

Studies on Sputter-deposited Cu nanocluster embedded ZnO Thin Films

A thesis submitted

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Submitted by

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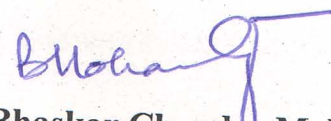
Dedicated

to

My Parents

Certificate

This is to certify that the report entitled "Studies on Sputter-deposited Cu nanocluster embedded ZnO Thin Films" submitted by Anubhav Gupta (301504007) of M.Sc. (Physics), Thapar University, Patiala was carried out by him under my supervision. He has not submitted this material for credit towards any other degree at Thapar University, Patiala or any other University.



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Abstract

We reported optical, magnetic, mechanical, structural and surface properties of sandwich structure of ZnO thin films with Cu as mid layer. ZnO was grown by RF sputtering and Cu was grown by DC magnetron sputtering technique. Deposition time of both the films were varied to study the evolution of its properties. The optical, mechanical, structural, surface and magnetic properties of the films were characterized by using UV-Vis Spectroscopy, Vicker hardness test, X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Vibrating Sample Magnetometer (VSM) respectively. Transmittance of as deposited decreases and after annealing transmittance increases due to presence of copper nanocluster reported by UV, increase in hardness of the film was reported by vicker hardness test, shifting of peaks due to compressive strain was reported by XRD, presence of nanoparticles and uniform film deposition was reported by SEM and diamagnetic phase was reported by VSM.

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Chapter 1

INTRODUCTION

Thin films are layers of any material with their thickness ranging from micrometer to nanometer [1]. In the past few decades, many research groups have investigated the synthesis and characterization of many oxides thin films such as (ZnO, TiO₂, SnO₂, In₂O₃ and HfO₂) [2].

1.1 Dilute Magnetic Semiconductors (DMS)

Those semiconductors in which a lattice ions is substitute by magnetic ions is called as diluted magnetic semiconductor. It is also called as semi-magnetic semiconductor. When these crystal are mixed it contain two connecting scheme. First scheme has delocalized electron in conduction band and some delocalized electron in valence band. Second scheme is arbitrary one, containing system of isolated magnetic moment having magnetic atoms related with them.

Most commonly used compounds are GaN and ZnO having metal ions of Fe, Ni and Co replacing its actual cations. Some other materials with this type of substituting ability are SnTe, InSb.

DMS has drawn intensive attraction because it has both charge and spin single substance. These are most promising candidate for spintronic application. Researches on DMS material which was carried out worldwide in past decades has been reviewed below.

These DMS material notice that when host matrix i.e. ZnO, GaAs etc was embedded with magnetic impurities by using transition metal, it reported ferromagnetism at 300K. Initial study showed that ferromagnetism in Mn doped semiconductor of III and IV group element are not used for practical application because curie temperature is low. Number of Groups elements show room temperature ferromagnetism in DMS materials are given below:

1.1.1 DMS materials showing room temperature ferromagnetism

- II-VI group elements : ZnMnSe, ZnCrSe, CdMnTe, ZnCrTe
- IV-VI group elements : PbMnTe, PbSnMnTe
- IV group elements : GeMn, SiMnC
- Oxides : ZnO:Mn, ZnO:Co, TiO₂:Co, SnO₂:Co, Cu₂O:Co
- Others : ZnSnMnAs, ZnGeMnP₂

Coming generation devices are based on the property of angular momentum, called as spin, has rapidly developed in the area of spin and electronic, combine known as spintronic. Magnetic ion containing semiconductor is considered as promising candidate for exhibiting spintronic function.

1.1.2 Application of DMS materials:

- DMS materials are used for storage the data in chips by magnetic spins of dopant atoms. They use both charge and spin of the electron to store the data.
- It is used to understand the material analysis i.e. defects, Nanostructures, Chemical composition etc.
- It is used as measurement characteristics such as frequency/noise characteristics, Thermal Stability etc.
- For small structure processing i.e. etching, isolation, interconnection etc.
- It is used in sensors, location detector like Automobile ABS control, Automated VCR etc.
- It is used in IC card, defence, space, digital mobile communication etc.
- It is used in storage of Data, HD display [3] etc.
- Future application of DMS will be in Spin FET, Spin Memory, quantum computing.
- It helps in to understand the theories of stimulation, Spin Polarization etc.

1.2 Choice of ZnO as a DMS Matrix

In past decades, ZnO attracted every one because it maintained the possibility of DMS materials when we doped with some metal and theoretical calculation also carried out to predict Curie temperature above room temperature T_c . But experimental results of ZnO based are still controversial. Creation of ferromagnetism in Zinc oxide based semi-magnetic semiconductor material also in controversial. While other concluded that an intrinsic carrier-mediated mechanism was responsible for the ferromagnetism.

Some experimental works has been done on these DMS such as ZnO, TiO₂, SnO₂, In₂O₃ and HfO₂ to confirm the ferromagnetism (FM). Due to void in oxygen some oxides like TiO₂, SnO₂, In₂O₃ and HfO₂ reveal ferromagnetism. But in Zinc oxide (ZnO) thin film the ferromagnetism nature is not due to oxygen vacancies. The ferromagnetism in ZnO is because defect in Zn⁺² sites which much influence the magnetism of the systems [4].

Some groups reported that a perfect ordering of crystal may be destroyed the FM or having large number of oxygen atoms could reduce the magnetic ordering. Firstly, we need to clarify that undoped ZnO thin films can show ferromagnetic [5]. Some reported that metal doping

in thin film does not play significant role in magnetic properties. It has potential for range of application in the area of optoelectronics. It is candidate for blue or UV light sources & it also has used as transparent conductive oxide in solar cells.

1.3 Zinc Oxide (ZnO)

Zinc based thin films have been widely studied over the years due to its optical and electrical properties suitable for a wide range of applications including gas sensor, solar cells, transparent electronic etc. Zinc oxide exhibit three structure mainly given below:

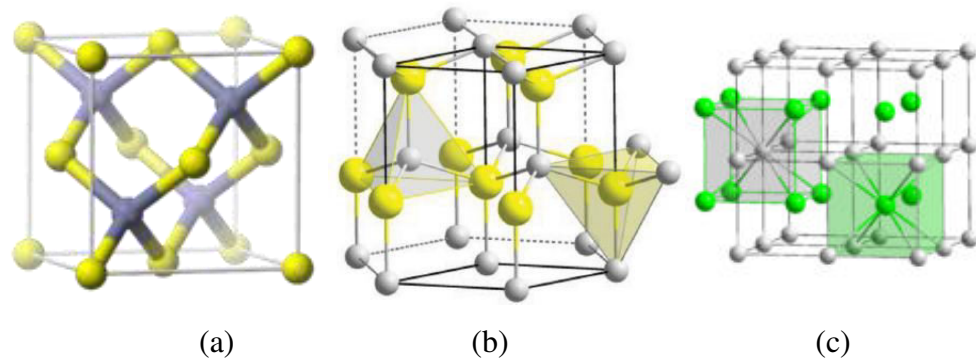


Fig. 1.1: 3d model of ZnO structure (a) Zinc blende, (b) Wurtzite (c) Rocksalt

In **Fig. 1.1** ZnO has three crystalline structure: cubic zinc blende, hexagonal wurtzite, and cubic rocksalt [6]. In surrounding condition, wurtzite structure is most secure. By growing ZnO on substrate with cubic structure zinc blende can be stabilized. Tetrahedral Structure is reported in above both cases of ZnO. No inversion symmetry has been observed in hexagonal and zinc-blende polymorphs.

1.3.1 Specification of Zinc Oxide

Molecular formula	ZnO
Appearance	white solid
Odour	odourless
Melting Point	1975°C
Boiling Point	2360°C
Solubility in water	0.16mg/100ml (30°C)
Band gap	3.3eV (direct)

1.3.2 Application of ZnO

- It is used in cosmetics.
- Used as manufactured of rubber as rubber cure.
- Pigments for paints and coatings.
- ZnO application as transparent conducting electrodes for photovoltaics (Solar cell) and light emitting diodes
- In electronics like laser diodes, light emitting diode (LED).
- It enhance the performance of solar cell.
- It is used in electrodes, displays in window materials and optoelectronic devices [6].
- Can be flexible electronics.
- Easy Fabrication at various shapes.
- It is piezoelectric and semiconducting coupled materials.

