Chapter - 2
Experimental and Characterization Techniques
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In this chapter, the different synthesis and deposition techniques for the preparation of undoped and doped ZnO nanoparticles and thinfilms are discussed, respectively. Also, the different characterization techniques involved in the investigation of the different physical, structural, chemical, electronic, optical, luminescence and gas sensing properties of synthesized materials are discussed briefly.

2.1. Experimental

2.1.1. Solution Combustion Technique

The solution combustion technique (SCT) has been an unique method of synthesis of nanocrystalline materials in as-synthesized form with large surface area at low synthesis temperatures without further need of heat treatment [1-3]. The SCT has greater advantages, as it produce fine, large surface area and sinter active particles by using different precursors and fuels in as-synthesized form itself without any further heat treatment. This method has all the advantages of wet-chemical processes like homogeneity, control over stoichiometry, purity and incorporation of desired amount of impurity ions. Therefore, in this work, SCT has been adopted to synthesize pure and transition metals (Co, Fe) doped ZnO nanoparticles. In the present investigations, we have used different new fuels (L-Valine, L-Glutamine and Leucine) to synthesize pure ZnO nanoparticles and the effects of fuel to oxidizer ratio on the properties of synthesized ZnO nanoparticles are studied. Further, L-Valine is used to synthesize transition metal (Co and Fe) doped ZnO nanoparticles. The general synthesis procedure is given below in Fig. 2.1.
Stoichiometric amounts of oxidizer (O) and fuel (F) were taken based on the condition that the valency of F/O to be unity, using total oxidizing and reducing valencies of the oxidizer and the fuel, using propellant chemistry [1]. According to this concept, the valencies of C = +4, Zn = +2, H = +1, Co = +2, Fe = +3, N = 0 and O = 2. The total oxidizing valency of metal nitrates can be calculated from the arithmetic summation of oxidizing and reducing valencies of elements present in oxidizer. Similarly, the total reducing valency of a reducer (fuel) can be obtained from the arithmetic summation of oxidizing and reducing valencies of elements present in it. That is,

$$\frac{\text{Fuel}}{\text{Oxidizer}} = \frac{\sum_{\text{oxidizing and reducing valencies of Fuel}}}{(-1)\sum_{\text{oxidizing and reducing valencies of Oxidizer}}} \quad \ldots \ldots (2.1)$$
Therefore, The F/O ratio was calculated based on oxidizing [O] and fuel [F] valencies of the reactants, keeping F/O = 1, in order to have the complete combustion. Also, one can vary F/O ratio in order to see the effect of fuel on the properties of the final product. These stoichiometric amounts of starting materials were dissolved in double distilled water and stirred thoroughly to get transparent solution. The transparent solution was then dried on a muffle furnace at 100 °C to remove water content in the solution. So obtained sticky gel (water free) was then placed inside a pre-heated muffle furnace at 400 °C for the combustion process. Within a short duration (< 5 min), the gel auto ignites with flame and with the rapid evolution of enormous amounts of gases to produce voluminous foamy product (ash). The final foamy product was collected and ground using agate pestle and mortar.

2.1.2. RF- magnetron sputtering

Recently, the devices on flexible substrates received considerable attention due to the very advantage of flexibility. However, due to the poor thermal tolerance of these flexible substrates, the devices on these substrates need to be deposited at low substrate temperature. This leads to a compromise on the crystalline quality of the deposited films. Hence, it has been a major challenge for the researchers to deposit high quality crystalline films on flexible substrates. In this regard the advantages of rf magnetron sputtering, over other techniques, are exploited in depositing the films of high crystalline quality with required resistance and the transparency at temperatures less than 100 °C, often without additional heat treatment. Magnetron sputtering is a low-cost and easy control method for film growth, especially suitable for large-scale film deposition. The rf magnetron sputtering technique has its own advantages to produce good quality of films having high surface area and surface roughness which are pre-requisite for many technological applications such as TCO’s and Sensors. In addition, many parameters can be varied in order to obtain good quality of films with high reproducibility.

