SYNTHESIS AND CHARACTERIZATION OF BINARY AND TERNARY METAL OXIDE NANOSTRUCTURES FOR GAS AND HUMIDITY SENSING APPLICATIONS

Ph.D. Thesis

By ALFA SHARMA



DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE AUGUST 2020

SYNTHESIS AND CHARACTERIZATION OF BINARY AND TERNARY METAL OXIDE NANOSTRUCTURES FOR GAS AND HUMIDITY SENSING APPLICATIONS

A THESIS

Submitted in partial fulfillment of the requirements for the Award of the degree Of DOCTOR OF PHILOSOPHY

> By ALFA SHARMA ROLL NO: PHD1501181005



DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE AUGUST 2020



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled SYNTHESIS AND CHARACTERIZATION OF BINARY AND TERNARY METAL OXIDE NANOSTRUCTURES FOR GAS AND HUMIDITY SENSING APPLICATIONS in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July, 2015 to July, 2020 under the supervision of Dr. Parasharam M. Shirage, Associate Professor, Discipline of Metallurgy Engineering and Materials Science.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date (ALFA SHARMA)

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ACKNOWLEDGEMENTS

First and foremost, I owe this unique opportunity to express my indebtedness and a profound sense of gratitude to my revered teacher Dr. Parasharam M. Shirage, Associate Professor, Department of Metallurgy Engineering and Materials Science, IIT Indore for his invaluable guidance, sustained interest, prudent suggestions & persistent endeavour throughout the work. I heartfully obliged my teacher for his constructive criticism, enthusiastic encouragement & for the time out of his busy schedule to meticulously go through the whole manuscript for making necessary corrections in a very short time. His effort in culminating the materialization of this dissertation work & to put it in the final form is incomparable. He is not only an advisor of my research but also a friend and mentor of my whole life and future venture.

I would like to extend my sincere gratitude to Prof. Pradeep Mathur, founding director, and Prof. Nilesh Kumar Jain, officiating director, IIT Indore for providing the research facilities and ambient environment involved in this work.

I would like to encompass a deep sense of reverence to my PSPC members Dr. Rupesh S. Devan and Dr. Santosh S. Hosmani, Department of Metallurgy Engineering, and Materials Science, IITI, for their encouragement and invaluable suggestions.

During my Ph.D. years, I was fortunate enough to get financial support from IIT Indore and CSIR, Govt. of India for providing me the fellowship as a Teaching Assistant (TA) and Senior Research Fellow (SRF). I owe my sincere thanks to the Department of Metallurgy Engineering and Materials Science, IITI for providing generous funding, laboratory facilities, and a rich environment to explore new ideas. I am also grateful to all the academic and administrative staff of IITI for providing practical support with friendly enthusiasm and grace. I thank Mr. Mayur Dhake for helping me in a lot of technical and non-technical works. I am thankful to the staff of SIC and workshop, IITI for their experimental help. The help received from Mr.

Santosh Pai (Excel Instruments, Mumbai) and Mr. Dilip Mahajan (PCI Analytics, Mumbai) is highly appreciated.

I am incredibly grateful to my colleagues Dr. Yogendra Kumar, Dr. Prateek Bhojane, Dr. Kushal Mazumder, Dr. Amit Kumr Rana, P.R.Chikate, and K. Narasimharao, with whom I learned a lot of experimental works. I thank them for their constant encouragement and contribution to accomplish my research. It has always been a great pleasure for me to work with them. I am also thankful to all my friends, present, and past lab mates Dr. Yogendra, Dr. Prateek, Dr. Kushal, Dr. Amit, Subhash, Akshay, Sarthak, Rituraj for their co-operation and support during my Ph.D. work.

I gratefully acknowledge Prof. G. Neri, University of Messina; Prof. Jaime Herran, IK4 CIDETEC; Prof. N. Venkataramani, IITB, and Prof. P. Elumalai, C-GET, Pondicherry University for their valuable guidance and thoughtful insights behind the present work.

I am always thankful to my best buddies Manu, Vivek, Param, Yogendra, and Shivendra Kaundilya for their moral support during my good as well as awful times and being my constant source of encouragement and confidence. A special thanks to Vivek for his selfless and compassionate caring in the most needed days.

Most importantly, I owe heartfelt devoutness to my immediate family; Mother, Father, and siblings (Annapurna, Dr. Akash, Asish) and extended family for their countless blessings, unmatchable love, affection & incessant inspiration that has given me the strength to overcome all the odds & shaped my life, career till today.

On a very special note, I extend regards from the core of my heart to my parents for their encouragement and inspiration without whom none of this will be possible.

Date: 08-09-2020

Alfa Sharma

Dedicated

To my parents

Sabita Sharma And

Santosh Sharma

LIST OF PUBLICATIONS

PAPER - 1

Alfa Sharma, Prateek Bhojane, Amit Kumar Rana, Yogendra Kumar, and Parasharam M. Shirage, Mesoporous nickel cobalt hydroxide/oxide as an excellent room temperature ammonia sensor, *Scripta Materialia*, **128**, 65-68, 2017.

PAPER - 2

Alfa Sharma, Yogendra Kumar, Kushal Mazumder, Amit Kumar Rana, and Parasharam M. Shirage, Controlled $Zn_{1-x}Ni_xO$ nanostructures for an excellent humidity sensor and a plausible sensing mechanism, *New Journal of Chemistry*, **42**, 8445-8457, 2018.

PAPER - 3

Alfa Sharma, Yogendra Kumar, and Parasharam M. Shirage, Structural, optical and excellent humidity sensing behaviour of ZnSnO₃ nanoparticles: Effect of annealing, *Journal of Materials Science: Materials in Electronics*, **29**, 10769-10783, 2018.

PAPER - 4

Alfa Sharma, Yogendra Kumar and Parasharam M. Shirage, Synthesis of humidity sensitive zinc stannate nanomaterials and modelling of Freundlich adsorption isotherm, *AIP Conference Proceedings*, **1942**, 050095(1-4), 2018.

PAPER - 5

Alfa Sharma, Rupesh S. Devan, and Parasharam M. Shirage, Deciphering the role of thermal treatment on correlation between sensitivity and hysteresis of humidity sensors based on ZnSnO₃ (**To be communicated**).

LIST OF CONFERENCE/WORKSHOP ATTENDED

1. Participated in RSC Symposium on "*Advances in Chemical Sciences*", at Indian Institute of Technology Indore, Indore, India, 30th January, 2018.

2. Oral presentation at "*Department of Atomic Energy, Solid State Physics Symposium (63rd DAE-SSPS)*", at Guru Jambeshwar University, Hisar, India, 18th – 23rd December 2018.

3. Poster presentation at "*Department of Atomic Energy, Solid State Physics Symposium (62nd DAE-SSPS)*", at Bhaba Atomic Research Centre, Mumbai, India, 25th – 30th December 2017.

4. Oral presentation at "International conference on nanotechnology: Ideas, Innovations & Initiatives (ICN: 3I-2017)", at Indian Institute of Technology, Roorkee, India, $6^{th} - 8^{th}$ December 2017.

5. Poster presentation at "*Fourth International Symposium on Semiconductor Materials and Devices (ISSMD 4)*", Jadavpur University, Kolkata, India, 8th – 10th March 2017.

6. GIAN workshop on "*High-Pressure Synthesized Materials: A Chest of Treasure and Hints*", at Indian Institute of Technology Indore, India 11th – 19th July 2016.

7. GIAN workshop on "*Chemical Sensors: Principles, Technologies and Applications*", at Indian Institute of Technology Indore, India 1st – 9th July 2016.

8. Poster presentation at "*Ramanujan Conclave*", at Indian Institute of Technology Indore, India $22^{nd} - 23^{rd}$ December, 2015.

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NOMENCLATURE

Α

Ag Silver B BET Brunauer- Emmett- Teller BJH Barrett- Joyner-Halenda C

CB Conduction band **CoFe₂O₄** Cobalt Ferrite

D

DI Deionized water

DUT Device under test

DTG Differential Thermogravimetry

Ε

EDX Energy dispersive x-ray *Eg* Energy gap **EtOH** Ethanol

eV Electron Volt

F

FESEM Field emission scanning electron microscopy *fcc* Face Centered Cubic **FWHM** Full-Width Half Maximum

Η

H₂ Hydrogen H₃O⁺ Hydronium ion

I

IEC International Electrochemical Committee **IUPAC** International Pure and Applied Chemistry **ITO** Indium tin oxide

Μ

M Molarity MO Metal Oxide N NiCo2O4 Nickel Cobalt Oxide NCO Nickel Cobalt Oxide

NCH Nickel Cobalt Hydroxide

NH₃ Ammonia

NR Nanorod

NP Nanoparticle 0 O₂ Oxygen **OH**⁻ Hydroxyl ion Ρ PC Personal computer ppm Parts per million PCA Principal Component Analysis R **RT** Room temperature **RH** Relative Humidity rGO Reduced Graphene Oxide **RDR** Relative Deviation in Resistance S SSA Specific Surface Area SE Secondary Electron Т **TEM** Transmission electron microscopy TGS Taguchi gas Sensor TMO Transition Metal Oxide Tres Response Time Trec Recovery Time Tc Transition point **TG** Thermogravimetry U **UV** Ultraviolet V **VB** Valence band W W Watt X **XPS** X-Ray photoelectron spectroscopy **XRD** X-Ray diffraction Ζ **ZnO** Zinc oxide **ZnSnO**₃ Zinc Stannate **ZTO** Zinc Stannate

Physical Constants and Conversion Factors

Avogadro's number	$N_A = 6.02 \times 10^{23} \text{ molecules/mole}$
Boltzmann's constant	$k = 1.38 \times 10^{-23} \text{ J/K}, 8.62 \times 10^{-5} \text{ eV/K}$
Electronic charge (magnitude)	$q = 1.6 \times 10^{-19} \mathrm{C}$
Electronic rest mass	$m_{\rm e} = 9.11 \times 10^{-31} \rm kg$
Planck's constant	$h = 6.63 \times 10^{-34}$ J.s, 4.14×10^{-15} eV.s
Speed of light	$c = 3 \times 10^8 \text{ m/s}, 3 \times 10^{10} \text{ cm/s}$

Prefixes:

$1 \text{ Å} (angstrom) = 10^{-10} \text{ m}$	milli-, $m-=10^{-3}$
1 μ m (micron) = 10 ⁻⁶ m	micro-, μ- = 10 ⁻⁶
$1 \text{ nm (nano)} = 10^{-9} \text{ m}$	nano-, $n-=10^{-9}$
2.54 cm = 1 in.	pico-, $p-=10^{-12}$
$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$	kilo-, $k-=10^3$
	mega-, $M - = 10^6$
Chapter 1 Introduction

This chapter starts with the rudimentary impression of chemical (gas and humidity) sensor, semiconducting metal oxides as sensors, its fundamental aspects, and working mechanism. The fundamental aspects of sensors along with sensing characteristics are well explained. This chapter concentrates on binary and ternary metal oxides as the material of concern in this thesis. This segment comprises of a brief review on the choice of materials: ZnO (binary) and NiCo₂O₄ and ZnSnO₃ (ternary), its chemical sensing properties depending on synthesis and morphology. Apart from these, it covers a specific study on adsorption-desorption models which provide a physical significance to the sensing mechanism of metal oxides.

1.1. Background

The sensors are simple devices, measuring a quantity of interest, and producing some form of mechanical, electrical, or optical output signal. Sensors become practically inexorable in our life due to their presence in every sector. The last decade has seen incredible developments in sensor technology which focused on the developments in miniaturization technologies, cost-effectiveness, microelectronic circuit compatibility, and advances in signal processing. It is an incessant pursuit to develop competent, and reliable, sensors for commercial affordability. Currently, improvements in sensor output, simulation technologies, and design aides are playing decisive roles for merchandise eminence. In this chapter, we briefly introduce basics of sensor along with their classification, and emphasises various aspects and parameters involved in semiconductor metal oxides based gas and humidity sensors.

1.1.1. Basic Introduction

The sensor recognizes variation in a quantifiable magnitude and alters it into a resultant signal processable by a data acquisition system [1- 4]. The definition of sensor according to the International Electrotechnical Committee (IEC) states that "the sensor is the primary part of a measuring chain which converts the input variable into a signal suitable for measurement" [5]. The sensors must have some characteristic features like high sensitivity, high stability, good reproducibility, excellent selectivity, less hysteresis and wide linearity, which determines their efficiency over a certain operation range. Hence monitoring all the above-stated sensor fingerprints are strongly recommended to observe during operation.

1.1.2. Chemical Sensors



Figure 1.1. Signal processing in biological and technical systems (Adapted with permission from ref. [7]).

Chemical sensors as an analytical device identifies and informs any small variation in chemical composition in ambient environment where the signal is directly associated with the nature and concentration of test analyte. They are also named as artificial noses or artificial tongues due to pertinent resemblance to the biological systems. Fig. 1.1 illustrates the similarity between biological and technical systems in use. Generally, in a biological system, receptor organs recognize and convey signals to the brain through sensory neurons. Similarly, in the technical systems sensing element acts as a receptor that retorts to its surroundings by altering its intrinsic property. A transducer alters this prime information into an electrical gesture which is then delivered to a data acquisition system like a computer that functions similarly as the central nervous system of the brain. Hence, for the effective operation of sensors two vital steps are intricate, *i.e.* recognition and transduction. In chemical sensors, the recognition step deals with the selective interface of analyte molecules with receptor sites or molecules of

sensing elements. Consequent changes in representative physical factors are transformed utilizing integrated transducers which generate a suitable analytical signal.

The various definitions of chemicals sensors prescribed by several researchers and organizations are listed below;

- The International Union of Pure and Applied Chemistry (IUPAC)
 [6] defined chemical sensors as, "A chemical sensor is a device that transforms chemical information, ranging from concentration of a specific sample component to total composition analysis, into an analytically useful signal".
- Wolfbeis [7] defined chemical sensors as "small-sized devices having a recognition element and a signal processor competent of continuously and reversibly reporting a chemical concentration".
- According to Göpel and Schierbaum [8], chemical sensors are devices that transform a chemical state into an electric signal. Chemical sensors are therefore a measuring string between the chemical domain and the world of electronics.
- Stetter and Penrose have quantified some representative features of chemical sensors [9] and these are as follow: "A sensitive layer in contact with analyte/test molecules alters the chemistry of layer due to certain reaction of the analyte, transduction of the corresponding change to an electrical signal, physically miniature, performing in real-time, economical and appropriate for the same chemical measurements over another equivalent instrument".

1.1.3. Classification of Chemical Sensors

The taxonomy of chemical sensors can be carried out in numerous ways. The classification based on the transducer's operating principle, as given by IUPAC [6], is shown in Fig. 1.2.



Figure 1.2. Classification of chemical sensors based on operating principles of transducers (Adapted with permission from ref. [10]).

1.2. Gas Sensors

The main objective and concern of the present peers are to monitor air quality and discourse the allied health problems. Air pollution has been persistently growing as a result of emergent industrial development. Hence, industrialization entails the detection and monitoring of toxic pollutants and gases springing from refineries, explosives, and processing establishments for environmental fortification and safety monitoring. The recognition, quantification, and possible eradication of a specific hazardous gas from the ambient is a key part of product development and process control. The gas sensor is a subgroup of chemical sensors and has several applications in both domestic and industrial processes. In gas sensors the receptor function mostly subject to sensing materials being used for identification of analyte, whereas the sensor signal is transduced into an electrical resistance alteration. In various circumstances capacitance, resonant frequency, electromotive force, optical absorption, and emission also utilized as a sensing signal for different sensing elements [11].

1.2.1. Types of Gas Sensors

The gas sensors are generally divided into three groups based on the technology engaged as follows:

- (a) Optical
- (b) Spectroscopic
- (c) Solid State

Optical sensor records change in analyte concentration via variation in specific absorption spectra which itself a complex measurement system. Spectroscopic techniques employed are infrared spectroscopy, chromatography, ultraviolet fluorescence, etc. which are very accurate and sophisticated but require expertise ceasing its common use. Whereas solidstate gas sensors are extensively engaged due to miniaturization possibility, feasibility for use through the Internet of Things (IoT), easy operability [12, 13]. Solid-state gas sensors are decent entrants for commercial use for a broad range of applications [14-16]. Signs of progress in nanotechnology have paved various paths like manipulation of nanostructured systems, fabrication of novel nanomaterials with better gas sensing properties, etc. These types of gas sensors in form of pellets, thin or thick films are centred on reversible chemical reactions of materials with an analyte and can be monitored through the minute variation in conductivity, capacitance, mass, work function, etc. Theoretically, any material such as solid electrolytes, semiconductor metal oxides, polymers, organic materials based on their physio-chemical properties can be used to design solid-state gas sensors [17-28]. However, as all gas sensors are not similarly effective, hence the strategic difficulty is the assortment of best gas sensor material with required operating parameters for the design and fabrication of a good and effective gas sensor [29-34].

		Тур	pes of Gas S	Sensors		
Parameter	Semi-	Catalytic	Electro-	Thermal	Infrared	
	conductor		chemical	conductive	absorption	
Sensitivity	E	G	G	В	E	
Selectivity	Р	В	G	В	E	
Accuracy	G	G	G	G	Е	
Response	Е	G	Р	G	Р	
Time						
Stability	G	G	В	G	G	
Durability	G	G	Р	G	E	
Maintenance	Е	E	G	G	Р	
Cost	Е	E	G	G	Р	
Portability	Е	G	Р	G	В	
E: Excellent, G: Good, P: Poor, B: Bad						

Table 1.1. Comparison of various types of gas sensors [35].

Generally, three main types of gas sensors based on solid-state electrolyte, catalytic combustion, and resistance variations are manufactured on a large scale and termed as electrochemical, pellistor, and conductometric or chemiresistive sensors, respectively [11]. Table 1.1 presents an assessment of semiconductor gas sensors with other types of solid-state gas sensors [35]. The present thesis is based on the chemiresistive chemical (gas and humidity) sensor prepared from various metal oxides. Chemiresistive semiconductor gas sensors are widely used to detect numerous toxic gases due to their simplicity in operation and low cost. The chemiresistive sensor based on the principle where interaction between an analyte gas molecule and a semiconductor leads to a change in the electrical resistance of the sensor [29]. Such types of sensors demonstrated high sensitivity, quick response/recovery time, design compatibility, portability, and cost-effectiveness.

1.3. Semiconductor Metal Oxide Gas

Sensors



Figure 1.3. Illustration of different processes occurring in metal oxides during gas sensing and their significances for polycrystalline metal oxides properties (Reproduced with permission from ref. [35], copyright from Elsevier (2007)).

In 1962, Seiyama *et al.* reported for the first time ZnO as a chemiresistive gas sensor [36] and in the same year, Taguchi discovered SnO₂ resistive gas sensor based on the same principle and Figaro Engineering *Inc.* commercialized the famous Taguchi gas sensor (TGS) [37]. Since then there has been an uninterrupted expedition to develop gas sensing materials and associated technology to accomplish several performance parameters vital for diverse applications. There is an everlasting research quest dedicated to examine innovative gas sensing materials and mechanisms for

understanding the science behind the practices. The performance factors of a gas sensor can be augmented by monitoring the crystalline phase, grain size, morphology, and engaging a multi-component system through doping (by noble metal, transition elements, *etc.*) or composites, heterojunctions, *etc.* Such adoptions along with desired microstructures affect the physicochemical properties [**35**]. As stated above, the construction of a chemiresistive gas sensor is easy, where a semiconducting material is deposited on an insulating substrate and contacts made over it using metals (Pt, Au, Ag, Cr, etc.). The sensor signal is produced due to variation in the conductance of semiconductor metal oxide upon analyte adsorption. Although these gas sensors suffer from a deficiency in selectivity, other sensor routine norms such as low cost, reliability brand them as fastestgrowing gas sensor devices in the market.

1.3.1. Working Principle of Metal Oxide Gas Sensor

The primary mechanism of metal oxide semiconductor-based gas sensors irrespective of *p*-type or *n*-type is centered on surface reactions with the target analyte (Fig. 1.4). Initially, the surface oxygen species are homogenously constructing a continuous electron depletion layer and hence high resistance, however, on exposure to a test analyte, the surface reactions neutralize these oxygen species and lower the resistance [**38-40**]. In *n*-type semiconductors with the electron as a majority carrier, O₂ adsorption on the surface results in the trapping of electrons from the semiconductor conductor band (CB). This generates an electron depleted layer on the surface within Debye length (δ) leading to a rise in sensor resistance (Fig.1.4).

 $MO + 2O + e^- \rightarrow MO + O_2^-$ (Between 30°C and 150°C) (1.1)

 $MO + O + e^- \rightarrow MO + O^-$ (Between 150°C and 300°C) (1.2)

On exposure to reducing gas, the electrons produced due to oxidation are guided back to the CB causing a release of electrons. This increases electron

mobility and reduction in sensor resistance takes place. Whereas, in a *p*-type semiconductor-based sensor, the holes are major charge carriers and resulted in an opposite effect on exposure to a reducing gas **[41]**.



