

**THIN FILMS GROWTH AND STUDY OF MANGANESE DOPED ZINC
NITRIDE DILUTE MAGNETIC SEMICONDUCTORS FOR SPINTRONIC
APPLICATIONS**

BY

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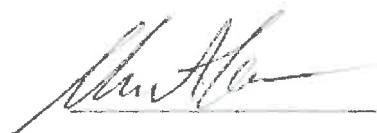


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Dedication

Deeply gratitude goes to Allah, for the worth gifts of life to complete the MS program.

To my family who are pillars of my life.

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LIST OF ABBREVIATIONS

LED	Light Emitting Diodes
SP-FET	Spin -Field Effect Transistors
DMS	Dilute magnetic semiconductors
RF	Radio Frequency
DC	Direct Current
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
MBE	Molecular Beam Epitaxy
RMS	Root Mean Square roughness

ABSTRACT

Full Name : Ali Alnoor Abaker Sulieman

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Abstract

Spintronics is an emerging field of physics where spin of the charge carriers is combined with the traditional electronics. Dilute magnetic semiconductors are a class of materials (DMS) that can be used in spintronic applications. DMS are formed by lightly doping a semiconductor with a transition metal element of uncompensated spin. The resultant material will be ferromagnetic as well as semiconductor. Here we report the growth and study of manganese doped zinc nitride thin films to fabricate DMS. Thin films were grown by RF/DC magnetron sputtering on Si (100) and glass substrates at different Mn concentration in the films. The films were studied using spectrophotometry, X-ray diffraction, Hall effect measurement, atomic force microscopy and X-ray photoelectron spectroscopy. The concentration of manganese dopants in zinc nitride films affected the surface morphology as well the optical, electronic, and chemical properties of the films. XRD diffractometer study revealed that all the grown films are polycrystalline in nature with a prominent Zn_3N_2 (411) peak presents in all the films. A red shift in the bandgap was observed with the increase in manganese concentration in the films. Hall Effect measurement revealed that all the grown films are n-type semiconductors and carrier density of the films is higher for the films with higher concentration of manganese. X-ray photoelectron spectroscopy confirmed the presence of manganese in the films due to existing of Mn 2p peaks in the films and the manganese was found to be in the second (Mn^{+2}), third (Mn^{+3}) and fourth (Mn^{+4}) oxidation state. Magnetoresistance measurements have confirmed the existence of magnetization in the films due to change the electric resistance of the films with the applied magnetic field.

ملخص الرسالة

الاسم الكامل : علي النور أبكر سليمان
عنوان الرسالة : دراسة الاغشية الرقيقة من أشباه الموصلات المغنطيسية المخففة لنتريد الزنق المطعم بالمانجنيز المحضر بواسه المغنطرون لتطبيقات اجهزه الالكترونياات المغزليه
التخصص : فيزياء
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اجهزه الالكترونياات المغزليه مجال ناشئ في الفيزياء حيث ان عزم الالكترتون تقترن مع الشحنة الالكترونية. أشباه الموصلات المغنطيسية المخففة فرع من المواد يستخدم في أجهزه الالكترونياات المغزليه. اشباه الموصلات المغنطيسية المخففة يتم تحضيرها بأشابه أشباه الموصلات بكميه قليله من العناصر الانتقاليه. ماده الناتجه تكون شبه موصل ولها خواص مغناطيسيه في نفس الوقت. في هذا البحث تم تحضير ودراسه الاغشية الرقيقة من أشباه الموصلات المغنطيسية المخففة لنتريد الزنق المشوب بالمانجنيز عن طريق قذف هدف الزنق باستخدام مدفع رش يعمل بالتيار المباشر بينما تم قذف هدف المنجنيز باستخدام مدفع رش يعمل بالتيار المتردد في وجود غازي الارجون والنتروجين لتكوين اشباه الموصلات المغنطيسية المخففة بتركيز مختلفه من المنجنيز في الافلام الرقيقه. تمت دراسه الخواص التركيبية, السطحيه, البصريه, الكهربيه والكيميائيه باستخدام حيود الاشعه السينيه, الفحص المجهرى للقوة الذريه, القياس الطيفي, أثر هول والتحليل الطيفي الضوئي للاشعه السينيه. زياده تراكيز نسب المنجنيز المختلفه في الافلام الرقيقه لنتريد الزنق اثرت على الخواص التركيبية, السطحيه, البصريه, الكهربيه والكيميائيه للافلام الرقيقه. أكدت دراسه حيود الاشعه السينيه أن كل هذه الافلام الرقيقه المحضره متعدد الكريستالات في طبيعتها. وجدت ان هنالك ازاحه ناحيه الطيف الاحمر في فجوه حزمه الطاقه عند زياده تركيز المنجنيز في نتريد الزنق. أكدت دراسه أثر هول بأن كل هذه الافلام أشباه موصلات من النوع السالبه و أن كثافه حاملات الشحنة أعلى في الافلام التي تحتوي على تراكيز عاليه من المنجنيز. أكدت التحليل الطيفي الضوئي للاشعه السينيه أن هذه الافلام تحتوي على عنصر المنجنيز نسبه لوجود اوربتال مستوى الطاقه الثاني للمنجنيز. ووجدت أن المنجنيز في حالات الأكسده الثانيه , الثالثه والرابعه في الافلام المحضره.

CHAPTER 1

INTRODUCTION

Twentieth century has seen tremendous growth in the technology owing mostly to silicon based semiconductors. The semiconductor electronics and photonics devices such as computers, cellphones, laser diodes, optical amplifiers and many other devices have revolutionized the world. Semiconductors are based on the manipulation of electric charge of the material. With time the size of the semiconductor devices have reduced to few nanometers whereas the operating frequency have increased reaching a limit where further reduction in size is not possible due to substantial heating of the device during its operation. This limits further advances in technology in semiconductors, hence there is a need to look for a different approach to manufacture high frequency and more efficient devices. A new generation of devices have been proposed where not only charge but also spin degree of freedom of the charge carriers can be exploited, this field is named as spintronics. The devices based on spintronics are anticipated to upgrade the conventional electronics devices in terms of reduced power consumption, faster in speed operation and providing a platform for quantum-computation. The potential examples of such devices include spin-polarized light emitting diodes (LED), spin -field effect transistors (SP-FET) and spin-based qubits for quantum computations. To achieve spintronics based devices we require material that can have spin-polarized carriers and bandgap as well. Ferromagnetic materials are a type of material that have spin-polarized carriers but do not have bandgap hence cannot be used for charge manipulation. A proposed material that can have spin-polarized carriers and a bandgap as well is dilute magnetic semiconductors.

1.1 Dilute Magnetic Semiconductors materials

Dilute magnetic semiconductors are a new class of materials that have been appeared in 1980s [1]. These materials combine both electric and magnetic properties, hence they are both semiconductor and ferromagnetic materials simultaneously, actually they are semiconductors materials slightly doped with one of the transition metals elements such as Mn, Fe, Co, Cr, etc. To make these materials are practically applicable, the origin of ferromagnetism in dilute magnetic

semiconductor, it is imperative should be carrier mediated and have Curie temperature (T_c) well above room temperature [2]. Transition metal-doped (III-V) semiconductor to fabricate dilute magnetic semiconductor was firstly reported in 1980s for investigating ferromagnetism in InMnAs, for this compound low temperature molecular beam epitaxy (LT-MBE) was used as the technique for the growth [1]. Then many other transition metal doped semiconductors have been studied as well, include GaMnSb, GaMnP, GaMnN, CaCrN, InCrN, and InMnN [1]. (DMS) are the best proposed materials for fabricating spintronics devices. They have been appeared through generation after generation in terms of increasing their Curie temperature. The first generation of these materials was in the early of 1980s, this type consists of manganese-doped with the II-VI elements of the periodic table elements. They take the form of $A_{1-x}Mn_xB$ for instance: $Cd_{1-x}Mn_xTe$ and $Hg_{1-x}Mn_xTe$. There were distinct reasons that make these compounds were appealing such as their bandgaps are readily could be tuned just by adjusting the concentration of their compositions. This type of materials are suitable for making heterostructure devices. Furthermore, the property of manganese related electroluminescence was very efficient and making them attractive for optoelectronic applications [1]. But the Curie temperature of the first generation was very low ($T_c \sim 2$ K) as a result, it was not easy job for doping these materials. Practically this generation of materials was not applicable for the mentioned reasons above. These lead to appearing the second generation of them which was in the late of 1980s and until the early of 1990s. this generation consists of III-V group elements semiconductors doped with transition metals developing using (LT-MBE) [1]. They have wide applications in electronics and optoelectronics industries, the manganese acts as acceptor when substituting to III elements. This type has been intensively studied from 1990s until today. The third generation of DMS was emerged in 2000. This class of materials consists of wide bandgap oxides such as ZnO and nitrides like CaN doped with 3d transition metals almost with Mn, Co and Fe. The main distinct characteristic of this generation with the previous two types is the bandgap [2]. The third generation was predicted to have ferromagnetism above room temperature. There were theories and models that were used to study the ferromagnetism for DMS material of transition metals, Zener model and bound magnetic polaron model are the most important ones of them.

Zener model of ferromagnetism description in DMS materials of transition metals is due to exchange interactions between conduction electrons and holes of the transition metals. This model was based on the three ideas. The first one is in isolated atoms, the lowest energy state is given by

electronic states where incomplete d-shell has the highest spin which means that all the spins are aligned in the same direction .The second idea is the exchange integral between d-shell of the adjacent atoms always leads to antiferromagnetic order. The third idea is the energy spin of incomplete d-shell is given by summation spins of the d-shell electrons and conduction electron and it is represented by the following equation:

$$E_{spin} = \frac{1}{2}\alpha S_d^2 - \beta S_d S_c + \frac{1}{2}\gamma S_c^2 \quad (1)$$

Where S_d^2 is the spin exchange interaction between d-shell electrons, S_c^2 is the spin exchange interaction between conduction electrons and $S_d S_c$ is the interaction between d-shell electrons, conduction electrons and α , β and γ are constants [2].

Zener studied ferromagnetism and explained Curie temperature T_c of $Ga_{1-x}Mn_xAs$ and also other compounds from II-VI groups [3]. Later on, Zener model was developed by Dietl for description the ferromagnetism of p-type DMS materials and also used for calculating the curie temperature of DMS materials. Dietl et al. studied ferromagnetism and calculated Cure temperature of Mn-doped InAs and GaAs and observed that its Curie temperature was above room temperature and matched very well with experimental observation done by Ohno et al, but the origin of ferromagnetism was not very clear [2].

Bound magnetic polaron (BMP) model was also used for ferromagnetism description of DMS in transition metals, the diagram representation of this model is shown in the following figure1:

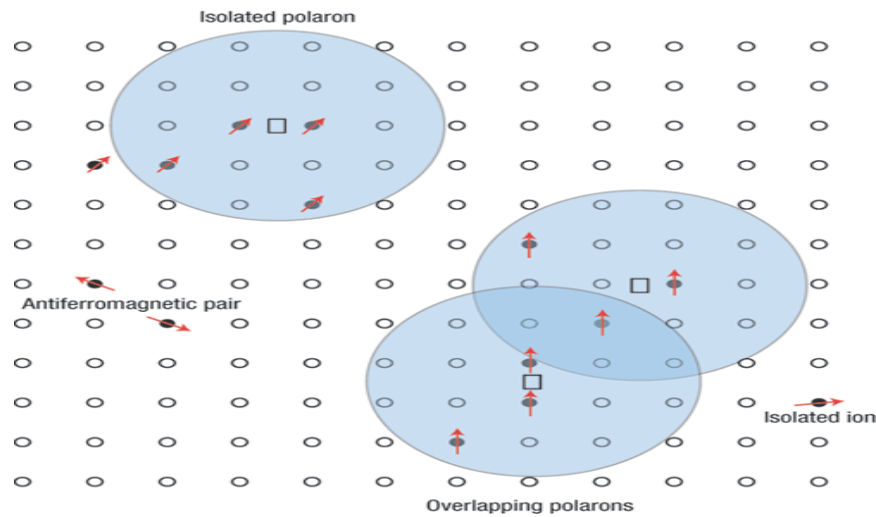


Figure 1: Representation of bound magnetic polaron [4]

The figure1 above, shows the magnetic polaron representation in a semiconductor lattice, where the white atoms are Ga for instance, the black ones are the magnetic atoms like Mn atoms and the square is called unoccupied oxygen or interstitial region just like a defects in the lattice. Also the isolated magnetic polaron can spin independently in any direction with no smooth motion with higher resistance. But after the overlapping of the magnetic polatrons, they all spin in the same direction with smooth motion and lower resistance. We expect to see negative magnetoresistance in this region where the magnetic polarons overlap, where there are enough defects, carrier concentration and polarons. Spinning of the atoms in the same direction means that they are in the ferromagnetic order. BMP is a collection of electrons or holes bound to impurity atoms through the exchange interactions with orbit [4].

Coey developed BMP model for description ferromagnetism of n-type DMS materials of the transition metals, and also for the wide bandgap oxides and nitrides of DMS materials for transition metals. According to BMP model, the materials should have large carrier density and ability of tuning charge carrier spin. Coey examined Mn –doped ZnO thin film using pulsed laser deposition and observed ferromagnetism at the room temperature moments [4].

In this thesis work, manganese doped zinc nitride dilute magnetic semiconductor thin films were prepared and the experimental results of the films were discussed.

1.2 Zinc Nitrides

Zinc nitride (Zn_3N_2) is a binary semiconductor compound that composed of (II-V) groups in the periodic table. Zinc is in the second oxidation state and nitrogen is in the third oxidation state. Zinc nitride has attracted research interest due to its potential use in an optoelectronics ,renewable energy and sensors applications ,in addition to its potential use to prepare p-type ZnO [5].Many properties of zinc nitrides are not yet fully understood because, it is a new material and still on its early stage of the progress. One of these aspects includes its direct optical bandgap which is regarded as one of the most significant keys and important properties of a semiconductor material. However, in the many reports, there were controversy about the exact value of zinc nitrides optical bandgap. In the one hand, Zn_3N_2 classified as a narrow band gap semiconductor due to the existence of the lattice defects which lower the optical band gap by introducing donors states to

electronic structure. In the other hand, it was classified it as a wide band gap semiconductor due to the unintentional formation of the oxide phase which leads to overestimation of the band gap value of this material. The exact and precise value of zinc nitride bandgap is yet to be determined which makes it an interesting material for research interest in semiconductors and thin films technology. There is no argument about the crystal structure of zinc nitride, it was resolved since 1940 to be a cubic anti-bixbyite structure [6]. In the same year 1940, Juza and Hahn were the pioneers who prepared zinc nitride powder samples [7]. The crystal structure of zinc nitride is similar to that of a cubic bixbyite structure material of Mn_2O_3 but the atoms are in the reverse position. Shown in Figure 2 below is the crystal structure of zinc nitride. In this type of the crystal structure the nitrogen atoms are in the eight corners of the cubic in addition to in the six faces of the cubic which form face centered cubic structure (fcc). Zinc atoms occupy the tetrahedral sites in which each of the zinc atom is bonded with four nitrogen atoms [6]. Zn_3N_2 exhibit n-type electrical conductivity and its magnetic properties exhibit non-magnetic order. The value of zinc nitride density is 6.46 g/cm^3 while its lattice parameter is $9.73 \text{ \AA}$ with the volume equal to $921.57 \text{ \AA}^3$, and this value of the lattice parameter of zinc nitride is comparatively enormous when compared to the lattice parameters of the other semiconductor materials such as zinc oxide ($a=4.56 \text{ \AA}$) and also it has high charge carrier concentration and this value of the charge carrier concentration which reported is in the range of $10^{19} - 10^{20} \text{ cm}^{-3}$ with the mobility of the charge carrier in zinc nitride thin films is between 33.18 to $2.30 \text{ cm}^2 / \text{V.s}$ with low resistivity which is in the range of $10^3 - 10^{-2} \text{ \Omega.m}$ [8]. There are various experimental techniques for preparing zinc nitride thin films such as pulsed filtered cathodic vacuum arc deposition, molecular beam epitaxy, chemical vapor deposition, physical vapor deposition and sputtering processes. Muhammad Baseer Haider prepared six samples of zinc nitride thin films on fused silica (quartz) substrates at the same time using radio frequency reactive magnetron sputtering of zinc target at 150 watts of the RF sputtering power in the presence of argon and nitrogen gases. He investigated the effect of the thermal oxidation on the electrical, optical and chemical properties of zinc nitride thin films. He found that the bandgap of the film is 1.85 eV , and it was increasing with the increasing temperature during annealing process like increased from 1.9 eV at 300°C up to 3.2 eV at 700°C [5]. Trapalis et al. prepared zinc nitride thin films on different wafers: glass, quartz, sapphire and silicon substrates by using DC sputtering process of the zinc target in the presence of the nitrogen plasma under the various of the different growth condition. The thin films were

investigated with the variety of characterization techniques. They applied a combination of physical electrical and optical characterization techniques to all of their grown thin films. They found that the bandgap of the films are in the range of 1.31 – 1.48 eV [9]. Here in this work, for the spintronic applications purposes, we prepared zinc nitride thin films samples by using DC/RF reactive magnetron sputtering of the metals zinc and manganese targets respectively in the presence of argon and nitrogen gases. After the growth we studied the structural ,optical,electrical,magnetic ,surface and chemical properties of the prepared thin films by using a combination of different characterization techniques which are discussed here in this these work.