2wt% Al doped ZnO (AZO) films were deposited onto clean quartz substrates by a 13.56 MHz rf magnetron sputtering technique using a 2 inch Al-doped ZnO (AZO) target of purity 99.99% [4]. The sputtering chamber was evacuated to a base pressure of about $1 \times 10^{-6}$ Torr using a turbo molecular pump. Working pressure was maintained at 5 mTorr under high-purity Ar (99.999%) gas. The quartz substrates were ultrasonically cleaned in acetone, methanol,
ethanol, and distilled water, sequentially, and finally dried with nitrogen gas. The AZO films were deposited onto clean glass substrates for 10 min at room temperature (RT) with varied RF power from 50 to 120 W under pure Ar plasma.

2.1.3. Sol-gel Spin Coating

Sol–gel process received much attention because of its low cost and its simplicity. This process is capable of producing high-quality coatings even on both large- and small-sized substrates which can be employed for advanced applications. In the present investigation, we have deposited pure and (1-3%) Al doped ZnO thin films by sol-gel spin coating method onto ITO coated glass substrates using 0.8 mol/L concentrated solution. The procedure is given below. Fig. 2.2 shows the flow chart of the procedure for synthesis of AZO thin films. Zinc acetate dihydrate (Zn(CH₃COO)₂. 2H₂O), Aluminum Chloride Hydrate (AlCl₃ xH₂O), 2-methoxyethanol and Di-ethanol-amine (DEA) were used as a source, dopant, solvent and stabilizer, respectively. The stoichiometric amounts of zinc acetate dihydrate, Aluminum Chloride Hydrate were dissolved in 2-methoxyethanol at room temperature to obtain source solution (A) and dopant solution (B), respectively. The mixture was stirred at 60 °C and diethanol-amine (DEA) was added drop wise to the solution A as a stabilizer until clear solution was achieved. Then solution B is added drop wise to the solution A in order to obtain the stoichiometric solutions of pure, 1, 2 and 3 mol% Al doped ZnO. The resulting precursor solutions were stirred at 60 °C for 2 h to form a clear and transparent homogeneous mixture. Then the solution (sol) was aged for 48 h at room temperature and then filtered and stored in a container. The concentration of the solution was 0.8 mol / L and molar ratio of DEA to zinc acetate was maintained at 1:1. Prior to the deposition, the glass substrates (Sigma Aldrich) were cleaned thoroughly with soap water, tap water, deionized water and consequently cleaned with acetone and with DI water for 5 min each with the help of ultrasonic bath, then dried with air blower. Finally the substrates were baked at 350 °C for 10 min and cooled down to room temperature. Pure, 1, 2, 3 mol% Al doped ZnO thin films were obtained by spin coating the sol at a rotation speed of 3000 rpm for 60 sec and the wet films were heated at 350 °C for 10 min and cooled down to room temperature. The process of coating and subsequent drying at 350 °C was repeated for 10 times to get the desired thickness of the film. Finally, the as-prepared films
were post annealed at 550 °C for 2 hr and cooled down to room temperature in a muffle furnace.

**Fig. 2.2** Flow chart showing the synthesis procedure for AZO thin films

### 2.2. Characterization Techniques

#### 2.2.1. Thermo-Gravimetry and Differential Thermal Analysis (TG-DTA)

Thermo-Gravimetry (TG) refers to the measurement of change in mass of a sample ($\Delta m$) with temperature ($T$). Differential Thermal Analysis (DTA) refers to the measurement of change in temperature of a sample ($\Delta T$) (with respect to a standard sample) with temperature ($T$). TG-DTA helps to understand (a) the thermal stability (melting point) or degradation (decomposition) of solid materials in various gaseous atmospheres; hence the volatilities and
the residues of the samples can also be determined. (b) It also helps to provide the quantitative information on the mass losses of different materials at different temperature ranges under different ambient gas environments such as, nitrogen, argon, oxygen and hydrogen individually or in a combination of two gases. (c) Phase transitions (e.g. glass transition, crystallinity, melting etc) and (d) Reaction kinetics in various gaseous atmospheres (e.g. oxidation, reduction, hydrogenation, adsorption etc) can also be studied.