1.4 Literature review:

Hong *et al.* [7] reported magnetism in insulating magnetic oxides by preparing the chromium doped Zinc oxide and nickel doped tin oxidethin films fabricated by physical vapor deposition. Preparation of thin film takes place under different condition, they conclude that oxygen and defect in film plays a significant role in magnetism and then they conclude that filled the oxygen vacanices and defect, it effect the magnetism in the films.

Chen *et al.*[8] reported that Cu embedded ZnO thin film deposited by nano-beam technique. When embedded Cu, it enhance the ferromagnetism at room temperature, measured by alternating gradient magnetometer (AGM). XRD depict that there is no secondary phase formed but CuO and Cu₂O secondary phase were detected by Transmission Electron Microscopy (TEM). Maximum magnetization is 2.61 emu per cubic centimetre with lower coercivity of 71 Oersted. Magnetization increase by increasing the amount of Cu upto certain amount and then start decreasing with the amount of Cu. X-ray photoelectron Spectroscopy (XPS) told that copper oxidation take place and reduction of Zinc and Oxygen spectra. The charge transfer in Nanocluster-matrix due to existence of defect verified by Photoluminescence (PL) spectra, and some interaction take place between them.

Feng Yu *et al.* [9] prepared nitrogen embedded ZnO:N film by physical vapor deposition. Secondary ions microscope is confirmed by Raman spectra due to presence of N ion in ZnO. Result mechanism based on Model construction which has one electron from d-orbital of Zn will compensate with Nitrogen ions and resultant give net spin of one-half in Zn orbit.

Chang *et al.* [10] prepared copper doped ZnO prepared by pulsed laser ablation. They developed different films that produced n-type ZnO which is non-magnetic and p-type has ferromagnetism with curie- temperature above 350K. Magnetic moment decreased as Cu concentration increases. The explanation is based on distance between nearest neighbor copper atom.

Hong *et al.* [11] investigated the ferromagnetism in ZnO, HfO₂ and TiO₂ films. They told us FM in ZnO thin film is not due to oxygen vacancies as in case HfO₂ and TiO₂. They also told that magnetization of thicker film is very lower as compared to thin film. They prepared Fe and Mn doped ZnO thin films reveal clearly that metal doesn't play necessary role in magnetic properties of doped films. They told us that FM is not in bulk ZnO but in thin film form it has FM in room temperature. The dopant participate in tuning of FM in ZnO thin film.

Brize *et al.* [12] investigated that ferromagnetic can be identify in undoped semiconductor oxides. Semiconductor oxides such as ZnO, TiO₂, HfO₂, In₂O₃ etc is investigated. XMCD measurement of TiO₂ show that the FM is due to TiO₂ host matrix not with transition metal doping. But in ZnO the FM is not from vacancy in O but due to some defects in Zinc sites. They give a model on electronic structure i.e. exchange interaction between of the oxygen atom surrounded by electron provide local field symmetry could lead to FM in lower state. The model suggested that low dimension system effects has significant role in magnetic properties.

Senay *et al.* [13] prepared ZnO by RF sputtering in the presence of Argon and Oxygen (1:1). They investigate the properties of the ZnO thin film by XRD, UV-Vis, AFM, tensiometer. They adopted a tauc method to find the optical band gap. They conclude the estimate band gap 3.4eV which tell us how thickness affected the band gap of a film. There result told us surface composition of film play significant in optical band gap.

Yang *et al.* [14] investigated Langasite substrates effect the structural and nano-mechanical properties of ZnO thin film on at 200°C by rf sputtering at 200W power and at deposition time i.e. 1,2 and 3hours. AFM and XRD characteristics were examined. Different phase like (100), (002) and (101) of hexagonal phase at 31.75°, 34.35° and 36.31° resp. are introduced. ZnO film oriented along c-axis (002) decreases, when sputtering time increases and roughness also decreases with increase in sputtering time. From nano-indentation, young modulus measurement they concluded that deposition time of 3 hour give best result of ZnO thin film. Hardness of 9.2to 10.8 GPa are result of 1-3h deposition of ZnO thin film.

Shafiet *al.* [15] examined the effect on microstructure and electrical properties of ZnO thin film by introducing copper layer in them deposited on a substrate reported as glass which was deposited by sputtering technique i.e. RF. Cu thickness posses good microstructural and electrical

properties in ZnO thin film. Elementary analysis was carried out by SEM, structural analysis by XRD, surface topography and electrical properties were investigated by AFM and four probe respectively. They conclude that Cu/ZnO film has high crystallinity having very intense peaks in plane (002) of hexagonal structure. Higher Copper thickness in Zinc oxide thin films gives us equal grains which was heavily arranged and carried grain boundary also. This multilayered film has lowest resistivity of $1.53 \times 10^{-3} \Omega/\text{cm}$ and sheet resistance is $5.06 \times 10^2 \Omega/\text{sq}$. It shows that resistivity values decreases with Cu thickness.

1.5 Objective and Motivation

Motivation:

As the literature review presented above reveals ZnO thin films with incorporated transition metal shows room temperature ferromagnetism depending upon the growth conditions of the films. The saturation magnetization and coercivity strongly depends on the amount of transition metal in the films and the films processing conditions. It has been shown that despite Cu being diamagnetic when incorporated in ZnO results in ferromagnetism. Although a few reviews on Cu doped ZnO films have been carried out, Cu nanocluster embedded ZnO thin films have not been widely studied and forms the basis of this work.

Objective:

- Synthesis of Cu embedded in ZnO thin films by the sputtering techniques.
- Characterization of Cu embedded ZnO thin film;
 - Transmittance and Absorbance by UV-Visible Spectroscopy (UV-visible).
 - Hardness of film by Vicker hardness test (HV).
 - Surface morphology by Scanning electron microscope (SEM).
 - Structurally is identified by X-ray diffraction (XRD).
 - Room temperature magnetism by Vibrating Sample Magnetometer (VSM)

Chapter 2

EXPERIMENTAL TECHNIQUES

In this chapter, experimental techniques were used to grow and characterize the samples have been briefly presented.

From literature one can find a various techniques used for the deposition of ZnO based thin films. However, the sputtering based techniques have been recognized as the most popular one to prepare ZnO thin film, due to easy control over the process parameters, large area deposition, high reproducibility and high yield. In the following a brief overview of the techniques is presented.

2.1 Sputtering technique

There are number of techniques used to growth thin films e.g. sol-gel techniques, vapor deposition by chemical, spin-coating, sputtering, thermal evaporation, pulsed laser ablation deposition, etc. Above all techniques, sputtering is interesting method to deposition ZnO based thin films due to low substrate temperature, uniform deposition of film, less complicated, high adhesion, high yield.

The sputtering process take place in high vacuum chamber in which substrate is fixed in substrate holder in sputtering chamber, chamber contain an non-reacting gas, usually “Ar” and which generate plasma by applying a negative charge to a target source material that will be deposited onto the substrate fixed opposite to the target [17] as shown in **Fig. 2.1**

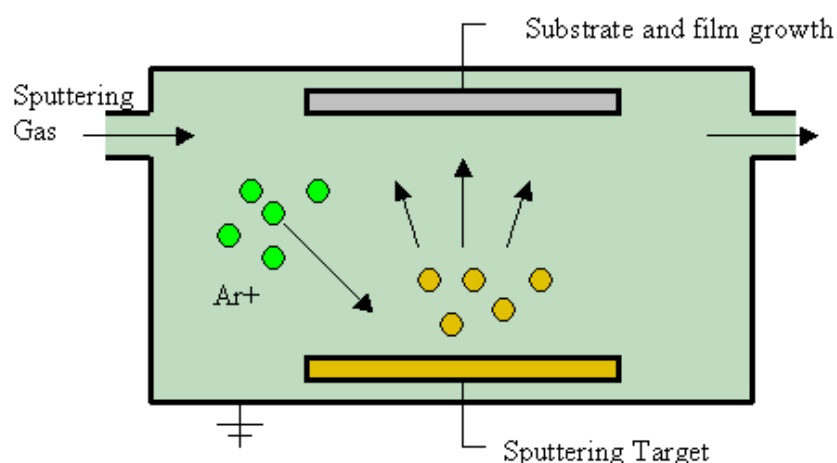


Fig. 2.1: Schematic diagram of Sputtering from target to substrate[16]

When kinetic energy of the bombarding particles are very high, much higher than normal then thermal energies in the plasma environment causes sputtering to be take place. By providing high energy to target source material, it deposits a uniform and pure film on the substrate [17].