Figure 1.4 Schematic of resistance change upon exposure to the target gas (reducing gas) for both *n*-type (left) and *p*-type (right) metal oxide semiconductor sensors (Reproduced with permission from ref. [42], copyright from MDPI (2009)).

Table 1.2. Chemiresistive behavior of semiconductors oxide-based gas

 sensors in reducing and an oxidizing atmosphere.

	<i>n</i> -type	<i>p</i> -type
Reducing Gas	Resistance decreases	Resistance increases
Oxidizing Gas	Resistance increases	Resistance decreases

1.3.2. Fundamental Aspects of Gas Sensors

The conductivity of these semiconductor-based sensors is primarily administered by the adsorption/desorption of O_2 molecules [38-40]. The gas adsorption mechanism and subsequent resistance alteration in a

semiconductor metal oxide gas sensor largely include three major tasks: receptor function, transducer function, and utility factor (Fig.1.5) **[43, 44]**.



Figure 1.5. Three main factors controlling semiconductor gas sensors: (*a*) Receptor Function, (*b*) Transducer Function, and (*c*) Utility Factor (Reproduced with permission from ref. [45], copyright from MDPI (2017)).

The receptor function is essentially ascribed to the sensitivity and selectivity of the device and response of individual components to the immediate environment comprising oxygen and the other analyte gases [45]. In this step, the surface depletion layer is formed based on the quantity of oxygen adsorbed mostly governing the sensing competencies of the device. This depends on the structure-specific surface area (SSA), predominantly on the particle size d_p of the sensing structure [45]. If $d_p >> 2\delta$, the mechanism is resulted by relocating electrons at the particle's grain boundary ensuing low sensitivity (Fig. 1.5) [38, 39]. If $d_p > 2\delta$, a hefty share of the bulk contributes to the sensing mechanism leading to moderate sensitivity (Fig. 1.5 *a*) [12, 20]. On contrary, if $d_p \leq 2\delta$ the entire surface is electron exhausted with an itinerant charge carrier, leading to considerably high resistance [38, 39]. The transducer function, as the second key factor, is an interparticle concern associated with alteration of the surface phenomenon with the change in resistance of the sensor [46] (Fig. 1.5 *b*). The chemical reciprocity at the semiconductor surface generates an electrical signal in the transducer function, which is mainly subjugated by the surface potential and potential barriers shaped between grains, trapping states in grain boundaries, and defect states in the semiconductor structure [38, 47, 48]. Schottky barriers among two grains hinder electrons to relocate across the boundary and acted as transducer upon augmentation of analyte [48, 49].

Lastly, the utility factor (Fig.1.5 *c*) is associated with the morphology of the metal oxide semiconductor and subsequent diffusion and reaction of target analyte through the structure **[45, 50]**. The utility factor regulates the sensing performance, which is largely pretentious by the device structure, porosity, *etc.* **[39]**. In a very porous structure, the target gas particles infiltrate into the lowest layers of the film causing an effective resistance variation of the sensing device (Fig.1.5*c*) **[39]**. However, the utility factor might be worthless for monolayer structures such as MoS_2 where the material structure is atomically thin and the gas adsorption is not connected with the diffusion through the material **[45]**.

1.3.3. Glossary of Sensing Characteristics

Some of the characteristics, which are used to judge for optimal operation of each sensor are defined here [51-53].

Response: The gas sensor response is defined as the ratio of resistance in the air to that in the presence of an analyte. The gas response "*S*" is stated as

$$S = \frac{R_{air}}{R_{gas}}$$
 (for *n*-type semiconductor) (1.3)
and $S = \frac{R_{gas}}{R_{air}}$ (for *p*-type semiconductor) (1.4)

Where, R_{air} and R_{gas} are the resistance values of the sensor in the air and gas environment, respectively.

Sensitivity: Change in the measurement signal per concentration unit of the analyte, *i.e.* the slope of a calibration graph.

Detection limit: The lowest concentration value which can be detected by the sensor in question, under definite conditions. Procedures for evaluation of the detection limit depends on the kind of sensor considered.

Dynamic range: The concentration range between the detection limit and the upper limiting concentration.

Resolution: The smallest detectable change of the input which can lead to a measurable change of the output.

Response time: The time for a sensor to respond from zero concentration to a step-change in concentration. Usually specified as the time taken to reach 90% of the final value of output signal.

Hysteresis: The maximum difference in output when the value is approached with (a) an increasing and (b) a decreasing analyte concentration range. It is given as a percentage of full-scale output.

Stability: Represents an ability of sensing element/system to produce the same output after measuring the same input for a certain period.

Selectivity: An expression of whether a sensor responds selectively to a group of analytes or even specifically to a single analyte. Quantitative expressions of selectivity exist for different types of sensors.

Linearity: The relative deviation of an experimentally determined calibration graph from an ideal straight line. Usually, values for linearity are specified for a definite concentration range.

Life cycle: The length of time over which the sensor will operate. The maximum storage time (shelf life) must be distinguished from the maximum operating life. The latter can be specified either for continuous operation or for repeated on-off cycles.

Accuracy: An expression of the agreement between the measurement results (given as the average value of a measurement series) and the true

value. It is also a measure of the systematic error, *i.e.* deviation from the true value (normally given as a percentage).

Precision: An expression of the random error of a measurement series. The generally accepted way to express precision is with the standard deviation (STD). The latter is the mathematical term for the width of the Gaussian error distribution curve given in the form of σ (the distance between the center and the inflection point of the Gaussian curve). For practical purposes, instead of σ , the estimated value *s* is determined from a finite population of single values. The approximate values are given by the equation (1.5):

$$s = \sqrt{\frac{\Sigma(x-y)^2}{n-1}}$$
 -----(1.5)

Where (x) is every individual value, (y) the average value, and (n) is the number of measurements [52].

1.4. Selection of Metal Oxides

The characteristics of solid-state gas sensors can be elevated through engineering of metal oxides. It has been witnessed that sensing performances such as sensitivity, selectivity, stability can be upgraded through optimization of the surface of metal oxides. However, for gas sensing applications, the assortment of particular metal oxides is significant as they convey a comprehensive scope of electro-physical properties. Electronic structures are divided into two categories [35]:

1. Transition-metal oxides (TMOs, e.g. NiO, Fe2O3, Cr2O3)

2. Non-transition metal oxides: segmented into *a*) pre-transition metal oxides (*e.g.* Al₂O₃), *b*) post-transitions-oxides (*e.g.* SnO₂, ZnO, *etc.*).

Pre-transition metal oxides cannot be simply oxidized or reduced due to their large bandgap. It is difficult to optimize their properties by generating defects or using dopants or additives. Post-transition metal oxides with wide oxidation state and direct bandgap can be revamped through doping. Again, it is well known that transition-metal oxides demonstrated diverse bonding properties due to variable oxidation states made them more delicate towards the ambient atmosphere. Therefore, suboptimal and structural variability parameters regulate the suitability of some oxides over the others.

Table 1.3. Gas sensors investigated using various binary, ternary, and doped metal oxides.

Binary Metal Oxides						
Metal	Morphology	Analyte Test Gas	References			
Oxide						
ZnO	Nanopillars	H ₂ , C ₂ H ₅ OH	[66]			
TiO ₂	Nanotubes	O ₂	[67]			
SnO ₂	Nanowires	NO ₂	[68]			
NiO	Microspheres	Butanol	[69]			
Fe ₂ O ₃	Nanotubes	C ₂ H ₅ OH, H ₂	[70]			
CuO	Nanospheres	H ₂ S,C ₂ H ₅ OH	[71]			
WO ₃	Hollow sphere	C ₂ H ₅ OH, acetone,	[72]			
		H_2S				
V ₂ O ₅	Nanobelts	C ₂ H ₅ OH	[73]			
In ₂ O ₃	Microsphere	Formaldehyde,	[74]			
		Ethanol				
Co ₃ O ₄	Nanorods	Acetone	[75]			
CdO	Nanowires	NO _x	[76]			
MoO ₃	Nanoparticles	H_2S	[77]			
Nb ₂ O ₅	Nanoporous film	H ₂	[78]			
	Ternary	Metal Oxides				
Metal Oxide	Morphology	Analyte Test Gas	References			
ZnSnO ₃	Nanocages	H ₂ S	[79]			
ZnFe ₂ O ₄	Nanoparticles	C ₂ H ₅ OH	[80]			
NiFe ₂ O ₄	Nanoparticles	LPG	[81]			
ZnTiO ₃	Nanoparticles	LPG	[82]			
CoTiO ₃	Nanoparticles	C ₂ H ₅ OH	[83]			

SrTiO ₃	Nanoparticles	O ₂	[84]
NiMn ₂ O ₄	Nanoparticles	Humidity	[85]
CoFe ₂ O ₄	Nanocubes	Humidity	[86]
NiCo ₂ O ₄	Nanoflakes	NH ₃	[87]
LaFeO ₃	Honeycomb	C ₂ H ₅ OH	[88]
BiFeO ₃	Nanoparticles	Acetone, C ₂ H ₅ OH	[89]

Effect of dopants in metal oxides						
Metal oxide	Dopant	Analyte Test Gas	References			
ZnO	Sn	NO ₂	[90]			
ZnO	Cu	СО	[91]			
NiO	Li	H ₂	[92]			
NiO	Fe	Ethanol	[93]			
NiO	Cr	Xylene, Toluene	[94]			
SnO ₂	Ag	Propane	[95]			
SnO ₂	Fe	CO,C ₂ H ₅ OH	[96]			
SnO ₂	In	CO, H ₂ , methanol	[97]			
WO ₃	Pt, Au	H ₂ S	[98]			
WO ₃	Ni	NO ₂	[99]			
Fe ₂ O ₃	Cd	LPG	[100]			

A thorough literature inspection demonstrates that simple metal oxides do not comply with all gas sensing performance factors to construct an impeccable gas sensor, hence it is obligatory to transform the binary metal oxides by doping, using multi-element systems like ternary metal oxides, hetero-junctions, *etc.* [54-56]. These tactics deliver different physicochemical properties to sensing elements which affect gas sensing properties. Gleiter *et al.* documented for the first time that integration of supplementary phase through addition of (noble metals, transition metals) in nanocrystalline metal oxides leads to development in materials for sensor applications [57, 58]. An additive can considerably modify catalytic properties of the host oxide, through the formation of active phases, stabilization of definite valance state, and increment in the electron exchange rate [59-65].

1.5. Background of Humidity Sensing

Humidity is a very common component in our environment, measurements, and/or control of humidity is important not only for human comfort but also for a broad spectrum of industries and technologies [101,102]. Humidity sensors have gained increasing applications in industrial processing and environmental control. For manufacturing highly sophisticated integrated circuits in the semiconductor industry, humidity or moisture levels are constantly monitored in wafer processing. There are many domestic applications, such as intelligent control of the living environment in buildings, cooking control for microwave ovens, and intelligent control of laundry, etc. In the automobile industry, humidity sensors are used in rearwindow defoggers and motor assembly lines. In the medical field, humidity sensors are used in respiratory equipment, sterilizers, incubators, pharmaceutical processing, and biological products. In agriculture, humidity sensors are used for green-house air conditioning, plantation protection (dew prevention), soil moisture monitoring, and cereal storage. In the general industry, humidity sensors are used for humidity control in chemical gas purification, dryers, ovens, film desiccation, paper and textile production, and food processing. Generally speaking, a humidity sensor has to fulfil most of the following requirements to satisfy the wide strange of applications good sensitivity in a wide humidity range, quick response, good reproducibility with no hysteresis, fitness to circuitry, tough durability and long life, resistant to other contaminants (selectivity), insignificant dependence on temperature, simple structure, and low cost [103,104].

1.5.1. Introduction of Humidity Sensors

Humidity is perhaps the most difficult environmental factor to monitor. Although accurate and relatively simple instantaneous measurement is feasible, no practical, reliable, continuous humidity measurement is available. Humidity measuring equipment is usually calibrated only in terms of relative humidity. There are many methods for measuring humidity. Humidity measurement techniques include gravimetric, elongation, volumetric, psychrometric, hygroscopic, electrolyte resistance, electrolytic, radiation refraction, piezoelectric, electrical capacitance, thermal, etc. Direct measurements of humidity require isolation of the gas and a means of measuring the water content (chemical absorption, condensation, gravimetric) and are therefore impractical as a routine technique for monitoring humidity. Such measurements are usually employed during calibration. Almost regardless of the technique used, most sensors are not accurate throughout the entire humidity span. Several functional materials like polymers, inorganic, and organic materials have been explored for the fabrication of humidity sensors. Due to their high sensitivity, low power consumption, and low manufacturing costs, humidity sensors have a significant role in a wide range of applications in meteorology, agriculture, industrial control, and medical instrumentation [105-112]. Different transduction mechanisms have been researched for the detection of humidity in the environment, including capacitance [109, 110, 113], resistance [111, 112, 114], field-effect transistor [111], microbalance [115, 116] and photonic crystal [117, 118], etc. Many efforts have been given to an improvement of the performances of humidity sensors, where the main focus was on the development of novel sensing materials, such as carbon-based materials [119, 120], electrospun fibers [118], metal oxide nanowires [121-123], semiconductor particles [124], and composite nanofilms [125, 126]. The resistive humidity sensors are the most frequently used sensors for the detection of the humidity in the commercial field, because of their high sensitivity, low power consumption and low production prices [127, 128].

1.5.2. Descriptions related to Humidity

Generally, the term moisture refers to the amount of water content in liquid or solid (absorption or adsorption), which can be removed without altering its chemical properties.

The term humidity is reserved for the water vapor content in gases. Absolute humidity is defined as the density of water vapor content per unit volume or the mass (*m*) of water vapor to per unit volume (*v*) of wet gas which is dw = m/v [129].

Mixing ratio (humidity ratio) r is the mass of water vapor per unit mass of dry gas. It is also referred as absolute humidity.

Relative humidity (RH or ϕ) is the ratio between water vapor pressure (P_w) and saturated vapor pressure (P_s),

$$RH = 100(P_W/P_S)$$
 (1.6)

Or the ratio between current absolute humidity and the highest possible absolute humidity at a certain temperature; the value of RH expresses the vapor content as a percentage of the concentration required to cause the vapor saturation. An alternative way to present RH is as a ratio of the mole fraction of water vapor in space to the mole fraction of water vapor in the space at saturation. The value of P_w together with the partial pressure of dry air P_a is equal to pressure in the enclosure or to the atmospheric pressure (P_{atm}) if the enclosure is open to the atmosphere:

$$\boldsymbol{P}_{atm} = \boldsymbol{P}_w + \boldsymbol{P}_a \tag{1.7}$$

The Dew point is the temperature at which relative humidity is 100%. In other words, the dew point is the temperature that the air must reach for the air to hold the maximum amount of moisture it can. When the temperature cools to the dew point, the air becomes saturated and fog, dew, or frost can occur. The equation (1.8) allows calculating the dew point from relative humidity and temperature:

$\mathbf{EW} = \mathbf{10}^{(0.66077 + 7.5t/(237 + t))} \quad (1.8)$

The Frost point is the temperature (below 0° C) at which the vapor condenses to ice [130].

1.6. Semiconducting Metal Oxide Humidity Sensors

Metal oxides are crystalline materials which are very useful in sensor fabrication. The reason why these materials are widely used is that they exhibit several specific features that enable their cost to become lower and their reliability to increase. There are two types of semiconductors: (i) intrinsic in which electrical conductivity doesn't depend on impurities and (ii) extrinsic in which electrical conductivity depends on impurities which can be obtained by doping (either by diffusion or ion implantation). In intrinsic semiconductors, holes are promoted by electron mobility so the number of electrons is equal to the number of holes. Extrinsic semiconductors have different concentrations of electrons and holes, generally p-type when the number of holes is more than that of electron and n-type in which the number of electrons is higher than that of holes. It is well known that the types of conduction are ionic (mostly for ceramics, metal oxides, *etc.*) and electronic (organic, polymers, *etc.*).

1.6.1. Water Adsorption Mechanism

Metal oxide follows a dissociative mechanism to form hydroxyl ions from water molecules. This is prompted due to the strong electrostatic field generated by high local charge density caused through metal cation upon interaction with adsorbed H₂O. So, the first layer of adsorbed water is chemically adsorbed and the subsequent layers are physically adsorbed. The first physisorbed layer is characterized by double hydrogen bonding of a single water molecule. Other layers are singly bonded and form a liquid-like network. Physisorption takes place at temperatures below 100° C. In the case of porous microstructure, the most important factors are the size of the pores and their distribution which are responsible for capillary condensation. Even it is possible to evaluate the pore radius at which

capillary condensation occurs at different temperatures (T) by using the Kelvin equation (1.9);

$$r_k = \frac{2\gamma M}{\rho RT ln(\frac{P_s}{p})} \quad (1.9)$$

Where r_k is the Kelvin radius, P is the water-vapor pressure, P_s is the watervapor pressure at saturation, and γ , ρ , and M are the surface tension (72.75 dyne cm⁻¹ at 20°C), density and molecular weight of water, respectively. Water condensation takes place in all the pores with radii up to r_k , at given temperatures and water-vapor pressures. The smaller the r_k , or the lower the temperature, the more easily condensation occurs [131]. These physical interaction mechanisms between water and oxide surfaces are largely recognized to be the basis of the operative mechanisms of a wide range of different humidity-sensor materials.

1.6.2. Ionic Type Humidity Sensors

The detection mechanism of ionic-type humidity sensors is strictly related to the above water-adsorption mechanisms. Moisture can be detected by measuring humidity-sensitive variations in conductivity, which ionic-type oxides undergo as a result of water adsorption: the oxides react to humidity by decreasing their resistivity [132]. The conduction mechanism depends on the surface coverage of adsorbed water. When the first physisorbed water layer is continuous, charge transport is governed by proton hopping between neighbouring water molecules in the continuous film. The easy dissociation of physisorbed water, due to the high electrostatic fields in the chemisorbed layer, produces H_3O^+ groups. The charge transport occurs when H_3O^+ releases a proton to a nearby H_2O molecule, ionizing it and forming another H_3O^+ , resulting in the hopping of protons from one water molecule to another [132]. This process is known as the Grotthuss chain reaction (Fig 1.6).



Figure 1.6. (*a*) A brief illustration of the Grotthuss mechanism of proton conductivity in water [133], (*b*) Multi-layer structure of condensed water [134].

This mechanism means that higher resistivity of the oxides is observed at low RH values. This is because mobile protons may arise from the dissociation of the hydroxyl groups or of the water molecules, but the activation energy required to dissociate hydroxyl ions is higher than that necessary to dissociate water molecules. A higher carrier concentration is found when more than one layer of the physisorbed water molecule is present on the surface. These molecules are singly hydrogen-bonded and form a liquid-like network, which greatly increases the dielectric constant and, therefore, the proton concentration. Moreover, in addition to the protonic conduction in the adsorbed layers, electrolytic conduction occurs in the liquid layer of water condensed within capillary pores, thereby resulting in an enhancement of conductivity. Thus, the primary concern of ionic type humidity sensor is controlling porosity and surface activity where highly porous and large surface area is desirable for the enhancement of sensitivity towards humidity. Pore size distributions ranging from 20-500 nm shows the best performance [132].

Another model proposed that ionic and electronic conduction coexists in porous ceramics at any humidity. The resistance of a sensor is then given by the sum of electronic conduction of the crystal grains and the proton hopping between two water molecules adsorbed on the grain surfaces [132]. The following equation (1.10) was derived:

$$l_g R_{\phi}/R_0 = (l_g \alpha - l_g \phi)/(1 + b/\phi)$$
 ------ (1.10)

Where R_{ϕ} and R_0 are the resistance of the porous ceramic element at any relative humidity and 0% respectively, ϕ is the concentration of quasi liquid water (equal to $(RH)^n$, where *n* is the correction index) and *a* and *b* are theoretical constants depending on the composition of the ceramic and the pore structure. This model takes into consideration the Grotthuss protontransfer mechanism and the intrinsic resistivity of the materials [135, 136]. Whereas for single crystals, capillary condensation cannot be responsible for humidity sensing and surface conduction in multi-layered water molecules cannot be ignored [132, 135]. The ceramic sensors suffer from their high resistance to low humidity due to prolonged exposure to humidity and environmental pollutants which requires periodic heating to recover to the initial sensor properties.

1.6.3. Electronic Type Humidity Sensors

The demand for humidity sensors able to operate at higher temperatures led to the development of humidity sensing devices based on different detection mechanisms. To this aim, semiconductor humidity sensors using metal oxides were investigated. In this case, water molecules behave as a reducing gas, so electrons transfer from them to the metal oxide sensing material. Firstly, the surface of metal oxides adsorbs oxygen ions from the air which determines the resistivity of the oxide surface. Secondly, oxidative reactions take place between reducing gases and oxygen ions resulting in releasing electrons which increase the electrical conductivity of the oxide surface. However, another proposed mechanism indicates that during the chemisorption where two OH^{-} groups are formed with H^{+} bonds to the oxide ion and OH^{-} bonds to metal ion there is no electron transfer [137]. In perovskite, the donation of electrons from water molecules is attributed to the presence of surface defects which trap electrons which are liberated by the adsorption of water molecules [138]. So, released electrons can be restored in the conduction band in the case of *n*-type semiconductors and valence band in the case of *p*-type ones.