In the present work, TG-DTA analysis of combustion redox mixture was carried out to understand the nature of the reaction process in the combustion synthesis; in other words the decomposition of gels or the thermal stability of the final product (combustion material). Initially the precursor (redox mixture) was dried on hot plate to form the dried gel. Then the dried gel was subjected to the TG-DTA characterization, carried out at CoE-MS, Thermax, Pune using NETZSCH STA 449F3 instrument. The studies were carried out in a synthetic air atmosphere (80% N₂ and 20% O₂) with a flow rate of 80 mLmin⁻¹ N₂ and 20 mLmin⁻¹ O₂ in the temperature range of 25 – 1000 °C at a heating rate of 10 °C/min. The accuracy of the TG-DTA microbalance is 1 µg and the accuracy of temperature sensor is 0.1 °C. Hence the quantitative analysis carried out on the data obtained from TG-DTA, to determine the decomposition of precursor material, crystallinity and residues, etc.

2.2.2. X-ray Diffraction

X-Ray Diffraction (XRD) is a finger print analytical technique, which uses X-Rays (Cu Kα) of wavelength 1.5418 Å to probe crystallographic information in a material. That is the phase purity, structure, lattice parameters, lattice micro-strain, dislocation density, stress, crystallite size, bond length and bond angles, etc. The XRD was carried out through two methods; (a) Powder XRD for powder samples and (b) GIXRD (Glancing Incidence XRD) for thin films. In both cases, the data obtained from XRD characterization can be quickly compared with the data stored in a standards database called JCPDS (Joint Committee on Powder Diffraction Standards) patterns and the contents (phases) of the material of interest can be determined by a search-match process. In the thesis work, the XRD patterns of undoped and doped ZnO samples were indexed by comparing with the corresponding JCPDS patterns of ZnO and other possible impurity phases. Hence the purity / impurity of the prepared samples
are indentified. Rietveld refinement was carried on PXRD patterns using Fullprof suite [5], to investigate the possibility of presence of impurities and also to obtain the refined lattice parameters. After comparing and identifying the crystal structure, the \((h \ k \ l)\) indices are indexed for the crystal reflections in the XRD patterns. The crystallite size, strain, dislocation density, lattice parameters, unit cell volume, stress and the bond length parameters of the samples were estimated from the XRD patterns using following equations.

The mean or average crystallite size and strain are calculated using Williamson-Hall equation [6].

\[
\beta \cos \theta = \frac{k \lambda}{D} + 4 \varepsilon \sin \theta \quad \text{.................. (2.2)}
\]

where, \(\beta = \sqrt{\left(\beta_0^2 - \beta_i^2\right)}\) is the effective FWHM, \(\beta_0\) is the observed FWHM, \(\beta_i\) is the instrumental broadening, \(\theta\) is the Bragg angle, \(k\) is the Scherer’s constant \((0.9)\), \(\lambda\) is the wavelength of the X-ray used, \(D\) is the mean crystallite size and \(\varepsilon\) is the strain present in the crystal. Synthesized micro-crystalline ZnO powder \((\sim 0.7 \ \mu m)\) was used for the estimation of the instrumental broadening. Crystallite size and strain were determined from the intercept and slope obtained by plotting \(\beta \cos \theta\) along y-axis and \(4 \sin \theta\) along x-axis.

or

The crystallite size \((D)\) and strain \((\varepsilon)\) was calculated for highest intensity peak, using Scherer’s formula;

\[
D = \frac{k \lambda}{\beta \cos \theta} \quad \text{.................. (2.3)}
\]

and

\[
\varepsilon = \frac{\beta \cos \theta}{4} \quad \text{.................. (2.4)}
\]

respectively.