The number of atoms ejected from the target is called the sputter yield. The sputter yield varies by controlling by the energy of incident bombarding ions. Several methods are widely used in sputter coaters, including reactive sputtering in an O gas surrounding, gas flow and magnetron sputtering[17].

Thin films are deposited by sputtering technique in today's world. **Fig. 2.2** show a sputtering machine which was used to deposit film at very high vacuum chamber.



Fig. 2.2: Outside Photograph of sputtering machine

By knowing, the biasing of target, sputtering is divided into two methods: direct current (DC) or radio frequency (RF) sputtering. Both processes are briefly given below:

2.1.1 Direct Current (DC) Magnetron Sputtering

DC sputtering is a thin film coating technique carried by Physical Vapor Deposition (PVD) in which target is ionized by inert gas which causes ions to sputtered out from a target material deposited on the substrate. The vaporization of ions from target material with the help Ar give a plasma to deposit thin film on a substrate [18].

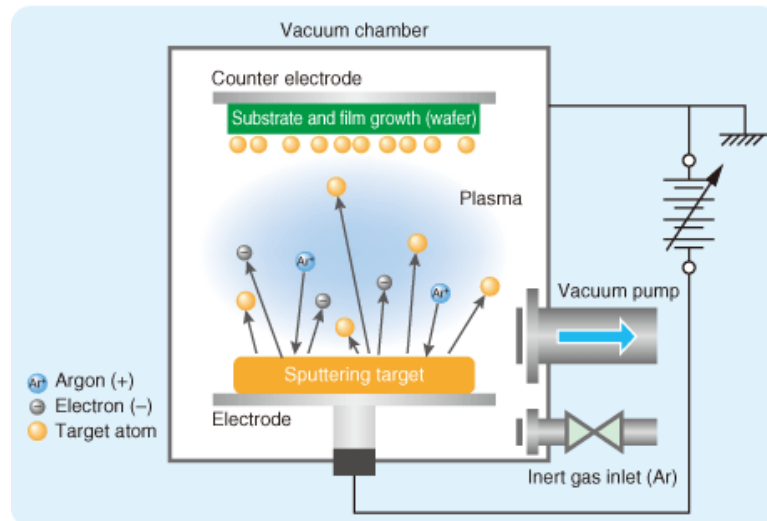


Fig. 2.3: Schematic diagram of Direct Current (DC) Magnetron Sputtering [19]

The schematic diagram of DC Sputtering coating system from target material placed in a vacuum chamber opposite to the substrate is shown in **Fig.:2.3**

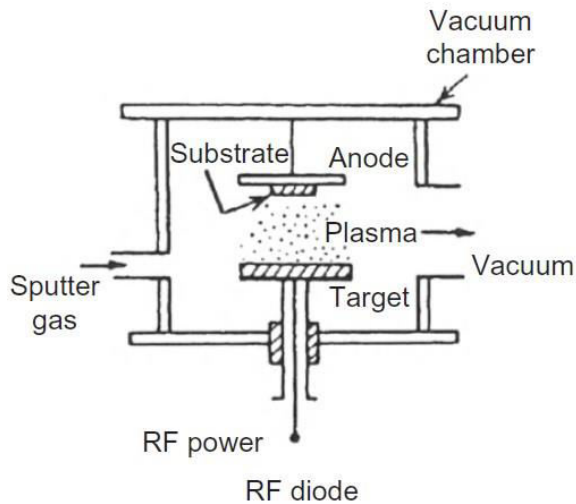
The vacuum chamber is evacuated by removing air from it and then backfilled with a high purity inert gas – usually Argon which has convey kinetic energy to high energy molecular collisions in the plasma that creates the gas ions used for sputter thin film. Typical sputter pressures range from 0.5mTorr to 100mTorr [18].

Electrically neutral Ar gas atoms are first ionized by colliding with gas atoms onto the surface of the negatively charged target, which remove atoms from it and turn into the plasma – a hot gas-like state containing half gas ions and half electrons which visible as plasma [18].

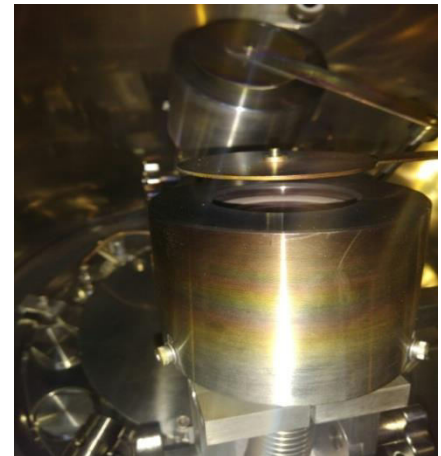
2.1.2 Radio Frequency (RF) Magnetron Sputtering

RF sputtering stand for Radio Frequency Sputtering. RF sputtering is the technique which involved alternating current in the highly evacuated chamber. RF does not generate charge on target material as in DC which turn to plasma [20].

In RF sputtering magnets are used in negative cathode to catch the electrons over the negatively charged target material, no atom are free to bombared on the substrate, It offers several advantages depending upon the specific application.



(a)



(b)

Fig. 2.4: (a) Schematic Diagram of RF magnetron sputtering, (b) Inside Photographs of RF and DC target loader

Above **Fig. 2.4 (a)** shows schematic diagram of RF and (b) RF and DC target loader. RF Sputtering can hold the plasma at lower pressure (1-15 mTorr). The result is fewer ionized gas collisions give more efficient deposition of material.

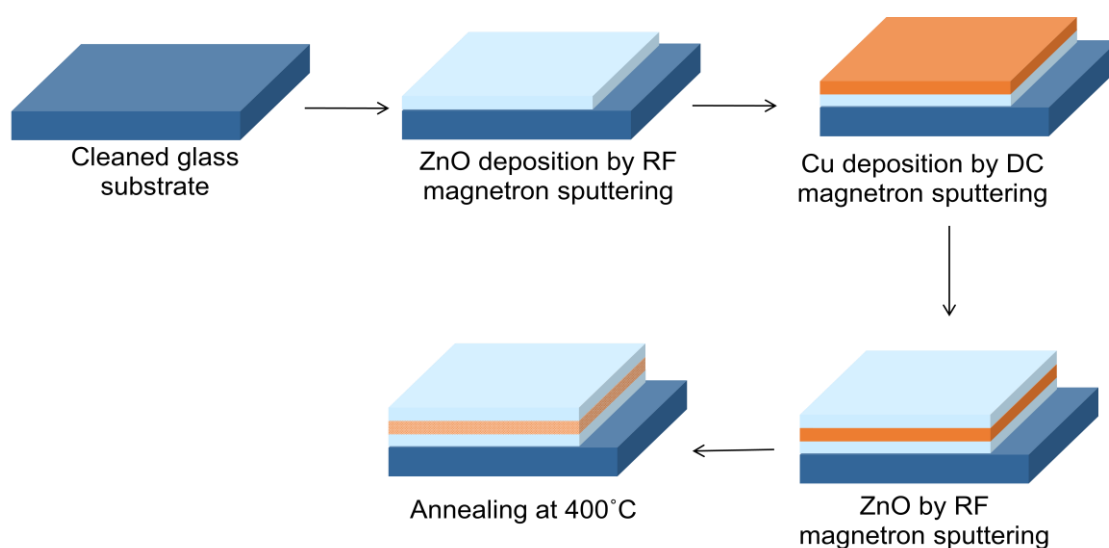
RF Sputtering avoid the creation of “Race track erosion” on the surface of the source material. With Magnetron Sputtering, a circular pattern is formed on surface of the target material as a result of the circular magnetic field of the magnetron focusing the charged plasma particles close to the surface of the sputter target. The diameter of the circular pattern is the result of the magnetic field.

2.2 Fabrication of Cu embedded ZnO thin film:

The ZnO thin films with various amount of Cu was prepared via two schemes. In the first scheme, a thin Cu layer was sandwiched between two identical ZnO layers, followed by a high temperature annealing. The ZnO films were prepared by RF magnetron sputtering while the Cu layer was prepared by DC magnetron sputtering.