1.7. Adsorption-Desorption Models

The affiliation among the adsorbed equilibrium amount and concentration of the analyte (gas or vapour) at a particular temperature is designated as adsorption isotherm [**139**]. It defines the thermodynamic functions ascribed to the adsorption complex and the isosteric heat of adsorption [**140**]. Several isotherm models have been established to pronounce the adsorption process out of which Langmuir, Brunauer-Emmett-Teller (BET), Freundlich, Wolkenstein models are noteworthy.

1.7.1. Langmuir Model

Langmuir model is the classical adsorption model which states that, "the adsorption rate is proportional to the bulk concentration and the number of unoccupied adsorption sites, whereas desorption rate is proportional only to the number of sites occupied by solute molecules". Thus, the adsorption/desorption processes governed by the nature of the adsorbate and adsorbent, accessibility of adsorbates, and on the temperature.

Generally, the Langmuir isotherm is resultant of the following assumptions:

- a) homogeneity of surface adsorption sites
- b) monolayer coverage
- c) a single adsorbate per site

- d) generation of a constant amount of adsorption heat energy from individual site-molecule interaction process and the independent bonding energy between the adsorbent and the adsorbate irrespective of covering rate
- e) Independency between sorption/desorption rate and energy regardless of neighbouring sites or population of nearest adsorbed molecules.

Assuming θ , a unit-less quantity is the fraction of surface coverage, $(1-\theta)$ the fraction of unoccupied surface active sites by target gas molecules, *C* is analyte concentration. A dynamic equilibrium, rate of adsorption, and desorption are equal. Therefore, the net adsorption-desorption rate can be expressed by the Langmuir theory as **[194]**:

At dynamic equilibrium; $\frac{d\theta}{dt} = 0$,

$$k_{ads} (1-\theta)C = k_{des}\theta \qquad \dots \dots (1.12)$$

Where k_{ads} and k_{des} are the rate constants for adsorption and desorption process, respectively.

Thus, the resultant equilibrium coverage θ is independent of time, and thus results in Langmuir isotherm:

$$\theta = \frac{N(t)}{N} = \frac{KC}{1+KC} \qquad \dots \dots (1.13)$$

Where $K = \frac{k_{ads}}{k_{des}}$ denotes the ratio of adsorption rate to desorption

rate.

1.7.2. Brunauer, Emmet and Teller (BET) Model

The Brunauer-Emmet-Teller (BET) theory is an addendum to the Langmuir model. The derivation of the BET model **[141]** is established on the following presumptions:

- a) surface homogeneity of adsorption sites
- b) gas molecules physically adsorb on individual solid layers

- c) there is no interaction between each adsorption layer
- d) the second and subsequent layers are feebly adsorbed than the first layer and
- e) the Langmuir theory can apply to each layer

In a multi-point linear form, the BET-equation is written as:

f)
$$\frac{p}{(p_0 - p)V} = \frac{1}{\alpha V_m} + \frac{\alpha - 1}{\alpha V_m} \frac{p}{p_0}$$
(1.14)

Where,

p = partial pressure of adsorbate gas at a given temperature, in Pascals;

 p_0 = saturation pressure at a given temperature;

V = volume of gas adsorbed at standard temperature and pressure (STP) [273.15K and atmospheric pressure $(1.013 \times 10^5 \text{ Pa})$], in milliliters;

 V_m =volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, in milliliters.

 α = dimensionless constant related to the adsorption enthalpy of the adsorbed gas.

The above equation is for multilayer adsorption. With, $\frac{1}{\alpha V_m} = 0$, a single-point BET equation can be applied to shorten the measurement time [142].

1.7.3. Freundlich Model

The Freundlich isotherm is a rational adaptation of Langmuir isotherm to pronounce the multisite adsorption behavior and significances of surface heterogeneity of semiconductor films [143, 144]. The adsorption behavior is described by the isotherm as:

$$\theta = \frac{N(t)}{N} = \frac{\alpha C^{\beta}}{1 + \alpha C^{\beta}} \left(1 - \exp\left(\frac{t}{t_A}\right) \right) \qquad \dots \dots \dots (1.15)$$

Where α is a proportionality factor, and β is the exponent. Depending on the characteristics (*i.e.* α and β) of the semiconducting material, the amplitude

resemble αC^{β} at low gas concentrations and 1 when the concentration of gas inclines to infinity. But in simplified form, the Freundlich isotherm can be represented as **[144]**:

$$\theta = \frac{N(t)}{N} = \alpha C^{\beta} \text{ for } 0 < \beta < 1 \qquad \dots \qquad (1.16)$$

The relative response of the sensor can be correlated to concentration by a Freundlich isotherm of the form [145]:

$$S = \frac{\Delta R}{R} = \frac{\alpha C^{\beta}}{1 + \alpha C^{\beta}} \qquad (1.17)$$

Where *S* is the sensitivity, *C* is the analyte concentration.

1.7.4. Wolkenstein Model

The Wolkenstein adsorption model includes the electronic interactions and their influence on the semiconductor adsorptivity for the depiction of chemisorption. The model contemplates both chemical and electronic equilibrium between the surface and the gas phase and at semiconductor surface, respectively **[146, 147]**. The elementary presumptions of the Wolkenstein adsorption isotherm are (i) presence single gas species (for adsorption) and, (ii) chemisorption is the only basis of surface charging. Basically, in two consecutive steps, the Wolkenstein adsorption process ensues by altering adsorbed particles from the neutral (*i.e.* weak chemisorbed species) state to the ionized (*i.e.* strong chemisorbed species) state, and vice versa **[148, 149]**. Considering these two steps, the development of the surface coverage with chemisorbed gas θ is defined by the rate equation of non- dissociative chemisorption as **[147-149]**:

$$S_{0}(1-\theta)(1-\theta)\frac{p}{\sqrt{2\pi mkT}}$$

= $N^{*}\theta^{0}\vartheta^{0}\exp\left(-\frac{E_{ads}}{kT}\right) + \exp\left(-\frac{E_{ads}}{kT}\right) + N^{*}\theta^{-}\vartheta^{-}\exp\left(-\frac{E_{ads}+E_{c}^{b}-E_{ss}}{kT}\right)$ (1.18)

where S_0 is the adsorption probability, p is the partial pressure of ambient gas, m is the molecular mass of the test analyte, k is the Boltzmann constant,

T is the thermodynamic temperature (in K), $\theta = (N^0 + N^-)/N^*$ is the resultant coverage from both neutral and charged adsorbates (N^{*} is the number of adsorption sites per unit surface area), $\theta^0 = N^0/N^*$ is the partial coverage of neutral adsorbates (N⁰ is the number of neutral adsorbates per unit surface area), and $\theta^- = N^-/N^*$ is the partial coverage of charged adsorbates, (N⁻ is the number of chemisorbed ions per unit surface area), Ec^b is the conduction-band edge in the bulk of the sensor, v^0 and v^- are the desorption probabilities for neutral and ionized chemisorbed species, respectively [149]. Wolkenstein adsorption isotherm for non-dissociative chemisorption on semiconductor expressed as:

$$\theta = \frac{\beta_p}{1 + \beta_p} \quad \dots \quad (1.19)$$

Now the Wolkenstein adsorption isotherm mimics the Langmuir isotherm. The major difference is coefficient β_0 which is independent of surface coverage θ in Langmuir, and dependent on θ in Wolkenstein model [147].

1.8. Materials of Choice

Here in this section details about all the metal oxides utilized in the thesis for sensing applications along with their corresponding literature survey are presented.

1.8.1. Nickel Cobalt Oxide (NiCo₂O₄)

In spinel NiCo₂O₄, nickel resides in the octahedral sites whereas cobalt lies in both O_h (octahedral) and T_d (tetrahedral) sites (Fig.1.7). NCO is nontoxic, low cost, and abundant [20, 21]. NCO exhibits higher electronic conductivity of ~10² orders as compared to pure NiO or Co₃O₄. NiCo₂O₄ is a well-known electrochemical material and has been applied in various applications like a supercapacitor, Li-ion battery, photo electrochemical cell, photodetector, and electro-catalyst [19, 22-25]. In oxide nanomaterials, the physiochemical properties vastly morphology (shape and size) dependant and this has potential applications in the microelectronics industry **[26-29]**. Thus, the fabrication of sensors using nanomaterials also has decent electronic compatibility for the development of signal processing circuit architectures. However, *p*-type ternary metal oxides so far lack significant application in gas sensing, hence attracts research interest **[30]**.



Figure 1.7. Crystal structure of NCO unit cell with the spinel structure (Adapted with permission from ref. [19]).

Here in Table 1.4, we have compiled literature regarding the synthesis techniques of various morphologies of NCO and their gas sensing characteristics.

Material	Method	Test	Response	Tres/ Trec	Ref.
		gas	(%)	(in sec)	
NCO nanorod	Hydrothermal	NH ₃	3.4	249/33	[150]
			(25ppm)		
NCO-rGO	Hydrothermal	NH ₃	1.07	57/185	[151]
nanorod			(100ppm)		
NCO nanorod	Hydrothermal	NH ₃	1.03	NA	[151]
			(100ppm)		

Table 1.4. Gas sensing characteristics of various NiCo₂O₄ morphologies.

NCO	Hydrothermal	TEA	1.38	49/54	[152]
microspheres			(50ppm)		
NCO@SnO ₂	Electro-	EtOH	8.87	115/148	
	spinning		(100 ppm)		[153]
	followed by				
	hydrothermal				
Zn doped	Hydrothermal	NO _x	~19	28/30	[153]
NCO			(10 ppm)		
mesoporous					
rod					
NiCo ₂ O ₄	Hydrothermal	NO _x	NA	51/53	[153]
nanorods					
NCO/rGO	Hydrothermal	H_2S	3.51	2/449	[154]
nano-		NO_x	(100ppm)		
composites		NH ₃	1.15		
			(100 ppm)		
			1.05		
			(100 ppm)		
Coral like	Template-free	Xylene	16.4	26/27	
NCO	hydrothermal		(100 ppm)		[155]
nanospheres					
Solid like	Hydrothermal	Xylene	4.3	39/39	
NCO			(100 ppm)		[155]
nanospheres					
NCO cubic	Urea assisted	O ₃	NA	32/60	[156]
structure	co-			(28 ppb)	
	precipitation				
	method			48/390	
				(165ppb)	
NCO	Template	Xylene	9.25	20/9	[157]
microtubule	assisted route		(100ppm)		

1.8.2. Zinc Oxide (ZnO)



Figure 1.8. Stick and ball representation of the ZnO crystal structures, cubic rock salt, cubic zinc blende, and hexagonal Wurtzite (O= red and yellow ball, Zn= white, and dark green ball) **[166].**

ZnO has rich literature as it is not new in the field of inorganic semiconductors. Research on different configurations to design ZnO nanostructures is carried out way back in time in the early 1900s [158-165]. It shows a high degree of surface "activity" in terms of interacting via chemisorption with the surrounding ambient. It is known as key technological material and leads to potential applications in field emission displays, chemical sensors, nanoresonators, and nano-cantilevers, etc. Zinc oxide is an *II-VI* compound semiconductor. It can crystallize in a variety of crystal structures including wurtzite, zinc blende, and rock salt as presented in Fig. 1.8. In general, ZnO has a stable hexagonal wurtzite structure composed of two interconnecting hexagonal close-packed (hcp) sub-lattice in a hexagonal lattice, each of which consisted of one of the Zn²⁺ and O²⁻ atom along the threefold *c*-axis involving sp^3 convent bonding where each anion is surrounded by four cations at the corners of a tetrahedron. The lattice parameters, $a_0 = 0.32495$ nm and $c_0 = 0.52069$ nm, in the ratio of c_0/a_0 =1.602, which is close to the ideal value of 1.633 expected for the hcp unit cell, and it belongs to the space group of $P6_{3}mc$.

Material	Synthesis	RH-	Tres/ Trec	Sensitivity	Ref.
	method	range	(in sec)		
		(%)			
ZnO NR	Hydrothermal	35-90		-4.4 mV/% RH	[168]
				(35-55%)	
			3.8/2.2	-10mV/% RH	
				(55-70%)	
				-24.6mV/%	
				RH (70-90%)	
ZnO	Sol-gel	40-90	336/370	162	[169]
	immersion				
Fe-	Sol-gel	40-90	287/119	197	[169]
doped	immersion				
ZnO					
Sn-	Sol-gel	40-90	NA	3.36	[170]
doped	immersion				
ZnO					
Sn-	Sol-gel	40-90	230/30	3.41(40-70%)	[171]
doped	immersion			1.41(70-90%)	
ZnO					
ZnO	Sol-gel	40-90	300/350	1.28(40-70%)	[171]
	immersion			1.40(70-90%)	
ZnO NR	CBD	33-95	NA	61.23%	[172]
ZnO NR	Sol-gel	20-90	~1/1	1.3	[173]
ZnO NR	Vapour-phase	12-97	3/20	183	[174]
	transport				
	method				

 Table 1.5. Humidity sensing characteristics of various ZnO morphology.

Zinc oxide is considered as an *n*-type semiconductor with a direct wide bandgap of $3.4 \ eV$ with a considerable fraction of ionic bonding. The cause

for the natural *n*-type nature of ZnO is due to the sensitiveness of ZnO lattice constants to the presence of structural point defects (vacancies and interstitials) and extended defects (threading/planar dislocations) that are commonly found in ZnO resulting in a non-stoichiometric compound $Zn_{1+d}O$ with an excess Zn. These excess Zn atoms tend to function as donor interstitials that give its natural *n*-type conductivity. In ionic form, the excess zinc exists as Zn⁺ interstitials that are mobile, and they tend to occupy special interstitial sites. These special sites offer passage routes for Zn interstitials to migrate within the ZnO wurtzite structure easily. This combination of optical and semiconductor properties make ZnO a contender for new generations of devices [167]. Here Table 1.5 presents the synthesis method of ZnO nanorods along with their sensing properties to support its stand in the development of next-generation humidity sensors.

1.8.3. Zinc Stannate (ZnSnO₃)



Figure 1.9. (*a*, *b*) Crystal structures of LN-type ZnSnO₃ (reprinted with permission from ref. [183], Copyright ACS 2012). (*c*) Crystal structures of cubic perovskite ZnSnO₃ (reprinted with permission from ref. [184],

Copyright IOP Publishing 2011). (**d**) Crystal structures of cubic inverse spinel Zn₂SnO₄, (reprinted with permission from ref. [187], Copyright ACS 2014).

Although binary semiconducting metal oxide nanostructures like ZnO, TiO₂, SnO₂, due to their distinctive physio-chemical properties establish them for extensive applications in energy conversion, catalysts, and sensing [175-179]. Still, then there is a recommence interest in the exploration of ternary oxide semiconductors (II-IV-VI oxides) due to their enhanced chemical stability towards applicability in extreme conditions, making them ideal for investigation [180]. There are two main outlooks on the structure of ZnSnO₃, including LiNbO₃ (LN) type and perovskite-type oxide. $ZnSnO_3$ has a polar LiNbO₃-type structure (space group: R3c, No. 161, Eg = 3.0 eV) [181, 182]. A typical atomic structure of LN-type $ZnSnO_3$ is shown in Fig. 1.9 (a, b) using octahedral units where the octahedral SnO_6 and ZnO_6 share both edges and faces with the adjacent octahedral architecture [183]. Cubic perovskite is another type of crystal structure of $ZnSnO_3$ (Fig. 1.9(c, d) [184] including face-centered-cubic and orthorhombic phase [185, 186] and can be fabricated by annealing different $ZnSn(OH)_6$ precursors. Zinc stannate ($ZnSnO_3$ and Zn_2SnO_4), usually retains distinctive physical and chemical properties that have acknowledged much responsiveness in recent decades. Noteworthy exertions have been fervent towards the assessment of ZTO micro/nanostructures due to their high electron mobility, high electrical conductivity, striking optical properties, and worthy stability in comparison to their binary counterparts (ZnO, SnO₂). Here Table 1.6 presents the synthesis method of ZnSnO₃ nanostructures along with their humidity sensing properties.

Table 1.6. Humidity sensing characteristics of various ZnSnO₃ morphology

Material	Method	RH-	Tres/ Trec	Sensitivity	Ref.
		Range	(in sec)		
		(%)			
SnS ₂ /ZnSnO ₃	LbL self	0-97	18/1	10709pF/%	[188]
	assembly			RH	
ZnSnO ₃	Hydrothermal	11-97	7/16	89.18%	[189]
cubic					
crystallites					
ZnSnO ₃	Chemical	10-100	NA	3GΩ / %	[190]
nanoparticles	Precipitation			RH	
ZnSnO ₃	Glucose	11-95	14.5 /30	NA	[191]
nanoparticles	assisted				
	hydrothermal				
ZnSnO ₃	Dual-	20-90	76.1/9.6	21	[192]
nanoparticles	hydrolysis-				
	assisted liquid				
	precipitation				
	reaction with a				
	subsequent				
	hydrothermal				
	procedure				
Sb-doped	Dual-	20-90	7.5/33.6	130	[192]
ZnSnO ₃	hydrolysis-				
nanoparticles	assisted liquid				
	precipitation				
	reaction with a				
	subsequent				
	hydrothermal				
	procedure				
ZnSnO ₃	Wet chemical	8-97	19/22	4155	[193]
nanoparticles					

1.9. Scope and Goals of the thesis

The main aspiration of this thesis is to synthesize various binary and ternary metal-oxide based nanostructures. The controlled growth of metal-oxides NiCo₂O₄, ZnO, and ZnSnO₃ was achieved by precisely controlling the reaction parameters. The prepared transition metal(TM) based oxides were evaluated for their gas and humidity sensing behavior at room temperature. Further, the experimental results were matched with available surface phenomenon to develop insight into the available sensing mechanism.

1.9.1. Thesis Objectives

The precise objectives of the research work plan are as follows:

1. Controlled growth of binary (ZnO) and ternary (NiCo₂O₄, ZnSnO₃) nanomaterials using simple and economical wet chemical methods followed by physico-chemical characterizations.

2. To investigate the anomalous room temperature NH_3 gas sensing properties of $NiCo_2O_4$.

3. To study the effect of transition metal (Ni) doping on ZnO nanomaterials and application in room temperature chemi-resistive humidity sensing behavior in association with physical model.

4. To explore the role of annealing temperature on humidity sensing behavior of $ZnSnO_3$ nanostructures and Freundlich isotherm modeling of the experimental results.

5. To study the influence of thermal treatment on the correlation between sensitivity and hysteresis induced error in ZnSnO₃ humidity sensors.
1.9.2. Thesis Outline

Regarding the selected objectives, and examining all the information gained from the literature review, the controlled growth of binary and ternary metal oxide nanostructures were executed. The growth of metal oxides (ZnO, NiCo₂O₄, and ZnSnO₃) nanostructures were carried out by a simple and economical wet chemical route followed by properties investigations. In conjunction with nanostructures, two prime factors *i.e.* effect of doping and effect of post-treatment temperature were also explored to understand their role in the enhancement of gas and humidity sensing applications. The experimental results are in correlation with available physical model like Freundlich adsorption isotherm to realize a plausible sensing mechanism. This work has been divided into seven chapters circumscribed between the introduction chapter 1 and the conclusions and future scope of chapter 7. The chapter-wise organization is summarized as follows:

Chapter-wise organization of the thesis:

Chapter 1, entitled, "Introduction" primarily discusses the brief overview of gas and humidity sensors, their classification, semiconducting metal oxide-based sensors, and their sensing mechanism, various adsorption/desorption models along with basic terminology used in sensors. The chapter also projects a literature review concerning the gas and humidity sensing behavior of binary (ZnO) and ternary (NiCo₂O₄ and ZnSnO₃) metal oxides.

Chapter 2, entitled, "Experimental Techniques and Sample Characterization" present the adopted materials synthesis technique for metal oxides and characterization techniques that are used in this thesis.

Chapter 3, entitled, "Mesoporous Nickel Cobalt Hydroxide/Oxide as Room Temperature Ammonia Sensor", describes the room temperature ammonia gas sensing properties of NiCo₂(OH)₆ and NiCo₂O₄. The anomalous sensing performance of NiCo₂O₄ is briefly explained based on the role of annealing temperature. Chapter 4, entitled, "Zn_{1-x}Ni_xO Nanostructures as an Excellent Humidity Sensor", discuss the chemi-resistive humidity sensing behavior of Zn_{1-x}Ni_xO(x=0, 0.05, 0.1) at room temperature.