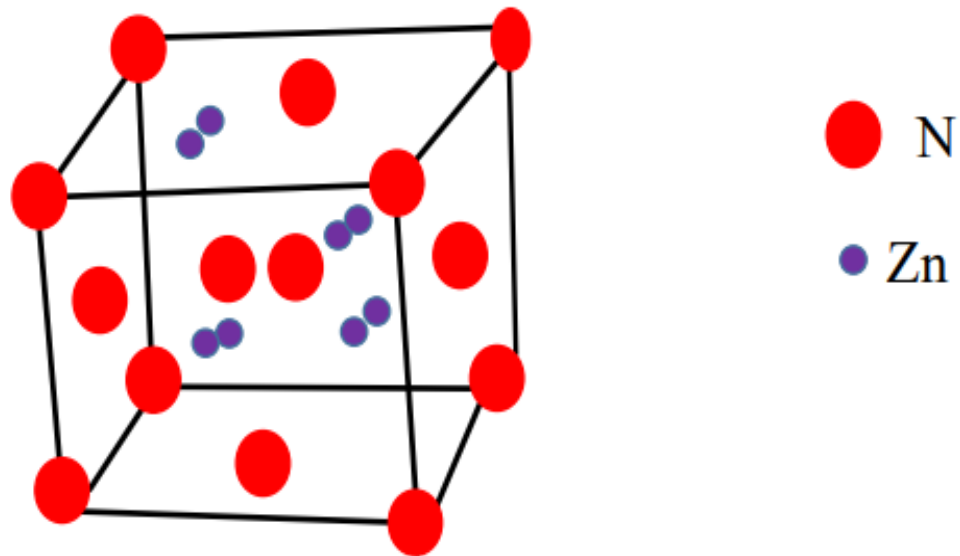


Figure 2: Crystal structure of Zn₃N₂.

CHAPTER 2

LITERATURE REVIEW

In 1990, Ohno et al have prepared manganese doped indium arsenide ($\text{In}_{1-x}\text{Mn}_x\text{As}$) thin films by using low temperature molecular beam epitaxy technique. They found that the samples had ferromagnetic order up to 35K Curie temperature and this was coincided with the emergence of the second generation of the dilute magnetic semiconductor (III-V) and the successes of the growth of ($\text{In}_{1-x}\text{Mn}_x\text{As}$) by resulted in progressing of manganese doped GaAs ($\text{Ga}_{1-x}\text{Mn}_x\text{As}$) even with the higher Curie temperature [10].

In 2003, Saito et al have prepared ZnCrTe dilute magnetic semiconductor thin films and they reported its ferromagnetic order at the room the temperature [1].

Volkan Şenay et al have grown zinc nitride (ZnN) thin films on two glass substrates (75mm x 25mm x 1mm) using reactive radio frequency magnetron sputtering for 60 minutes at room temperature. They investigated its optical and surface properties using UV-Vis spectrophotometry and atomic force microscope respectively. They discussed the effect of the film thickness on the optical properties [11].

Despite having a high curie temperature, Mn-doped Ga As ($\text{Ga}_{1-x}\text{Mn}_x\text{As}$) was developed as a result of the success of $\text{In}_{1-x}\text{Mn}_x\text{As}$ using (LT-MBE) technique for the growth. GaAs and InAs are well-known III-V semiconductors with several uses in the electronics and optoelectronics industries, making them especially appealing for the application [10].

Matsumoto et al has prepared Co-doped TiO_2 thin films and they found that it had ferromagnetic order at high Curie temperature also high levels of p-type Mn doping in ZnO. GaN were anticipated by Dietl et al. to reach Curie temperatures above room temperature, and wide-gap dilute magnetic semiconductor materials have been shown to exhibit ferromagnetism both at and above room temperature. Particular focus was paid to the materials Mn and Fe-doped GaN and Co and Mn-doped ZnO. Even in the absence of further carrier doping [10].

In 1990s, Matsumoto et al have prepared cobalt doped TiO_2 thin films and they reported that it had ferromagnetism at high Curie temperature for the first time and also Dietl et al predicted that semiconductor with highly p-type manganese doped and wide band gap materials ZnO and GaN could be obtained with the ferromagnetism above room temperature. The materials p-type like cobalt and manganese doped zinc oxide and manganese and iron doped GaN had received a particular attention [10].

In 1996, Ohno et al has prepared $\text{Ga}_x\text{Mn}_{1-x}\text{As}$ and they found that it had 60K Curie temperature and it was showed a huge progress in achieving Curie temperature which was higher than what was reported for transition metal doped (II-VI) generation of dilute magnetic semiconductor which was showed low Curie temperature about ($T_c \sim 3\text{ K}$). Generally, the magnetism of transition metal doped for (II-VI) generations of dilute magnetic semiconductor was explained by sp-d exchange interaction which takes place between d-shell electrons in the magnetic ions and s-p shell electrons in the host semiconductor materials resulted in the generation of the observed magnetism and this is known as sp-d exchange interaction theory [1].

Ando et al has prepared and reported strong magnetic hysteresis loop in GaN: Mn at Curie temperature 300K using superconductor quantum interference device (SQUID) measurement and considered as ferromagnetic dilute magnetic semiconductor [1].

Sato et al. and Dietl et al. reported ferromagnetism at ambient temperature in P-type materials and in ZnO and GaN, respectively [10].

In 1989, Munekata et al have prepared InMnAs thin films using low temperature molecular beam epitaxy technique and they found that it had ferromagnetic order at high Curie temperature [1].

In June 2005, Haider et al have grown Cr-doped GaN thin film on sapphire substrate (0001) at temperature of 650 and 700 $^\circ\text{C}$ using radio frequency N-plasma molecular beam epitaxy (N-plasma-MBE). They reported the study of chromium doped gallium nitride (CrGaN) and the surface morphology of the film by using atomic force microscope (AFM) of Ga-rich GaN growth surface. They found that N-rich and metal-rich growth conditions resulted in room temperature ferromagnetism. Also they discussed the influence of Cr on the surface reconstruction and the influence of annealing on the properties of the CrGaN thin film and they investigated how the structural and magnetic properties of (CrGaN) rely on the condition of the growth thin film [11].

Lee et al, have prepared (CrGa₂N) thin films on sapphire substrate and reported the ferromagnetic order in the samples of chromium doped gallium nitride (CrGa₂N) for Curie temperature up to 320K using ion implantation of chromium [11].

Park et al. have prepared and reported the order of ferromagnetism in single crystal grown of chromium doped (CrGa₂N) thin films at Curie temperature $T_c = 280\text{K}$ using the method of sodium flux [11].

Hashimoto et al. have prepared and reported the order of ferromagnetism in chromium doped gallium nitride (CrGa₂N) samples grown on sapphire substrate (001) above the room temperature using the method of electron –cyclotron-resonance plasma assisted molecular beam epitaxy (ECR-MBE) [11].

Liu et al. have prepared and observed the order of ferromagnetism in chromium doped gallium nitride (Cr-Ga₂N) thin films above Curie temperature 900K using the method of reactive molecular beam epitaxy [11].

Nanke Jiang et al. have grown and discussed the computational study of pure zinc nitride thin films and its native points defects and dopants Cu, Ag and Au. They investigated the atomic geometry, formation energy and the electronic structure of the defects in zinc nitride and computed the lattice constants of zinc nitride films and found that to be equal $9.839\text{\AA}$ which is close to the exact value of the lattice constant which is $9.76\text{\AA}$ [12].

Trapalis et al. have prepared zinc nitride thin films on different wafers: glass, quartz, saphair and silicon substrates using DC sputtering of the zinc target in the presence of the nitrogen plasm under various of the different growth condition, the films were resulted with variety of compositions and he applied combinations of physical, electrical and optical characterization techniques to all of the growth thin films [9].

Nanke Jiang et al. have deposited zinc nitride thin films on glass and silicon substrates which were mounted on the rotating holder at 10cm distance from the zinc target and the substrates temperature was controlled up to 400C° at the base low pressure in the range of 10^{-4} Pa he maintained by dry mechanical pump and turbo molecular pump using radio frequency magnetron sputtering by sputtering zinc target of 3-inch diameter and 99.995% purity, Kurt J. lesker company for five minutes. RF sputtering power was 80 watts in the presence of nitrogen gas and using argon gas with 1% oxygen to obtain zinc oxyntride in the controllable way. They investigated the effect of

the different nitrogen concentration and the substrate temperature on the grown thin films and also he investigated the crystallinity of the film with XRD [13].

V. Kambilafka et al have grown zinc nitride thin films using radio frequency magnetron sputtering by sputtering zinc nitride target with argon gas and then nitrogen gas. They found that the films which grown by argon gas were opaque and conductive because of the excess of more zinc atoms in the structure of the films and the process of annealing the films were transparent and stoichiometric. After further annealing the electrical properties of the films were deteriorated and the films which grown by nitrogen gas were transparent but they were resistive even after the annealing process. Then they converted both types of the films into p-type ZnO by thermal oxidation at 400 °C and then he investigated the effect of nitrogen on the properties of zinc nitride thin films and their conservation into p-ZnO: N thin films. They examined their properties after annealing up to 550C in the nitrogen and oxygen environment [14].

Haider et al have grown six samples of zinc nitride thin films on fused silica (quartz) substrates at the same time using radio frequency reactive magnetron sputtering of zinc target at 150 watts of the RF sputtering power in the presence of argon and nitrogen gases. They chemically cleaned the substrates using sonicating first by acetone and isopropanol. Finally dried them in air before placing them into the sputtering chamber growth which he evacuated it into the pressure of 1.0×10^{-3} Pa then he introduced 20 (sccm) standard cubic centimeter per minute of argon gas into the sputtering chamber, pre-growth he treated the substrates by heating them up to 500C°, the plasma formed at DC power supply of 20 watts. They reduced the temperature into 300C° and the argon gas flow rate into 10 sccm and introduced nitrogen gas of 99.999% purity at the flow rate of 6 sccm. During the growth the chamber pressure was about 3.0×10^{-1} Pa with rotating the substrates at 6 round per minute (rpm) for about two hours of the total growth time. They investigated the effect of thermal oxidation on the electrical, optical and chemical properties of zinc nitride thin films. After the growth of the samples they annealed them in the presence of oxygen ambient in order to convert n-type zinc nitride film into p-type zinc oxide thin films. They performed systematic depth profiling x-ray photoelectron spectroscopy (XPS) for studying of the growth films and the thermally oxidized zinc nitride thin films [5].

Toyoura et al. have prepared zinc nitride thin films by means of the direct chemical reaction between zinc and NH_3 then they annealed the films in the presence of nitrogen and NH_3 . They found that the optical band gap of the grown films in the range of 3.2 eV and this was at the Curie temperature of 300K [5].

Kambilafka et al. have fabricated zinc nitride thin film by using reactive sputtering of the zinc nitride target in whether with pure argon gas or pure nitrogen gas in the ambient and found that the optical band gap of the films to be about 3.4 eV. There was a huge variation in the reports about the optical bandgap values of zinc nitride thin films ranging from 1.1 to 3.2 eV [5].

H. Ohno; A. Shen et al have successfully grown a new $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ -based of III–V alloys dilute magnetic semiconductor materials thin films using molecular beam epitaxy technique with different concentration from $x = 0.015$ to $x = 0.07$. By using XRD. They investigated that the lattice constant of the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ thin films increased linearly proportional with the increasing of manganese concentration in the film, by using superconducting quantum interference device measurement. They observed ferromagnetic order at Curie temperature about 60K. They used magneto transport measurement and Hall effect measurement revealed that the concentration of holes to be in the order of manganese concentration [15].

Yuji Matsumoto et al have prepared and reported his observation of the transport in the ferromagnetism of cobalt doped anatase thin films with different concentration of cobalt between zero and eight percent. They also observed the structure of magnetic domain in the thin films with magnetic microscope image which showed the existence of long range ferromagnetic order above room temperature with magnetic moment about 0.32. They also showed that the thin films were electrically conductive and exhibit positive magnetoresistance of about 60 percent at Curie 2K. They took a series of magnetic images using the scanning of superconducting quantum interference device (SQUID) measurement at Curie temperature of 3K for the anatase thin films with different concentration of cobalt doping [16].

Takahiko Sasaki et al .have prepared manganese doped gallium nitride (GaMnN) thin films by using molecular beam epitaxy technique and considered a tentative model based on the band theory of ferromagnetism in dilute magnetic semiconductor which was introduced by Sato and Katayama for discussing his obtained experimental results and he investigated the transport characteristics

and the magnetism on high Curie temperature ferromagnetic of manganese-doped GaN thin films [17].

Lei Zhang, et al have prepared B and gallium cobalt-doped ZnO (BGZO) thin films using radio frequency magnetron sputtering technique. Then they investigated the effects of substrate temperature on the optical, electrical structural and morphological properties of B and gallium cobalt doped ZnO thin films. From XRD data they revealed that the deposited thin films were textured along c-axis and maintained the symmetry of the crystallinity. As he increased the temperature of the substrate up to 200 °C, the thin films crystallinity were more improved and the crystallite sizes also became much larger. And at the substrate temperature of about 200 °C, the films showed lower resistivity, higher Hall mobility and higher optical band gap. He also observed that all films showed high transparency in the visible range (400–800 nm), which did not change obviously with the temperature of the substrate. They investigated the effect of substrate temperature on the properties of B and gallium cobalt-doped ZnO thin films prepared by using radio frequency (RF) magnetron sputtering [18].

Z. Yang et al .have prepared (MnZnO) manganese –doped zinc oxide diluted magnetic semiconductor thin films by using plasma-assisted molecular-beam epitaxy technique on sapphire substrate. The films showed ferromagnetic order at the highest saturated magnetization which was happened at temperature of 700 °C and the Curie temperature of manganese doped zinc oxide dilute magnetic semiconductor was above the room temperature and the order of the ferromagnetism was weakly anisotropic .Before transferring into molecular beam epitaxy growth chamber. They chemically cleaned the substrate with hot up to temperature about 150 C⁰ aqua regia solution for twenty minutes. They rinsed with de-ionized water the dried it with the nitrogen gun. They applied x-ray photoelectron spectroscopy for identification the elemental composition of the thin films and estimation the quantity of manganese concentration in the samples and also he performed advanced X-ray diffractometer for investigation the crystallinity of the grown thin film deposited [19].

Dan Li et al have grown ferromagnetic manganese doped titanium nitride thin films by using the plasma assisted molecular beam epitaxy technique. They investigated that the post preparation of the annealing treatment in the plasma of nitrogen vacancies defect improves manganese incorporation on the titanium lattice sites when the magnetization of the sample increased .Also he investigated that the magnetization of the sample could be activated using plasma implantation

by reducing the nitrogen vacancy and this reducing of the nitrogen vacancy defects leading to the improvement of the ferromagnetic order of the samples [20].

T. S. Herng et al. have fabricated carbon doped zinc oxide ZnO: C thin films by using ion beam method, he found that the thin films exhibit Curie temperature above the room temperature. The magnetization moment of the films was $1.35 \mu_B$ per the atoms of carbon. They investigated that the electrical conductivity of the films was p-type containing about $5 \times 10^{17} \text{ cm}^{-3}$ concentration of the holes and anomalous of the Hall effect .They found that the magnetoresistance of the carbon zinc oxide film can be detected and the properties of the magnetoresistance for the films indicated that it contained spin polarized charge carriers [21].

Yu Kumagai et al have studied band gap variation in Zn_3N_2 due to point's defects and charge carriers from the first principles. They found that the band gap increased from 0.85 to 3.2 eV based on Burstein-Moss effect phenomenon [22].

CHAPTER 3

EXPERIMENTAL TECHNIQUE

3.1 Sputtering Process

There are many techniques that are used for thin films deposition, some of them are chemical methods such as chemical vapor deposition while others are physical methods for example physical vapor deposition, molecular beam epitaxy and sputtering process. In this work we used the sputtering process system in which the atoms of the material target is removed by the kinetic energy of inert ions (high energetic ions), and the resultant thin film is plasma-based deposition. There are different types of sputtering systems; DC sputtering, RF sputtering and magnetron sputtering. In DC sputtering, only electrically conductive materials; mostly metallic targets and doped semiconductors can be sputtered, while the non-conducting materials cannot be deposited using DC sputtering power since non-conducting coating on the target material prevents the electrons flow through the anode and leading to the charge build-up and this will stop the sputtering process with the time. In RF sputtering, the plasma will be created using radio frequency sputtering power instead of DC sputtering power. Both conductive and non-conductive materials can be deposited as there will be no charge build-up in the target material. In magnetron sputtering, the magnetic field is applied in addition to the electric field to increase the flux of inert ions without increasing the pressure. The magnetic field will be perpendicular to the electric field and parallel to the substrate. Under the influence of magnetic field, the electrons will spiral around the magnetic field and there will be more collisions of electrons and inert ions. Hence more ionization and produce high density of plasma containing high density flux of ions maintain greater sputtering of atoms and the result will be high growth rate yield of the thin film deposition.

3.2 The principle of Sputtering System

The general principle of the sputtering process is based on the interaction between the high energetic ions (inert gases ions) and the surface of the target material used. The idea of using inert gas is that it is low reactivity and has high sputtering yield and this process will be carried out under the high vacuum closed chamber with working pressure about 10^{-5} Torr. In this process, the deposition chamber is evacuated by pumping it down until the working pressure which is around 10^{-5} Torr. Then it will filled back by sending the argon and nitrogen gases into the vacuumed

sputtering chamber. Negative potential difference will be applied between the target and the gun (anode). The electrons in the atoms of argon and nitrogen gases gain kinetic energy from the applied potential difference and they kick out from the atoms. Then argon became positive ions and these positive ions will be attracted by the negative target material used. Actually plasma will be generated here is a mixture of argon and nitrogen gases. After the plasma hitting the target material ejects atoms from the target, and these atoms will be deposited onto the substrate and growth the intended thin film. Figure 3 below show the schematic diagram of the sputtering system.