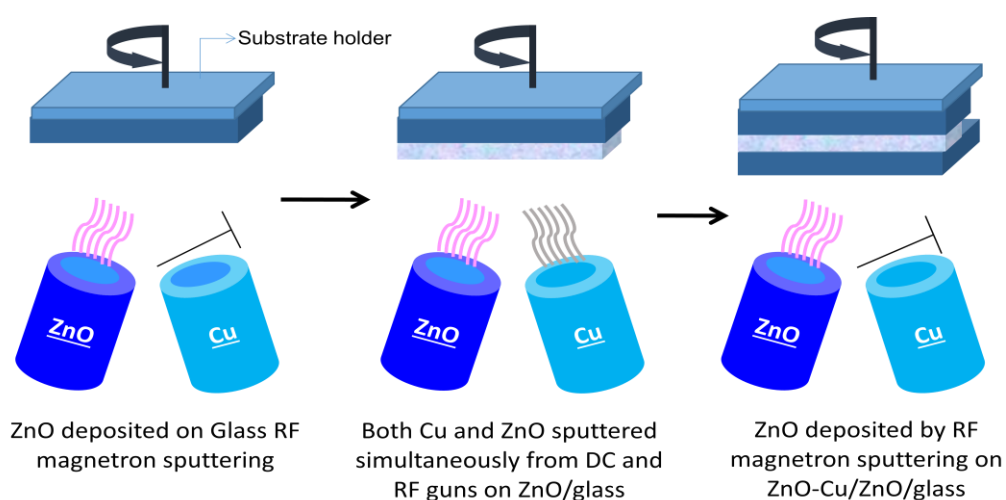
In Second Scheme, ZnO and Cu films were Co-Sputtered by using RF and DC magnetron Sputtering assembly respectively. The Schematic diagram of the growth process of the samples is presented in figure below:

Scheme-1



Schematic diagram of Sandwich structure ZnO/Cu/ZnO by sputtering

Scheme-2



Schematic diagram of Sandwich structure ZnO/ZnO+Cu/ZnO by sputtering

All samples were grown on sodalime glass substrates. The substrates were first cleaned by liquid soap and removing impurities by doing ultra-sonication for 1min before being wiped by acetone. In all cases, the base pressure was 2×10^{-6} mbar. A working pressure of 4.5×10^{-3} mbar was achieved by allowing “Ar” gas into the chamber through a gas mass flow controller limited at 100 SCCM. During sputter deposition of the films, the substrates were rotated at 7 RPM. ZnO was deposited from a compound ZnO target by RF magnetron sputtering while Cu was deposited by DC magnetron sputtering from a metallic target.

For the samples grown via Scheme 1, the RF power for the ZnO target was kept fixed at 50 W and the DC power for the Cu target was at 25 W. The top and bottom ZnO layers were grown for a typical period of 60 min each (~150 nm). The Cu target was sputtered for various times ranging from 10 to 540 s.

For the samples grown via Scheme 2, the RF power for ZnO was varied from 50 to 200 W during the co-sputtering stage (stage 2) while the DC power for Cu was fixed at 25 W. **Figure 2.5** shows a photograph during co-sputtering inside the chamber.



Fig. 2.5: Photograph of the plasma during the co-sputtering from RF and DC targets

Deposition time for ZnO (Zinc Oxide) layer was 30 minutes at same power i.e. 50W at condition mention above on the glass slide. The film formed on this condition was transparent. Amount of copper varied in all the sample. The timing of copper amount was 0, 10, 20, 30, 40 seconds as shown in top row in **Fig. 2.6**. The film started darken when the copper amount varied

The same was happen in the 3min, 5min, 7 min & 9 min copper deposition on ZnO film as shown in second row in **Fig. 2.6**. Then another layer of ZnO was deposited on the ZnO/Cu layer so it become ZnO/Cu/ZnO films or sandwich structure film was formed as shown below:

Then multi layered or sandwiched structure films were annealed at 400° C for 1 hour. The color of layer as compared to as deposited layer, after heating change as shown in third row in **Fig. 2.6**.

The deposition of ZnO in co-sputtered sample take place in different condition i.e. 50W, 100W, 150W, 200W at different deposition time, then shuttered of Cu was also opened at sputtering power i.e. 25W and both ZnO and Cu was deposited at same time for some time, on

glass substrate, after that third layer of ZnO was deposited and shuttered of Cu was closed. Different amount of copper deposition give different color to the sample as shown in fourth row of **Fig.2.6**

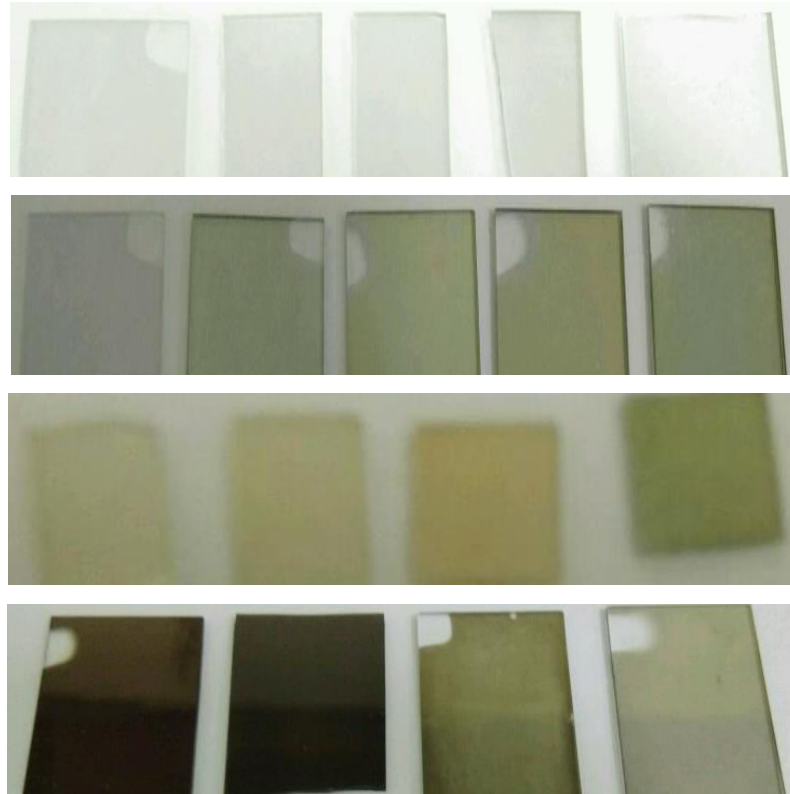


Fig. 2.6 Photographs of the as-deposited sandwich structure film i.e. ZnO/Cu/ZnO on glass substrate; First row: As-deposited samples with Cu of 0, 10, 20, 30 and 40 seconds of growth time; Second row: As deposited sample with Cu of 0, 3, 5, 7 and 9 minutes of growth time; Third row: The ZnO/Cu/ZnO/glass samples annealed 1hr at 400°C; Fourth row: The ZnO/ZnO+Cu/ZnO/glass samples with different amount of copper.

2.3 Characterization Techniques: A variety techniques were used to characterize the sample. In the followings they are briefly described:

2.3.1 X-ray diffraction (XRD)

XRD is used to characterization to find the crystal structure of any material. It gives us lattice constants, geometry, preferred orientation of poly-crystals, orientation of single crystal, etc. In XRD, collimated beam is fall on the sample having wavelength between 0.7 to 2 Å and it was diffracted by the sample crystalline phases according to bragg's equation

$$n\lambda = 2d\sin\theta$$

d = distance between planes in atomic crystalline phases

λ = wavelength falling X-ray on the sample

θ = incident angle of the beam

n = integer (Reflection Order)

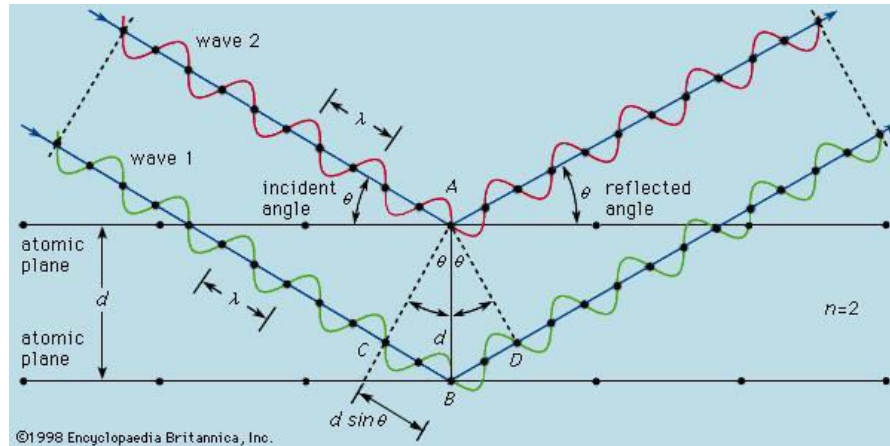


Fig. 2.7: Bragg's Diffraction Law (Encyclopaedia Britannica, Inc.)