Chapter 5, entitled, "Controlled growth of ZnSnO₃ nanomaterials as Humidity Sensors", presents the effect of annealing temperature on growth and humidity sensing properties of ZnSnO₃ nanostructures.

Chapter 6, entitled, "Correlation between Sensitivity and hysteresis induced error in ZnSnO₃ humidity sensor", summarizes the role of thermal treatment on the relationship between sensitivity and hysteresis induced measurement error in ZnSnO₃ based humidity sensors.

Chapter 7, "Conclusions and Future Scopes", recapitulates the main findings of the previous chapters and describes the probable future scope of the research work that can be undertaken in this area.

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Chapter 2

Experimental Techniques and Sample Characterization

This chapter elaborates on the experimental methods employed to synthesize and characterize the different nanostructured metal oxides i.e. NiCo₂O₄, ZnO, and ZnSnO₃ that are described in this thesis. The nanostructures presented in this thesis are prepared by using a simple and economical wet chemical method. Finally, a brief review of the various analytical tools including their principle of operations for material characterizations is summarized along with the gas and humidity sensing measurement processes of metal oxides. In recent years, several synthesis and characterization practices were invented for nanostructured materials. However, it's a persistent journey for the development of nanomaterials with improved properties for the preferred applications. This chapter gives an ephemeral details regarding the synthesis and characterization techniques utilized in current research.

2.1. Synthesis of Nanomaterials

This section details, the steps involved in the wet chemical synthesis method for synthesizing AB_2O_4 type cubic spinel structures of NiCo₂O₄, Zn_{1-x}Ni_xO (x=0, 0.05, 0.1), and *fcc*-phases of ZnSnO₃. This method involves a variety of routes for producing different types of nanostructures at relatively low temperatures.

It is a very simple and effective technique that requires only the beaker, precursor materials, hot plate, and magnetic stirrer. This technique has several advantages such as high and stable yield, uniform and reproducible, does not require sophisticated instrumentation, room temperature, economical, and minimum loss of material. The growth process is mainly governed by some fundamental factors like nature and concentration (molarity) of the precursors/complexing agent, pH of the solution, temperature, duration, and the reaction medium. The wet chemical method involves two steps, nucleation and particle growth, and is based on the formation of a solid phase from a solution.

2.1.1. Synthesis of Ni-Co hydroxide/oxide

1. All the appropriate metal salt precursors, *i.e.*, Ni(NO₃)₂· $6H_2O$, Co(NO₃)₂· $6H_2O$, and ammonium hydroxide solution are used for the synthesis.

2. The metal precursors are taken in 0.05 M concentration in deionized (DI) water by keeping the ratio of A: B as 1:2.

3. The (above) precursors are vigorously stirred for 30 min to obtain a homogeneous mixture.

4. pH of the solution maintained at 13, using the addition of NH₄OH solution drop wise. This reaction solution was made alkaline to promote the growth of nanomaterials, and to obtain the desired nanostructures i.e. nanoflakes.

5. The growth of nanomaterials was governed by parameters like pH, temperature, and time, *etc*. The reaction temperature was maintained at 100° C for ~ 3 h.

6. This resulted in a dark green precipitate, and once the reaction was completed, the precipitate was filtered using Whatman filter paper. The filtered product was repeatedly rinsed with DI water and several times with ethanol, to remove the unreacted precursors. Then the washed product was allowed to dry naturally.

7. The dry product was collected and further annealed at 450°C for 4 h to obtain AB_2O_4 *i.e.* NiCo₂O₄ from NiCo₂(OH)₆.

2.1.2. Synthesis of Zn_{1-x}Ni_xO

1. Analytical grade of appropriate metal salt precursors *i.e.* $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and ammonium hydroxide solution are used for the synthesis.

2. The metal precursors are taken in 100 mM concentration in deionized (DI) water by maintaining the Ni- concentration of x=0, 0.05, and 0.10 to obtain desired Zn_{1-x}Ni_xO nanostructures.

3. The precursors are vigorously stirred for 30 min to obtain a colourless homogeneous mixture. The resulting solution pH maintained at ~11 using

the drop wise addition of NH₄OH solution which directs the growth of nanomorphology. The reaction temperature was maintained at 90°C for ~ 2 h.

4. Thus obtained white precipitate was filtered using Whatmann filter paper after repeated rinsing with DI water. Then the washed product dried overnight and collected.

2.1.3. Synthesis of ZnSnO₃

1. All the appropriate metal salt precursors, *i.e.*, $ZnSO_4.7H_2O$, $Na_2SnO_3.3H_2O$, and ammonium hydroxide solution were used for the synthesis.

2. The metal precursors were taken in 10 mM concentration in deionized (DI) water by keeping the ratio of Zn: Sn as 1:1.

3. Firstly, clear solutions of zinc sulfate and sodium stannate separately were prepared by vigorous stirring. Then sodium stannate solution was added to the zinc sulfate solution and stirred for 6 h.

4. Here the growth of nanomaterials was governed by reaction temperature which was maintained within 25-100°C.

5. The precipitate was collected using centrifugation and dried naturally. The obtained product was annealed at various temperatures.

2.2. Characterization Techniques

2.2.1. X-ray Diffraction

The X-ray diffraction technique is one of the dominant, fast and nondestructive diagnostic tool usually implemented for phase identification, crystallite size calculation, strain, and anisotropic growth of nanomaterials. Both powder and thin films can be used for analysis **[1, 2]**.

Theory: Typically, a monochromatic beam of X-rays whose wavelength analogous to atomic spacing, strikes the sample and diffraction in a specular

manner to endure constructive interference. X-rays are diffracted at a specific angle (θ) by lattice planes and their constructive interference creates (*hkl*) planes whose path difference is an integral multiple of the incident light wavelength. The condition essential for constructive interference is mathematically expressed by Bragg's law:

$$2d \, \sin \theta = n\lambda \qquad \dots \qquad (2.1)$$

where *d* is the interplanar spacing, θ is the glancing or rather diffraction angle, *n* is the order of diffraction and λ is the wavelength of the incident ray. The intensities, broadening, and shape of the obtained peaks deliver data about the atomic basis, crystal perfection, and particle size of the sample. The experimentally acquired diffraction pattern is unique for a sample and is compared with various standard existing data by the joint committee on powder diffraction standards (JCPDS), thus the definite composition of the sample can be realized. XRD measurements of the powder samples were performed at room temperature and pressure using an X-ray diffractometer (Bruker D8 Advance, Germany). The X-ray source was Cu X-ray having a wavelength of Cu K α lines with a wavelength of 1.5406 Å. The filtered Cu K α radiation was used for recording the diffraction pattern where the value of 2 θ was varied from 10° to 80°. Fullprof software was used for X-ray profile analysis, further to determine structural parameters.

In case of nanomaterials, widening of XRD peaks due to induced stress causes decrease in the particle size. Usually, the crystallite size (D) is calculated by the Scherrer's formula which is expressed as:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (2.2)$$

Where β is Full-width half maxima (FWHM) of XRD peak at angel θ . λ is the incident wavelength X-ray beam.



Figure 2.1 Scheme of different components of an XRD. The circle represents the goniometer where the sample is placed in the center. A divergent source of X-rays is focused on the flat plate sample which then diffracted and collected by the detector. The diffraction pattern is recorded by rotating both the source and the detector at an angle θ , keeping the sample fixed. (Adapted with permission from ref. [3])

2.2.2. Field Emission Scanning Electron Microscopy

Scanning electron microscope (SEM) is a type of microscope used to investigate the topological (surface features), morphological (size, and shape), and the compositional (the elements, compounds, and the relative amounts) details of the materials. SEM is used to observe and characterize the materials in the regime of microscopic (μ m) to nanoscopic (nm) scale [4].

Theory: SEM is one of the most widely used instruments because of its extremely high magnification, larger depth of focus, high resolution, and ease of sample observations. There are a few basic steps involved in its working operation (1) a stream of electrons was produced in vacuum by an

electron gun, (2) this focused high energy e-beam was accelerated towards the sample by a system made up of electromagnetic lens, (3) then the sample was irradiated with the beam and the interaction occurs inside the irradiated sample, the resulting changes in the e-beams were collected by the detectors, and (4) the detected signals were further processed and transformed into an image. SEM operated at a voltage between 2-50 kV and its beam scan the sample using a raster scan method.

An electron beam created by an electron gun at the top of the microscope was focused on the sample through different lenses. The top columnar part was placed under a high vacuum which resulted in increment of the electron mean free path to proficiently pass electron beam towards the sample. Thermionic tungsten filaments are extensively used in SEM, whereas lanthanum hexaboride (LaB₆) field emitter filaments are used in FESEM. FESEM requires an applied potential of 30 kV to hasten electrons. Upon striking an electron beam on the sample, the interaction of the sample surface generates elastic and inelastic waves. The backscattered electrons (BSE) are deflected due to inelastic scattering upon the interaction of the electrons with the nucleus of an atom. This interaction produces auger electrons and secondary electrons (SE) and causes characteristic X-rays. The signals due to Backscattered electron (BSE) and secondary electron (SE) are administered to generate topographic images of a sample. The elemental identification is made by evaluating the characteristic X-rays formed. The X-rays are generated when high energy orbital electrons relocated to low energy orbitals after they are detached by an incident beam of electrons. X-rays are then identified and deliver distinguishing evidence about elements existing in the sample.



Figure 2.2. Schematic representation of electron-sample interaction in FESEM. (Adapted with permission from ref. **[5]**)

In this work, the high quality microscopic and nanoscopic images of the synthesized samples were obtained using FESEM Supra 55 Zeiss, UK and JEOL 7610F plus, JAPAN. Both FESEM instruments were equipped with an EDS (Energy Dispersive Spectroscopy) analyzer from Oxford Instruments, UK, which is used for analyzing compositional analysis and elemental mapping of various TM-based materials.

2.2.3. Transmission Electron Microscopy

A transmission electron microscope (TEM) is another most efficient and versatile technique for material characterization on the microscopic scale. A TEM provides information regarding the microstructural, crystal structure, and chemistry with a high spatial resolution from each of the microscopic phases individually by application of an electron beam of 100-400 keV potential **[6]**.

Theory: TEM uses a high energy electron beam to 'see-through' the specimen. The electron beam interaction (Fig. 2.3) with the sample gives the following results:

- A part of the highly energetic electron beam gets transmitted, and part of it scattered while passing through the specimen.
- Transmitted electrons suffer no interaction and no loss of energy in the specimen which carries information about the structure of the sample. Elastically scattered electrons get diffracted from their original path while passing through the specimen, without loss of energy and transmitted through the remaining portion of the specimen.
- All incident electrons which are scattered by some atomic spacing will be scattered by the same angle and will follow the Bragg's law. This diffracted beam carries the information about the orientation, atomic arrangements, and phases present in the area being examined.
- The transmitted beam gives a bright-field image of the specimen. A dark field image is formed when one of the diffracted beams is selected for imaging.
- The incident electrons also inelastically interact with the specimen, then lose their energy due to this interaction and transmitted through the rest of the specimen. The loss of energy due to the inelastic scattering of electrons (Electron Energy Loss Spectroscopy (EELS)) can be measured. This information can be used to determine the elemental composition, chemical bonding, and valence and conduction band electronic properties.



Figure 2.3. Schematic representation of TEM imaging system including Diffraction Mode (SAED) and Imaging Mode. (Adapted with permission from ref. **[7]**)

HRTEM is composed of filament, an objective lens system, a magnification system, a specimen stage, and a data recording and chemical analysis system. The sample preparation is essential since the sample must be thin enough so that it can pass the e-beam through it. JEOL JEM-2100 and JEOL 3010 with UHR pole piece which was a computer-controlled high-resolution transmission electron microscope (HRTEM) were used to characterize the samples in our research work.

The samples were prepared by sonication of the samples in ethanol. In the case of directly grown nanostructures, the substrates as a whole were immersed in ethanol then the dispersion was cast on the copper grid using a micropipette, which was further dried for 1 h inside a heating furnace to evaporate the solvent. HRTEM images were analyzed using ImageJ software, which is a public domain Java-based image processing program developed at the National Institutes of Health, USA.

2.2.4. N₂ adsorption/desorption Analysis

Chemical sensing is a surface phenomenon that is much dependent on surface area and porosity of employed material. The surface area and porosity are figured out from N_2 adsorption-desorption measurement which usually takes place at ~77K at liquid nitrogen temperature.

Theory: To investigate the N₂ adsorption-desorption properties, out of various models Brauner-Emmett-Teller (BET) adsorption isotherm model is employed. According to the BET model, gas molecules are physically adsorbed on a solid by forming a multilayer, there is no interaction between each adsorption layer. Depending on the different types of pore structure of the different materials the International Union of Pure and Applied Chemistry (IUPAC) has classified the pores into micropores (< 2 nm), mesopores (~2-50 nm), and macropores (>50 nm).

The N₂ adsorption-desorption isotherm can be classified into various types [8-10]. Type-I isotherm generally occurs in microporous solids having relatively small external surfaces (e.g., activated carbon, molecular sieve zeolites, metal-organic frameworks, and certain porous oxides). In the BET equation, when $P/Po \ll 1$ and $c \gg 1$, then it leads to monolayer formation. Type-II is a reversible isotherm that indicates the non-porous/macroporous materials. The isotherm represents the unrestricted monolayer-multilayer adsorption. Type-III isotherm is the vapor adsorption; it also indicates the unrestricted multilayer formation process. It forms due to the lateral interactions between adsorbed molecules which are stronger in comparison to the interaction between the material's surface and the adsorbate. Type-IV and V isotherms with the hysteresis loop indicate the presence of capillary condensation in mesoporous materials. The initial part of the hysteresis type IV is attributed to monolayer-multilayer adsorption. Type VI isotherm, the sharpness of the steps depends on the system and the temperature. It represents the stepwise multilayer adsorption on a nonporous surface. The step height represents the monolayer capacity for each adsorbed layer. The hysteresis loop in the isotherm curve is usually related

to the thermodynamic or network effects or the combination of these two. The hysteresis loops are classified into four types, *i.e.*, from H1-H4 and the steepness of the isotherm decrease from the H1-H4. H1: it suggests the shape of the hysteresis is governed by agglomerates/spherical particles arrangement uniformly, cylindrical pore geometry which indicates the relatively high pore size uniformity and facile pore connectivity. H2: suggests the pore with narrow openings (ink-bottle pores), relatively uniform channel-like pores, and pore-network/connectivity effects. H3 loop of the isotherm illustrates the loose assemblages of plate-like particles forming a slit-like pore and H4 loop, indicates the narrow slit-like pores, with internal voids irregular shape and broad size distribution, hollow spheres with walls composed of ordered silica.



Figure 2.4. Schematic representation of the N_2 adsorption-desorption analysis instrument. (Adapted with permission from ref. [11])

The BET method was used for calculating the specific surface area in the relative pressure of 0.05-0.3 (classical BET range) for multipoint BET, and at a relative pressure of 0.3, the single point BET was obtained. The pore size distribution curves were derived from the desorption part of the isotherm using the Barret-Joyner-Halenda (BJH) method. The total pore volume was calculated from the adsorption quantity at a relative pressure of $P/Po\approx 0.99$ [11]. The samples synthesized in this work were tested to understand the surface area analysis and pore size distribution and carried

out at 77 K using N_2 adsorption-desorption study with an automated gas sorption analyzer Quantchrome Autosorb iQ2.



2.2.5. Thermogravimetry Analysis (TGA)

Figure 2.5. Schematic representation of Thermogravimetric analysis (TGA) instrument. (Adapted with permission from ref. **[13]**)

Thermogravimetry (TG) is the division of thermal analysis scrutinizing the mass change of a sample as a function of temperature (in scanning mode) or as a function of time (in isothermal mode). TG analysis is one of the essential analysis tools, which measure the changes in the physical and chemical properties of the material as a function of temperature at a constant heating rate in various atmospheres [12]. It measures the change in the mass of a sample due to various thermal processes like adsorption, desorption, sublimation, vaporization, oxidation, reduction, and decomposition concerning the change in temperature. The instrument used for TG analysis is a programmed precision balance called Thermo balance; it consists of an electronic microbalance, a

furnace, and a temperature programmer and a recorder. The instrument plots the TGA curve in percentage mass change versus temperature/time. TGA curves are classified according to their shape. Each contributes to the unique thermal events which they undergo like: (1) no change (indicating no mass change, *i.e.*, the decomposition temperature is greater than the temperature range of the instrument), desorption/drying (volatile materials/polymerization process, where the mass loss is large), (2) single-stage decomposition, (3) multistage decomposition (decomposition process occurs as a result of various reactions), (4) atmospheric reaction (it may occur due to the surface oxidation reaction in the presence of interacting atmosphere) [13]. So, TGA studies help to explicate the decomposition mechanisms, characterize the material, to fingerprint the materials for identification and quality control, allowing the compositional analysis, kinetic studies through weight loss/gain through chemistry or predictive studies. Thermogravimetric and differential thermogravimetric analysis of the prepared samples were carried out using TGA-DSC (Mettler Toledo Thermal Analyzer) at a heating rate of 5°C/min in air.

2.2.6. Ultraviolet-Visible Spectroscopy (UV-Vis)

UV-Visible spectroscopy is ideal instrumentation for exploring the optical and electronic properties of various nanostructured materials in the form of powders, thin-film, and liquids **[14]**. It provides information about the interaction of electromagnetic radiations in the ultra-violet and visible region with molecules. When a molecule absorbs light of an appropriate wavelength; an electron is promoted to a higher energy molecular orbital and the molecular state is termed as an excited state. An electronic transition is caused due to the absorption of the appropriate wavelength of ultraviolet and visible with material **[14, 15]**.

Theory: According to the Beer-Lambert, the absorbance is proportional to the concentration of the substance in the solution. The Beer-Lambert Law can be expressed in the form of the following equation [16]:

$$A = \log_{10} \frac{I_0}{I} = \epsilon c l \quad (2.3)$$

Where *A* is the absorbance, I_0 is the intensity of the incident light, *I* is the intensity of the transmitted light, I/I_0 is called the transmittance, *l* is the dimension of the cell or cuvette (cm), *c* is the concentration of the compound, and ε is the extinction coefficient, which is constant for a particular substance at a particular wavelength.



Figure 2.6. Schematic diagram of UV-Vis-NIR spectrophotometer. (Adapted with permission from ref. **[15]**)

The wavelength of the absorbed light provides information about the bandgap of the substance. The instrument used in ultraviolet-visible spectroscopy is called a UV-Visible spectrophotometer. UV-Visible spectrophotometer has several components: the light source, monochromator, detector, and sample holder as depicted in Fig.2.6. UVvisible spectrophotometer possesses two light source: (a) tungsten filament (300-2500 nm) for visible region, and (b) deuterium arc lamp (190-400 nm) or Xenon arc lamp (160-2000 nm) for UV region. The photomultiplier R955 detector was used for the high energy ultraviolet-visible range, whereas a Peltier cooled PbS detector was used for the whole near-infrared range. When a light beam passes through the monochromator; the light beam gets split by a half mirror device before it reaches the sample. The half of the light passes through a reference cell which contains the solvent only, and

another half of light passes through the sample (compound) cell. The container or cuvette for the reference and sample cell must be transparent to pass the radiation. The detector records the difference between the reference and sample cell intensities of the transmitted lights, and it displays the value on the LED screen. In this work, Varian Cary 100 Bio UV-Visible Spectrophotometer was used for UV-Visible spectroscopy. The optical bandgap of samples is determined in absorption spectroscopy mode.

2.2.7. Gas Sensing Measurement

The response (change in resistance) of different metal oxide samples in the presence of various test gases like ethanol, ammonia, and carbon monoxide was studied. An indigenous instrumental set up for gas sensing experiments was fabricated in the lab. A gas sensing setup consists of several parts. This can be broadly classified into 4 segments.

- i) Gas Chamber
- ii) Sample and Contact
- iii) Resistance measurement unit
- iv) Gas cylinders and controllers

2.2.7.1. Gas Chamber

The gas chamber was custom made using high-grade SS to continuously withstand high temperature (>500 °C) during sensor operation. A specially designed heater from Excel instruments (India) was used for heating the samples. The controller for the heater was also customized as to be operated with 16A current and was from Heat and Control Systems Mumbai, India. The sample holder was made of stainless steel and consisted of gold plated copper probes for electrical measurements.

2.2.7.2. Sample and Contact Preparation

Dried powder samples were initially ground using motor and pestle. 0.1 gm of each sample was pressed to pellet using stainless steel die of 10 mm diameter and applying a uniaxial pressure of 1.44 MPa. Electrical contacts were made by painting with silver on the pellet. The contact was restricted
to approximately 8 mm diameter on the bottom side and approximately 2 mm diameter on the top side to allow the sample to expose to the gaseous atmosphere. The pellet was kept for drying in a hot air oven after painting on each side for 15 minutes for the paint to dry properly. The sample was preheated for 24 hr. in zero air (air with 0% humidity) atmosphere at 30 °C before starting the sensing measurements.