Further, the lattice parameters ‘\(a = b \neq c\)’ were estimated using the following equation;

\[
\frac{1}{d^2} = \frac{4}{3} \left[ \frac{h^2 + k^2 + l^2}{a^2} \right] + \frac{t^2}{c^2} \quad \text{........ (2.5)}
\]

Where, \(d\) is the lattice spacing, which is calculated using the Bragg’s law,
\[ d = \frac{n\lambda}{2\sin\theta} \]  \hspace{1cm} (2.6)

Where, \( n \) is the order of diffraction (taken as 1), \( \lambda \) is the X-ray wavelength and \( \theta \) is the Bragg diffraction angle.

The unit cell volume for hexagonal system was determined using the equation;

\[ V = 0.866 \ a^2 c \]  \hspace{1cm} (2.7)

The estimated lattice parameters \( a = b \neq c \) and unit cell volume values are compared with the standard values of JCPDS card no. 36-1451.

The dislocation density \( (\delta) \), defined as the length of dislocation lines per unit volume is estimated using the following equation;

\[ \delta = \frac{1}{d^2} \]  \hspace{1cm} (2.8)

The stress in the films is estimated using the biaxial strain model [7-8].

\[ \sigma = -232.8 \times \varepsilon \ (GPa) \]  \hspace{1cm} (2.9)

The bond length \( L \) of Zn-O is estimated using the following equation [9-10];

\[ L = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2} \]  \hspace{1cm} (2.10)

For hexagonal wurtzite structure, \( u \) is given by following relation;

\[ u = \frac{a^2}{3c^2} + 0.25 \]  \hspace{1cm} (2.11)

2.2.3. Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS)

A Scanning Electron Microscope (SEM) is basically an imaging tool used to study the surface morphology of materials up to a magnification of 1,00,000X. It is called a scanning electron microscope because images are obtained by scanning the surface of a sample by an electron beam and detecting the electrons scattered from the surface of the sample. Generally, an electrically conducting sample such as a metallic sample can be studied without much of a
sample-preparation. Whereas, electrically insulating materials such as polymers, biological samples, ceramics, glasses sometimes need to be coated with a thin layer of electrical conductive material such as gold or carbon for obtaining better images. From the SEM micrograms the morphology, such as, voids, cracks, porosity, agglomeration, grain distribution and the average grain size was determined. On the other hand, for thin films, the cross-sectional SEM helps to estimate the thickness of the film on the substrate, adhesivity and layered structure if any can be studied. The X-rays produced by the electrons scanning the surface of the material can be studied using an attachment called Energy Dispersive X-ray Spectrometer (EDS). The quantitative information on chemical composition of contents of the sample can also be estimated. That is, EDS is best suited for detecting and mapping the elements present on the surface of a sample. Samples were characterized for their morphology and elemental composition using SUPRA 55 FESEM/ EDX (M/s Carl Zeiss, Germany) equipment at UGC-DAE-CSR, Kalpakkam.

2.2.4. Transmission Electron Microscopy

Transmission Electron Microscope (TEM) is known to be a very powerful, efficient and versatile imaging tool for material science which uses electrons as light source and their much lower wavelength makes it possible to obtain a resolution much more than SEM. In TEM, the interactions between the high energetic electrons and the atoms of the sample can be used to observe features such as the crystal structure and features in the structure like dislocations and grain boundaries. Transmission electron microscopy provides us with high resolution TEM (HR-TEM) images that show structures at the atomic scale. That means we are able to identify features on the size of 2 Å (i.e. 2 x 10^{-10} m). We can use this tool to take a look at the arrangement of atoms in a crystal. HRTEM is the best method used to determine the size and size distribution of nanoparticles samples.