The X-rays intensity depends on diffraction angle 2θ and sample orientation. Bragg's Law is used to find the structural properties and phases of crystalline. XRD is non-destructive. In XRD, sample preparation does not require to elaborate them. The diffraction peaks in XRD give us the best method for characterization of homogenous and inhomogeneous strains. For shift in peak position, there is strain in them due to change in d -spacing.



Fig. 2.8: Photographs of X-ray Diffraction Machine

2.3.2 Nano-indentation:

It gives mechanical properties of the material. It is variety of test in which we find hardness at very small volume.

Vickers Test:

Vickers test is the method in which we indent diamond in test material, in right pyramid square base which make an angle of 136° between opposite faces. Load is varied to indent the diamond from 10 to 500gf as shown in **Fig. 2.13**. Load is applied for 10 to 20 seconds. The two diagonals of the indentation left in the surface of the material after removal of the load are measured using a microscope and their average calculated. **Fig. 2.12** show instrument diagram of vicker hardness. The area of the inclined surface of the indentation material is calculated. The hardness calculation is carried out by quotient obtained by dividing the load by the mm^2 area of indentation. [21].



Fig. 2.9: Photograph of Vicker Hardness Instrument

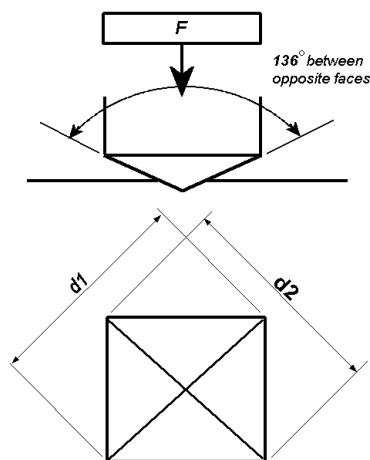


Fig. 2.10: Schematic diagram of Vickers Hardness Instrument [21]

F= Load in gf

d = mean of the two diagonals i.e. d1 and d2 (in mm), $d = \frac{d1+d2}{2}$

HV = Vickers hardness, $HV = 1.854 \frac{F}{d^2}$

2.5.3 Scanning Electron Microscope (SEM)

SEM is used to characterize the nano-material and nanostructure. The resolution of SEM is few nanometers and the magnification which can be adjustable varies from ~10 to over 30,000. SEM gives us topographical information and also provide the chemical composition of the surface. In SEM, electron providing source is focused on the surface from very fine spot size ~5nm and energy required for this material is varied from few hundred eV to 50KeV that move over the surface of the film and it was detected with the help of detecting coils. As the electron strikes the surface of the specimen and penetrates through it, a number of interactions happen with those of the specimen and give result in the emission of photons and electrons from the specimen.



Fig. 2.11 Outside photographs of scanning electron microscope machine

SEM images were produced by collecting the emitted electron by sample on the cathode ray tube (CRT). SEM images mainly produced by three type of emission electron:

- Secondary electron images
- Backscattered electron images
- Elemental X-ray maps

When a powered primary electron fall on the atom, it follow two type of scattering i.e. elastic and inelastic scattering, in elastic scattering take place with atomic nucleus and inelastic with atomic electrons. In inelastic scattering, the interaction is take place by transmit some part of energy of primary electron to other electron.

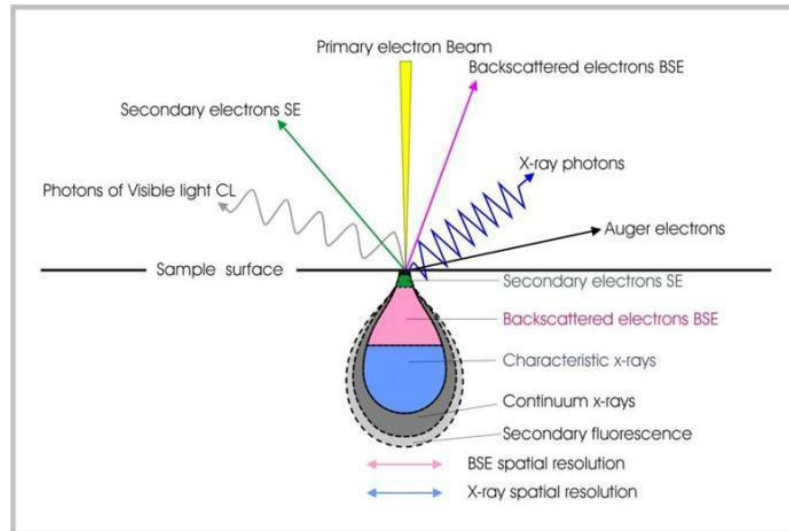


Fig. 2.12 Interaction of primary electron beam with sample surface[22]

Energy transmitted is higher enough, so the other electron will released by the specimen. The electron released from specimen has energy $<50\text{eV}$, regard as secondary electron. In back scattered has electron of higher energy which is elastically scattered and it has same energy as incident primary electron. Backscattering possibility increases when atomic number of the sample increases. Elemental identification does not carried by backscattering images.

X-ray Photon is emitted in SEM when excited atom will fall back to its lower state. X-ray photon is also called Auger electron. Auger electron or X-ray photon or both were used to find the chemical characterization called as EDX.

Theoretical limit of instrument is identified by calculating the resolving power by using the wavelength of the electron and the numerical aperture of the system. The Resolving power is denoted as R, so

$$R = \lambda / 2NA$$

λ = wavelength of the electron beam,

NA= Numerical aperture of the system

2.5.4 UV-Visible Spectroscopy

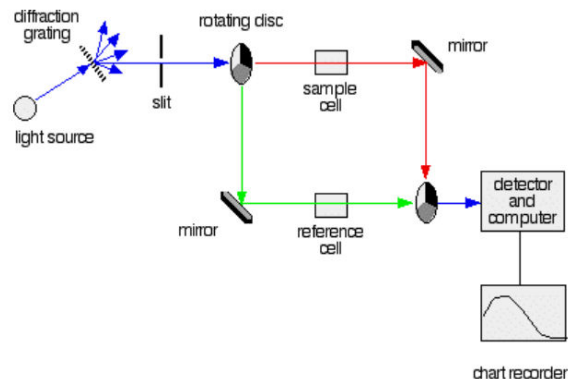


Fig. 2.13 Schematic diagram of UV-Visible Spectroscopy [23]

UV-Vis spectrophotometers are widely used in various fields for applications to measure the transmittance or reflectance of optical elements. Various measurement techniques are available for a sample to characterize physically e.g. if the substrate is opaque then reflection of that sample gives the thickness or if the substrate is transparent then the transmission of that film gives the thickness of the films.

The **Fig. 2.16** schematic diagram above shows the internal working of a UV-Visible instrument. A source light passes through the diffraction grating and a rotating disc is placed in it which directs the monochromatic light pass through reference sample and sample formed by us. After passing through sample, it is reflected towards the detector by mirror. It made a chart on the recorder. A Reflectance specular involves shined light fall on the sample and reflected by the sample at same angle as that of incident angle. It is useful especially for measuring the thin film on the mirror.

The UV-visible is based on Beer's law. It has a linear relationship with absorbance and concentration of absorbing sample.

The above Law is written as:

$$A = a(\lambda) \cdot b \cdot c$$

Here, A = absorbance of the sample

λ = wavelength depend on absorptivity

b = Path length, c = Analytic concentration.

When concentration is in molarity form, then Lambert law is written as :

$$A = \epsilon \cdot b \cdot c$$

E wavelength of dependent molar absorptivity coefficient units are $M^{-1}cm^{-1}$.

Relation between Transmittance (T) and Absorbance(A) is given by : $A=-\log T=-\log(I/I_0)$

2.5.5 Vibrating Sample Magnetometer (VSM)

VSM has common choices for measurements on magnetic material. A uniform magnetic field is applied to the sample. With this instrument it vibrates a sample and change the position of the sample. Due to vibration and change in position causes the amount sample flux, which was captured by a set of sense coils as shown in **Fig. 2.17**. The changing flux produce voltage proportional to sample magnetic moment. The actual dimension require to calculate the magnetic moment of sample was 10 mm x 10 mm because the sample moment is proportion to have a moment i.e. 4x higher than the moment of other size. VSM instrument made a graph between Magnetization versus applied field. It made a hysteresis loop.