2.2.7.3. Resistance measurement unit

This measurement was done by Keithley 2401 source meter. The current was varied according to the resistance of the sample from $0.1 - 1\mu A$. The ohmic nature of the contacts was confirmed at the start of the measurement by varying the current and noting the voltage. The Keithley instrument was interfaced to a PC for finding the time-dependent factors (like response time and recovery time). This was done using LABVIEW[®] software and GPIB USB interface from National instruments. Interfacing requires a PC, instrument to be interfaced, and a connector. NI-USB HSS was used for interfacing Keithley 2401 to the PC. LABVIEW[®] software helps in running the commands and plotting the results simultaneously. The software must be used in conjecture with drivers, one for identifying NI-USB HSS viz. NI 488.2 and other for Virtual instrument software architecture (VISA).

2.2.7.4. Gas cylinders and controllers

The accuracy of measurements depends on the test gas used for measurement. All the test gases were procured from Ultra-Pure Gases Pvt. Ltd., Gujarat, India (99.9 % purity). The gas flow was controlled using digital mass flow controllers with flow rate 0-200 mL/min (Dakota Instruments, USA), out of which one is dedicated to zero air and the other one was calibrated for use of various test gases like CO, CO₂, NH₃, C₂H₅OH, etc. To take care of the effect of humidity on the gas sensing, synthetic air (zero air) was used for measurements. In this work concentration varying from 1 - 100 ppm was studied. The concentration of the gases was controlled by DigiFlow[®] software interfaced through PC.



Figure 2.7. Schematic diagram of In-house developed Gas sensor testing setup.

2.2.8. Humidity Sensing Measurement

A schematic diagram of the experimental setup used for humidity sensing measurement is depicted in Figure 2.8 (a). The two terminal sensor device is fabricated on ITO-coated glass substrates as shown in Figure 2.8 (b). The ITO substrates were patterned by using Zn-dust and conc. Hydrochloric acid (HCl) to make the active sensing area of 0.10 cm² [10 mm length (L) and 1 mm width (W)]. Then the sensing materials were drop casted in the active channel and dried in a furnace at 50°C overnight to remove any other functional materials in the binder before sensing experiments. To obtain environments with a controlled relative humidity value, the saturated aqueous solutions in a closed vessel were utilized. The experiment was performed at room temperature. The saturated solutions of KOH, MgCl₂.6H₂O, K₂CO₃, Mg(NO₃)₂, NaNO₃, NaCl, KCl and K₂SO₄ in closed conical flasks were used to obtain 8%, 33%, 43%, 52%, 63%, 75%, 86% and 97% RH levels, respectively [**17**, **18**]. The electrical resistance of the present film sensor was measured in DC mode using a Keithley 2401 source

meter, which was interfaced with the computer through LABVIEW[®] software.



Figure 2.8. Schematic diagram of (a) In-house developed humidity sensor testing setup and (b) two- terminal humidity sensor device.

In summary, the synthesis techniques and characterization of various metal oxide nanostructures are discussed. The indigenously developed gas and humidity sensing measurement setup are also discussed.

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Chapter 3

Mesoporous Nickel Cobalt Hydroxide/Oxide as Room Temperature Ammonia Sensor

We report NH_3 gas sensing behavior at room temperature (RT) using highly mesoporous nanostructures of Ni-Co hydroxide/Oxide synthesized by facile and economical wet chemical methods. The dynamic sensing of NiCo₂(OH)₆ (NCH) and NiCo₂O₄(NCO) illustrates nearly 3 and 2 fold rise in sensitivity by varying NH₃ concentrations indicating excellent sensitivity following the Freundlich equation. NCO being a well-known p-type material, showed anomalous n-type sensing behavior towards low NH₃ concentration at room temperature. The abnormal sensing characteristics were attributed to the transition of majority charge carriers due to the surface reaction of chemisorbed oxygen ions and ammonia gas vapors.

3.1. Background of the Work

Environmental pollution has become one of the most serious issues that have attracted considerable attention from the scientific community to investigate various environmental safety issues. The major reason for atmospheric pollution is the release of harmful gases, liquids, and chemicals to the air through industrial effluents, agricultural chemicals, fertilizers, and so forth [1, 2]. Ammonia (NH₃) is one of the toxic gases, hazardous air pollutants with a distinct irritating odour, and is widely employed in refrigeration systems, livestock breeding, food processing, and fertilizer production [3, 4]. It has been known that exposure at around 50 ppm of NH₃ gas in the air may cause acute poisoning or life-threatening situations, such as permanent blindness, lung disease, respiratory disease, skin disease, and so on. Therefore, it became highly necessary to design and fabricate a longterm-reliable, highly-sensitive, miniaturized, and room-temperatureefficient ammonia gas sensor, which can detect and monitor NH₃ concentration in real-time in the surrounding environment [5]. Hence, it is an environmental concern because of serious health with exposure to a high concentration of ammonia [6]. A standard for safe exposure of ammonia gas was set below 35 ppm for less than 15 minutes by the US Occupational Safety and Health Administration (OSHA). The National Institute for Occupational Safety and Health recommends that the exposure level in workroom air be limited to 50 ppm for > 5 minutes [7]. Therefore, it is a bit challenging idea to develop such types of sensors so that the people working in an ammonia gas environment or laboratories to detect the ammonia at room temperature and to reduce serious injuries to human health if the exposure reaches above its safe limits. Although a large variety of metal oxide-based ammonia gas sensors are available, still search for more effective gas sensor materials is continued with high sensitivity, fast response and recovery time, and selectivity to detect gases at lower concentrations or to eliminate cross-sensitivity. A typical portable novel gas

sensor with high performance based on semiconducting metal oxides relies principally on continuously monitoring the direct changes of conductance in adsorption and desorption of target gas molecules. In this context complex oxides like spinel oxides have attracted much more interest with the possibility to optimize the physical and chemical properties of the gas sensor [8]. Due to fundamental sensing mechanisms, metal oxide semiconductor gas sensors generally operated at elevate temperatures *i.e.* above 150°C [9]. Current research is focusing on reducing the operating temperature of the sensors for safety demand, low power consumption, and various industrial applications. In the process of developing different oxide sensors, the majority of these gas sensing devices operated only at high temperatures and not used in the existing environment at room temperature. The major issue is that the recovery performance of sensors is very poor at room temperature because desorption of gas molecules from the sensor takes long time [1]. Till now approaches like noble metal decoration (Pd, Pt) [10-13] CNT-based combined structures [14, 15] self-powered gas sensing system [16, 17], metal elemental doping and UV light activation [18, 19]. Nanostructured materials such as nanowires, nanotubes, nanoparticles, and nanoflakes are promising because of their high surface area, high surface-to-volume ratio, small size, low energy consumption, and unique electronic properties [20-23]. It has been known that the cobaltcontaining spinel oxides *i.e.* MCo₂O₄ where M= Ni, Cu, Zn, Mg, Mn, Cd, etc. have many applications in the areas like chemical sensors, electrode materials for supercapacitor and Li-ion batteries, electro-catalysts and as pigment [24]. In this chapter, we present the economical wet chemical synthesis method of mesoporous spinel Nickel Cobalt hydroxide (NCH) and NiCo₂O₄ (NCO) nanoflakes and investigate ammonia gas sensing properties of fabricated gas sensing devices. The results shown that the sensor exhibits excellent compatibility between stability and sensitivity, operability at room temperature for ammonia gas detection. The response of the sensor was measured within 2-100 ppm NH₃ gas concentration at

room temperature, with main focus on sensor behaviour towards lower concentration (2, 5, 10 ppm).

3.2. Synthesis Procedure

The mesoporous nanoflakes of NCH and NCO were obtained using a facile and economical wet chemical process. A 50mM aqueous solution of Ni(NO₃)₂.6H₂O and Co(NO₃)₂.6H₂O (Alfa Aesar) was prepared (1:2 ratio, respectively) in DI water and stirred for 30 min. Then the NH₄OH solution (Merck) was slowly added under constant stirring and *pH* maintained at ~13 to obtain desired mesoporous flake-like structures [**25**]. Upon heating at 80°C, a thick viscous dark greenish fluid was obtained which was washed several times with DI water and ethanol and dried in air overnight. NCO was formed after annealing the as-prepared NCH at 450°C for 4 hours [**26**]. The plausible mechanisms are given as follows:

$$NH_3 + H_2 O \to NH_4^+ + OH^-$$
 (3.1)

 $Ni^{2+} + 2Co^{2+} + 60H^{-} \rightarrow NiCo_2(0H)_6$ (3.2)

(Nickel Cobalt Hydroxide (NCH))

$$NiCo_2(OH)_6 + \frac{1}{2}O_2 \rightarrow NiCo_2O_4 + 3H_2O \uparrow (3.3)$$

(Nickel Cobalt Oxide (NCO) after annealing)

3.3. Results and Discussions

3.3.1. Structural and Morphological Analysis

Fig. 3.1 (*a*) depicts the XRD pattern of NCH (Mixture of Cobalt hydroxide and Nickel hydroxide). All the diffraction peaks are broad indicating nanocrystalline NCH, which can be indexed to the mixed-phase of hexagonal close packed (*hcp*) Ni(OH)₂ peaks (001), (006), (100) (JCPDS card no: 01-1047) and face centred cubic (*fcc*) Co(OH)₂ peaks (001), (102), (104) planes (JCPDS card no: 51-1731). Fig. 3.1 (*b*) and (*c*) shows the XRD pattern of nickel cobalt oxide (JCPDS card no: 02-1074) and its corresponding Reitveld refinement, respectively. The lattice parameters obtained from Reitveld refinement for NCO are $a=b=c=8.120\pm0.005$ Å [27].



Figure 3.1. XRD patterns of (*a*) NCH, (*b*) NCO, and (*c*) Reitveld refinement of NCO.

The gas sensing process is closely related to the surface reactions, which is an important parameter of gas sensors since the test gases react with the adsorbed surface species on the material. The ability to direct the selective uptake of gaseous species relies on the pore size, increased surface area, and the effectiveness of the materials for gas and vapor detection. Fig.3.2 shows the FESEM image of (*a*) NCH and (*b*) NCO sample and the inset shows the high magnification image indicating well interconnected, highly dense mesoporous flakes. The intersected topographies of flakes were seamlessly reserved even after thermal transformation demonstrates materials stability and considered to provide high surface area for better adsorption of ions [28].



Figure 3.2 FESEM images of (*a*) Ni-Co hydroxide (NCH) and (*b*) NiCo₂O₄ (NCO) and (*c*) HRTEM image of NiCo₂O₄ (NCO).

Fig. 3.2 (*c*) represents the HRTEM image of the mesoporous NiCo₂O₄. HRTEM indicates interplanar spacing of 0.135 nm for (440) plane (spacing between two consequent fringes) which was calculated by ImageJ software. The (440) plane orientation of the NCO was confirmed by the *d*-spacing calculated from the lattice fringes of HRTEM and XRD.

3.3.2. N₂ Adsorption-Desorption isotherm Study

The adsorption-desorption isotherm can be classified as type-IV for NCH suggesting complete pore filling due to the monolayer-multilayer adsorption and capillary condensation. In the case of NCO, adsorption-desorption isotherm is categorized as type-III proposes weak adsorptive-adsorbent interactions and incomplete pore filling **[29, 30].** BET multipoint surface area of NCH and NCO measured that of 118.933 m²g⁻¹ and 45.481 m²g⁻¹, respectively. The corresponding BJH pore size distribution for NCH was between 2 nm to 4 nm (Fig. 3.3 (*a*)) and for NCO few of the pores lies in the between 2-5 nm whereas the majority of the pores lie in the region of

5-50 nm (Fig. 3.3 (b)). The high surface area with an advantageous mesoporous structure promotes enhanced sensing properties as well as high selectivity for ammonia gas.



Figure 3.3. N₂ adsorption-desorption isotherms of (*a*) NCH and (*b*) NCO. Inset shows Barrett-Joyner-Halenda (BJH) pore size distribution.

3.3.3. Ammonia (NH₃) Sensing Properties

3.3.3.1. NH₃ Sensing Measurement

For ammonia sensing measurements a homemade setup was used (as shown in Fig.2.7). The NCH and NCO samples exist in the powder forms were pressed into pellets for ammonia sensing using hydraulic press under a constant load of 1.4 MPa. The sensing element was fabricated by designing ohmic contacts on the pellet with the help of silver paste at a separation of 2 mm on the surface. To record the dynamic ammonia gas sensing response of the Ni-Co oxides, studies were carried out on these sensing elements in a closed gas chamber pre-filled with ambient air at ambient temperature. The sensing element was placed directly over a sample holder in the gas chamber and the operating temperature was noted down (here the temperature was kept constant at room temperature *i.e.* ~ 30° C). The known volume of the ammonia gas was introduced into the gas chamber pre-filled with balanced air by using mass flow controllers, to control the desired concentration of ammonia gas and it was maintained at atmospheric pressure and temperature.

3.3.3.2. Analysis from Resistance Measurements

To explore the potential applicability of the mesoporous nanostructured spinel NCH and NCO as a room temperature NH_3 gas sensor, we have studied the variation of gas sensing behavior of both samples at room temperature. The gas sensing experiment for Ni-Co hydroxide/oxide samples was carried out at low concentrations of NH_3 gas (*i.e.* 2, 5, 10 ppm). The gas response is expressed by the following equation,

$$S(\%) = \frac{R_g - R_a}{R_a} \times 100$$
 (3.4)

Where R_g and R_a represent the resistance of Ni-Co hydroxide/oxide sample in the presence of NH₃ gas and air respectively. The operating temperature is important for the study of gas sensing properties because of its considerable influence on the surface state of materials on which the gasdetection process usually takes place [**31**]. For practical application, a sensor that operates at room temperature is essential which is challenging with the employment of simple metal oxides. To the best of our knowledge, for the first time, we report the room temperature gas sensing behavior of mesoporous NCH and NCO for the detection of ammonia.



Figure 3.4. NH₃ sensing behaviour of (*a*) NiCo₂(OH)₆ (NCH) and (*b*) NiCo₂O₄ (NCO).

Fig. 3.4 shows the ammonia gas concentration-dependent sensing property of (*a*) NCH and (*b*) NCO. Fig. 3.4 (*a*) showed ammonia gas sensing

behavior of *p*-type NCH [32], within subjected gas concentration from 2-10 ppm. When NCH was exposed to ammonia gas, the resistance of the material sharply increases indicating an excellent response to ammonia gas. Upon purging with ambient air, the resistance drastically decreases to a minimum and forming a plateau, which can be explained by the saturation of reaction sites on the surface changing a little or without causing any effective variation of electrical resistance [33]. From Table 3.1 it was observed that the response of NCH got increased by 1.65 and ~3 times by changing the analyte concentration from 2 to 5 and 10 ppm, respectively. Figure 3.4 (b) demonstrated the sensing behavior of NCO where the ionic and molecular forms like hydroxyl ion, water molecules were removed after annealing. Table 3.1 showed an increase in response from 31% to 109% with varying NH₃ concentrations from 2 ppm to 10 ppm for NCO samples. The most interesting fact about NCO is that its ammonia gas sensing shows a typical *n*-type metal oxide sensing pattern although it is known that $NiCo_2O_4$ is *p*-type in nature [37]. Here the correlation among pore properties of sensing materials with their gas sensitive electrical response has been discussed. The porosity (ϕ) of both NCH and NCO are calculated using the formula,

$$\phi = \frac{\rho}{\frac{1}{SSA.APS} + \rho} \qquad (3.5)$$

Where ρ is the density of sensing materials, SSA and APS are specific surface area and average pore size respectively **[54-56]**. The porosity of NCH and NCO are calculated to be 96% and 71% respectively. It is observed that the larger SSA value leads to higher porosity in sensing material. Based on this higher response of NCH can be ascribed to the larger specific surface area and porosity. Other than this it is well known that materials with lower surface area have lower gas sensing response as the surface reactions occur only on the geometrical surface area. Combined these two facts the sensing response of NCH and NCO can be related to the porosity, specific surface area etc.

Conc. (ppm)	Response (%)	Tres (S)	Trec (S)	Response (%)	Tres(s)	Trec(s)
	NCH		NCO			
2	165	44	16	31	20	45
5	272	28	20	60	30	13
10	439	44	18	109	62	27

Table 3.1. The gas response, response and recovery time for NCH and NCO samples at different NH₃ concentrations.

3.3.3.3. Plausible Sensing Mechanism

The sensing performance of semiconductor oxides is usually attributed to the adsorption and desorption of oxygen and analyte gas on the surface of the oxides. It is known that the oxide surface of a *p*-type semiconductor is readily covered with chemisorbed oxygen, even at low oxygen partial pressure and within 25°C- 500°C [**34**, **35**]. When exposed to reducing gas like NH₃, the gas molecules are chemisorbed at the active sites on the NCH surface. The free electrons released via the interaction between the NH₃ molecules and the pre-adsorbed O_2^- neutralize the holes or the majority carrier in *p*-type sensing material. This compensation results in a decrease in the hole carriers in NCH and consequently, an increase in the resistance. The equations can be represented as: [**36**]

$$O_{2(ads)} + e^- \leftrightarrow O_{2(ads)}^- \tag{3.6}$$

$$4NH_3 + 3O_{2(ads)}^- \rightarrow 2N_2 + 6H_2 \ 0 + 6e^- \qquad (3.7)$$

Whereas Fig. 3.4 (*a*) showed a typical *p*-type sensing response of NCH to reducing gas (NH₃), the annealed counterpart *i.e.* NCO illustrated anomaly in sensing response. Here we assumed certain reasons for this abnormal sensing behavior of NiCo₂O₄ ternary metal oxide. The facts can be classified such as:

(i) Due to annealing certain functionalized groups like hydroxyl (- OH), H₂O molecules got removed and redistribution of surface active sites took place which causes a possible transition from p- to n-type with increased electron concentration. On the exposure to NH₃ gas to NCO yet again rise electron concentration upon reaction between surface adsorbed oxygen ions which narrow the surface depletion layer width leading to a decrease in the resistance [38]. (ii) Another fact to anomalous *n*-type gas sensing behavior of NCO is the rigorous interaction of chemisorbed $O_2^{-}_{(ads.)}$ and NH₃ and nature of sensing material. When the sensor is placed in the air, oxygen molecules adsorb on the film surface to form $O_2^{-}(ads.)$ ions by capturing electrons from the conductance band, leading to the formation of an electron depletion layer and thus increase in sample resistance. Dang et al. reported that in NiCo₂O₄ the oxygen distribution mostly arises from lattice oxygen (O_{laff}), oxygen defect (O_{def}) and adsorbed oxygen (O_{ads}). Among them O_{laff} used to be stable oxygen species and had no contribution towards gas sensing. Whereas the O_{def} referred towards the initial oxygen ionization state which promotes the gas adsorption on surface of sensing material and O_{ads} represents the chemisorbed oxygen species which considered to main species participating in gas sensing process [50]. Again, Yamazoe et al, reported that porosity of sensing layer generally contributes more concentration of chemisorbed oxygen ions [51]. Collectively it can be concluded that due to mesoporous flake like NiCo2O4 structure the NH3 gas molecules can diffuse freely throughout the sensing layer. These NH₃ molecules further react with chemisorbed Oads2- present over the surface of sensing material to dissociate into N_2 , H_2O and free electrons [52]. It is well known that gas sensors based on metal oxide semiconductors generally proceed through adsorption-oxidation-dissociation process [53]. Hence as per the gas sensing mechanism these chemisorbed O_{ads}^{2-} available in mesoporous NCO acts as the main site which takes part in sensing process, hence can be termed as surface active sites [39, 40]. This general process describes where electrons are simultaneously fed back into the sensing

body, leading to increased conductance and thereby to *n*-type NH₃ sensing behavior [41, 42].

3.3.3.4. Freundlich Isotherm Model

The gas response is related to the overall surface area of sensing materials and the concentration of gas molecules adsorbed on the surface [43, 44]. The isotherm model in Fig. 3.5 shows the variation of response (*S*) of NCH and NCO with ammonia concentration (*C*) on the log-log scale which is similar to the Freundlich adsorption isotherm model. In general, the Freundlich isotherm curve correlates the concentrations of solute on the surface of an adsorbent and the solute concentration and the relationship between *S* and *C* can be expressed as, $S = k.C^{\alpha}$ where *k* and α are the proportionality and exponent constants and represent the adsorption capacity and adsorption strength respectively [45]. It is evident that in our case the variation of sensitivity with ammonia concentration is sub-linear (0(α <1) for both NCH and NCO where α value of NCH and NCO is found to be 0.786 and 0.606, respectively. The higher α value indicates the presence of more surface active sites for sensing enhancement purposes in NCH and this result is in correlation with BET measurements.



Figure 3.5. Log-Log plot of response *vs*. ammonia concentrations of NCH and NCO.

