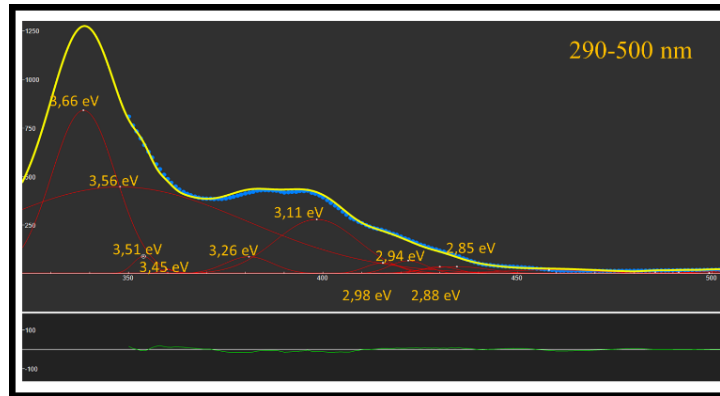


Figure 4.31: Fit of photoluminescence of TiO₂ growth at 950 °C (290 nm -500 nm).

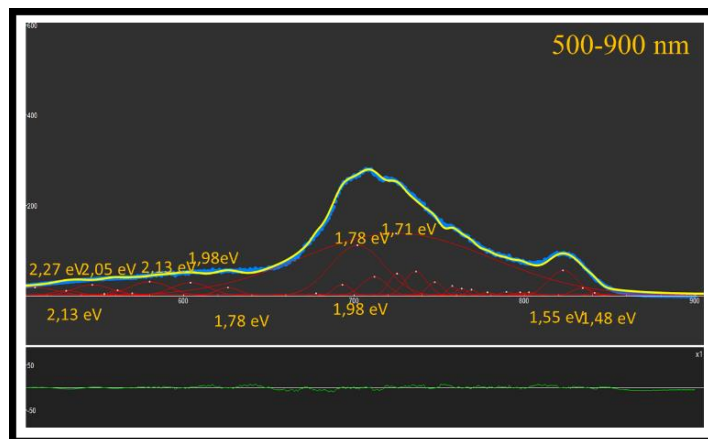


Figure 4.32: Fit of photoluminescence of TiO₂ growth at 950 °C (500 nm- 900 nm).

According to results of fit in Figure 4.32 and Figure 4.33, Oxygen vacancy energy levels are exist from 2,98 eV to 2,85 eV and 2,27 eV – 1,48 eV in TiO₂ rutile phase (Bandgap 3,0 eV)

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APPENDICES

Appendices A: Studies

Ozkal B., Karatas O., Okay C., Kazan S., Rameev B., Khaibullin R.I., Güler S., Arda L., (2018), “Magnetic Resonance And VSM Studies Of Co Implanted TiO₂ Single Crystals”, Poster presentation, Graduate Studies Symposium and Promotion Days, Institute of Natural and Applied Sciences, Gebze Technical University, Turkey.

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