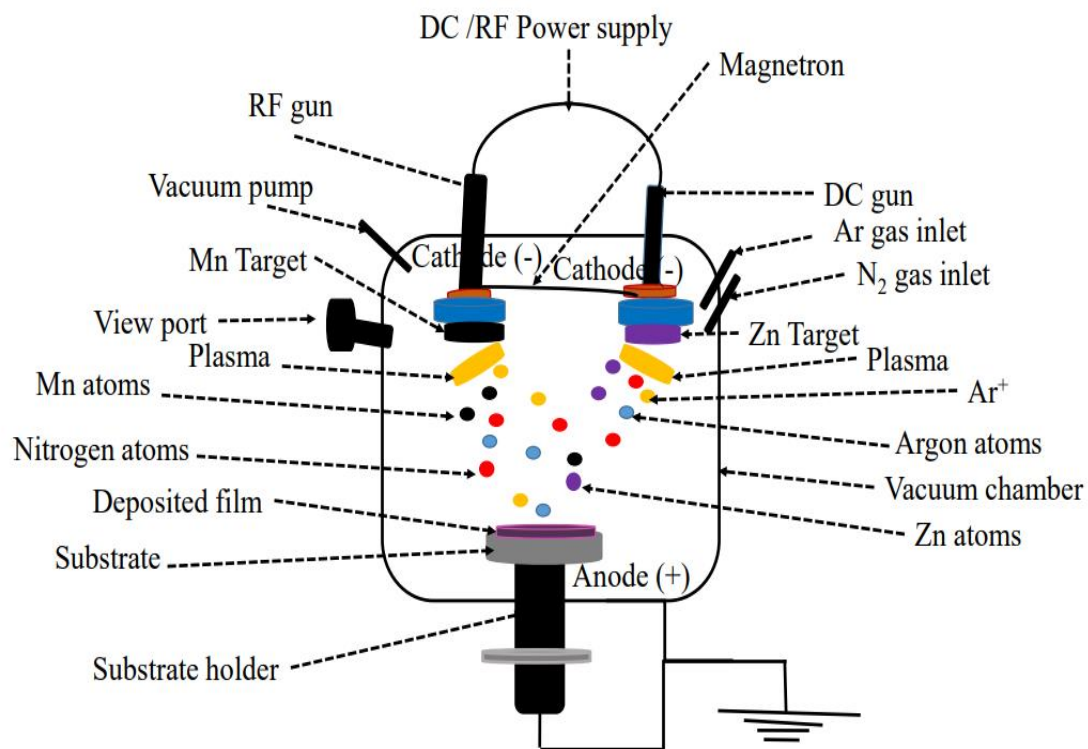


Figure 3: Schematic diagram of the sputtering system.

Below are the experimental techniques that we used them for the characterization of the deposited thin films:

3.3 X-Ray Diffraction

X-ray was discovered in 1895 by German physicist Wilhelm Rontgen and X-ray ray diffraction is the basic technique that based on the X-ray in its operation and it is used to study and identify the crystal structure of the material under the study whether it is crystalline or amorphous structure .It is regarded as fingerprint for any crystalline material . Also it used to investigate the lattice parameters and the interplanar spacing between the parallel crystal planes of atoms or ions. Currently, XRD is very important technique and used in many fields such as physics, chemistry and biology for studying the crystal structure of different compound materials. Basically, XRD is used to study the crystalline materials with the surface depth about 10µm and from the crystalline material and by identifying the lattice parameter (a), and using the Bragg's law the d-spacing between the planes of the crystalline material can be determined. Then the corresponding Miller indices can be found using equation 3 below. The pattern results of XRD give us the intensity (I) versus diffraction angle (2θ) and the interaction between X-ray monochromatic beams. The sample of the material result in constructive interference in which the diffracted waves will be in phase and this happens when the Bragg's formula is satisfied. The main purpose of using XRD here is to check the crystallinity of the prepared samples.

Bragg's Law:

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

Where λ is the wavelength of the XRD anode material which is constant (1.5406 Å for CuKα). Therefore, we can find the Miller indices of our material using the following relation in the case of cubic crystal structure:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3)$$

XRD technique is independent on the state of the material.

3.4 Principle of X-ray diffraction

As mentioned earlier x-ray diffraction is versatile technique for the crystalline materials, so it is also dependent on the constructive interference of the monochromatic X-ray beam which interacts with the material sample. Figure 4 illustrates theta to two theta scan of X-ray diffractometer instrumentations.

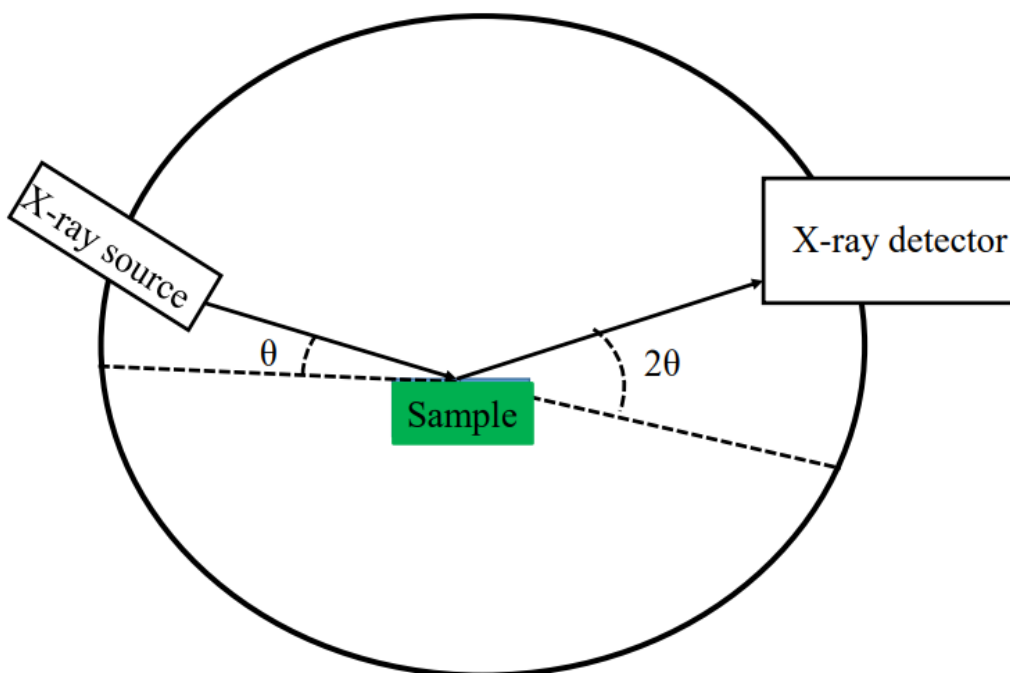


Figure 4:X-ray instrumentation.

In the X-ray instrumentations, the apparatus of XRD are generally consist of the source of x-ray, the generator which is used to generate x-ray, the detector which is associated with the electronics, diffractometer which is mechanical system that is used to orient and hold the sample for enable the detector to measure the scattered x-ray around the sample and the computer which is regarded as the control unit to conduct the experiment and also to prepare data file for the post-processing. The most common materials that are used for x-ray targets are Mo, Cu, Cr and Co. The accelerating

voltage is in the range of 40- 80 KV which is corresponding to 50-25 mA current. The powder x-ray voltage tube requires higher voltage for generating, the main function of the detector is to convert x-ray voltage into the current, then into the pulse of voltage which will be counted electronically. The ideal detector responds only for the characteristic x-ray wavelength used.

3.5 UV-Vis Spectrophotometry Technique

Spectrophotometry is a technique that used for analyzing the intensity of the incident light at the preferable specific selected wavelengths by estimating the light intensity as a function of the wavelength and used for studying the optical properties of the specimens. The main reason for using UV-Vis spectrometry is to measure the transmitted light from the samples. This technique depending on light quantity that emitted by the analyzed specimen. The charge–coupled device are used to detect the incident intensity of light and the result will be shown in the graph on the display unit. The major constituents of the spectrophotometry are represent in 1. The first one is the source of light: this is the most important component that used to provide the light with multicolor to the monochromator that will diffract light and it is rely on the kind of spectrophotometry instrument used for the characterizations. For instance in the ultraviolet light, the prevalent light sources used in the device is represented in the lamps of deuterium and hydrogen, and in the visible light, the dominated one is the filament of tungsten and carbon lamps, and in the infrared one, the prevalent one is the Global and glower Nernst. 2. Monochromatic: It is the second component of the UV-Vis spectrophotometry and it separates the light of multicolor into different and single wavelengths and these wavelengths have small bands. 3. Sample holder: It is responsible for the holding the specimen and make the particular wavelength for passing via itself due to its transparency and it is the third component .4. Detector It is the fourth component and very sensitive for detecting the light .5. display device: It the fifth component and its responsibility is interpreting the signals after detecting [23].

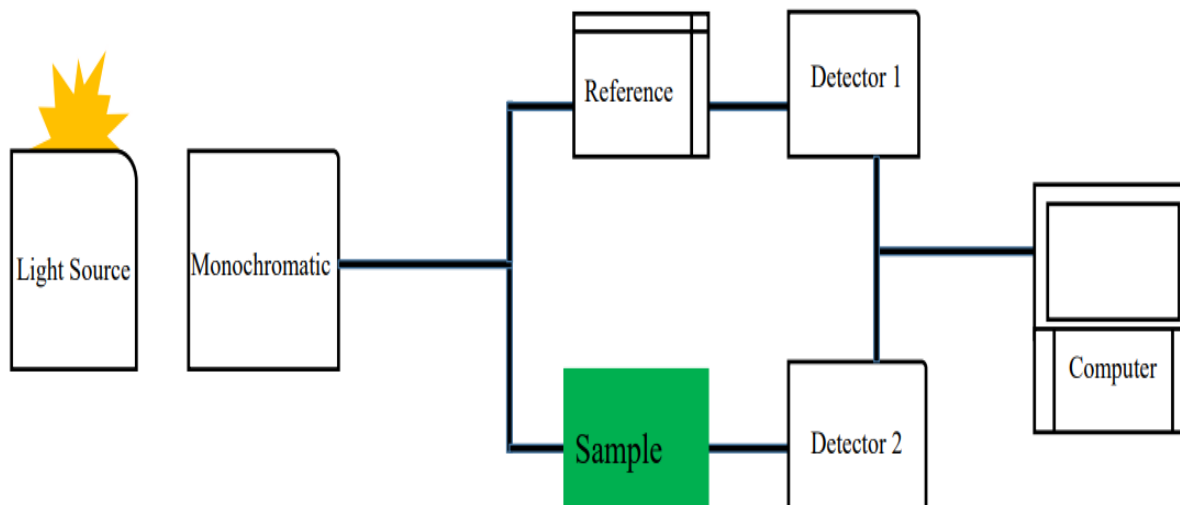


Figure 5: Instrumentation of UV-Vis Spectrophotometry.

Advantages of UV-Vis spectrophotometry: Cheaper and very sensitive for the light. Disadvantages of UV-Vis spectrophotometry: Spectrophotometer of one beam is not suitable because of the following reasons:

- Take time for the analysis, has fluctuation in the circuits of electronics and voltage.
- Spectrophotometry has two types according to their beams.

3.5.1 Spectrophotometer of one beam

Allows one beam to go via the specimen in the holder and the reference sample will be used for the standardization and the transmittance or absorbance light of the reference will be subtracted from the specimen.

3.5.2 Spectrophotometer of two beams

In this case one of the beams go to the reference while the other go to the specimen and both of the beams will be compared [23].

3.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is also called electron spectroscopy for chemical analysis (ESCA) is a technique used to investigate the chemical composition of the material surface and it is based on the principle of photoelectric effect which is discovered by Hertz in 1887 and later

enhanced by Siegbahn who was won 1981 Nobel prize in physics for his work for developing the XPS technique. The interactions of XPS take place between the incident X-ray photons and the surface atoms of the material used in the experiment and which will lead to the emissions of the photoelectrons. These electrons called photoelectrons because they are emitted due to the photons, the generated photoelectrons have kinetic energy given by Einstein's equation:

$$E_k = h\nu - (E_B + \phi_s)$$

Where E_k is the kinetic energy of the photoelectron, E_B is the binding energy and ϕ_s is analyzer (spectrometer) work function. The main reason of using XPS is to check the elemental composition of the samples and to find their oxidation states. By using XPS spectroscopy we get the following information from the studied material: elements compositions and chemical bonding information. XPS spectroscopy detect all the chemical elements except He and H due to the dependence of incident photons on the interactions with the core electron of the material sample and in He and H atoms no core electrons exist. Ultra high vacuum is required for operating XPS technique to reduce the contamination and prevent the scattering of ions from its path in the chamber, figure 6 illustrates XPS instruments.

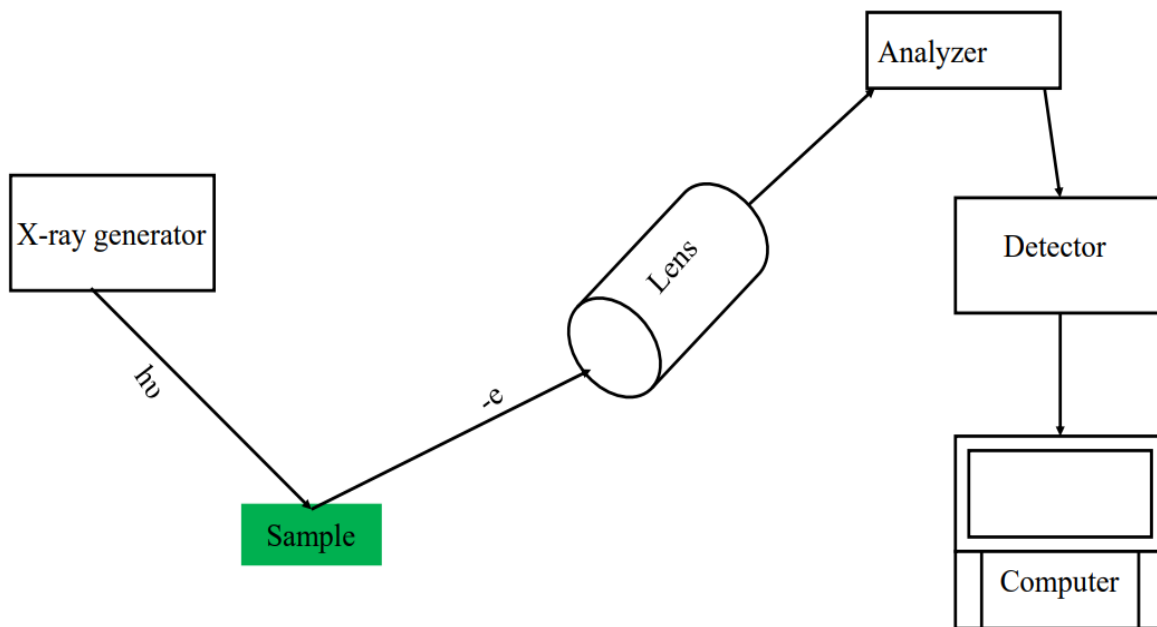


Figure 6: Illustration of XPS spectroscopy.

3.7 Atomic force microscope

In order to develop the materials and comprehend their physical nature and properties, we need to know and understand what happens inside the materials and understanding their characterizations and structures. AFM is one of the innovative technique that is used for the mapping surface topography of the materials, characterizing and studying the materials at the atomic levels. It is introduced in the beginning of 1986 by Gerd Binnig as a result of extending for scanning tunneling microscope (STM) for characterizing the non-electrical conductive samples hence it covers the limitations of STM because STM was dedicated only for investigating the surface of the conductive materials like metals and doped semiconductors while AFM investigates both of the conducting and non-conducting materials. This technique plays very important role and applied in many fields such as physics, chemistry, for studying semiconductors in electronics industry and material science. AFM is a three dimensional image technique that is used for map the surface imaging topography and providing the information in three dimensions. Understanding properties

of the sample on the nanoscale level and force measurement. The main reason for using AFM is to study the roughness of the films. Figure 7 shows the instrumentations of AFM.

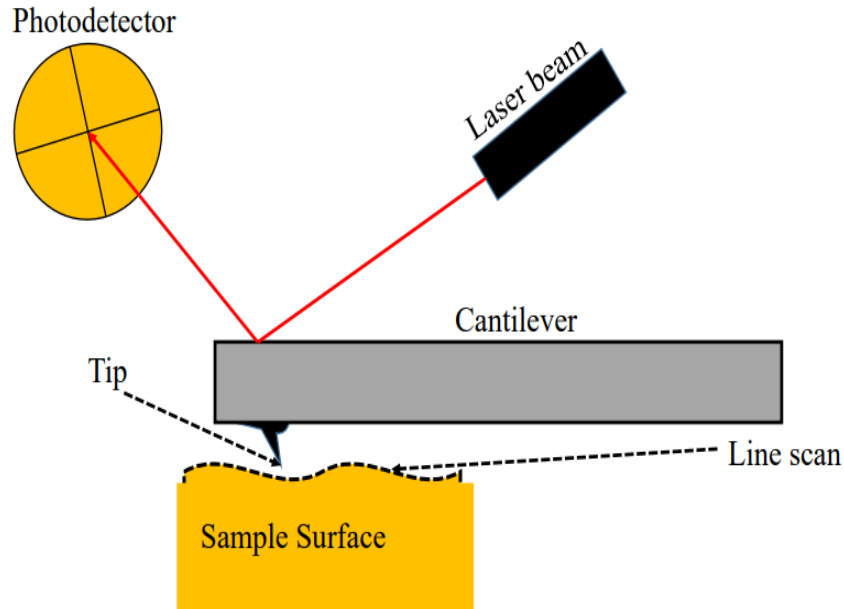


Figure 7: Schematic diagram of AFM instrumentations.