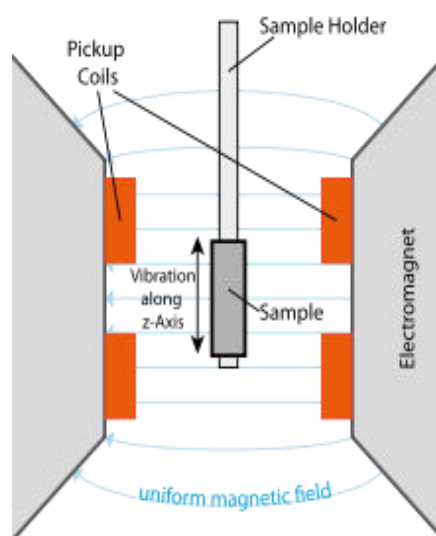


Fig.2.14: Schematic diagram of VSM [24]

Specifications:

1. Range: 0.00001 to 10000 e.m.u.
2. Temperature range: 77 to 1050 K
3. Magnetic field: -10 to +10 kOe
4. Rotation: up to 360° w.r.t magnetic field
5. Recording: X-Y(t) Recorder
6. Sample size: 10mm x 10mm

Chapter 3

RESULTS AND DISCUSSION

3.1 Optical Analysis:

The analysis of optical transmission spectra which is relate to glass substrate for a sandwich structure i.e. ZnO/Cu/ZnO thin film by changing the copper thicknesses. Generally, in the visible region, average transmittance of the films is about 82% including substrates and as in **Fig. 3.1** ZnO/ZnO show transmission is about 82% over the visible range of wavelength. Generally, transmittance decreases with increase in thickness of the film. As shown in **Fig. 3.1** when Copper layer was added at different time i.e. 3 min, 5min, 7min, 9min range show transmission drop to about 70% as copper concentration increased. This decrease in transmittance of Zinc oxide after Cu layer can is justified by structural modification of ZnO thin films. And it can be also be supposed that Cu ions embedded in ZnO lattice creating structural deformation. And Spectra also clearly show that the band edge of all the films is in range of 385 to 394 nm with band gap start decreasing by increasing the concentration of the Cu. In **Fig. 3.2**, when we annealed the samples. However, from shorter wavelength transmission is maximum and for higher wavelength the transmission was decreasing simultaneously the absorbance of the film increasing. So we can say that copper thickness effected the transmittance.

This increase in transmittance at wavelength below 600nm this is due to at higher wavelength in which free-carrier absorption influence and screening effects also arising from bound electrons which lead to increase in transmission when wavelength decreased.

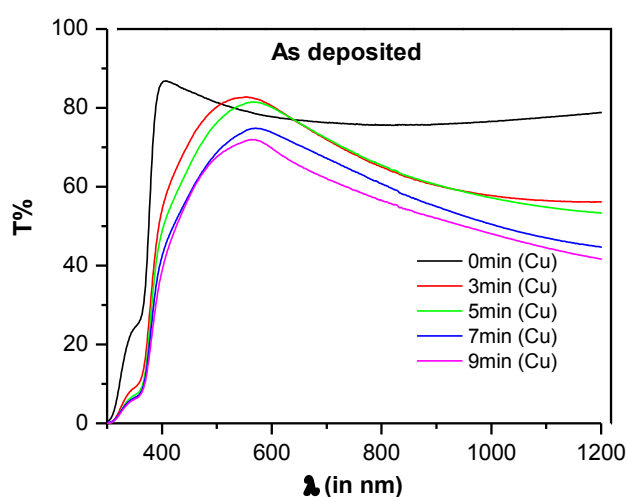


Fig. 3.1 Optical transmittance of as deposited samples

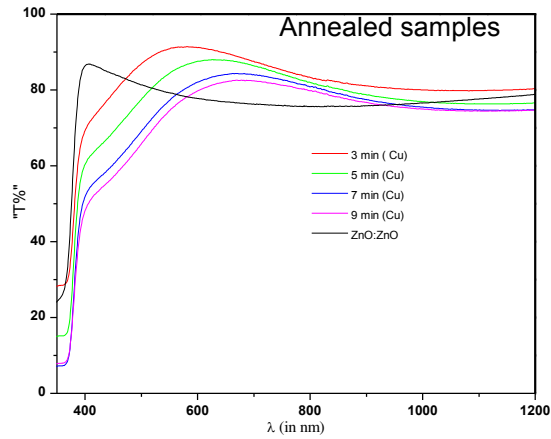


Fig. 3.2 Optical transmittance of annealed samples

3.2 Mechanical Analysis:

The analysis of mechanical properties of Zinc oxide thin films deposited in various sputtering power i.e. 50W, 100W, 150W, 200W and copper concentration were investigated by nano-indentation. At different sputtering power hardness of the also varied, ranging from 2 Gpa to 8 Gpa. In addition, the nano-indentation characteristics affected by load of indentation which is vary from 10gf to 500gf. The results as shown in **Fig. 3.3** confirmed that various sputtering powers and copper amount plays a significant role in the characteristics of indentation of ZnO film. So, at 200W and maximum amount of copper give maximum hardness.

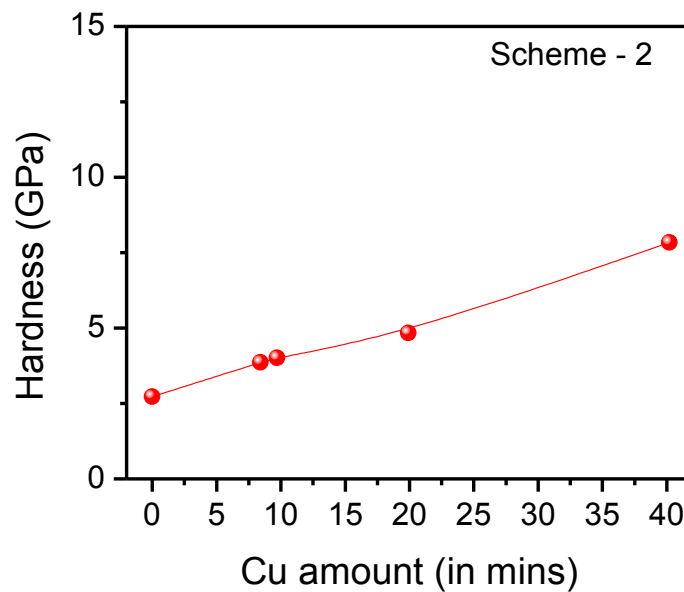


Fig. 3.3: Hardness vs Cu amount (in min)