3.3.3.5. Transient Sensing Behaviour

Fig 3.6 depicts response and recovery times for NCH and NCO samples with a varied low concentration of ammonia gas at room temperature. It is noted that for NCH the response (T_{res}) and recovery (T_{rec}) time are 44 s/ 16 s, 28 s/ 20s, and 44 s/ 18 s for 2 ppm, 5 ppm and 10 ppm NH₃ concentration respectively. Whereas for NCO samples the response (T_{res}) and recovery (T_{rec}) time are 20 s/ 45 s, 30 s/ 13 s, and 62 s/ 27 s for 2 ppm, 5 ppm, and 10 ppm NH₃ concentrations, respectively. Reproducibility is another key criterion for practical sensor applications, which is related to various factors including the stability of sensing materials, contact stability between sensing materials and electrodes, and storage stability in air. Sensor instability generally results in an error in measurements and provides abrupt response and recovery signals.



Figure 3.6. Response and recovery time plot of NCH and NCO for 2, 5 and 10 ppm NH₃ gas concentration.

Fig 3.7(*a*, *b*) demonstrates that both NCH and NCO sensors have excellent long-term operability and stability for low ammonia concentration. A nearly similar type of response was observed for both NCH and NCO in the presence of ammonia gas with negligible variation in resistance values confirmed the wide sensing behavior of ternary cobaltite materials. Fig. 3.7 (c & d) shows the resistance variation with time for NCH and NCO respectively in 10-100 ppm NH₃ gas concentration. It is observed that for NCH the variation in resistance (Δ R) increase upto 40 ppm after which the Δ R value started decreasing and attained saturation. This confirms the increase in sensitivity of NCH sensors upto 40 ppm. Similarly in case of NCO the saturation of sensor response takes place after 40 ppm. The saturation in sensor response can be ascribed to decrease in number of active sites taking part in gas sensing.



Figure 3.7. Transient response trend of (a) NCH and (b) NCO sample towards 2, 5 and 10 ppm NH₃ gas concentration. Variation of resistance with time (c) NCH and (d) NCO against 10-100 ppm NH₃ gas.

3.3.3.6. Selectivity

Selectivity is a critical parameter in the evaluation of gas sensor performance. Here the selectivity is considered by response measurement with 10 ppm of carbon monoxide, acetone, ethanol and ammonia at room temperature (~30°C). Fig 3.8 shows selectivity histograms, that NCH shows an outstanding ammonia sensing response in comparison to other gases and even has ~4 fold higher response than that of NCO at same experimental conditions. MCo_2O_4 (M= Ni, Zn *etc.*) materials are among the least studied spinel candidates in gas sensing despite of the presence of multi-cation sites. This hitherto deficient literature strives for the present investigation of NiCo₂O₄ as ammonia gas sensor and Table 3.2 represents a comparative chart among available spinel cobaltite and their ammonia sensing characteristics.



Figure 3.8. Selectivity histogram with 10 ppm of carbon monoxide (CO), acetone, ethanol and ammonia for Ni-Co hydroxide/oxide sample at 30°C.

MCo ₂ O ₄ Type	Operating	NH ₃ Conc.	Response	Ref.
	Temp.	(ppm)	(%)	
	(°C)			
ZnCo ₂ O ₄	300	100	4	[46]
nanoparticles				
Zn _x Co _{2-x} O ₄	250	40	5	[47]
nanomaterial				
ZnCo ₂ O ₄	175	100	7.5	[48]
microspheres				
NiCo ₂ O ₄	200	_	3	[49]
Thin films				
NiCo ₂ (OH) ₆	30	10	439	This work
Nanoflakes				
NiCo ₂ O ₄	30	10	109	This work
nanoflakes				

Table 3.2. Comparison of MCo_2O_4 (M= Zn, Ni) based NH₃ sensors.

3.4. Summary

In summary, we have investigated the sensing behavior of mesoporous flakes of NCH and NCO for low concentrations of NH₃ gas at room temperature. The synthesis of mesoporous NCH and NCO was carried out by an economical and simple wet chemical bath method. The XRD, HRTEM confirmed the formation of phase pure and the high-quality NCH and NCO materials. FESEM represents flake like morphologies with high porosity. HRTEM indicates the material was oriented along (400) direction which agrees with the XRD of NiCo₂O₄. The porosity behavior of prepared samples was carried out by BET studies which confirm the mesoporous

morphologies of Ni-Co hydroxide/oxides. Mesoporous NCH samples at room temperature demonstrate higher sensitivity, fast response, and recovery time even at 2 ppm NH₃ concentration with better cyclability due to the surface chemisorbed oxygen ions, uniform pore distribution along the higher surface of interaction. Whereas lowering of charge depletion width, increased chemisorbed oxygen ions assumed to help in reverting the major charge carriers on the surface of NCO to cause abnormal *p*-type (i.e. *n*-type) response towards NH₃ gas at room temperature. The variation of sensor sensitivity with ammonia concentration shows a Freundlich adsorption isotherm like behavior also correlates the higher sensitivity of NCH over NCO towards NH₃ gas. Interestingly the sensitivity and Freundlich constant show similar exponential enhancement which advocates the improvement in low detection limit shown experimentally. The overall work demonstrates NCH and NCO as potential candidates for low concentration ammonia detection at room temperature, hence technologically important.

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Chapter 4

Zn_{1-x}Ni_xO Nanostructures as an Excellent Humidity Sensors

In this chapter, we have discussed the chemi-resistive humidity sensing behavior of $Zn_{1-x}Ni_xO$ materials synthesized using a wet chemical method. At room temperature, x=0.10 sample shows a combined excellent humidity sensitivity of 152% and response/recovery time of 27/3 s within 33-97% relative humidity range. The experimental data observed over the entire RH range fitted with the Freundlich adsorption isotherm model, which revealed two distinct water adsorption regimes. The obtained results suggest that with doping the adsorption strength increases. Theoretical humidity detection limits for the x = 0, 0.05 and 0.10 samples are found to be about 7.24% RH, 6.31% RH and 3.71% RH, respectively. The outstanding humidity sensing observed in the ZnO and Ni-doped ZnO nanostructures is attributed to the Grotthuss mechanism.

4.1. Background of the Work

Humidity sensors have drawn enormous consideration and became a widely important device for its use in daily life for monitoring the ambient moisture for human comfort. They are also employed in various industries ranging from automotive, medical, construction, semiconductor, meteorological, and food processing industries [1-4]. The utilization of any sensor in revealing actual humidity and environmental monitoring under various conditions stresses for its quality, high sensitivity and selectivity, fast response/recovery, low hysteresis, high stability, operability in wider humidity and temperature range, miniaturization, and economic viability, etc. [5, 6]. The possibilities to achieve these characteristics by sensors constructed from bulk materials under concurrent conditions are stalled due to their lower surface area in comparison to nano colleagues [7]. However, chemically, and thermally stable metal oxide nanostructures [8], wellknown to deliver a larger surface-to-volume ratio for their interaction with the environment are observed to be suitable candidates for humidity sensing with high sensitivity, fast response, etc. In the last decades, metal oxide NWs and nanostructures such as ZnO [9-11, 17], SnO₂ [12, 13], TiO₂ [14], In₂O₃ [15], and WO₃ [16] are employed for the production of a range of chemical sensors. Among them, ZnO is a favourable humidity sensing material due to its morphological assortment (e.g., NWs, nanorods, nanoparticles, etc. [18]) with an exceptional sensing performance [17, 18]. The chemical sensing capability of metal oxides can be enriched through confinement effect, surface area, controlled morphologies, and sensing mechanism [19-21]. However, doping is an effective policy to amend the properties of semiconductor metal oxides and augment their humidity sensing [22-25]. However, to our best knowledge, a humidity sensor based on Ni-doped ZnO nanostructures have not been discussed so far. In the current study, we devote a simple approach to construct Ni-doped ZnO humidity sensors. Freundlich isotherm model has been deliberated to

apprehend the humidity sensing mechanism of metal oxides. 10% Ni-doped ZnO nanostructures showed excellent sensitivity, long-term stability, and reproducibility, indicating that the doped ZnO is a potential candidate for the fabrication of high-performance humidity sensors at an industrial scale.

4.2. Synthesis Procedure

Ni-doped ZnO nanostructures were synthesized using a simple wet chemical process. The ZnO nanostructures doped with different Niconcentration of x= 0, 0.05, and 0.10 are indicated as ZnO, Ni5ZnO, and Ni10ZnO, respectively. The synthesis process involves analytical grade metal nitrates *i.e.* Nickel Nitrate hexahydrate (Ni(NO₃)₂ .6H₂O), Zinc Nitrates hexahydrate (Zn(NO₃)₂ .6H₂O) without any further purification for preparing 100 mM solution in DI water. After 30 min., stirring ammonia solution (NH₄OH) was added which increased the *pH* of the solution up to ~11. These solutions heated at 90°C for 2 hrs. was filtered using Whatmann filter paper and further washed several times with double-distilled water. Pure and Ni-doped ZnO samples were collected after overnight drying and heating at 150°C for 2 hrs.

4.3. Results and Discussion

4.3.1. Structural and Morphological Analysis

XRD analysis of pure and Ni-doped ZnO is in correlation with earlier literature [**10**, **27**, **28**, **33**]. XRD result in Fig. 4.1(*d*) shows that all the samples are phase pure and reveal a pure hexagonal phase of the wurtzite type structure of ZnO, with growth direction along the *c*-axis. No impurity peak related to Ni phase were detected up to 10% doping in ZnO due to almost similar ionic radii of Ni²⁺ (0.69Å) and Zn²⁺ (0.74Å), this indicates successfully doping of Ni ions into ZnO structure.



Figure 4.1. FE-SEM images of (*a*) Ni0ZnO, (*b*) Ni5ZnO, and (*c*) Ni10ZnO (at 20 KX) and (*d*) X-ray diffraction pattern of $Zn_{1-x}Ni_xO$ (*x*=0,0.05,0.1).

FE-SEM images of pure and Ni-doped ZnO nanostructure is represented at Fig.4.1 (*a*-*c*), with a magnification at 20 KX. In a wet chemical method, the structure and morphology of obtained ZnO nanostructures depend on parameters such as reaction temperature, reaction time, *pH* value, solute concentration, *etc.* These factors are playing an important role in the physicochemical properties of ZnO [**26**]. A typical FESEM image of pristine ZnO (Fig.4.1 (*a*)) shows the realization of nanoneedles in the form of a flower-like structure. The average diameter (from the middle) and the length were estimated to be ~200 nm and 1-2 μ m, respectively and with Ni 5% doping nanoneedles converted into thick and top flat face nanoneedles with a slight increase in average diameter 280 and 294 nm respectively. It was also observed that the cone tapered part of the nanoneedles was broken and the formation of nanorods had started. Again, with a further increase of Ni concentration, nanoneedles were fully converted into nanorods and finally, in Ni 10% doping there was a decrease in the average diameter of

nanorods, less than ~100 nm with formation nano-sheets started in between the thin nanorods.

4.3.2. Humidity Sensing

4.3.2.1. Device Fabrication and Measurement Setup

A 1 cm x 1 cm ITO coated glass substrates is used for fabrication of twoterminal device as shown in Fig. 2.8 (b) where ITO electrodes present on both side of the channel act as source and drain. The device has an effective working area of 0.10 cm² [10 mm length (L) and 1 mm width (W)]. Humidity sensors were prepared by a drop-casting technique where a paste of pure and Ni-doped ZnO samples was subjected to the channel and dried in an electric furnace at 50°C for 10 hours before the experiment. The relative humidity environment was achieved using saturated aqueous solutions of inorganic salts of MgCl₂.6H₂O (33%), K₂CO₃ (43%), Mg(NO₃)₂ (52%), NaCl (75%), KCl (86%), and K₂SO₄ (97%) in a closed container respectively [29-32]. These RH levels were scrutinized using a standard hygrometer (MEXTECH IT-202). The room temperature chemiresistive humidity sensing properties were characterized by the variation of resistance with time (R-t) of the pure and Ni-doped ZnO sensors at different relative humidity. The device under test (DUT) was attached on a rubber seal where two conducting wires attached between the DUT and external power source (Keithley 2401 source meter) and the data recorded through LABVIEW[®] programming.

4.3.2.2. Sensitivity

For transient response measurement, initially, the DUT *i.e.* in the present case $Zn_{1-x}Ni_xO$ (x = 0, 0.05, 0.1) was retained in a container with RH of 33%, to attain a steady response, after which it was quickly switched to another RH% container. The switching time was kept very low of 1-2 sec. to minimize any possible interference during the measurement. The humidity sensing analysis was carried out within 33–97% RH range. The

current-voltage (*I-V*) measurements confirm the connectivity between the electrodes and the sensing layer. The measurement was performed at individual RH level at 10V bias and the plot is shown in Fig.4.2.



Figure 4.2. *I-V* plots of (*a*) ZnO, (*b*) Ni5ZnO, and (*c*) Ni10ZnO samples at various humidity levels.

The slope of the *I-V* curve increases with an increase in RH from 33% to 97%. Fig. 4.2 shows that ZnO has a distinctive current behavior at each humidity, whereas with an increase in Ni-dopant concentration to 5% and 10% the current values repressed to a larger magnitude at low RH. This notable $Zn_{1-x}Ni_xO$ behavior can be ascribed to Ni-doping for the quick electron conduction due to the creation of an energy level beneath of conduction band [**34-39**]. The alteration in current at room temperature is the competitive replacement of chemically pre-adsorbed oxygen species on the surface with physisorbed H₂O molecules [**40-42**]. The bias dependent non-linearity in $Zn_{1-x}Ni_xO$ humidity sensors can be ascribed to variation of
Schottky barrier. Semiconducting oxides usually possess surface states associated with adsorbed oxygen species. At low RH condition the barrier height is affected by the presence of extrinsic surface states, which can be formed by chemisorption of H₂O. Whereas, at higher RH condition, exposure of the device to high concentration of H₂O molecules causing physisorption over chemisorbed layer, this causes further decrease in height of Schottky barrier resulting an increase in forward current.



Figure 4.3 A typical plot of resistance and response *vs.* relative humidity for (*a*) ZnO, (*b*) Ni5ZnO, and (*c*) Ni10ZnO based RH sensor.

The response of pristine and Ni-doped ZnO based humidity sensor can be expressed as:

$$S(\%) = \frac{R_{33\%} - R_{\Delta R\%}}{R_{\Delta R\%}} \times 100$$
 (4.1)

Where, *S* (%) is sensor response, $R_{33\%}$, and $R_{\Delta R\%}$ are the resistance of the device at lower humidity and after the change in humidity respectively [32, 43, 44]. Fig.4.3 displayed a nearly linear increase in humidity response of Zn_{1-x}Ni_xO with an increase in RH much noticeable in the case of high RH. A linear fitting to the sensor resistance exhibited an increase in slope value from 0.06359 to 0.0665 and 0.06848, with an increase in the Ni dopant concentration from 5% and 10% in ZnO, respectively (Fig. 4.4). The surge in the sensor response with RH value is ascribed to the augmentation in surface active sites for H₂O adsorption due to an increase of oxygen vacancies in the ZnO_{1-x} lattice site [10, 27, 28].



Figure 4.4 Linear analysis of resistance vs. relative humidity for $Zn_{1-x}Ni_xO(x=0, 0.05, 0.1)$ based RH sensor.

The bar plot in Fig. 4.5 shows that the sensitivity of the Ni10ZnO sample is much higher in comparison to ZnO and Ni5ZnO within 33-97% RH. Ni10ZnO has shown the highest sensitivity value of 152.82% at 97% RH value which is nearly 7.66 and 7.69 times higher than that of ZnO and Ni5ZnO, respectively. Chou *et al.* [17(c)] have reported that ZnO nanorods with lower surface area, larger pore size shows lower sensitivity than that of samples with larger surface area and smaller pore size. According to previous literature [10], an increase in the surface area has been observed in a sequence of Ni10ZnO>Ni5ZnO>ZnO along with the pore size distribution lying at low pore radius range. Hence the collective result of higher surface area and lower pore size traits for enhanced humidity sensing performance of Ni-doped ZnO than that of pure.



Figure 4.5 Comparative sensitivity values plot for ZnO, Ni5ZnO, and Ni10ZnO sensing element from 43-97% RH.

4.3.2.3. Hysteresis Behaviour



Figure 4.6 Typical hysteresis characteristics of (*a*) ZnO, (*b*) Ni5ZnO, and (*c*) Ni10ZnO based sensor.

To demonstrate the hysteresis behavior, the variation of resistance of the sensor devices made of pure and Ni-doped ZnO nanorods were recorded. The resistance through the device was measured at various humidity levels (with increasing humidity from 33% to 97% and then decreasing it back to 33% again). Hysteresis is the resistance drift observed by the device due to the variation in adsorption and desorption rates of H₂O vapors on the sensing material. From Table 4.1, it can be seen that the hysteresis values are quite small for most of the humidity levels. The hysteresis error in humidity sensors was calculated using the equation (4.2) as,

$$H_{\rm e} = \pm \frac{\Delta R_{max}}{2F_{FS}} \qquad (4.2)$$

Where ΔR_{max} is the difference of resistance between adsorption modes and desorption modes whereas F_{FS} is the output of full-scale [18-20, 27].

Table 4.1. Hysteresis values at different levels of RH for ZnO, Ni5ZnO, and Ni10ZnO.

RH%	ZnO	Ni5ZnO	Ni10ZnO	
33	0.0011	0.0010	0.0009	
43	0.0040	0.0178	0.0033	
52	0.0170	0.0194	0.0070	
63	0.0321	0.0047	0.0051	
75	00146	0.0041	0.0013	
86	0.0010	0.0009	0.0001	
97	0.0011	0.0010	0.0009	

Fig.4.6 shows a nearly superimposing behavior between adsorption and desorption curves for the $Zn_{1-x}Ni_xO$ sensor at high RH condition. During the experimented adsorption-desorption process, the highest absolute value of H_e came around 0.032, 0.02, and 0.007 in the 33-97% RH change for ZnO, Ni5ZnO and Ni10ZnO, respectively, with better reliability of the sensors. The lowering of hysteresis in Ni-doped ZnO inferred their feasibility in electronic devices [22, 47, 48].



4.3.2.4. Response-Recovery Analysis

Figure 4.7 Transient resistance behavior of (*a*) ZnO, (*b*) Ni5ZnO, and (*c*) Ni10ZnO based sensors within controlled RH levels (33-97-33%) and (*d*) response and recovery time $Zn_{1-x}Ni_xO$ samples.

Fig.4.7 (*a-c*) shows the transient resistance behavior of the pristine and Nidoped ZnO nanostructures. With 33% RH as a reference, the cyclability of ZnO based RH sensors was continual for a longer period. The discrepancy witnessed in resistance variation of pristine and Ni-doped ZnO sensors can be endorsed to (i) formation of oxygen vacancies in doped metal oxides and (ii) hydroxyl poisoning. Due to the presence of excess Zn interstitials and oxygen vacancies in Ni10ZnO, the related donor effect assists in suppression in hydroxyl poisoning, and a reduction in resistance was observed [10, 41, 42]. The response (T_{res}) and recovery (T_{rec}) time is defined as the time taken by the sensor to achieve 90 % of resistance change in case of water adsorption and desorption, respectively. The observed response/recovery time for a cycle of 33-97-33% for undoped ZnO, Ni5ZnO, and Ni10ZnO samples found to be 202s/9s, 14.4s/4s, and 27s/3s.

4.3.2.5. Stability Study

Long term stability is an essential feature for the evaluation of sensor performance. Fig. 4.8 shows the long-term stability of the sensor where the variation of resistance with applied humidity was monitored for 60 days at various humidity levels. The average resistance variation in the case of pure and Ni-doped ZnO samples throughout the RH range is within a permissible limit.



Figure 4.8 Stability test of (a) ZnO, (b) Ni5ZnO, and (c) Ni10ZnO sensors.

The effect of polarization on the sensing response of the $Zn_{1-x}Ni_xO$ sensor under different polarities was monitored at the DC bias voltage. The duration of polarity inversion was kept very short and a negligible degree of variation in sensing response as shown in Fig. 4.8. The measured humidity response demonstrated a nearly superimposing behavior with the polarity variation as per available literatures [47, 49-52].



4.3.2.6. Freundlich Isotherm Model Analysis

Figure 4.9 Humidity transient response measurement at RT of (*a*) ZnO, (*b*) Ni5ZnO, and (*c*) Ni10ZnO with RH% ranging from 33-97-33% under an applied bias voltage of 5V.

Relative deviation in Resistance (R.D.R or ΔR_H) indicates the variation in resistance during operation of the **D**evice Under Test (DUT) between different RH environments. The relative deviation in resistance (ΔR_H) values was calculated for the samples by using the expression 4.3 [18-20, 27, 32]:

$$\Delta R_{\rm H} (\%) = (R_{\rm LH} - R_{\rm H}) / R_{\rm LH} \times 100\%$$
(4.3)

Where, R_{LH} and R_H are the sample resistance at the lowest RH (i.e. 33% RH) and that of other relative humidity values. For pure and Ni-doped ZnO humidity sensor samples, the values of RDR increase with applied relative humidity whereas the plot of ΔR_H against relative humidity does not show linearity (Fig. 4.10(*a*)) which is associated with the conduction mechanism.