In this technique, laser beams incident into cantilever and reflected into photodetector for analyzing the beam. The basic function of the tip on the cantilever is to interact with the sample and results into the repulsive or attractive force. Therefore, the force gives us the information about the sample topography and these interactions depend on the positions between the sample and the tip. When they are near to each other the attractive force deflects the cantilever near to the specimen and when they are in contact then the repulsive force deflects the cantilever far away from the specimen and cantilever represents as the sensor of the force and these deflection can be detected by the laser beam. The detector is used to register changes that are happened by the deflection and magnifies it.

These deflections, the piezoelectric xyz scanner is moving between the specimen and the tip, then it allows us to make three dimensional image. Generally, AFM works on different modes contact

mode (static mode), tapping mode and dynamic mode (non-contact mode). There is a dominator force for them, in contact mode there is repulsive force while in non-contact mode the attractive force can be seen [24]. The comparison between these modes is showed in the table 1 below:

Table 1: The comparisons between AFM modes.

Type of operation mode	Contact Mode	Non-contact Mode	Tapping Mode
Principle of working	The tip and the surface of the sample will be in contact	There will be no contact between the tip and the surface of the sample	Brief and intermittent touch between the tip and the surface of the sample
Advantages	High scan speed and high resolution	No damage to the sample	High resolution and minimal damage to the sample
Disadvantages	Distorts the soft samples	Low scan speed and low resolution	Scan speed is lower than contact mode and higher than non-contact mode

3.8 Hall Effect Measurement

Hall Effect is a technique that used to identify the charge carriers concentration and its mobility for semiconductor materials. It is considered as the basic concept in solid state physics and effective tool for characterizing the materials especially semiconductors. It was discovered by Edwin Herbert Hall in 1879 during his studying on his PhD's degree at the university of Johns Hopkins in Baltimore, Maryland, USA. In Hall Effect measurement, when a conductor carrying an electric current and placed in the magnetic field which is perpendicular to the direction of current the corresponding electric field will be generated perpendicular to both of the current and magnetic field. Therefore, this field called Hall field and the corresponding effect is known as Hall effect. The existing of the magnetic field will generate Lorentz force on the electron because of moving electron in the direction perpendicular to both magnetic field and electric current. The

charge carriers will be deflected in a certain direction due to applied magnetic field. The potential difference across the conductor or semiconductor will be measured. The main reason for using Hall effect measurement is to identify the type of material used based on their electrical properties and to measure their carrier concentration. The diagram of Hall effect measurement is illustrated in following figure 8 below.

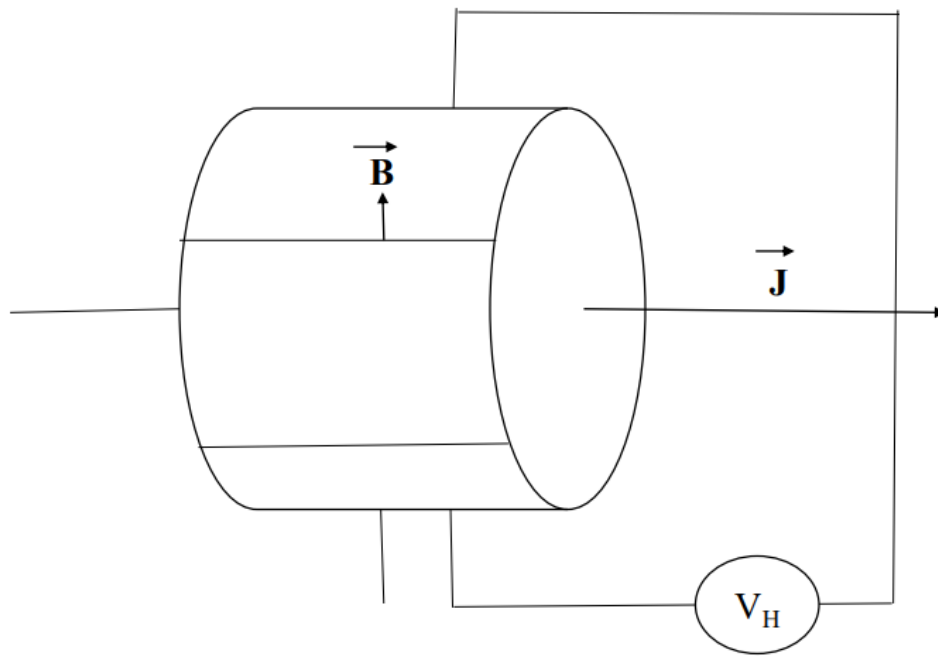


Figure 8: Schematic diagram of the Hall Effect Measurement.

Hall Effect is used for the following purpose:

3.8.1 Identifying the type of semiconductor material.

If the coefficient of Hall effect is positive, then the semiconductor is p-type and if it is negative then the semiconductor is n-type, and this coefficient theoretically can be found from the following equation:

$$R_H = \frac{1}{nq}$$

Where R_H is the Hall coefficient, n is the number of charge carrier concentration and q is the charge for carriers; q is negative for electron and positive for holes.

3.8.2 Determination of the charge carrier concentration

By identifying the Hall voltage and the Hall constant the charge carrier's concentrations of electrons in n-type semiconductor can be measured. Hole's concentrations in p-type semiconductor also will be determined, the Hall voltage will be found theoretically from this equation:

$$V_H = \frac{iBR_H}{d}.$$

Where d is the thickness of the Hall strip, V_H is the Hall voltage, B is the applied magnetic field, i is the electric current and R_H is Hall coefficient.

3.8.3 Measuring of charge carrier's mobility.

3.8.4 Measuring Hall coefficient [25].

3.9 Magnetoresistance measurement

Magnetoresistance is defined as the changing in the electrical resistance of the material with the applied magnetic field. Magnetoresistance measurement known as one of the common techniques that used to investigate the existence of magnetization in the sample by measuring its resistance as a function of a temperature. The measurement will be carried out in closed cycle cryostat connected to helium compressor in a four wire probe technique at cryogenic temperature with the help of temperature controller for recording the temperature. The sample will be placed inside the cryostat and the cryostat will be confined in the external magnetic field. There is a computer connected to the experiment for running the system and conducting the experiment. There are two different kinds of pumps: mechanical pump and diffusion pump for evacuating the system. Mechanical pump or rough pump firstly, helps in taking the system up to about 10^{-2} mbar and then secondly, operating the diffusion pump for evacuating the system up to 10^{-6} mbar. There is a constant current source for measuring the current passing through the sample and a constant voltage source for measuring the potential difference between the two terminals points of the sample. With using this technique, the resistance of the sample could be measured at different temperature values from room temperature to lower temperature values with applied and without applied magnetic field.

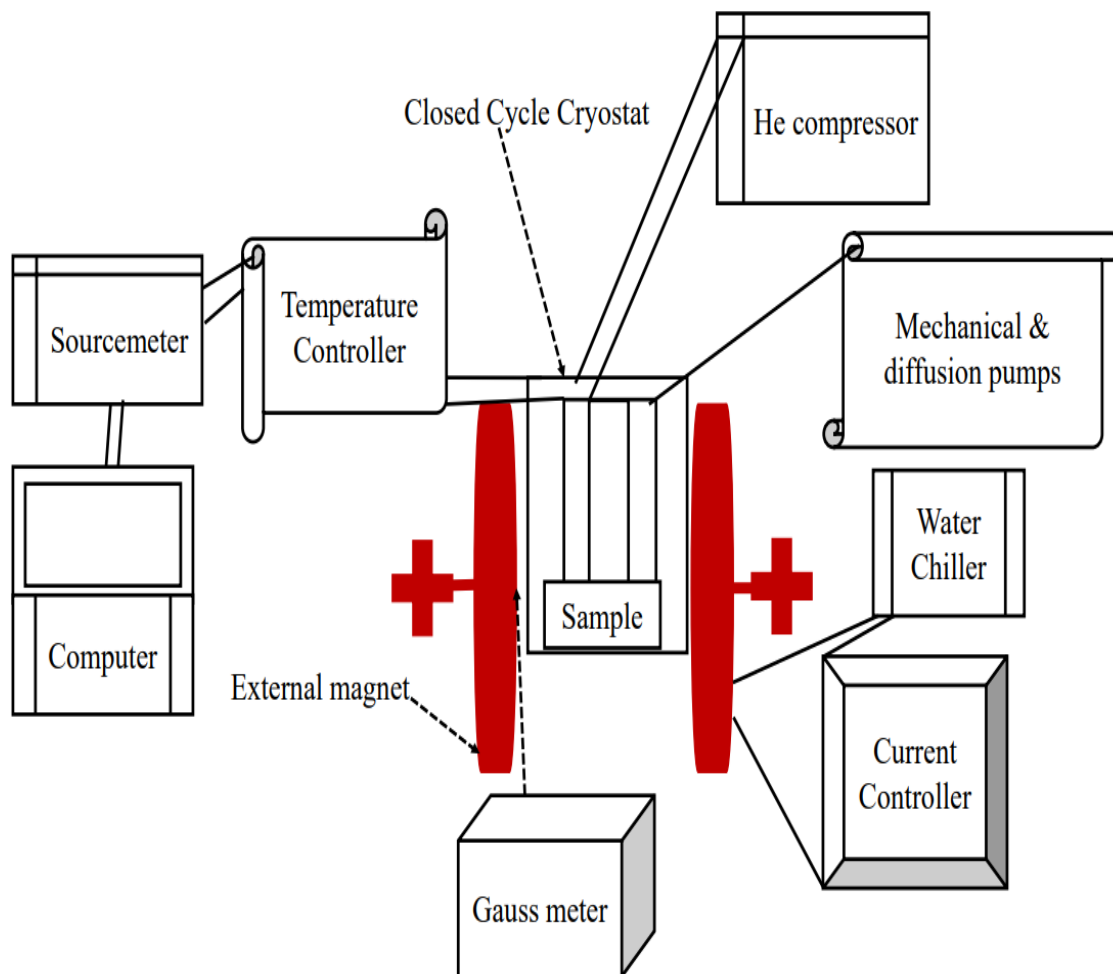


Figure 9: Setup of magnetoresistance measurement.

3.10 Objectives

The overall objectives of this work are

1. To grow pure zinc nitrides thin films using RF/DC magnetron sputtering to find the optimal growth condition of a pure zinc nitride thin films.
2. Grow manganese doped zinc nitrides thin films with different concentration of manganese.
3. Study the effect of manganese doping concentration on the surface morphology, structural, chemical composition, optical, electrical and magnetic properties of the grown films using atomic force microscopy, x-ray diffraction, XPS, UV-Vis spectrophotometry, Hall effect, and magnetoresistance measurement respectively.
4. Study the magnetic properties of the grown films using magnetoresistance measurement and study the effect of manganese concentration on the magnetism of the films and investigate the origin of magnetism.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Experimental

Manganese doped Zn_3N_2 thin films were grown by using RF/DC magnetron sputtering on both glass and Si (100) substrates. The films which grown on glass substrates were used for the optical, electrical and magnetoresistance measurements. While the films which grown on Si (100) substrates were used for the structural, surface morphology and chemical composition measurements. Zinc metal target of 99.99% purity with size of 2-inch diameter $\times$ 0.125 -inch thick was sputtered by DC sputtering power. Manganese metal target of 99.9% purity with 50.8mm diameter $\times$ 3mm thick was sputtered by RF sputtering power of the NSC – 3000 Sputter coater NANO-Master sputtering technique. Before the growth process zinc and manganese targets were cleaned with the distilled water, then chemically sonicated with acetone first and ethanol for ten minutes for each solvent. Two different types of substrates; one glass substrate of 1-inch $\times$ 1- inch size and two silicon substrates ;1- cm $\times$ 1- cm and 1- cm $\times$ 5 - mm were cleaned with distilled water and then chemically sonicated for five minutes with both acetone first and then ethanol. Both kind of the substrates were place into substrate holder in the sputtering chamber at the same time. Manganese doped zinc nitrides thin films were prepared using reactive magnetron co-sputtering in the presence of the processing gas argon of 99.99% purity and reactive nitrogen gas of 99.999% purity ambient with the flow rate of 20 standard cubic centimeter per minute (sccm) for argon gas which was kept constant (20sccm) for all samples and (15,10,10,10,10) (sccm) of nitrogen gas for the samples (S_1, S_5, S_3, S_2 and S_4) per each one another sample respectively. DC sputtering power values were (11, 10, 10, 10 and 11) watts for the samples (S_1, S_2, S_3, S_4 and S_5) respectively. Radio frequency sputtering power was used at different values (0, 4, 5, 7 and 10) watts for the samples (S_1, S_2, S_3, S_4 and S_5) respectively. First to find the optimum DC sputtering power value for zinc target and then to control different concentration of manganese doping in the thin films. The thin films were grown at temperature of 14C° on both glass and silicon Si (100) substrates. At starting the growth time the initial chamber pressure was (6.09×10^{-5} , 5.44×10^{-5} , 1.2×10^{-4} , 5.44×10^{-5} and 6.56×10^{-5}) Torr for the samples S_1, S_5, S_3, S_2 and S_4 respectively. This initial pressure was achieved by pumping the system down for several hours to remove the air from inside to outside

and to create vacuum inside. The duration time of the growth for these samples was (135,120,120,120 and 120) minutes respectively. During the growth the substrates were kept at room temperature without rotating and the chamber pressure was maintained to 10^{-3} Torr .The crystallinity of the films was investigated by XRD Bruker instrument equipped with the Couper $K\alpha$ radiation of the wavelength of $1.5406\text{\AA}$. The electrical conductivity type of the films was confirmed by Hall effect using van der pauw with four wires resistance measurement. The transmission spectra of the thin films were studied by using Jasco V-670 double-beam spectrophotometer which were measured from the range of recording spectra from 200 nm - 1200 nm of the wavelength .Surface morphology of the films was obtained by using AFM Veeco technique and the elemental composition of the prepared films were investigated by using ThermoFisher scientific XPS technique and the growth parameters were shown in the table 2 below:

Table 2: The growth condition of all samples.

Sample #	Zn-DC sputtering Power (W)	Mn-RF sputtering Power (W)	Ar flow rate (sccm)	N ₂ flow rate (sccm)	Growth Pressure (Torr)
S ₁	11	0	20	15	5.17×10^{-3}
S ₂	10	4	20	10	4.71×10^{-3}
S ₃	10	5	20	10	4.71×10^{-3}
S ₄	10	7	20	10	4.71×10^{-3}
S ₅	11	10	20	10	4.71×10^{-3}

4.2 Chemical properties

The elemental chemical composition of Mn-doped Zn_3N_2 thin films and their oxidation state as well were studied using X-ray photoelectron spectroscopy. All the spectra were obtained after the first etching cycle of the samples by bombarding it with argon ions of 3KeV for 30 seconds at the chamber pressure of 10^{-10} Torr which is in the range of ultra-high vacuum. The experiment has been done based on the photoelectric effect. C1s peak at 284.8 eV was used as standard reference for correction the spectra of XPS from any chemical shifting caused by charging effect. The figure 10 below shows several peaks of full scan XPS spectra of a pure Zn_3N_2 Sample S_1 and Mn-doped Zn_3N_2 sample S_5 thin films scanning all energies from 0 to 1200 eV .Both of the spectra in the two films contain the peaks of Zn3d ,Zn3p ,Zn3s ,C1s,ZnLMM ,O1s ,OKLL ,Zn2p_{3/2} and Zn2p_{1/2} ,but Mn- Zn_3N_2 .Sample S_5 has extra Mn2p peak which is not existing in the spectrum of Zn_3N_2 sample S_1 .This peak is corresponding to manganese peak at around 657 eV [26,27] ,where the range of manganese peaks are reported between(630-665) electron volts [27]. The presence of oxygen O1s peak at around 531 eV is due to the oxidation of the sample when exposed to the air atmospheric after the growth and before transferring to XPS chamber. Carbon C1s peak at around 285 eV is existing as a result of the organic contamination of the samples surface resulted from exposing to the air atmospheric [5].

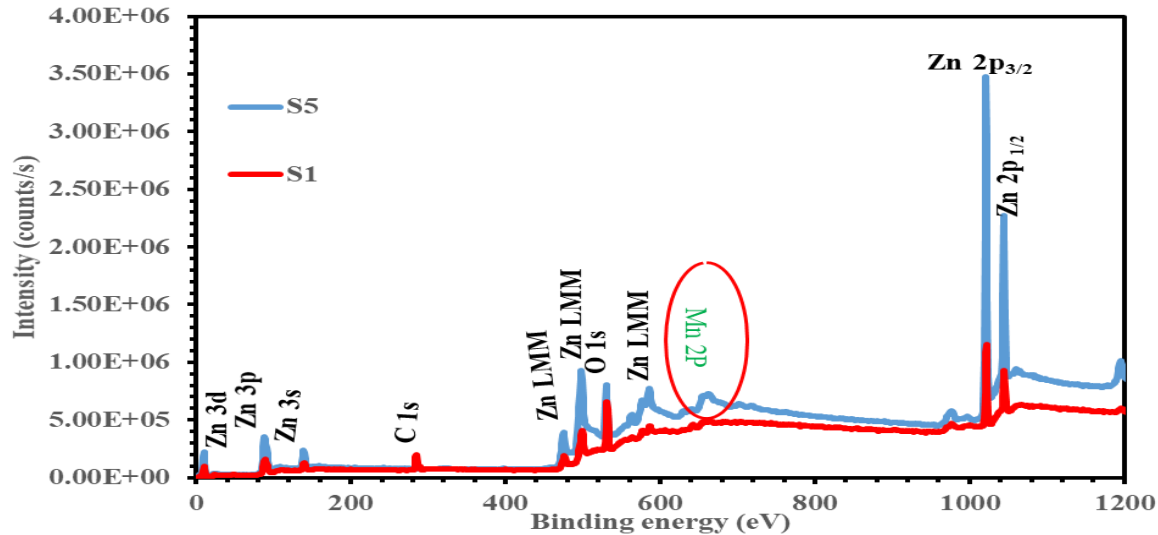


Figure 10: Survey of a pure and Mn-doped film for S_1 and S_5

The figure 10 above is the survey of the pure sample S_1 and Mn-doped sample S_5 shows the existence of different species in the film in the range of binding energy from (0-1200 eV).Zn

$2p_{3/2}$ and $Zn\ 2p_{1/2}$ are resulted from $Zn\ 2p$ peak. Zn LMM auger peaks are resulted from the second emission after electron from high energy level dropped into the hole in the lower energy level.