3.3 Surface Morphology Analysis:

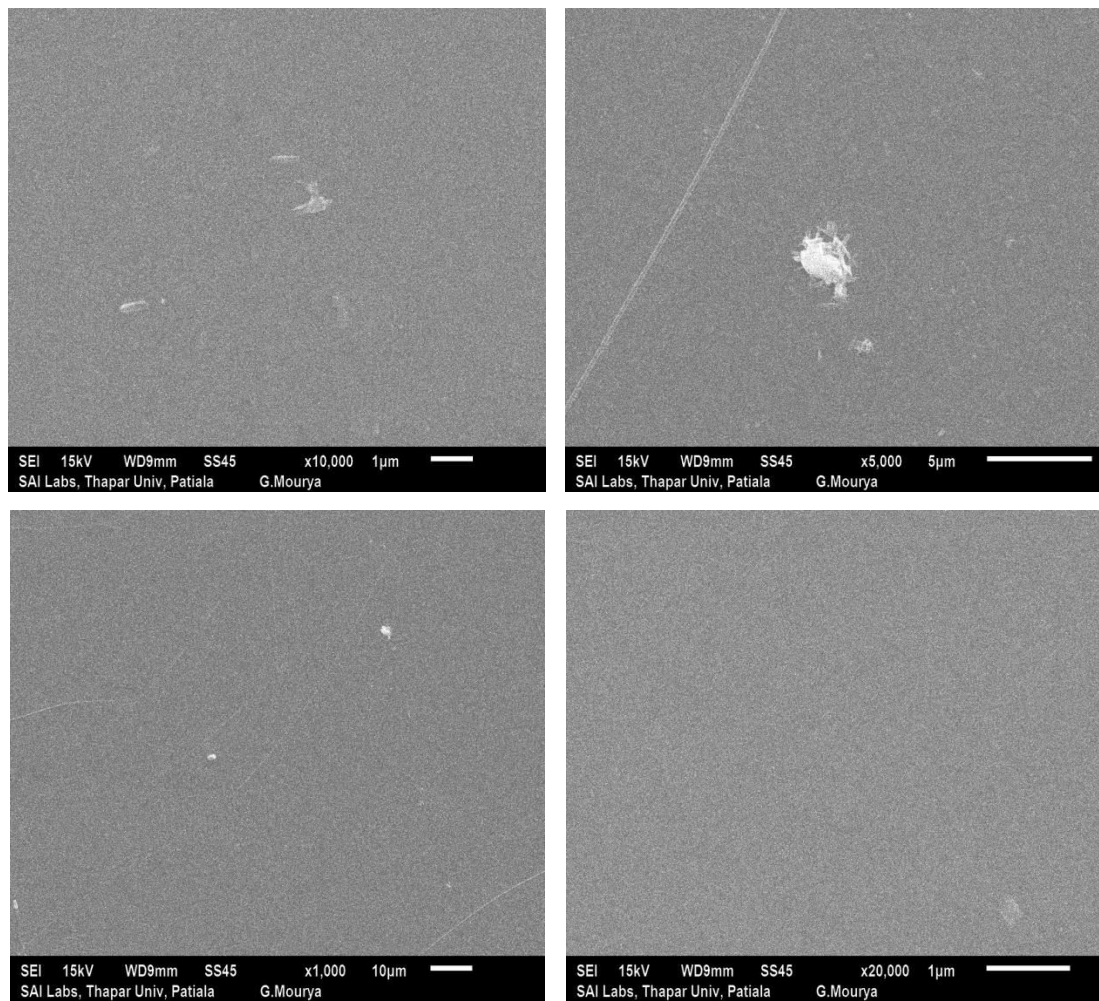


Fig. 3.4: Different Surface Morphology of ZnO/ZnO thin film by sputtering

SEM measurement was carried out to characterize the surface microstructure properties of ZnO/ZnO layer. SEM was taken at different magnification and different places on the films. A uniform layer of ZnO were observed and there is very small uniform grain in them.

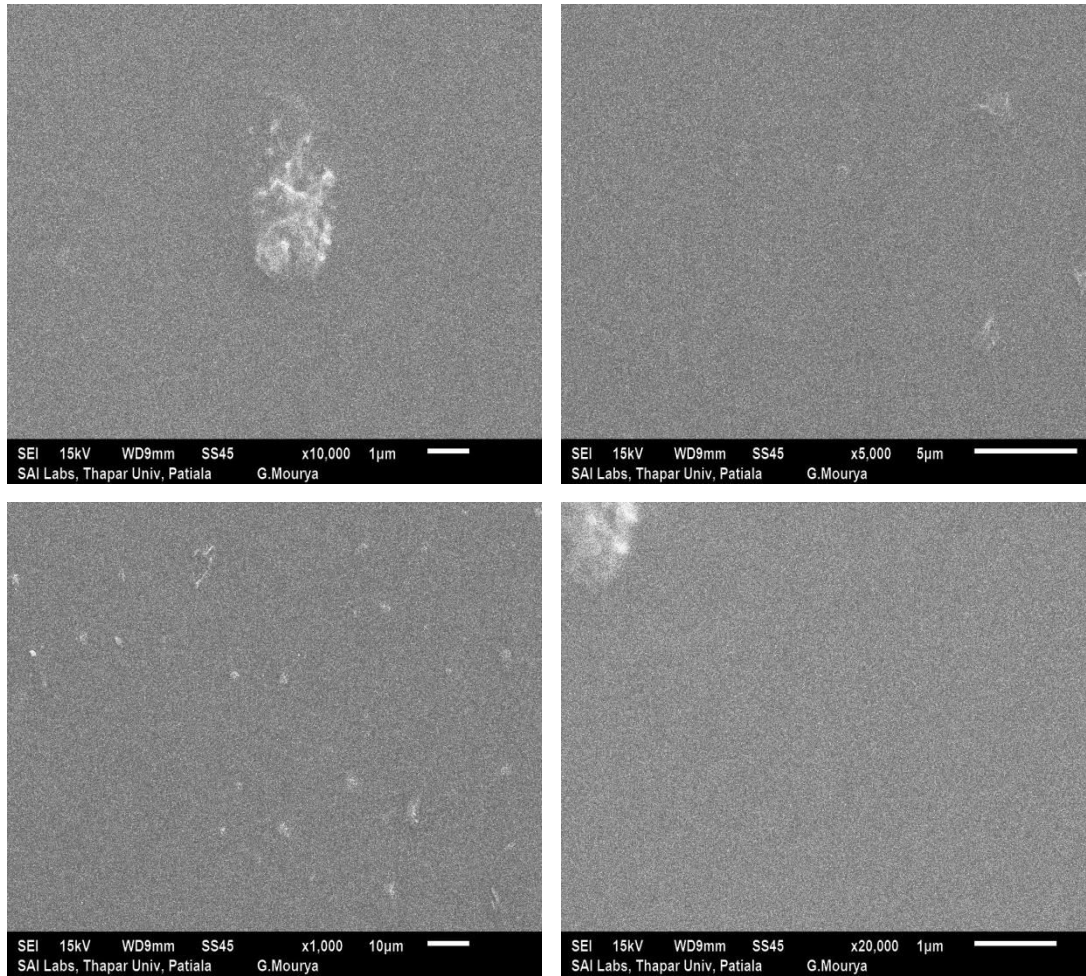


Fig. 3.5: Different Surface Morphology of annealed ZnO/Cu/ZnO thin film by sputtering

SEM measurement was used to characterize the surface microstructure properties of ZnO/Cu/ZnO layer. SEM was taken at different magnification and different places on the films. A uniform layer of ZnO were observed and there is very small uniform grain in them.

SEM measurement was characterize the surface microstructure properties of ZnO/ZnO+Cu/ZnO layer. SEM was taken at different magnification and different places on the films. In **Fig. 3.6**, we observed some pores and larger size pattern of grains.