The conduction process was ascribed to chemisorbed layers and physisorbed layers before and after transition point (T_c), respectively. Fig.4.10 (*a*) showed RDR values of 87%, 84%, and 10.45% for ZnO, Ni5ZnO, and Ni10ZnO sensors, respectively. The plots of RDR *vs.* % RH show different slopes for two different regions, justifying the idea of calibration of sensor devices to the electronic circuits. Hence lowering the value of T_c is another aspect for improvement of commercial deployment of sensors for real-time monitoring. During humidity sensing, adsorbed H₂O molecules are bonded with surface-active groups via hydrogen bonding, and surface interactions on and within the nanostructure account for the reversibility of the process.



Figure 4.10 (*a*) Relative Deviation in Resistance (RDR) *vs.* %*RH* and (*b*) log-log plot of measured and modelled (Freundlich) behavior of $\Delta R_H vs.$ % *RH* of Zn_{1-x}Ni_xO based sensor.

Freundlich model is well-known for describing the adsorption of gas on porous materials. The key feature of Freundlich adsorption model is the accountability of intermolecular interactions between adsorbate (gas) and adsorbent (solid) which implies the heterogeneity of adsorption sites. The isotherm is expressed as:

$$S = k * (RH)^{\alpha} \tag{4.4}$$

Where *S* is the relative deviation in resistance, *k* is adsorption capacity (i.e. availability of surface active sites in sensing materials), RH is the relative humidity percentage and α referred to the adsorption strength (i.e. relative distribution of energy of available surface active sites), respectively [**18-20**, **27**, **63**]. Where both *k* and α doesn't have any unit. To the best of our knowledge, it is indeed the first attempt to model Freundlich adsorption isotherm for any ZnO based humidity sensors to investigate the uptake of water vapor during the sensing process and the surface phenomena behind it. Fig.4.10 (*b*) shows a log-log plot between ΔR_H vs. % *RH* in the Freundlich model layout where two significant regions (*i.e.* 33-52% and 52-97%) were present. The transition point (*T_c*) was calculated from the intersection point of both region and the values were 48.28% RH, 50.31% RH, and 55.28% RH for ZnO, Ni5ZnO, and Ni10ZnO, respectively. Each region was fitted in agreement with the Freundlich model and the parameters (α and *k*) were determined and shown in Table 4.2.

Table 4.2. Freundlich Adsorption Isotherm Model results including the Adsorption Capacity (k), Adsorption Strength (α), correlation coefficient (R^2) value on humidity sensing of ZnO, Ni5ZnO, and Ni10ZnO.

Sample	Low RH Regime		High RH Regime			
	k	α	R^2	k	α	R ²
ZnO	1.94±0.05	4.57±0.10	0.96	1.43±0.20	1.05 ± 0.10	0.98
Ni5ZnO	1.91±0.47	4.52±0.92	0.98	1.59±0.18	0.48±0.09	0.97
Ni10ZnO	1.94±0.03	4.29±0.96	0.97	1.64±0.15	$0.47{\pm}0.01$	0.95

Generally the ' α ' value greater than unity indicates strong adsorption [56]. Table 4.2 shows that all Zn_{1-x}Ni_xO samples indicated a decrease in α value with an increase in doping concentration from 0-10% in both low (33-52%) and high (52-97%) humidity region. It was observed that α value in low and high RH region were 4.57/1.05 (ZnO), 4.52/0.48 (Ni5ZnO) and 4.29/0.47 (Ni10ZnO). As α value designates the relative distribution of energy of active sites, hence any increment of the value ascribed to lowering in energy of surface active sites which participates in sensing. Whereas with increase in RH above 50% the energy of active sites start increasing due to presence of multi-layered chemisorbed H₂O layer resulting in lower ' α ' value [56]. The calculated k value represents the adsorption capacity or concentration of available surface active sites of material for sensing at a particular RH state. From Table 4.2, it was observed that with an increase in Ni-dopant concentration from 0-10% there was an increase in k-value indicating a rise in active sites with an increase in doping. In a nutshell, both at low and high RH range, $Zn_{1-x}Ni_xO$ sensors have durable responsiveness for water vapor where a decrease in α values and an increase in k- value with an increase in Ni- doping was observed. An increase in number of surface active sites can be ascribed to the enhanced sensing performance of Ni-doped ZnO, signifying a positive effect of doping in metal oxides from the correlation between experimental and Freundlich model.

4.3.2.7. Theoretical Detection Limit

Generally, in humidity sensing, both adsorption and desorption of water vapor from the surface take place to attain equilibrium. Whereas it is described that the adsorption process initially proceeds very fast due to large number of accessible adsorption sites and then declines due to reduction in number of active adsorption sites after saturation in $Zn_{1-x}Ni_xO$ samples [57]. During this stage, the desorption process becomes more prominent and the rate of desorption surpasses that of adsorption. To overcome such problems of experimental detection of lower humidity the calculation of detection limit is much useful and provides theoretical information regarding optimization of the commercial sensor devices. According to available

literature **[59, 60]**, the detection limit can be calculated using the belowdescribed formula.

Detection limit: **DL** (%**RH**) = 3 rms/slope (4.5)

The RMS noise is given by: **RMS** = $\sqrt{V_{x^2}/N}$

(4.6)

Where N is the number of data points used in the curve fitting and V_{x^2} is given by,

$$V_{x^2} = \sum (y_i - y)^2$$
 (4.7)

Where y_i is the measured data point and y is the corresponding fitted value. According to IUPAC terms [60], a signal is regarded as a true signal if the signal-to-noise ratio (SNR) exceeds a value of 3. Hence by extrapolating the linear dependence of slope and RMS values from resistance variation in baseline using root mean square deviation delivers the detection limit in Zn_{1-x}Ni_xO humidity sensors. The lowest detectable humidity by ZnO, Ni5ZnO, and Ni10ZnO are 7.24% RH, 6.31% RH, and 3.71% RH, respectively. These details enlarge the opportunity of Ni-doped ZnO as next-generation high- performance humidity sensors.

4.3.2.8. Humidity Sensing Mechanism

Kulwicki *et al.* recommended that humidity sensing in ceramic and porous materials as surface-mediated conduction mechanism [**61**]. This section discussed the humidity sensing mechanism of pure and Ni-doped ZnO nanorods following the available literature [**62**]. Generally, overall humidity sensing resulted through two processes (i) chemisorption process for low humidity and which is followed by (ii) the Physisorption process at higher humidity level associated with the Grotthuss mechanism. Mostly, at room temperature the sensor placed in air adsorbs molecular oxygen and surface adsorbed oxygen ions formed $(O_2 + e^- \rightarrow O_2^-)$ [**54**]. Schaub *et al.* suggested that the defects in nanorods extend a durable electrostatic field and the simultaneous presence of localized charge density due to the preadsorbed O_2^- stimulates dissociation of chemisorbed H₂O molecules resulted in proton (H⁺) hopping on the surface [**63**]. Whereas in higher

humidity level, numerous H₂O molecules through physisorption get adsorbed over the surface and these molecules experience dissociation to produce hydronium ion $(2H_2O \rightarrow H_3O^+ + OH^-)$. As H₃O⁺ ion is energetically favored in physisorption hence act as a major charge carrier. According to Grotthuss mechanism H^+ and H_3O^+ ions impart the protonic and electrolytic conduction, respectively in the physisorbed layer affects the resistance variation in ZnO nanorods during its relocation from high to low then high humidity. It has been stated that doping induces defects in nanomaterials to provide more surface-active sites which aids charge transfer for enhancement of their humidity sensing over the pristine ZnO [22]. With Ni-doping, the increase in free electrons due to oxygen vacancies in ZnO lattice improves the humidity sensing performance as expressed in the following reaction:

$$H_20 + 0_0 + 2Ni_{Zn} \rightarrow 2(0H - Ni) + V0^{-} + 2e^{-}$$
 (4.8)

Where Ni_{*Zn*} denotes positive charges of Ni ions that occupy the Zn lattice and act as a donor; O_o is the oxygen ion in the inherent lattice, and VO[°] represents the neutrality. The experimental results along with available sensing mechanism confirm the positive effect of Ni dopant in ZnO for the improvement in humidity sensing due to increase in surface adsorption sites with an increase in defects and endorsement of easier charge transfer through water layers using H⁺ and H_3O^+ .

4.4. Summary

In this chapter, we demonstrated the humidity sensing behavior of pure and Ni-doped ZnO nanorods in comparison to existing conventional sensors. The FE-SEM images show a gradual conversion of ZnO morphology with respect to doping, from nanoneedles to nanorods. The $Zn_{1-x}Ni_xO$ sensor devices showed ohmic behavior at various relative humidity. The sensor characteristics like highest sensitivity (~153%), negligible hysteresis error, fast response/recovery time (27/3 s), robust stability, the lowest detection

limit of 3.71% RH, *etc*, accounts Ni10ZnO as the best candidate for the humidity sensing operation. The sensing mechanism is also correlated with the Freundlich adsorption model for a better understanding of the guiding adsorption phenomena in the high RH range. This reveals two distinct water adsorption regimes in ZnO nanostructures where low and high RH regime is due to chemisorption and physisorption, respectively. The fitted model for 10% Ni-doped ZnO sample bargain high adsorption capacity and adsorption strength than other ZnO nanostructures supports for its potential to serve as an excellent humidity sensor at room temperature.

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Chapter 5

Controlled Growth of ZnSnO₃ Nanoparticles as Humidity Sensors

In this chapter, we report the chemi-resistive humidity sensing behavior of as-synthesized and annealed face centred cubic (FCC)-ZnSnO₃ nanoparticles synthesized using wet chemical synthesis method. The effect of annealing on the evolution of varied nano-morphology of ZnSnO₃ is in accordance to Ostwald's ripening law. 500°C annealed ZnSnO₃ samples showed an excellent humidity sensitivity with the fastest response/recovery within 08-97% RH. Freundlich adsorption model is well fitted with the experimental data revealing two distinct water adsorption regimes, along with improved adsorption characteristics with a rise in annealing temperature. The admirable humidity sensing characteristics perceived in the annealed nanostructures are credited to the Grotthuss mechanism considering the availability and distribution of available adsorption sites. This present result suggests deployment of low-cost synthesis technique of ZnSnO₃ for its favourable competences as a prospective aspirant for the fabrication of next- generation humidity sensors.

5.1. Background of the Work

Humidity sensors have drawn great responsiveness as an integrated device in normal life for accurate monitoring and control of the environmental moisture towards human comfort along with prospective applications in industries ranging from automation, aerospace, agriculture to healthcare [1]. The instantaneous disposition of any sensor for environmental monitoring under several working conditions governed by physical parameters like high sensitivity and selectivity, fast response/recovery, low hysteresis, high stability, wider robustness in range of humidity and temperature, miniaturization of the sensor device and economic viability, etc. [1,2]. The potentials to achieve these features by sensors based on bulk materials under immediate monitoring circumstances are stalled due to their insignificant physio-chemical properties in contrast to analogous nanomaterials for recognition of fickle humidity levels in the current environment [3]. However, well-known metal oxide nanostructures such as ZnO, SnO₂, TiO₂, In₂O₃, WO₃, and CoFe₂O₄ are employed for the construction of diverse chemical sensors acknowledged being the appropriate nominee for sensing with high sensitivity, fast response than that of bulk materials [4-13]. Whereas the occurrence of a single cation site and constraint in hightemperature operation restricts it's much demanding prerequisites [14]. Zinc stannate, a multifunctional metal oxide, subsists as two types of oxide with different Zn/Sn/O ratios (ZnSnO₃ and Zn₂SnO₄) and have potential uses as photo catalysts [15], lithium-ion batteries (LIB) [16], gas sensors [17, 18], and dye-sensitized solar cells [19]. The humidity sensing aptitude of a metal oxide regulated by the interaction between H₂O molecules and the surface of interaction. The particle size, surface, defects, and interfacial properties of metal oxides primarily persuades its sensing performance where the synthesis technique plays a significant role. Recently, ZnSnO₃ nanostructures using various synthesis routes have drawn attention to obtaining better crystallites [20-25]. It has been known that wet chemical

synthesis of ZnSnO₃ in an aqueous medium is strenuous due to variation in precursor's reactivity for the formation of the desired material. To comprehend the aforementioned idea here we report the synthesis of Zinc Stannate (ZnSnO₃) nanoparticles by employing a solution-based method where variation in synthesis temperature followed by annealing steps implemented to get desired crystallites. Here in this study, a modest tactic fabricate humidity sensors employing ZnSnO₃ nanostructures to synthesized by wet chemical route. Freundlich isotherm model was employed to realize the humidity sensing of metal stannate. The effect of post-treatment temperature on humidity sensing has been explored in an appropriate method and it is witnessed that high temperature (400°C-500°C) annealed ZnSnO₃ nanostructures showed outstanding sensitivity, fast response, good recovery, and enduring operating stability shows that metal stannate as a prospective aspirant for the fabrication of nextgeneration high-performance humidity sensors at industrial scale to replace the conventional metal oxides and ceramics.

5.2. Synthesis Procedure

The ZnSnO₃ crystallites synthesized using wet chemical synthesis method with varied synthesis temperature. The obtained ZnSnO₃ nanomaterials are indicated as S-01, S-02, and S-03 where the synthesis temperature retained at 65°C, 85°C and 100°C, respectively. In a typical synthesis of ZnSnO₃ crystallites, 10 mM of Zinc sulfate heptahydrate (ZnSO₄.7H₂O) and sodium stannate (Na₂SnO₃.3H₂O) was dissolved in 100 mL of DI water and the mixed solution is stirred vigorously at 65°C for 6 hours. The precipitates were collected by centrifugation at 10,000 rpm and then washed repeatedly with distilled water and ethanol for removal of any impurities from the product. The final product was dried in a hot oven for overnight and grounded before any characterization. The same procedure was followed during the preparation of other ZnSnO₃ samples where only the synthesis temperature varied at 85°C and 100°C. The above as-prepared samples were further annealed at different temperatures *i.e.* at 250°C, 400°C and 500°C. The 250°C annealed samples are noted as SA-01, SA-02, and SA-03, 400°C annealed samples as SB-01, SB-02 and SB-03, and 500°C annealed samples are mentioned as SC-01, SC-02 and SC-03 throughout the chapter at proper places.

5.3. Results and Discussion

5.3.1. Structural Analysis

Fig.5.1 shows the XRD patterns of *fcc*- phase of as-prepared and annealed ZnSnO₃ samples in accordance with JCPDS No.11-0274. All diffraction peaks at $2\theta = 19.82^{\circ}$, 22.97° , 32.73° , 36.67° , 38.47° , 40.37° , 46.78° , 51.39° , 52.74° , 58.34° , 61.17° , 68.33° , 73.16° and 77.89° corresponding to (111), (200), (220), (013), (311), (222), (400), (331), (024), (422), (511), (440), (442), and (620) ZnSnO₃ planes, respectively **[29].** Absence of any impurity peaks such as ZnO and SnO₂, *etc.* indicate the formation of phase pure ZnSnO₃ with lattice constants *a* = 7.758 ± 0.004 Å.



Figure 5.1. X-Ray Diffraction patterns of (*a*) as prepared, (*b*) 250°C, (*c*) 400°C and (*d*) 500°C annealed ZnSnO₃ samples.

The average crystallite size of the NP's was determined by Debye-Scherrer's formula for all the samples using a more intense (200) peak. The formula can be expressed as:

$$D = \frac{\kappa\lambda}{\beta\cos\theta} \tag{5.1}$$

Where *D* is the crystallite size, β is the line broadening at full width half maximum (FWHM), λ is the wavelength of X-rays, θ is the Bragg's angle for the studied peak position and *K* is a dimensionless shape factor [**30**, **31**]



Figure 5.2. (*a*) Lattice strain calculations for the as-prepared sample (S-03) and its annealed samples (SA-03, SB-03 & SC-03), (*b*) Effect of annealing temperature on crystallite size and strain.

The average crystallite size calculated from Scherrer's formula is 14.72, 20.52, 21.57, and 23.46 nm for as-prepared (S-03) and annealed from 250°C to 500°C (SA-03, SB-03, and SC-03), respectively. As the annealing temperature increases up to 500°C, an increase in crystallite size specifies a growth in crystallinity as shown in Fig.5.1 (*b-d*). The lattice strain was calculated from the Williamson – Hall equation. The equation can be expressed as: **[30]**

$$\beta_{hkl} = \frac{\kappa\lambda}{D\cos\theta} + 4\varepsilon\,\tan\theta \qquad (5.2)$$

Where β_{hkl} is the full width at half maximum of the corresponding peak, K=shape factor (0.9), λ = wavelength of Cu- K_{α} radiation, D = crystalline size, ϵ is the induced strain value. The strain calculation was carried out for S-03, SA-03, SB-03, and SC-03 samples by using high intensity peaks. The curve $\beta_{hkl} \cos \theta vs.$ 4 sin θ shows approximately a liner variation, as represented in Fig.5.2 (a) [30]. The slope of equation (5. 2) gives strain while their intercept on Y-axis gives the crystallite size. The average crystallite size and strain concerning annealing temperature are shown in Fig.5.2 (b). It is observed that the crystallite size calculated from Scherrer's and W-H equation is consistent with each other. The positive slope of all samples indicates the presence of tensile strain in the crystal strain. The S-03 sample shows higher strain while it decreases from SA-03 to SC-03 samples, which is attribute the particle size effect. These observations lead us to purpose that the variation in lattice strain due to particle size is governed by the annealing temperature which in turn affects the humidity sensing.

5.3.2. Morphological Analysis

Analysis of FE-SEM images was used to identify the morphology of the synthesized ZnSnO₃ NP's as shown in Fig.5.3. An irregular morphology of the as-synthesized samples (Fig.5.3 (*a-c*)) can be related to the growth of ZnSnO₃ nanoparticles initiated by the reaction between Zn and Sn ions during wet chemical synthesis. With the variation of annealing temperature, the morphology changes from irregular nanoparticle to nanospheres (at 250°C), then to nanoplatelets and nanocubes (at 400°C) and finally uniform nanocubes formed at 500°C. The particle size calculated from FE-SEM ranged within 15-17 nm (for as-prepared), 18-23 nm (250°C annealed), 22-24 nm (400°C annealed), and 24-26 nm (500°C annealed) samples. The association of NP's can be ascribed to the annealing temperature where the spherical particles get associated to migrate into different types of morphology like spheres, platelets, cubes, *etc.* The growth is governed by Ostwald's ripening law assisted by the application of an optimized

annealing temperature following the synthesis temperature for such type of nanomaterials progression [**32-34**]. The particle size calculated from X-ray diffraction technique are in close relation with that obtained from FESEM.





Figure 5.3. FE-SEM images of ZnSnO₃ samples (*a*) S-01, (*b*) S-02, (*c*) S-03, (*d*) SA-01, (*e*) SA-02, (*f*) SA-03, (*g*) SB-01, (*h*) SB-02, (*i*) SB-03, (*j*) SC-01, (*k*) SC-02 and (*l*) SC-03.

5.3.2.1. Growth Mechanism

Considerable insight into the synthesis and growth mechanism of typical ZTO nanostructures is important for the synthesis of controllable highperformance architectures. Inorganic materials growth mechanisms include Ostwald ripening, oriented attachment, Kirkendall effect, oxidization etching, and their combined strategies **[52, 53].** The size-controlled synthesis can be represented through the following set of equations:

$$SnO_3^{2-} + 2H_2O \to H_2SnO_3 + OH^-$$
 (5.3)

$$Zn^{2+} + 4H_2O \to Zn(OH)_4^{2-} + 4H^+$$
(5.4)

$$H_2SnO_3 + Zn(OH)_4^{2-} + 2H^+ \rightarrow ZnSn(OH)_6 \downarrow + H_2O$$
 (5.5)

$$ZnSn(OH)_6 \to ZnSnO_3 + 3H_2O \tag{5.6}$$

Successively, the ZnSnO₃ nanoclusters aggregated promote the growth of cubic crystallites based on the Ostwald ripening mechanism. Lastly, the suspended amorphous nanoparticles were fully disbursed, and the well-defined cubic products were formed with the rise in annealing temperature. Hence, a facile solution-phase strategy associated with the consequent annealing process has been validated for the size-controlled synthesis of porous ZnSnO₃ cubes [**52**, **53**]. Here in our case the ZnSnO₃ nanostructures are engineered through a nucleation–dissolution–recrystallization mechanism and represented in Fig. 5.4.



Figure 5.4. Schematic growth mechanism of cubic ZnSnO_{3.} (Adapted with permission from ref. **[52]**).