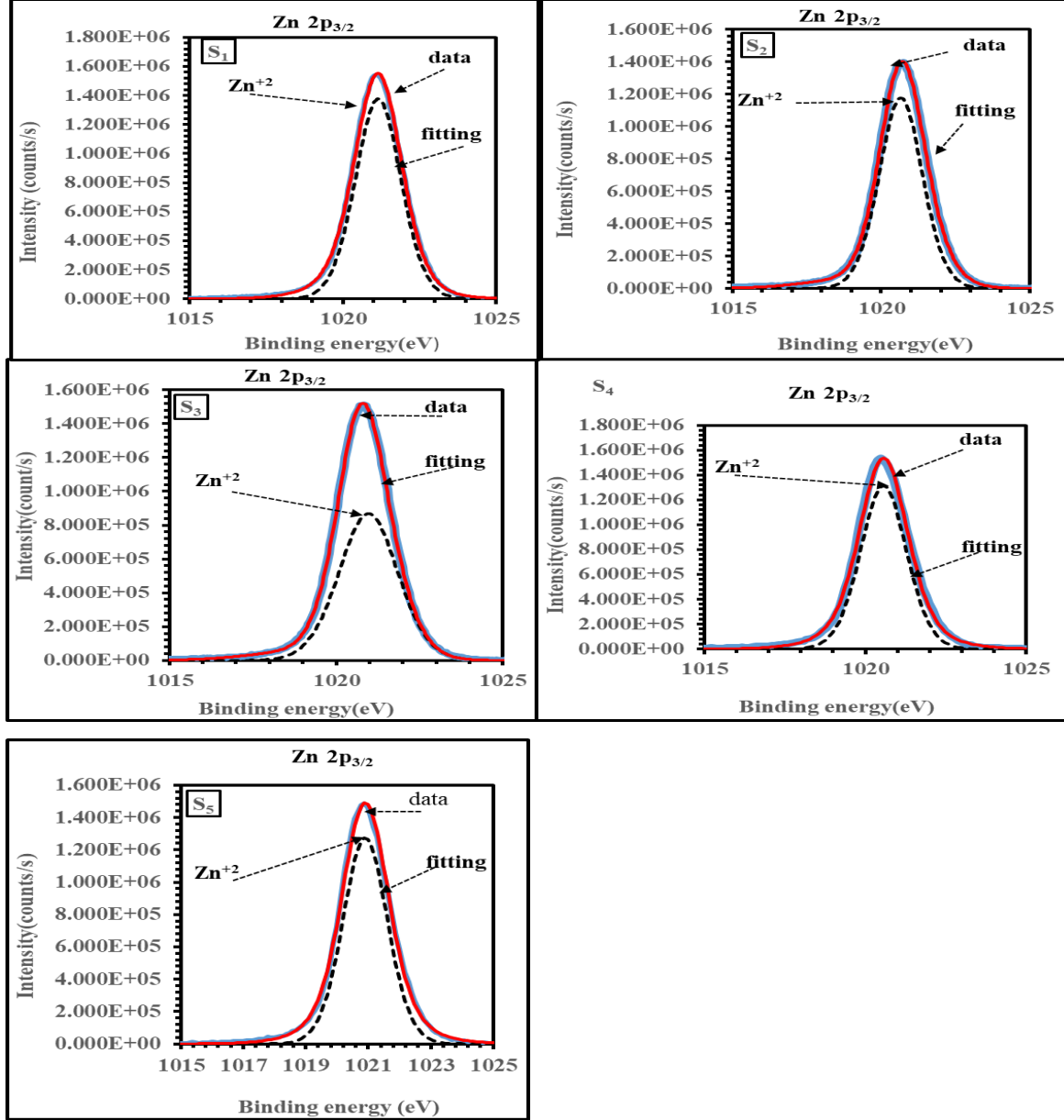


Figure 11: $Zn\ 2p_{3/2}$ for the all films.

Figure 11 above shows high resolution XPS analysis of $Zn\ 2p_{3/2}$ for the all samples, after the peak fitting analysis $Zn\ 2p_{3/2}$ has deconvoluted into other peak Zn^{+2} for all the samples [28].

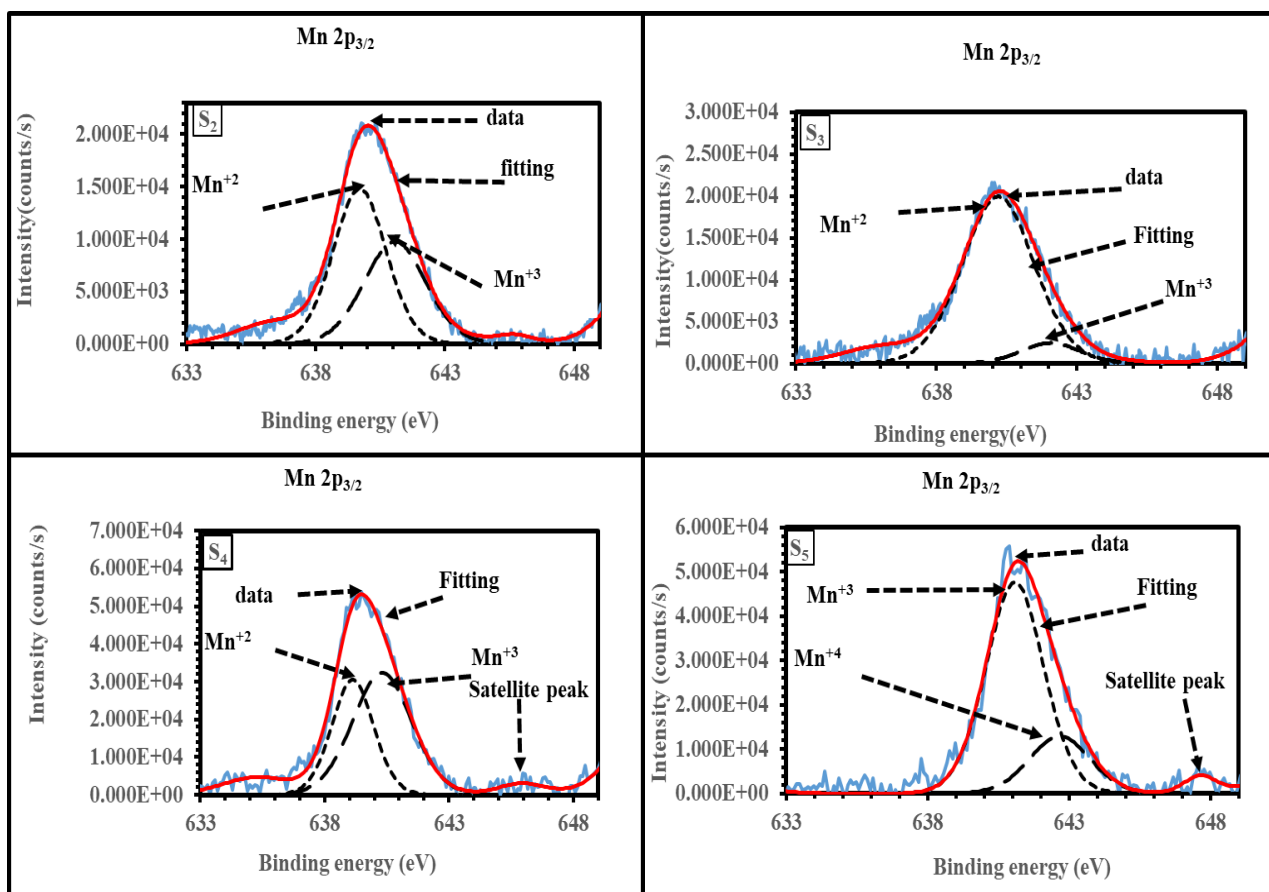


Figure 12: Mn 2p_{3/2} for the doped films.

Figure 12 above shows high resolution XPS analysis of Mn 2p_{3/2} for the doped samples. X-ray photoelectron spectroscopy confirmed that manganese was either in the second (Mn²⁺), third (Mn³⁺) or fourth (Mn⁴⁺) oxidation state. Sample grown with lower RF sputtering power for manganese (S₂, S₃ and S₄) have (Mn²⁺) and (Mn³⁺) oxidation state, which are high spin states. The intensity of manganese high spin state is increasing with increasing manganese concentration in the films which means that the most of manganese in the films is in the second oxidation state and most of manganese replacing zinc in the crystal lattice. Third manganese oxidation state either replacing nitrogen or goes into interstitial sites between zinc atoms. Fourth manganese oxidation state is interstitial defects in the crystal lattice. Sample with the highest Mn concentration (S₅) the Mn found to be in Mn³⁺ and Mn⁴⁺ oxidation state which are low-spin state, the relative intensity of high-spin was highest for sample S₃ indicating optimum Mn doping concentration in the Zn₃N₂ film. From the analysis it is clearly observed that the intensity of high spin (Mn²⁺) Mn 2p_{3/2} was increasing with the increasing RF sputtering power of manganese in the films until it reached RF

sputtering power of 10 watts (sample S₅) for which (Mn⁺²) peak does not exist. Hence the optimum Mn concentration in the film was obtained for sample S₃ (RF sputtering Power 5 watts), which resulted in the highest (Mn⁺²) oxidation state [29]. Mn 2p_{3/2} satellite peaks have appeared at about 646eV for sample S₄ [35].

But it is shifted to high energy at around 647.48 for the highest doped film, whereas it is absent for the lower doped films. The existing of satellite peak is associated with certain electronic excitations and interactions in the material and due to the different manganese concentration and oxidation states in the films the satellite peak appears for the high doped films while it is absent for lower doped films and it is high intensity for the high doped film which indicate to the effects of dopants concentration on the electronic structure in the films.

From the high resolution XPS data, due to spin-orbit coupling manganese Mn 2p peaks split into two major peaks Mn 2p_{3/2} and Mn 2p_{1/2} at the binding energy of about 640.46 eV and 652.99 eV respectively [26]. After the peak fitting analysis both of the splitted peaks deconvoluted into identical components for two peaks (Mn⁺²) and (Mn⁺³) in the sample S₂, S₃ and S₄ and into two peaks (Mn⁺³) and (Mn⁺⁴) in the sample S₅ in addition to the existing of satellite peaks in the samples S₄ and S₅ which associated with electronic interaction and interaction in the samples. The spin-orbit splitting energy difference between Mn 2p_{3/2} and Mn 2p_{1/2} is 12.5eV, 12.6eV, 11.8eV and 11.61eV for the samples S₂, S₃, S₄ and S₅ respectively. Whereas the splitting energy between Mn 2p_{3/2} and Mn 2p_{1/2} is 11.6eV and 11.7eV for Mn₃O₄ compound and 12 eV for manganese oxide nanoparticles [29,31]. The splitting energy difference between the states Mn⁺³ and Mn⁺⁴ for sample S₅ is 1.6 eV whereas it is 1.35 eV in MnO₂ compound [26]. The splitting energy difference between the states Mn⁺² and Mn⁺³ for samples S₄, S₃ and S₂ is 1.2eV, 1.95eV and 1.4eV respectively, whereas it is 1.46eV in Mn₃O₄ compound. Mn 2p_{3/2} peak binding energy of metal manganese Mn 2p_{3/2} is 638.7 eV.

Table 3: XPS peaks positions of Zn 2 P_{3/2} and Mn 2P_{3/2} for all the samples

Sample #	Zn 2P _{3/2} B.E (eV)	Mn 2P _{3/2} B.E (eV)			I _(Mn+2) /I _(Mn+3)	Satellite B.E (eV)
	Zn ⁺²	Mn ⁺²	Mn ⁺³	Mn ⁺⁴	Mn 2P _{3/2}	Mn 2P 3/2
S ₁	1021.53	-	-	-	-	-
S ₂	1021.13	639.98	641.78	-	1.66	-
S ₃	1021.18	640.73	642.13	-	8.84	-
S ₄	1020.48	638.98	640.78		0.89	646
S ₅	1020.98	-	641.78	642.58	-	647.48

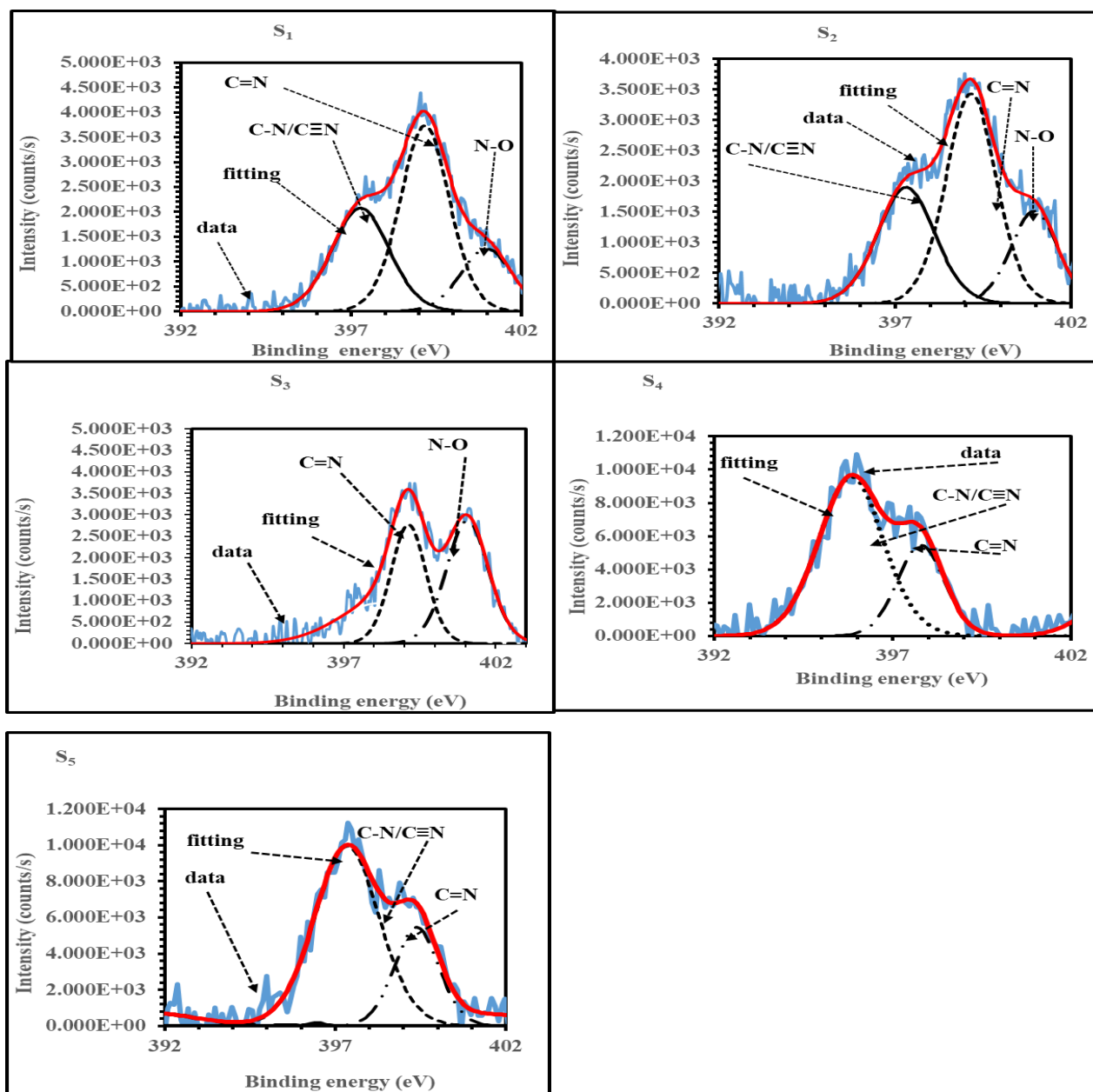


Figure 13: N 1s for the all films.

Figure 13 above shows high resolution XPS analysis of N 1s for the all samples, after the peak fitting analysis N 1s has deconvoluted into two peaks (C-N/C≡N) and (C=N) for the all samples [32]. In addition to N-O peaks in the samples S₂ and S₃ [32]. The peaks positions of Zn 2P_{3/2} and Mn 2P_{3/2} with their deconvolutions are shown in the table 7 below.