In detail, TEM also helps to estimate the shape, distribution and size of the particles accurately with high resolution. ZnO samples were characterized for their structure, morphology through HR-TFM using LIBRA 200 TFM (M/s Carl Zeiss, Germany) equipment at UGC-DAE-CSR, Kalpakkam. Once a representative group of images is obtained, the next task is to count as many particles as possible, so that good statistics on the size and size
distribution present can be obtained, which was done using ImageJ software [11]. Also, HR-TEM helps to study the morphology of the sample with more precisely and accurately. One can also perform Inverse Fast Fourier Transformation (IFFT) on the HR-TEM image to estimate the d-spacing of the crystalline sample; hence the orientation of the crystallites can be determined. It helps to estimate the possible presence of impurities which was not detected from the XRD due to its limitations. On the other hand, Selected Area Electron Diffraction (SAED) is an useful tool in determining crystal structure and structural parameters like, d-spacing, lattice parameters. SAED pattern consists of diffracted ring patterns, each ring is corresponding to a contented diffraction condition of the sample’s crystal structure, for which d – spacing values can be determined and corresponding (h k l) values can be assigned using standard JCPDS patterns. Having known the values of d-spacing and (h k l) planes, the lattice parameters for hexagonal crystal system can be determined using the formulae (2.5) – (2.7) and compared with the standard values.

2.2.5. Atomic Force Microscopy

Atomic Force Microscope is the imaging technique used to investigate the surface topographic features of the samples, basically thinfilms, using metallic tip as a probe. In AFM, three modes of operation is possible depending on the nature of the sample surface; (a) contact mode, (b) non contact mode and (c) tapping mode. The advantage of AFM is that, it extends the 2D line profile or surface to 3D view. Hence one can evaluate the topographic features.

For ZnO thinfilms, the surface topographic features were examined though Atomic Force Microscope (AFM) images recorded on an APF Research AFM A100 instrument available at MRC, IISc, Bangalore. From the AFM micrographs, topographic features such as, average roughness (Rq), rms roughness (Rq), skewness (Rsk) and kurtosis (Rsk) are determined. The average roughness (Rq) and the root mean square roughness (Rq) are the amplitude parameters give information about the height distribution of the surface features, deviation and standard height deviation, respectively. The parameters such as skewness (Rsk) and kurtosis (Rsk) are the measure of the asymmetry and the sharpness, respectively. Therefore knowing these parameter values the nature of the sample surface can be evaluated.
In particular, the skewness ($R_{Sk}$) is used to measure the profile symmetry about mean line. Hence, skewness ($R_{Sk}$) can either be zero, positive or negative. If the height distribution is symmetrical, the skewness factor $R_{Sk}$ is zero. If the height distribution is asymmetrical, and the surface has more peaks than valleys, the skewness ($R_{Sk}$) is positive and if the surface is more planar and valleys are predominant the skewness ($R_{Sk}$) is negative. The kurtosis ($R_{Ku}$) is a measure of surface sharpness of the films surface. If $R_{Ku}$ is 3, indicates a Gaussian amplitude distribution, and the surface is called Mesokurtic, but if kurtosis is smaller than 3 the surface is flat and called ‘Platykurtic’. If the kurtosis is higher than 3, the surface has more peaks than valleys.

2.2.6. Raman Spectroscopy

It is a spectroscopic technique used to observe vibrational, rotational and other low frequency modes in the material based on the Raman Effect. The Raman Effect is due to inelastic scattering of monochromatic light (laser) and it occurs when an electromagnetic radiation strikes on a molecule and it interacts with the polarizable electron density and the bonds of the molecule in the phase. Photons of the laser light are absorbed by the sample and then reemitted. The frequency of the reemitted photons is shifted up or down in contrast with the original frequency of the monochromatic light. This effect is called the Raman Effect. This Raman shift provides information about the vibrational, rotational and other low frequency transitions in molecules. Raman spectroscopy can be used to study solid, liquid and gaseous samples. It provides the complementary information to the IR (infra red) spectroscopy. Therefore IR and Raman are the most common vibrational spectroscopic methods for assessing molecular motion and fingerprinting species. In other words, Raman helps in determining the structure and symmetry of the molecules. Therefore it provides a finger print by which the molecule can be identified. This technique is also used to determine the presence of small impurities which is difficult to detect through XRD. The qualitative analysis can be performed by measuring the frequency of scattered radiations and quantitative analysis can be performed by measuring the intensity of scattered radiations.