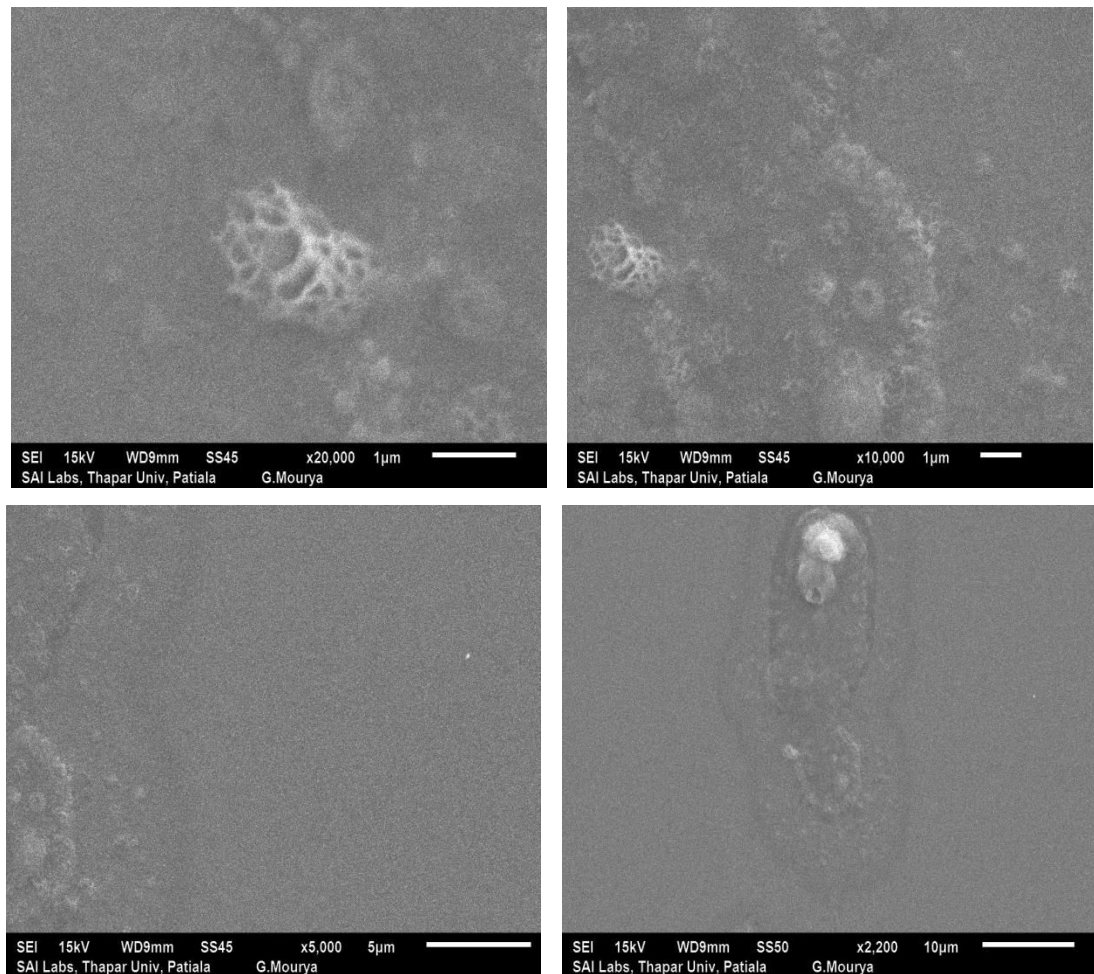


Fig. 3.6: Different Surface Morphology of ZnO/ZnO+Cu/ZnO thin film by sputtering

3.4 Structural Analysis

In **Fig. 3.7** show the X-ray diffraction spectra and the effect of Copper on crystallinity of the film. **Fig. 3.7** shows the XRD pattern of pure ZnO and Cu varied ZnO thin film with different amount of Cu thickness in them. Firstly, XRD peaks exhibit that film are highly crystallinity and having very sharp peaks.

The intense high XRD peaks corresponding to lattice reflection plane (002) of a hexagonal wurtzite structure with card number [00-001-1136]. High crystalline nature of ZnO thin film is identified by the presence of high intense peaks. It don't show any peaks of Copper because due to very less amount of copper thickness. Shifting in peaks is due to compressive strain in the layer.

It is clear from the **Fig. 3.7** that the (002) diffraction peak of sandwich structure ZnO/Cu/ZnO films shifted to higher angle as compared to ZnO/ZnO film. Shifting is mainly of 0.21° between a

pure ZnO/ZnO and ZnO/Cu/ZnO layer. This shifting of peaks is due ZnO/ZnO compressive strain and also due to small amount of copper presence between these layers.

In **Fig. 3.8** show the amorphous nature of the film at different amount of Copper and sputtering power of ZnO sputtered on it.

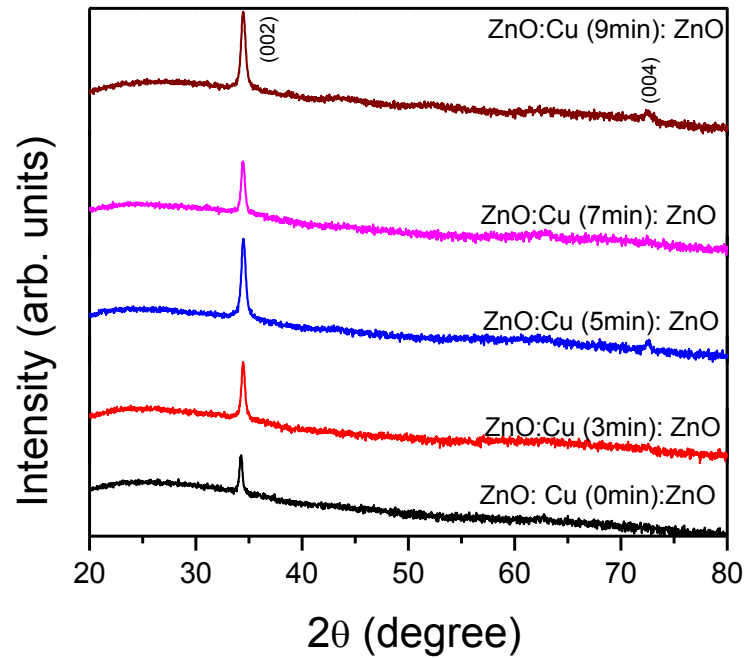


Fig. 3.7: XRD pattern of different ZnO/Cu/ZnO thin film by sputtering

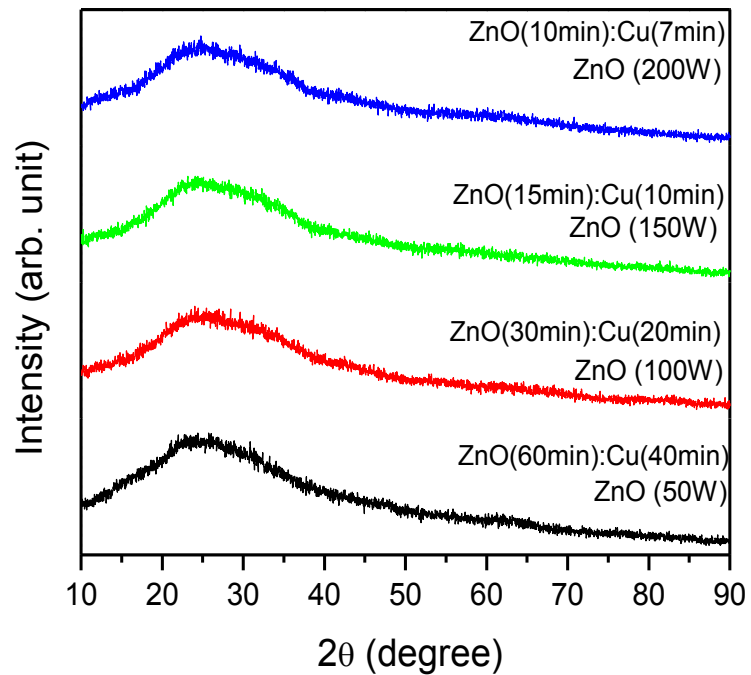


Fig. 3.8: XRD pattern of different amount of Copper in ZnO/ZnO+Cu/ZnO thin film by sputtering

3.5 Magnetic Analysis:

The magnetic analysis told us the magnetic behaviour of the ZnO thin films when it is embedded by Cu nanocluster. The magnetization versus applied field graph at room temperature for pure ZnO was diamagnetic because neither Zn^{+2} nor O^{-2} are magnetic in nature so there is no source of magnetism in them.

When we embedded Cu in different amount on it, still it show diamagnetic may be due to It show diamagnetism due to there is no interface effect between effect of nanocluster and matrix. There is no charge transfer between nanocluster-matrix and existence of defect and Copper species does not favourable for FM. The magnetism in ZnO films are reveals that it is a anisotropy, the film is basically diamagnetic behavior. We observed clearly in **Fig. 3.9** that both the films are diamagnetic.

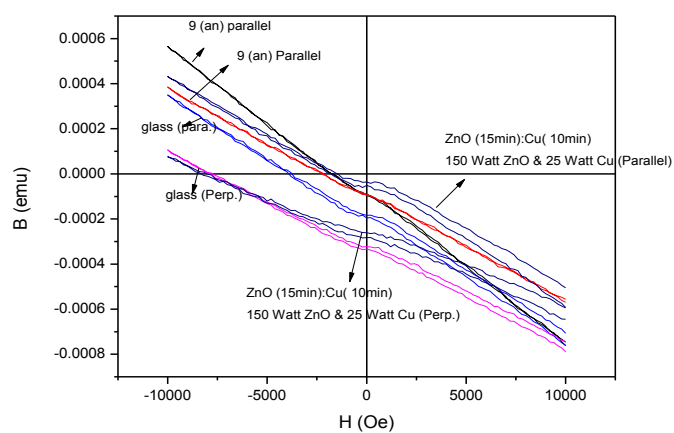


Fig. 3.9: Magnetic behavior of samples

Chapter 4

CONCLUSION

We conclude from all characterization that different amount of Cu nanocluster embedded in ZnO thin films prepared by sputtering play a significant role. The number of Characterization to analysis the films are UV-Visible Spectroscope, X-Ray Diffraction, Scanning Electron Microscope, Nano-indentation and Vibrating Sample Magnetometer.

- In optical analysis, amount of copper sputtered on ZnO thin film decreases transmittance in as deposited and increased by annealing.
- In structural analysis, all peaks in ZnO/Cu/ZnO sandwich structure confirm the crystalline nature. All samples were observed corresponding to wurtzite structure of ZnO and exhibit hexagonal phase. Shift confirmed the Cu effect on the films about 0.29° . In ZnO/ZnO+Cu/ZnO did not show any peak so it is amorphous.
- In surface morphology, pure ZnO has seemed to be spherical in shape and uniform formation of films by sputtering.
- The hardness of ZnO at different sputtering power and with different copper amount increases.
- The magnetic analysis give result diamagnetic nature of the film.

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