4.3 Structural analysis

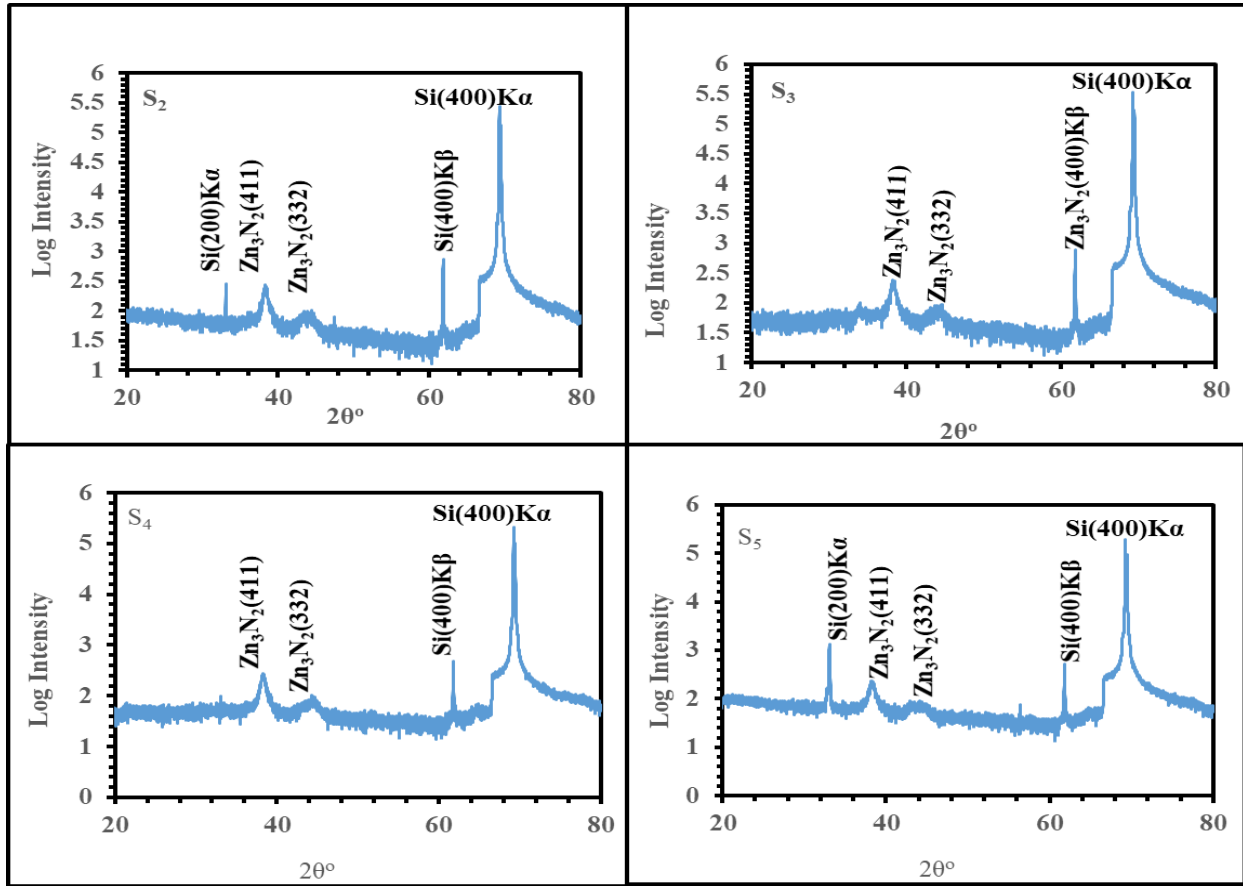


Figure 14: XRD for the all grown Zn₃N₂ thin films.

Shown in the figure 14 above are θ - 2θ scans of XRD spectra for Zn₃N₂ thin films which grown on Si (001) substrate. The highest intensity of Zn₃N₂ XRD peaks in the films is for Zn₃N₂ (411) which indicate that the growth direction of the films is along $\langle 411 \rangle$ direction, whereas a broad Zn₃N₂ peak is observed along $\langle 332 \rangle$ direction. XRD scans also contains stronger Si (400) and Si (200) peaks which referring into silicon substrate used for the growth. The d-spacing of the films was calculated using Bragg's equation.

The full width at half maximum (FWHM) for Zn₃N₂ (411) and Zn₃N₂ (332) is increasing with increasing manganese concentration in the films, which indicates that more introduction of manganese dopants into the films can lead to creating defects in the lattice which decrease the crystallinity of the films. More manganese create more defects which create strain in the films lattice and this is we obviously observed in the XPS analysis.

The crystallites size of the films were calculated from Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

D: is the crystallite size in nanometer, K: is Scherrer constant (k = 0.94), λ : is the incident wavelength of XRD radiation for Cu α_1 = 1.5406 nm, β : is the full width at half maximum (FWHM in degree), θ : is the peak position in degree .The calculations are consistent for the both XRD peaks of Zn₃N₂ (411) and Zn₃N₂ (332) directions. For the both peaks FWHM and strains are increasing with increasing manganese sputtering power in the films, whereas the crystallinity of these peaks decreasing. We conclude that more introduction of manganese into the films create more defects in the lattice which results in more strains with more peaks broadening and lower films crystallinity.

Table 4: peaks position, FWHM, crystallite size and strain of the all films.

Sample#	Peaks (degree)	FWHM(β)(degree)	Strain $\epsilon = \frac{\beta}{4 \tan \theta}$ (degree)	$D = \frac{K\lambda}{\beta \cos \theta}$ (nm)
S ₂	Zn ₃ N ₂ (411)38.34	1.159	0.833	0.132
	Zn ₃ N ₂ (332)43.80	0.162	0.101	0.965
S ₃	Zn ₃ N ₂ (411)38.30	1.233	0.888	0.124
	Zn ₃ N ₂ (332)44.49	0.222	0.136	0.703
S ₄	Zn ₃ N ₂ (411)38.32	1.244	0.895	0.123
	Zn ₃ N ₂ (332)44.51	0.273	0.167	0.573
S ₅	Zn ₃ N ₂ (411)38.26	1.405	1.013	0.109
	Zn ₃ N ₂ (332)44.31	0.556	0.341	0.281

4.4 Surface morphology

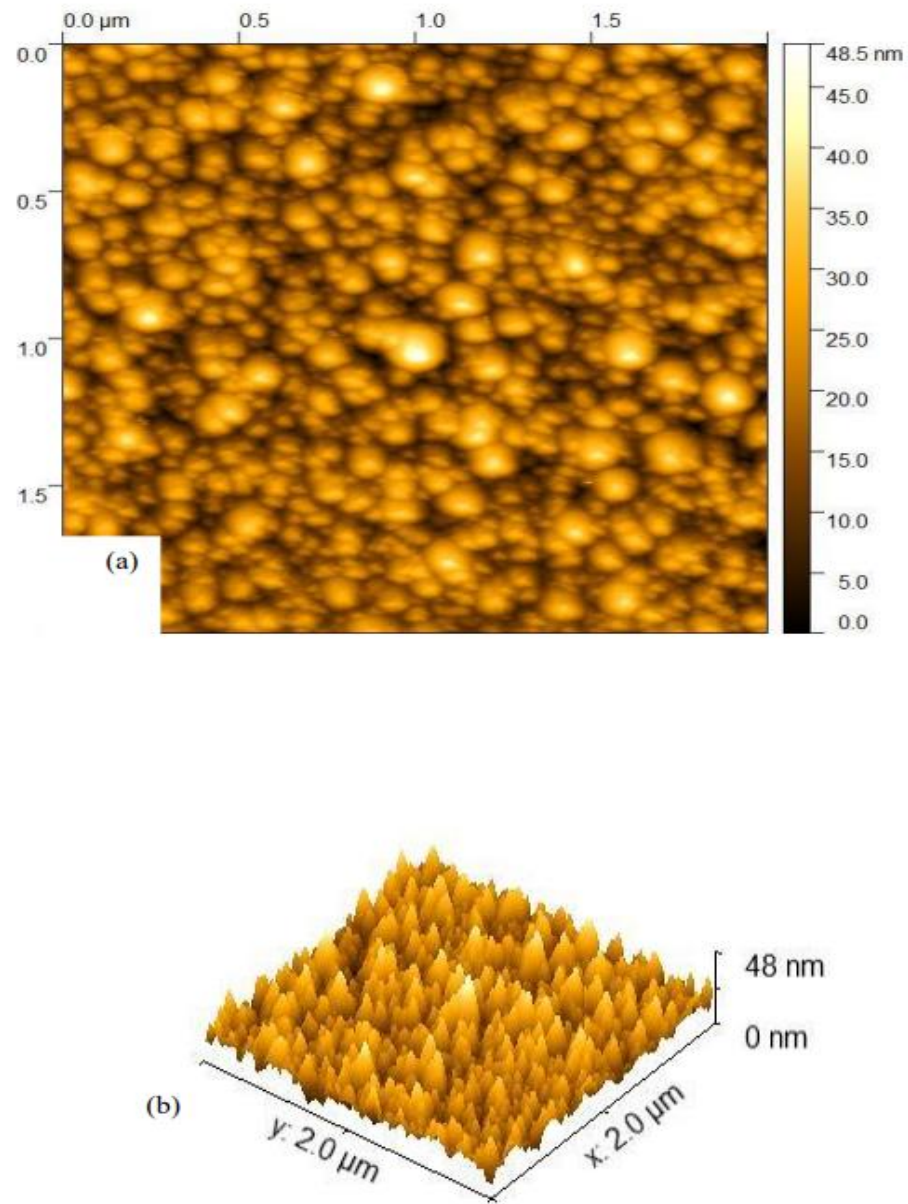


Figure 15: $2\mu\text{m}^2 \times 2\mu\text{m}^2$ area of two and three-dimensional AFM images of sample S_1

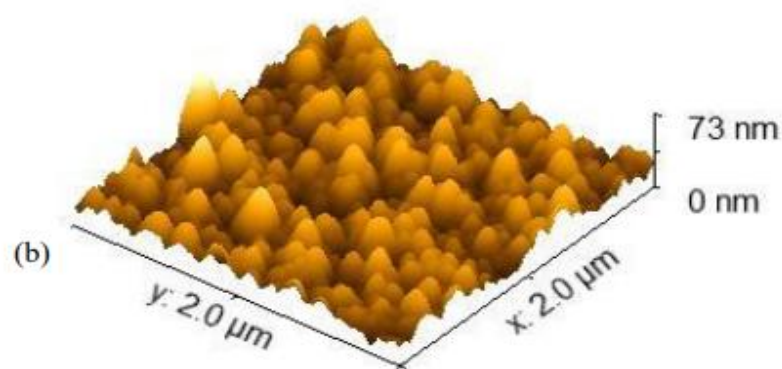
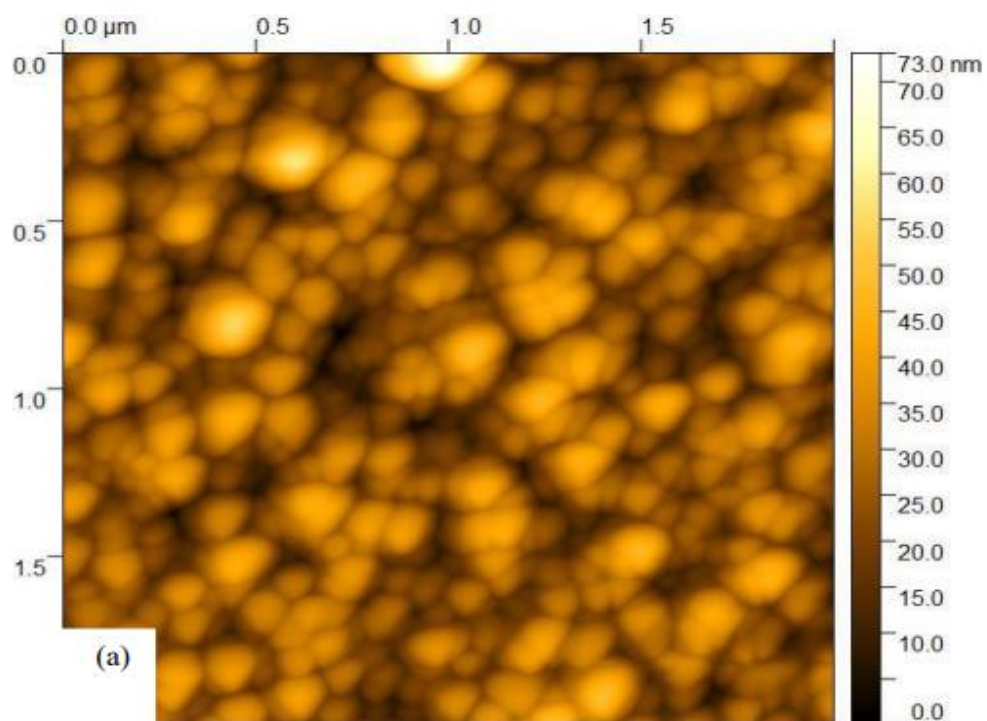


Figure 16: $2\text{m}\mu^2 \times 2\text{m}\mu^2$ area of two and three-dimensional AFM images of sample S_2

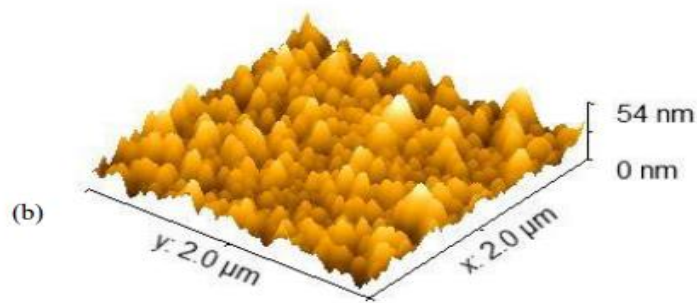
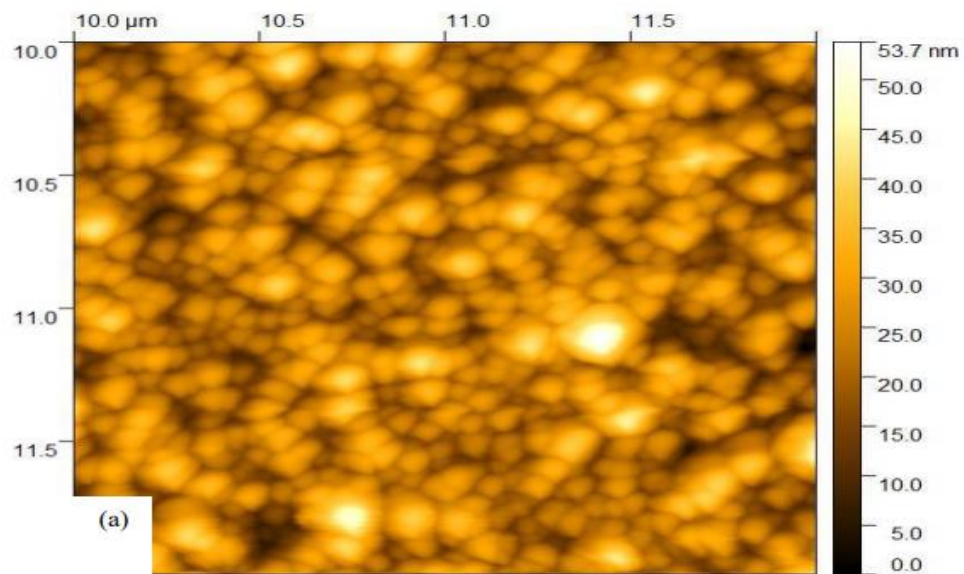


Figure 17: $2\text{m}\mu^2 \times 2\text{m}\mu^2$ area of two and three-dimensional AFM images of sample S_3

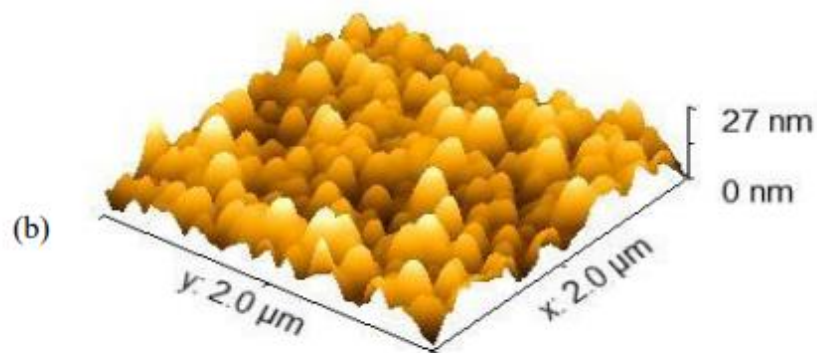
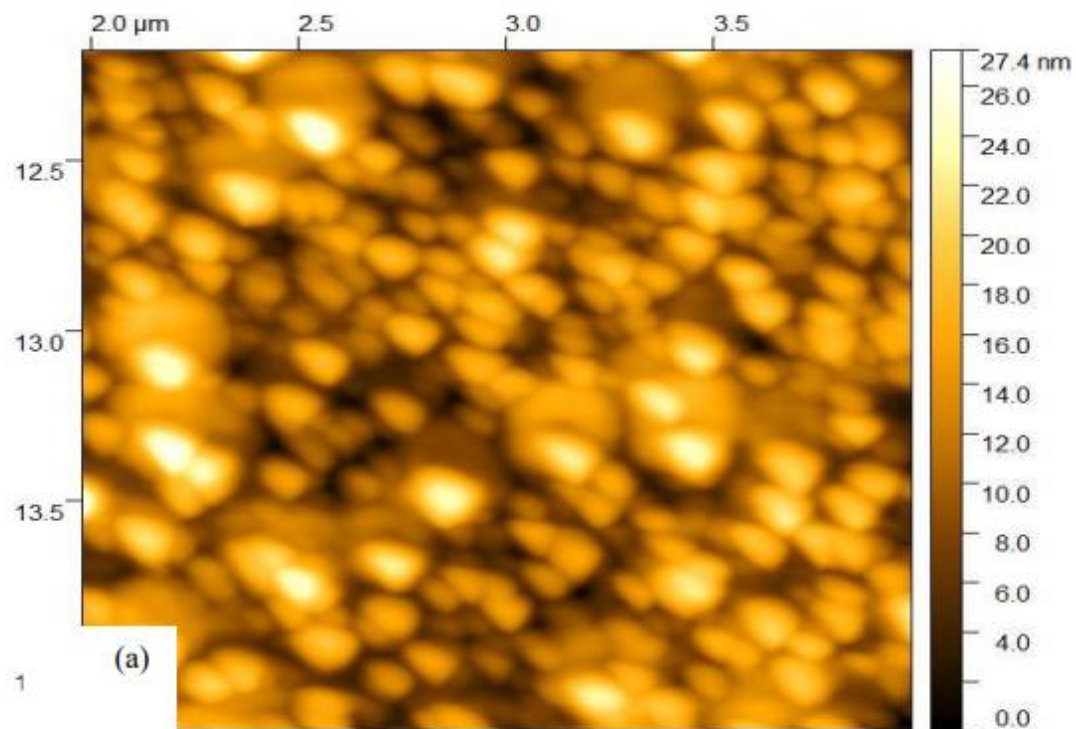