The thin films of Al doped ZnO were characterized using Horiba Jobin Vyon HR Raman – micro PL spectrometer instrument using the laser excitation source of wavelength 530 nm.
and power 15 mW available at CeNSE, IISc, Bangalore. The data obtained from the Raman measurements is plotted against Intensity vs Raman shift. Raman shifts are typically represented in wave numbers (cm⁻¹), which have the units of inverse wavelength, in turn directly related to the energy. The Raman spectra were studied for their molecular modes, structure, symmetry and possible impurities present in the material.

### 2.2.7. UV-Visible Spectroscopy and Diffused Reflectance Spectroscopy

UV-Visible characterization was carried out in the wavelength range 200 – 800 nm. The optical band gap of undoped and doped ZnO nanoparticles and thin films are estimated using the diffused reflectance spectroscopy (DRS) and UV-Visible spectroscopy (UV-Vis), respectively.

In UV-Vis, the optical absorption spectra can be used to determine the band gap energy of the material. The optical absorption coefficient, $\alpha(\lambda)$, was determined using the following equation [12]:

$$\alpha(\lambda) = \frac{A}{d} \tag{2.12}$$

Where, $d$ is the thickness of the thin film.

The band gap energy was calculated using the Tauc’s equation;

$$a\nu = B(h\nu - E_g)^n \tag{2.13}$$

Where, $B$ is a constant, ‘$\nu$’ is the photon energy, ‘$E_g$’ is the optical energy band gap and ‘$n$’ is a number which characterizes the transition process. The exponent ‘$n$’ takes the values; 2, 3, 1/2 and 3/2 for indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively. The experimental optical absorption data was successfully fitted using the above equation for $n = 1/2$ (direct allowed transition). The $E_g$ values are obtained by extrapolating the linear region of the $(a\nu)^2$ vs $\nu$ curve, that is, the $\nu$ value of x-axis at $(a\nu)^2 = 0$ gives the band gap energy ($E_g$).

In DRS, the acquired diffuse reflectance spectrum can be converted to Schuster-Kubelka-Munk function using the formula [13];
\[ F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{s} \quad \text{............... (2.14)} \]

Where ‘\(k\)’ is the absorption co-efficient, ‘s’ is the scattering co-efficient and ‘R_\infty’ is the Reflectance.

The vertical axis is converted to quantity F(R_\infty), which is proportional to the absorption coefficient. Hence, the ‘\(a\)’ in the Tauc equation can be replaced with F(R_\infty). Therefore, for direct allowed transition, the Tauc’s relation becomes;

\[ (h\nu F(R_\infty))^2 = A (h\nu - E_g) \quad \text{............... (2.15)} \]

The \(E_g\) values are determined by extrapolating the linear region of the \((h\nu F(R_\infty))^2\) vs \(h\nu\), that is, the \(h\nu\) value of x-axis at \((h\nu F(R_\infty))^2 = 0\) gives the band gap (\(E_g\)).

**2.2.8. Photoluminescence Spectroscopy**

Photoluminescence (PL) is contactless, non-destructive spectroscopic technique, for the determination of certain impurities in semiconductors. It is particularly suitable for the detection of shallow level impurities, provided the radiative recombination events dominate non-radiative recombination. Identification of impurities is easy with PL; but measurements of the concentration of impurities are more difficult. PL can provide simultaneous information on different types of impurities. The Photoluminescence measurements were carried out for ZnO samples at room temperature and at 77 K and the spectra were recorded in the wavelength range from 350 – 800 nm with different excitation wavelengths.