Figure 18: $2\mu\text{m}^2 \times 2\mu\text{m}^2$ area of two and three-dimensional AFM images of sample S_4

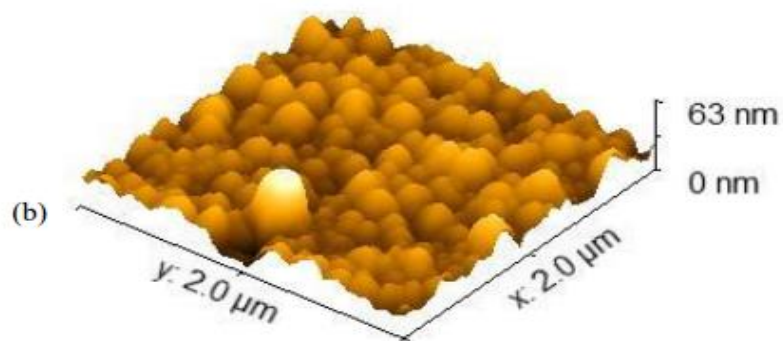
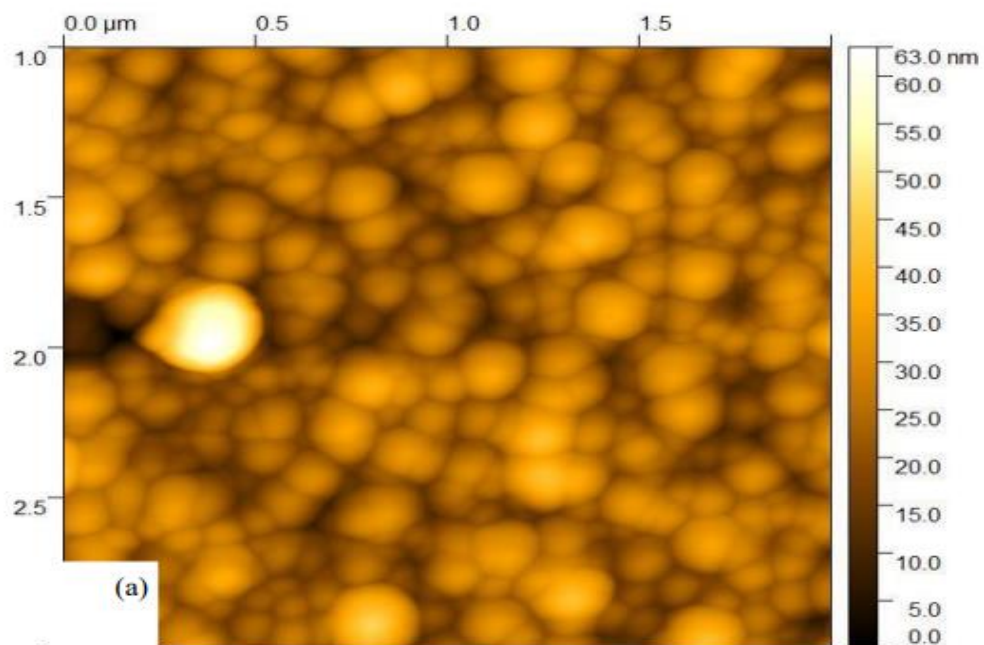


Figure 19: $2\mu\text{m}^2 \times 2\mu\text{m}^2$ area of two and three-dimensional AFM images of sample S_5

For the all films the surface morphology was studied using atomic force microscopy manufactured by veeco with non-contact mode. Figures (15, 16, 17, 18 and 19) (a) and (b) illustrate $2\text{m}\mu^2 \times 2\text{m}\mu^2$ area of two (a) and three-dimensional (b) images of AFM for a pure Zn_3N_2 and Mn-doped Zn_3N_2 thin films which prepared on Si (100) wafer. Root means square roughness of the all films were calculated from these images. Laplacian was used to mark the grains. The grain sizes were estimated by selecting appropriate threshold which resulted in maximum numbers of grains in the grains statistic. The films were found to be roughly in surface and grainy as well. Root mean square roughness (RMS) and the mean grain sizes of the films were calculated using Gwydion software. The results were shown in the table 5. It is noticed that they were increasing with the increasing RF sputtering power of manganese target which indicate the incorporation of manganese in the films. Root mean square roughness and the mean grains sizes were increasing with increasing RF sputtering power of manganese concentration due to increasing of strains introduced into the films and that we clearly observed in the XPS analysis.

Table 5: DC/RF Sputtering power, RMS and average grain sizes of the all films

Sample#	DC-Zn power(W)	RF-Mn power (W)	RMS(nm)	Mean grain size(nm)
S ₁	11	0	7.054±0.5	6.812± 1.4
S ₂	10	4	13.76± 1.7	6.897± 0.5
S ₃	10	5	19.19± 0.2	7.191± 1.1
S ₄	10	7	24.22± 1.2	9.43 ± 1.0
S ₅	11	10	35.63± 1.5	9.70 ± 0.5

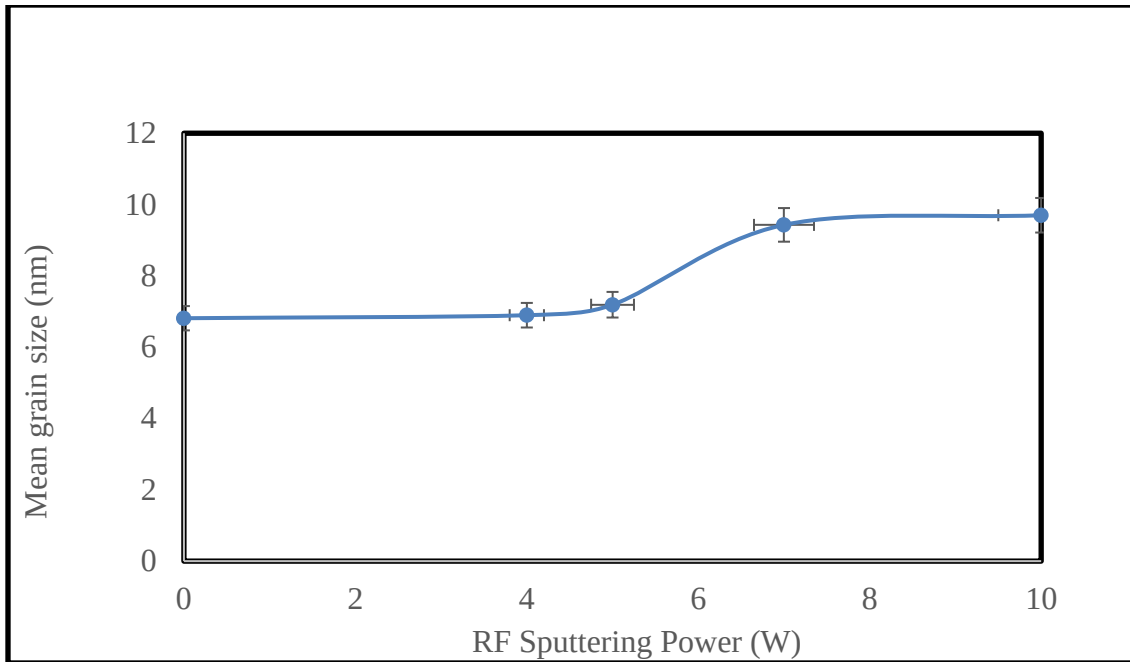


Figure 20: average grain size (nm) versus RF Sputtering power (W) for the all films.

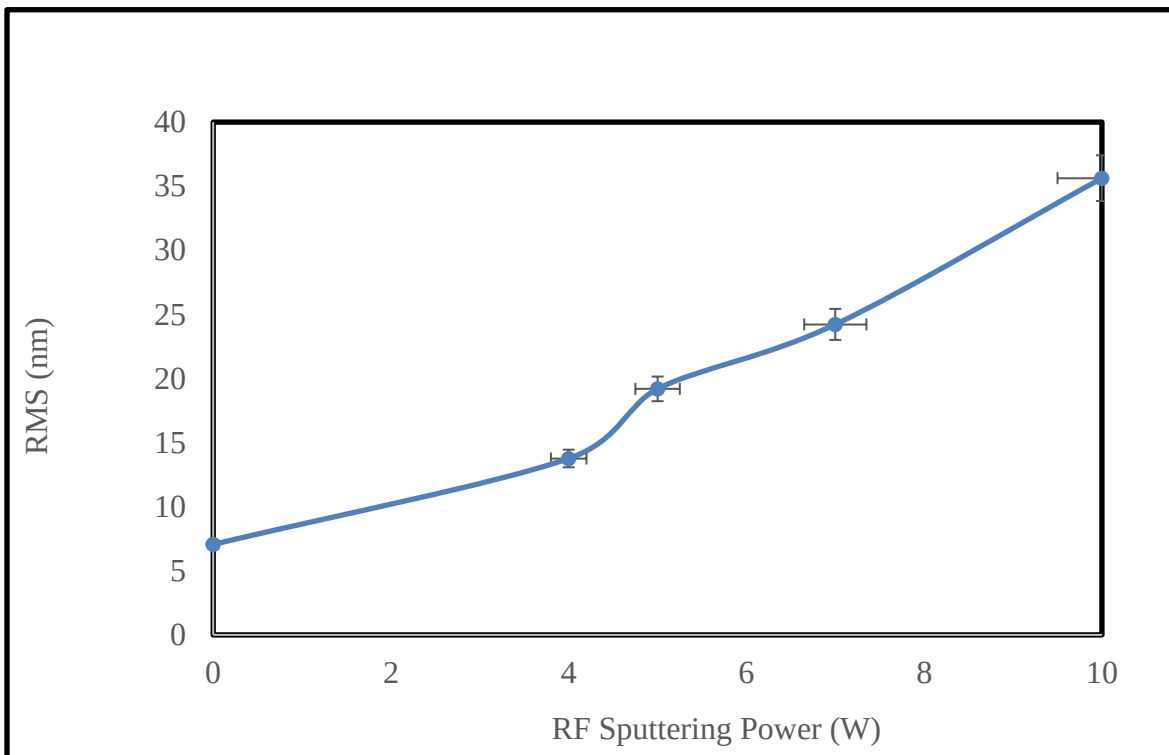


Figure 21: RMS (nm) versus RF power (W) for the all films.

4.5 Electrical properties

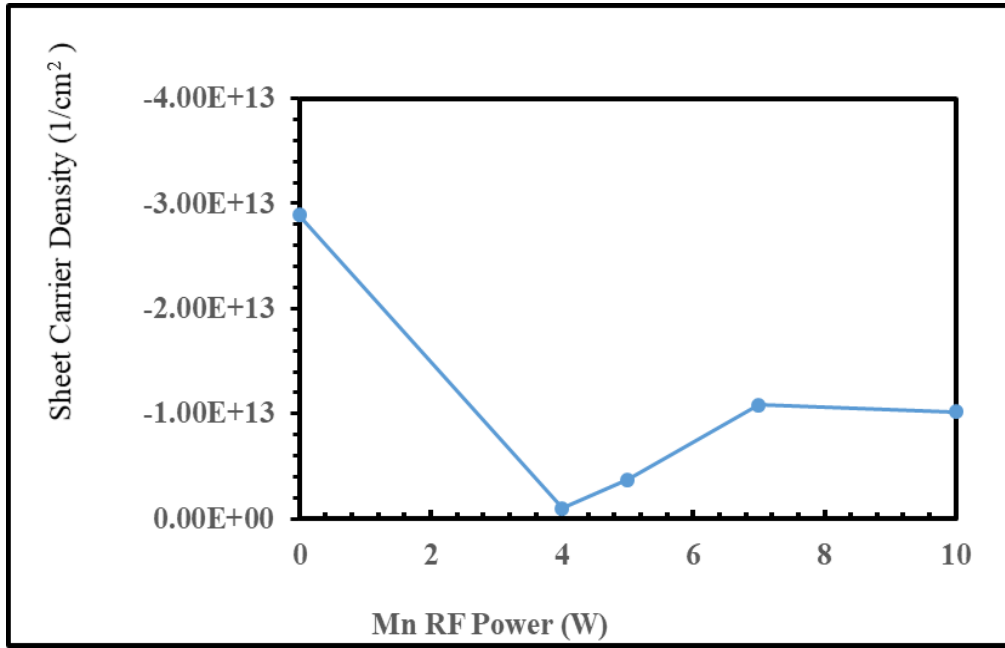


Figure 22: sheet carrier density Versus Mn-RF Sputtering power (W) for the all films.

The figure22 above shows sheet carrier density as a function of manganese sputtering power for a pure Zn_3N_2 and Mn-doped Zn_3N_2 thin films. The negative sign in the values of the carrier densities indicated for the electrons and the number of carrier densities increasing with increasing of doping manganese sputtering power in the films and this increase the electrical conductivity of the films with the decrease of their electrical resistivity. The pure Zn_3N_2 sample S_1 has higher carrier density this resulted from zinc vacancies defects in the films. These carriers were decrease for the lowest doped films due to filling of these defects with manganese dopants concentration in the films. With increasing of manganese concentration in the films the carriers increased a gain due to acting of manganese dopants as carrier's concentration.

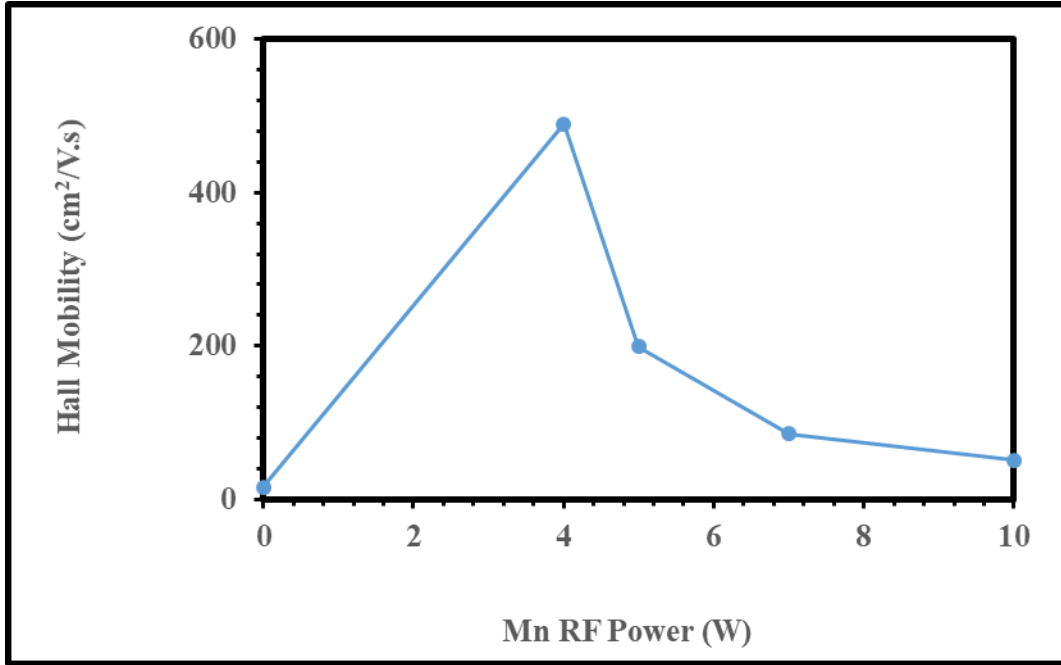


Figure 23: Hall mobility versus Mn-RF sputtering power for the all films.

Shown in the figure23 above is Hall mobility versus Mn sputtering power for the all Zn_3N_2 thin films. The films with higher carrier densities have lower Hall mobility, so the mobility will decrease when the charge carrier increase according to the following equation:

$\mu = \frac{1}{nef}$, where μ is the Hall mobility, n is carrier's density, e is the electronic charge, and f is the resistivity.

Hall Effect data confirmed that all the grown Zn_3N_2 thin films are n-type semiconductors., increasing in the applied magnetic field will increase the Hall voltage and the accumulation of the carrier on one side of the sample and this increase the carrier density according to the Hall voltage formula: $V_H = \frac{iBR_H}{d}$

, where V_H is the Hall voltage, i is the current, B is the applied magnetic field, d is the thickness of the sample, the mobility is decreasing with the increasing the applied magnetic field due to accumulation of the charge carrier in one side of the sample and they do not move to the other side and the mobility will decrease when the charge carrier increase according to the following

equation: $\mu = \frac{1}{nef}$

Table 6: Hall effect results taken in the applied field (- 5000) G.