**2.2.9. Magnetic Measurements by SQUID Magnetometer**

Superconducting Quantum Interference Device (SQUID) Magnetometer is useful, efficient technique to study the magnetic nature of the samples and it is capable of detecting incredibly small magnetic fields of the order of 10^{-18} T. Transition metal doped ZnO samples were characterized through Superconducting Quantum Interference Device (SQUID) magnetometer to investigate the magnetic nature of the samples. The data obtained from SQUID device was plotted as M-H plots. From the M-H plot, the nature of the magnetism of the sample such as,
paramagnetic, diamagnetic or ferromagnetic can be drawn. If the plot of M-H is linear and slope is positive / negative, then the nature of the magnetism is called paramagnetism / diamagnetism respectively. If M-H plots shows clear opening, showing ‘S’ like shape, called as hysteresis, then the magnetism is called ferromagnetism (FM). M-H plots (hysteresis curves), helps to determine the parameters such as saturation magnetization (M_s), remnant magnetization (M_r) and coercivity (H_c) and the possible origin for the existence of RTFM can be explored with the help of NEXAFS and XMCD measurements.

2.2.10. Electronic structure by NEXAFS and XMCD

NEXAFS and XMCD are considered to be powerful tools to investigate the electronic structure and element specific magnetic properties of the material. The near-edge x-ray absorption fine structure (NEXAFS) is an effective experimental tool and is an element specific technique, which can give information about the valence state, local environment, and hybridization of the specific cation in the material. On the other hand, x-ray magnetic circular dichroism (XMCD) can be used to probe information regarding the contribution of specific cation in any material towards the total magnetism of the system. It is also used to determine the spin and orbital contributions to the magnetism using sum rules [14-15].

NEXAFS measurements were carried out at different beam lines (BL-11A, 17C and 20A) available at National Synchrotron Radiation Research Center (NSRRC) in Taiwan. Together with SQUID, XMCD measurements were carried at 11A1 (Dragon) beam line of NSRRC, Taiwan. All the beam line X-ray absorption data was obtained in the fluorescence yield (FLY) mode, which is mostly bulk sensitive.

In detail, the line shape of NEXAFS spectra is the fingerprint for d- as well as p-state configuration. The NEXAFS is an element-specific technique, in which the spectral features are very much sensitive to the local environment of the probed ion. In other words, it is the fingerprint technique to determine the valence state of ‘Co’ ion and its substitution at ‘Zn’ site in the host ZnO. It also helps to determine the possibility of existence of ‘Co’ ion as clusters or in any other oxide phase. NEXAFS spectra were collected at O K-, Zn L- and Co L- edges and XMCD spectra were taken for fixed helicity of the light. Atomic multiplet calculations
(simulations) were performed for various symmetries with different crystal field splitting \((10Dq)\) values for all possible valence states of the ‘Co’ ions at the Co \(L_{3,2}\)-edge using CTM4XAS software [16]. Then the experimentally observed spectra were compared with the simulated one to determine the possibility of presence of impurities, valence state and crystal field splitting. Also XMCD spectra were analyzed to investigate the orbital and spin contribution to the magnetism as well as the source of ferromagnetism in Co doped ZnO samples.

2.2.11. Gas Sensing Measurements

In the present work, the sensor response of Al doped ZnO (AZO) films for NO\(_2\) gas was studied by exposing AZO films to the respective test gas diluted with zero air. The details of the gas sensor characterization setup can be found elsewhere [17]. The %Response \((S)\) was calculated using equation;

\[
\text{% of Response}(S) = \left(\frac{R_g - R_a}{R_a}\right) \times 100 \quad \text{--------------} (2.16)
\]

Where, \(R_g\) and \(R_a\) are the sensor resistances in presence of test gas and air, respectively. The sensors were tested on exposure of 100 to 600 ppm concentration of NO\(_2\) gas at 350 °C. The data obtained from the sensing measurements were analyzed and possible mechanism was discussed.
REFERENCES