Sample #	Mn RF sputtering power (W)	Zn DC sputtering Power(W)	Average Sheet resistivity (Ohm/sq)	Sheet Hall coefficient (cm ² /C)	Hall resistance (Ohm)	Sheet carrier density (1/cm ²)	Hall mobility(cm ² /Vs)
S ₁	0	10	1.40×10^4	-2.16×10^5	10.8	-2.89×10^{13}	15.8
S ₂	4	10	1.24×10^4	-62.6×10^5	313	-9.97×10^{11}	490
S ₃	5	10	0.839×10^4	-16.6×10^5	83.1	-3.76×10^{12}	199
S ₄	7	10	0.668×10^4	-5.76×10^5	28.8	-1.08×10^{13}	86
S ₅	10	10	1.34×10^4	-61.3×10^5	306	-1.02×10^{13}	51

4.6 Optical properties

The thickness of the all films were measured from profilometer Dektak Bruker stylus profiling measurement and found to be in the range of (150 – 283) nm .They were changing with the changing of RF sputtering power of manganese concentration in the films during the growth. The optical bandgaps of a pure Zn₃N₂ thin film sample S₁ and Mn –doped Zn₃N₂ thin films samples S₂, S₃, S₄ and S₅ were determined using the transmission spectra of UV-Vis double beam spectrum Jasco-760 spectrophotometry technique .The bandgap values of the films were found from Tauc Plot using the following formula : $(\alpha h\nu)^n = \beta (h\nu - E_g)$ of the direct transition of electron from valence band to conduction band.

Where; $h\nu$ is the incident photon energy in electron volt (eV), E_g : is the optical bandgap of the film in electron volt (eV) , α is the absorption coefficient, β : is constant , n is the parameter which measures the type of the optical bandgap ($n = 2$ for direct bandgap and $n = \frac{1}{2}$ for indirect bandgap). The bandgap of the all grown thin films were found from Tauc plot by extrapolating the linear part

of the plot and the intersection with the x-axis is equal to the bandgap value of the film and all the films have direct bandgap , where $(\alpha h\nu = 0)$ is a good linear fitting with the equation :

$$(\alpha h\nu)^2 = \beta (h\nu - E_g)$$

A red shift in the bandgap was observed in Mn-doped Zn_3N_2 samples with increasing manganese concentration in the films which indicating that Mn creating mid-gap states. The bandgap value of the pure Zn_3N_2 thin films sample S_1 is 2.6eV. The bandgap values of Mn- doped Zn_3N_2 thin films are 2.4 eV , 2.7 eV , 2.1 eV and 2.5 eV corresponding to the samples S_5, S_3, S_2 and S_4 respectively ,the optical bandgap values of Zn_3N_2 samples are reported in the range of 1.92 and 1.27 eV [9],also reported between (3.2 – 3.4) eV [33]. A pure Zn_3N_2 film has higher band gap due to the existence of more zinc vacancies defects which increase the bandgap by introducing carriers concentration into the conduction band. The band gap value is reduced for the lowest doped films due to filling of zinc vacancies with manganese dopants which reduced conduction band carriers and resulted in lowering the band gap values. With increasing manganese concentration in the films, the band gap values decreased a gain due to acting of manganese dopants as carriers resulted in creating mid donors states and reduced the band gap values and these clearly observed in the electrical measurements.

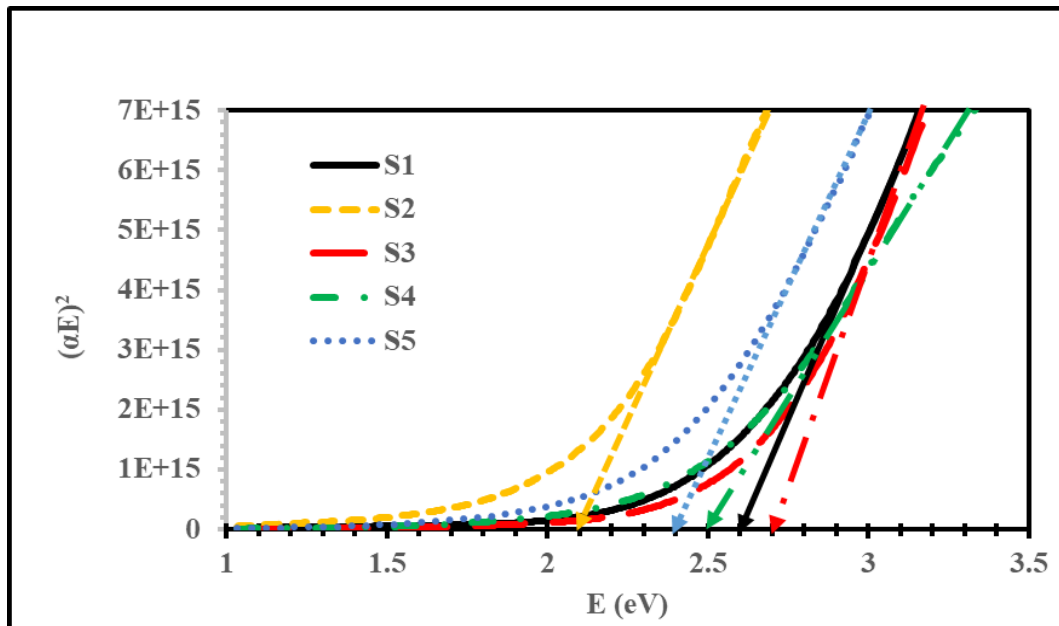


Figure 24: Tauc plot for a pure Zn_3N_2 and Mn-doped Zn_3N_2 thin films.

Table 7: RF Sputtering power, thickness and bandgaps of the all films

Sample#	RF-Mn power (W)	Film Thickness(nm)	Bandgap(eV)
S ₁	0	150± 4	2.6
S ₂	4	192±6	2.1
S ₃	5	238±5	2.7
S ₄	7	283±7	2.5
S ₅	10	249±7	2.4

4.7 Magnetic properties

To operate the magnetoresistance measurement system we followed the procedures below:

Firstly, by doing the electrical connection with a four wires probes technique into the sample by depositing silver paint into the surface of the sample and letting it up to the second day for drying. Secondly, by installing the sample into cryostat confined in the external magnetic field and the cryostat is connected into the pumps system, helium compressor, temperature controller, source meter and computer equipped with LABVIEW software for conducting the experiment. Thirdly, by turning on the mechanical pump and waiting until the pressure goes up to 10^{-2} mbar, then opening the diffusion pump and waiting until the chamber pressure goes up to 10^{-6} mbar. Fourthly, by opening the helium compressor for cooling down the sample. Then by opening the temperature controller with adjusting the heater of the controller in the high mode for measuring the temperature of the sample in the both cases cooling and heating. The heater will not be turn on unless there is enough cooling for the sample when it is under the vacuum to avoid heating in small area, the heat will not be dissipated out and this causes melting for soldering and connections which may cause damage to the experiment. A cold helium gas keeps coming to the cryostat through the supply line, it becomes hot and return through the return line continuously during the whole measurement. A source meter is used to measure the current passing through the sample and the potential difference between the two terminals of the sample. The sample will be cooled

down under the vacuum to avoid condensation of any contaminants molecules in the chamber. The parameters of the experiments will be adjusted from the LBVIEW software .The measurements were done with and without applied magnetic field in mli Tesla, therefore Gauss meter was used for sensoring the magnetic field in the cases of the applied magnetic field. The different values of the magnetic fields were adjusted using AC current controller. Water chiller was used to cool down the magnet due to heat generating from the high voltage-current. After completing the measurement the helium compressor will be turn off and waiting for the temperature to go up above liquid nitrogen temperature to release ,pumped out and avoid condensation in the chamber.Finally , the pumps system will be turn off.

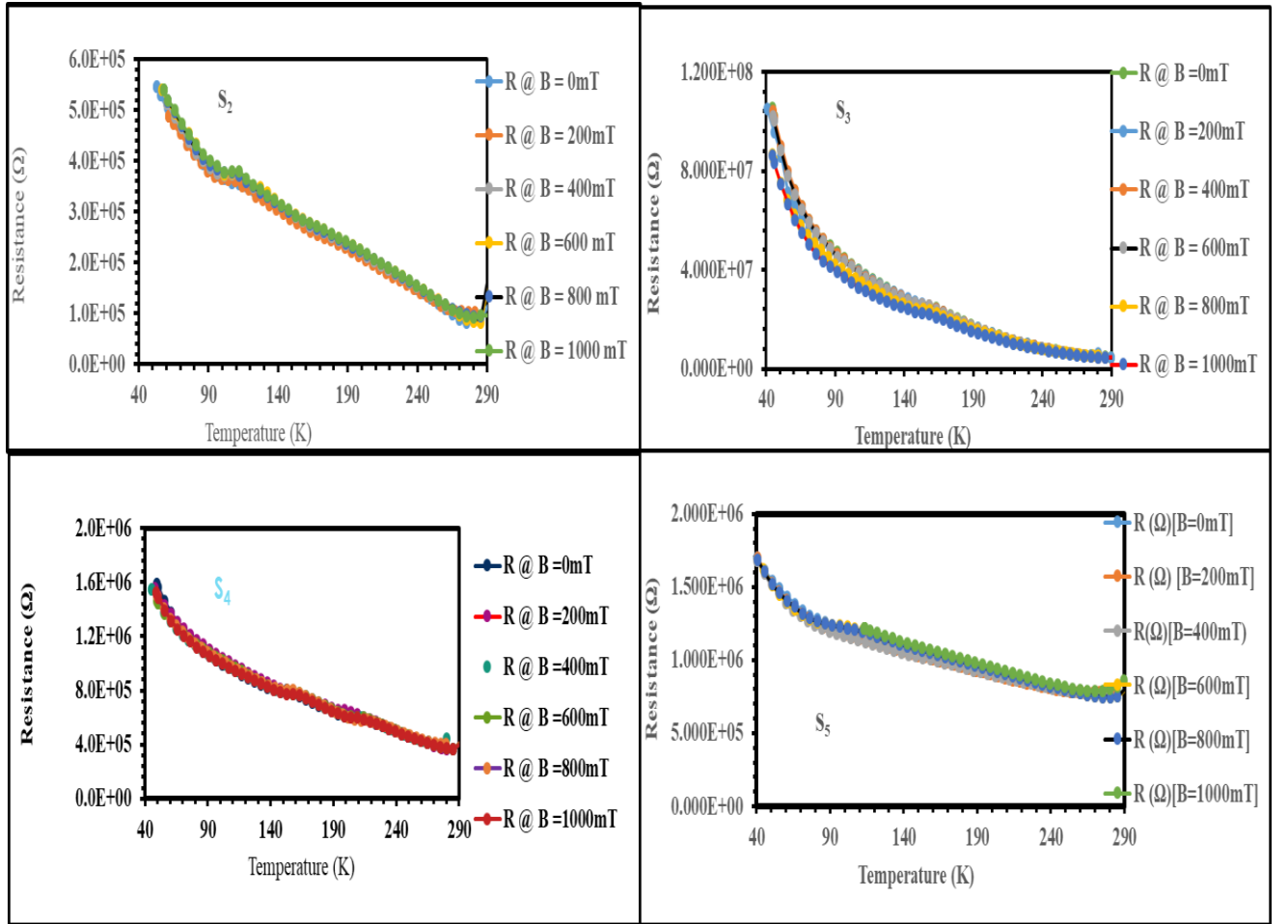


Figure 25: Resistance versus temperature for all films.

Shown in figures 25 above is the resistance versus temperature graph with different values of the applied magnetic field. Each line corresponds to the constant value of the applied magnetic field in (mT). Hence the resistance is changing with the applied magnetic field indicating that there is magnetoresistance in the thin films samples S_2 – S_5 - Mn-doped Zn_3N_2 . As the resistance of the samples decreases with increasing temperature it is strong evidence of semi conductivity behavior for the prepared films.

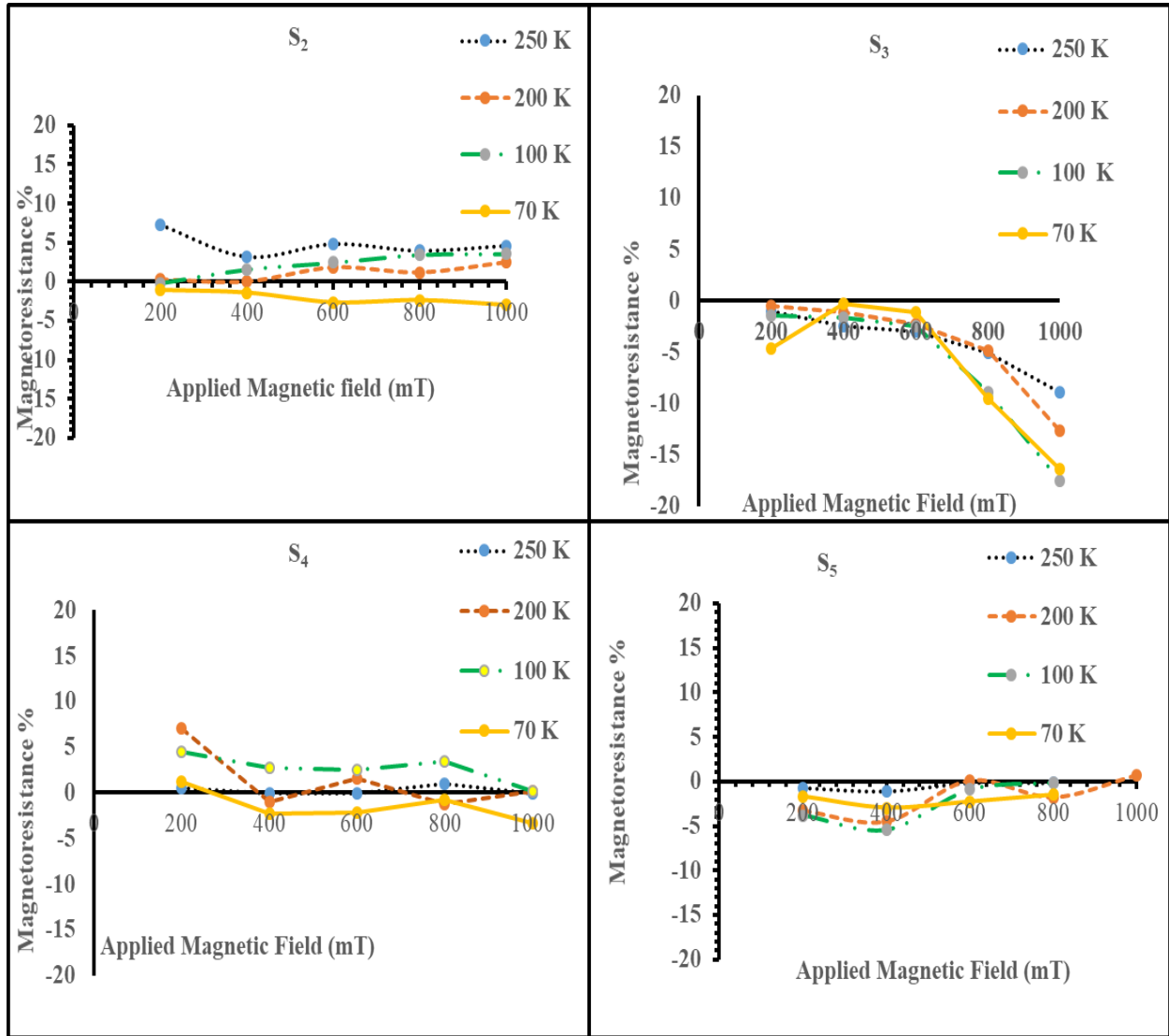


Figure 26: Magnetoresistance % Versus Applied Magnetic field in mT for the all films.

Shown in figures 26 above is magnetorsistance percentage versus applied magnetic field in mT for Mn-doped Zn_3N_2 thin films samples S_2 , S_3 , S_4 and S_5 . Magnetoresistance was calculated using the following formula:

$$\text{MR \%} = \frac{R_B - R_0}{R_0} \times 100$$

Where R_B is the resistance of the sample with applied magnetic field.

R_0 is the resistance of the sample without applied magnetic field.

Two types of magnetoresistance were observed in the prepared films. Positive magnetoresistance is due Zeeman splitting with the applied magnetic field, and the non-smooth motion of carriers from one hole to another resulted in high resistance which caused positive magnetoresistance in the film. Negative magnetoresistance is due to formation of magnetic polarons, when there is enough magnetic ions, carriers and defects and due to overlapping of magnetic polarons the hopping or tunneling of the carriers from one side to another result in smooth motion and lower resistance which leads to negative magnetoresistance in the films.

CHAPTER 5

CONCLUSION

Manganese doped zinc nitride thin films were prepared and studied in this work, Mn-doped Zn_3N_2 thin films have been grown by RF/DC reactive magnetron co-sputtering with different Mn concentration in the films. Two targets of the materials have been used, sputtering zinc target of 99.99 % purity has been sputtered using DC sputtering power for the gun and manganese target of 99.9 % purity has been sputtered using RF sputtering power for the gun in the presence of reactive nitrogen and processing argon gases. The RF sputtering power for manganese target was adjusted for the values of (0, 4, 5, 7 and 10 watts) to control the level of manganese doping concentration in the films and the prepared thin films were studied in details. The structural, surface, optical, electrical, chemical and magnetic properties of the films are affected by manganese dopants concentration in the films. The structural analysis confirmed that Mn-doped Zn_3N_2 thin films are polycrystalline with the preferential growth along $\langle 411 \rangle$ direction. Average grain size and RMS roughness of the films increased with the increasing of manganese concentration in the films. A red shift in the bandgap was observed in Mn-doped Zn_3N_2 samples with increasing manganese concentration in the films indicating that Mn creating mid-gap states. Carrier concentration decreased due to Mn incorporation in the film indicating Mn acting as carrier trap centers resulting in reduced carrier concentration. X-ray photoelectron spectroscopy analysis confirmed the existence of manganese in the films in three different oxidation states (Mn^{+2} , Mn^{+3} and Mn^{+4}). Manganese was found to be in the high and low spin states at the same time in sample S_2 - S_4 and intensity of high-spin state Mn increased with increasing Mn concentration. For sample with highest Mn concentration S_{10} Mn was not found to be in high-spin state indicating optimum Mn concentration for sample S_3 . Magnetoresistance measurements revealed the existence of magnetization in the films due to the changing of the electrical resistance with the applied magnetic field. Positive and negative magnetoresistance have been observed in the films.

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