5.3.3. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of as-prepared samples were performed to decide their performance with applied temperature. TGA provides weight loss of the synthesized material as a function of increasing temperature which helps to optimize the annealing temperature so that there will be minimization in loss of material with enhanced physio-chemical properties that can be attained. Fig 5.5 showed the thermal behavior of as-prepared samples where nearly 15- 16 % weight loss up to 250 °C and ~3 % within 250-900 °C was witnessed. The plot discloses the dehydration of H₂O from the ZnSnO₃ demonstrating almost 15% weight loss in the sample within 250°C. However, the H₂O molecules confined within the crystals require more energy to get rid of than that of bulk, that's why an additional peak of weight loss was observed between 250°C and 600°C.



Figure 5.5. TG-DTG plot of as prepared ZnSnO₃ samples.

The differential thermogravimetric (DTG) curves unveil an instantaneous weight loss within 0–230 °C with the presence of endothermic peaks at 200.93 °C, 209.99 °C and 227.46 °C, respectively for S-01, S-02 and S-03 resemble the removal of residual moisture. In addition to these two noticeable exothermic peaks for the S-02 sample at about 373.57°C and 558.17°C were also observed due to the decomposition of more stable functional groups. Hence there is an overall weight loss of 19.4-19.68%, nearly consistent with the observed value (19%) reported earlier [**35**, **36**].

5.3.4. Optical Analysis



Figure 5.6. (*a*) Absorption spectra, (*b*) $(\alpha hv)^2 vs$. photon energy, (*c*) linear fitting to $\ln(\alpha) vs$. hv to calculate Urbach energy and (*d*) variation in bandgap and Urbach energy with particle size.

Optical absorption spectra of ZnSnO₃ (S-03 and its annealed counterparts *i.e.*, SA-03, SB-03, and SC-03) were observed at room temperature to conclude the optical energy bandgap (E_g) and Urbach energy (E_u) or band tail width. A lower energy shifting of the absorption edge is shown in Fig. 5.6 (*a*) inset value. The optical bandgap energy was calculated from absorption spectra by using Tauc relation [**31**, **37**]:

$$(\alpha h\nu)^n = \beta(E_a - h\nu) \tag{5.7}$$

Where α , *h*, *v*, *n*, and E_g are the absorption coefficient, Planck's constant, light frequency, the transition mode ($n = \frac{1}{2}$ for indirect bandgap and n = 2 for direct band gap), the energy of optical bandgap, respectively. While β is a constant called the band tailing parameter. Fig. 5.6 (b) showed the bandgap values extracted from the plot $(\alpha hv)^2 vs$. photon energy (hv), where decrement in Eg value from 4.64 (S-03) to 3.84 eV (SC-03) and increase in particle size observed with increase in annealing temperature. The decrease

of bandgap can be attributed to the influence of grain size and lattice strain like parameters [**38**]. Wang *et al.*, [**39**] reported the bandgap of *fcc*-ZnSnO₃ which varies between 5.0-5.28 *eV*, while Placke *et al.*, observed bandgap variation within a range of 3.0- 4.2 *eV* for ZnSnO₃ nanoparticles [**40**]. Urbach energy is a significant factor which characterizes the material disorder. The relationship between (α) and (hv) at near optical band edge, is acknowledged as Urbach energy (E_u) and the empirical rule expressed as [**37**],

$$\alpha = \alpha_0 \exp (h\nu / E_u) \tag{5.8}$$

$$ln\alpha = ln\alpha_0 + \left(\frac{h\nu}{E_u}\right) \tag{5.9}$$

Where α_0 is a constant, (hv) is the incident photon energy and E_u is the Urbach energy or band tail width. The E_u value was calculated from the linear fitting of $ln(\alpha)$ against (hv) near the adsorption edges is shown in Fig.5.6 (*c*), where the value decreased from 792 to 712 meV. Fig.5.6 (*d*) showed that lessening in Urbach energy (E_u) can be ascribed to the increase in particle size concerning annealing temperature which causes a reduction in structural disorder.

5.3.5. Humidity Sensing

5.3.5.1. Device Fabrication and Measurement Setup

The detailed information regarding humidity sensor device fabrication and measurement procedure has already been described in section 4.3.2.1.

5.3.5.2. Sensitivity

Before measurement, initially, the DUT (Device under Test) was kept in a container with fixed humidity (here 8% RH). Once the initial resistance reached a steady state, the biased DUT was quickly switched to another humidity environment. The humidity sensing analysis was done within 8–97% RH range at 5V. The obtained results indicate that the H_2O molecules

act as electron donor **[41]**. The response ZnSnO₃ based humidity sensor was calculated using the equation:

$$S(\%) = \frac{R_{08\%} - R_{\Delta RH}}{R_{\Delta RH}}$$
 (5.10)

Where S (%) is the response, $R_{08\%}$ and $R_{\Delta RH}$ are the resistance of the device at lower humidity and change in relative humidity respectively [42, 43].



Figure 5.7. Response (%) *vs.* RH for (*a*) S-01, (*b*) S-02 and (*c*) S-03 and their corresponding annealed $ZnSnO_3$ samples.

According to equation (5.10), the humidity response for as prepared and their analogous annealed ZnSnO₃ samples are plotted against relative humidity as shown in Fig.5.7. It is observed that the humidity response of annealed analogous samples increases with an increase in annealing temperature. The response of as-prepared and annealed ZnSnO₃ samples measured at 97% RH, where the values are 133.27%, 715.44% for S-01 and SC-01 samples, 382.93%, 3310.73% for S-02 and SC-02, 408.56%,

4155.77% for S-03 and SC-03 respectively. The increase in sensitivity of samples with an increase in annealing temperature can be attributed to structural effects (*i.e.* increasing particle size, decrease in lattice strain, *etc.*). Again, the sensor behavior can be linked with annealing which causes the creation of more surface-active sites for water vapor adsorption and desorption process.



5.3.5.3. Hysteresis Behaviour

Figure 5.8. Typical hysteresis characteristics of the (*a*) as prepared, (*b*) 250° C, (*c*) 400° C, and (*d*) 500° C annealed ZnSnO₃ samples.

Hysteresis is the drift in output resistance of the sensor upon variation in applied RH from 8% to 97% and reverting to 8% again. The observed variation in output resistance from the initial value at the same RH is possibly triggered by the difference in rates of adsorption and desorption process. Fig. 5.8 showed the hysteresis behavior of ZnSnO₃ based humidity sensors, where the hysteresis error can be expressed as:

$$H_e = \pm \frac{\Delta R_{max}}{2F_{FS}} \qquad \dots \qquad (5.11)$$

Where the ΔR_{max} is the difference in the output for the process of adsorption and desorption and F_{FS} is the full-scale output [44, 45].

The adsorption and desorption curves for the ZnSnO₃ sensors nearly superimpose with each other at higher RH, where the maximum hysteresis error was 1.4 % obtained for the S-03 sample and it decreases down to 1.03 % for the 500°C annealed counterpart SC-03. The aforesaid results admit the positive role of annealing as an optimization tool to reduce hysteresis of metal stannate anticipated during its operation.

5.3.5.4. Analysis of Relative Deviation in Resistance

Relative deviation in resistance (ΔR_H) is an essential feature of any sensor to check its potential for real world application. Fig.5.9 showed two distinct regions for as prepared and annealed ZnSnO₃ samples with applied relative humidity. The distinction is associated with the conduction mechanism where the region before and after transition point (T_c) can be credited to chemisorbed layers and physisorbed layers respectively deal with the calibration of the device. The ΔR_H values are calculated by the following expression:

$$\Delta R_H (\%) = (R_{LH} - R_H) / R_{LH} \times 100$$
 (5.12)

Where, R_{LH} and R_H are the resistance of the sample at lower and desired humidity. From Fig.5.9, it is observed that ΔR_H values increase with an increase in the relative humidity and annealing temperature. The RDR values enhanced from 78 % (S-01) to 97.71 % for SC-01, similarly the value increases from 85 % (S-02) to 87.01 % (SC-02) and 75 % (S-03) to 87.73 % (SC-03). This confirms an affirmative effect of annealing on the electronic interfacing of ZnSnO₃ humidity sensors.


Figure 5.9. Relative Deviation in Resistance (ΔR_H) *vs.* relative humidity for (*a*) as prepared, (*b*) 250°C, (*c*) 400°C, and (*d*) 500°C annealed ZnSnO₃ samples.

5.3.5.5. Analysis of Freundlich Model

Freundlich adsorption model is employed for modeling of water vapor adsorption over the material, where the relationship can be expressed as:

$$\mathbf{S} = k. \ (\mathbf{RH})^{\alpha} \tag{5.13}$$

Where k and α are the adsorption capacity (*i.e.* availability of surface active sites for sensing) and adsorption intensification (*i.e.* relative distribution of energy of active sites), respectively [46-48]. Fig.5.10 showed the experimental sensing results plotted in the linear format of the Freundlich model with two distinct linear regions (*i.e.* low RH (8-52%) and high RH (52-97%)) within entire RH range. The two linear regions are related to two dissimilar conduction regimes and the transition point (T_c) is determined

from their intersection. Both RH regimes were fitted separately in agreement with the Freundlich model, and the calculated parameters (k and α) were displayed in Table 5.1.



Figure 5.10. The plot of log (ΔR_H) *vs.* log (*RH*) of (*a*) S-01, (*b*) S-02, and (*c*) S-03 and their corresponding annealed ZnSnO₃ samples.

A significant decrease and increase in α values for samples observed with an increase in annealing temperature in low and high RH regions, respectively. Whereas the *k* (adsorption capacity) value showed an increment in both low and high RH regions for the sample with an increase in annealing temperature. Shaheen *et al*, reported that annealing causes increment in specific surface area, creation of defects and vacancies etc. [54], which helps for an increment in number of surface actives sites. These active sites take part in sensing due to their strong affinity towards H₂O molecules and thus humidity sensing behaviour enhanced in annealed samples.

	Low RH regime			High RH regime		
Sample	k	α	R^2	k	α	R^2
S-01	1.07	2.34	0.99	1.16	1.95	0.99
	±0.08	±0.12		±0.22	±0.10	
SA-01	1.45	1.63	0.95	1.33	1.91	0.99
	±0.04	±0.07		±0.18	±0.11	
SB-01	5.15	1.49	0.99	2.37	1.78	0.97
	±0.16	±0.40		±0.13	±0.03	
SC-01	5.54	0.92	0.76	9.56	0.48	0.99
	±0.15	±0.11		±0.74	±0.04	
S-02	1.16	2.34	0.98	1.89	1.99	0.99
	±0.37	±0.21		±0.03	±0.05	
SA-02	1.18	2.32	0.87	5.63	1.95	0.99
	±0.20	±0.14		±0.14	±0.10	
SB-02	1.20	1.12±0.	0.97	6.45	0.52	0.99
	±0.31	14		±0.08	±0.02	
SC-02	2.10	0.90	0.93	8.45	0.32	0.99
	±0.27	±0.19		±0.05	±0.01	
S-03	1.04	2.47	0.90	5.78	1.75	0.97
	±0.33	±0.29		±0.29	±0.23	
SA-03	4.19±0	2.10	0.99	7.37	1.42	0.97
	.34	±0.19		±0.29	±0.06	

Table 5.1. Results from the Freundlich Adsorption Model including the Adsorption Capacity (*k*), Adsorption Strength (α), and correlation coefficient (R^2) value of as-prepared and annealed ZnSnO₃ samples.

SB-03	5.25	2.01	0.95	9.52	0.99	0.95
	±0.03	±0.18		±0.43	±0.17	
SC-03	8.39	1.98	0.88	9.60	0.91	0.96
	±0.12	±0.20		±0.34	±0.02	

The modelled data for 500°C annealed ZnSnO₃ samples showed improved water adsorption behavior within the subjected RH region provides an effect of post-treatment temperature optimization and its effect on humidity sensing.



5.3.5.6. Stability of Humidity Sensors

Figure 5.11. Stability behavior of (*a*) S-03, (*b*) SA-03, (*c*) SB-03, and (*d*) SC-03 where the inset shows the stability behavior of SC-03 at 75%, 86% and 97% RH.

Fig.5.11 shows the long-term stability of the ZnSnO₃ humidity sensor (S-03) and their corresponding annealed samples measured for 60 days within interval of 10 days at different RH levels and the variation over the period was found within the permissible limit. The average resistance variation for the samples was 14.15 Ω , 17.2 Ω , 4 Ω , and 0.072 Ω for S-03, SA-03, SB-03, and SC-03, respectively. The stability results indicate an improved humidity sensor property of annealed ZnSnO₃ signifies its concrete feasibility.



5.3.5.7. Response-Recovery Analysis

Figure 5.12. Effect of annealing temperature on (*a*) response and (*b*) recovery time of as prepared and their annealed equivalents, (*c*) transient response/recovery behavior of SC-03 during 8%-97%-8% RH cycle.

Fig.5.12 (*a*, *b*) displays the response and recovery time of as-prepared and annealed analogous $ZnSnO_3$ sensors subjected within 8%-97%-8% RH cycle, respectively. A sharp decrease in response/recovery time is observed

for sensors with an increase in annealing temperature. The trend for response/recovery time for S-01 (134s/102s) to SC-01(26s/44s), S-02(118s/99s) to SC-02(24 s/ 37s) and S-03(70 s/91 s) to SC-03 (19 s/22 s) confirms the above mentioned fact. This inclination of fast response/recovery was credited to the annealing temperature which improvises ZnSnO₃ surface property through modulation of morphology to enhance the H₂O vapors sorption/desorption process.

5.3.5.8. Humidity Sensing Mechanism

Humidity sensing is a well-known surface mechanism taking place over the metal oxides where water molecules act as an electron donor [49, 50]. The humidity sensing in general proceeds through two processes, (i) chemisorption and (ii) the Physisorption process. In low humidity levels, the chemisorbed layer dissociates resulting in proton as charge carriers [46, 51]. Whereas at high RH level, several water layers stacked above the surface by physisorption mechanism and experience dissociation to produce hydronium ion $(2H_2O \rightarrow H_3O^+ + OH^-)$. Again, Grotthuss mechanism suggests both protonic and electrolytic conduction for the disparity of resistance in ZnSnO₃ sensors during their relocation from low to high RH and vice versa. A plausible reason for enhancement in humidity sensing behavior with subjected annealed samples can be ascribed to the increment in defects for promising adsorption sites and stimulates easier charge transmission by tumbling the hydroxyl ion realization and its interaction. This can be expressed in the following reaction:

 $H_20 + 0_0 + A \rightarrow 2(0H - A) + V0^{-} + 2e^{-}$ (5.15)

Where O_0 is the oxygen ion in the inherent lattice, "A" represents the cation site present over the surface which can be either or both Zn^{x+} and Sn^{x+} and VO" represents the neutrality. This possible reason for the adsorption/desorption of H₂O molecules is closely associated with that of the isotherm model.

5.4. Summary

In summary, a facile chemical solution route combined with a subsequent annealing process was demonstrated for the synthesis of various types of fcc-ZnSnO₃ nano-morphologies of different particle sizes varying from 15-25 nm. The FE-SEM images show a gradual conversion of ZnSnO₃ morphology with respect to the reaction temperature and annealing from nanospheres to nanocubes confirms the Ostwald ripening law-governed formation mechanism. The simultaneous decrease in optical bandgap energy and Urbach energy with annealing confirms the formation of defectfree nanoparticles with improved sensing properties. The humidity sensors fabricated with annealed samples shows high sensitivity, fast response, and good recovery times within 8% - 97% relative humidity range at room temperature operation. The sensing characterizations like hysteresis and relative deviation in resistance were a compliment towards the use of annealed ZnSnO₃ crystallites as highly promising humidity sensors. The plausible sensing mechanism is also correlated with the Freundlich adsorption model for a better understanding of the guiding adsorption phenomena within the applied humidity range. This reveals two distinct water adsorption regimes in ZnSnO3 nanostructures where low and high RH regime is due to chemisorption and physisorption, respectively. The fitted model for ZnSnO₃ crystallites provides much deeper insight into the physical significance of water vapor adsorption and the role of synthesis controlling parameters for its potential to design an excellent humidity sensor at room temperature.

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Chapter 6

Correlation between Sensitivity and Hysteresis induced error in ZnSnO₃ Humidity Sensor

In this chapter, we study the correspondence between sensitivity and sorption/desorption hysteresis of humidity sensors made of as-prepared and annealed $ZnSnO_3$ samples. The as-prepared sample showed a higher degree of hysteresis induced error of 0.77±0.11% RH associated with sensitivity $(0.876\%(\% RH)^{-1})$ whereas the 500°C annealed analogous showed a decreased degree of measurement error value (0.71±0.12% RH) along with increased sensitivity of 3.32% (% RH)⁻¹) within the humidity range of 8-97% RH. Principal component analysis (PCA) confirms positive effect of thermal treatment on ZnSnO₃ humidity sensors through a significant increase in sensitivity along with reduction in hysteresis induced error. The statistical analysis illustrates the distribution of measurement errors which migrates from high to lower RH region upon annealing. An inverse correlation between sensitivity and hysteresis induced error in fabricated sensors with the enactment of annealing emphasizes the prominence of revising the sorption/desorption hysteresis as a crucial feature in the development of metal oxide-based humidity sensors.

6.1. Background of the Work

Relative humidity (RH) measurement is one of the most important aspect in the development of semiconductor-based chemical sensors and their wide utility[1-5]. The amount of water vapor that is present in the air can affect not only personal comfort but can also affect various manufacturing processes in industrial applications. For this reason, humidity sensors have considerable practice ranging from household applications to manufacturing units, food, and agriculture sector to significant services like metrology, aviation, medical, etc., [6, 7]. To cater needs from various industries humidity sensors should have various properties like low power consumption, lower hysteresis, fast response, wide detection range, highly sensitive and long stability towards humidity in harsh environments[1, 8, 9]. This has been achieved through tremendous progress in the utilization various metal oxides[10-15], polymers[1,8,16], carbon-based of nanomaterials including carbon nanotube and graphene [17-22]. Thin-film type humidity sensors of the above-mentioned sensing elements are widely used for measurements of relative humidity in a variety of environments because they are cheap, easy to handle, and reliable showing hassle-free calibration approach [23]. Many studies reported the utilization of binary metal oxides because of their advantage over single metal oxides [24-26]. Among perovskite-based semiconductors ZnSnO₃ is one of the promising candidate for multi-functional applications in photocatalysis [27,28], lithium-ion batteries[29], dye-sensitized solar cell (DSSC)[30], chemical sensor, etc. [31,32]. However, ZnSnO₃ shows significant humidity sensing properties due to their superior sensitivity towards the detection of low water concentrations[33]. However, most of the thin-film humidity sensors made out of carbon nanomaterials and polymers suffer from severe hysteresis effect during the sorption and desorption of water due to their vulnerable carbon backbone [34-36]. Similarly, pristine and doped zinc stannate also suffers substantial amount of sorption/desorption induced

hysteresis like 2.9 % for Sb-doped ZnSnO₃ within 25-95 % RH [37], zinc stannate cubic crystallites show absolute hysteresis value of 3.5 % within 11-97 % RH [38], ZnSnO₃ nanoparticles show hysteresis around 1.4 % within 8-97 % RH [13]. Similarly ZnSnO₃/TiO₂ heterojunctions have hysteresis of 3.5% RH [39]. The hysteresis obtained in humidity sensing can be attributed to the variance in water content anchored on the sensing material at specific humidity conditions dependent on either adsorption or desorption process [10,35,36,40,41]. Such sorption/desorption induced hysteresis might lay the foundation of a substantial measurement error in humidity measurements as it devises an ambiguity in the early calibration on matching to electric signal [42]. Hence, it is decisive to apprehend the idea about the effect of water content on the physical and chemical properties of the system. Considering its importance, the topic of water sorption behavior is a widely studied phenomenon [43,44]. Still, at present, there is no clear understanding of water sorption-desorption hysteresis in metal oxide-based chemiresistive humidity sensors, their limiting working environment or operating parameter which are of significant interest. From the device aspect, hysteresis is a result of the complex interplay between diffusion of water and relaxation of the sensory matrix. Although water diffusion is not the limiting factor, the sorption/desorption branches show clear hysteresis effects that are similar to those typically observed in bulk samples [43]. In comparison to carbon-based humidity sensors, the hydration-induced hysteresis is shown to be in excellent agreement with the onset of the sorption-desorption hysteresis as in metal oxide based humidity sensors. We suggest that the hysteresis effect is related to a difference in dynamical and structural properties of the metal oxide materials depending on the hydration history of the films. The sorption/desorption induced hysteresis error causes decrement in sensing capability of sensors, instead of its potential role in reduction of measurement accuracy it is one of the least studied sensing parameters. Thermal treatment is one of the most widely used technique to maximization of sensitivity of metal oxide based

sensors through the modulation of surface defect concentrations significantly affecting the interaction of H₂O molecule with metal oxides **[45].** In this regard, we revealed the relationship between the sensitivity and the hysteresis of humidity sensors based on ZnSnO₃ nanomaterial. The magnitude of hysteresis in ZnSnO₃-based sensors is symbolized by the hysteresis-induced error and its correspondence towards the sensitivity considered subject to variance of synthesis and annealing temperature of the sensing material. This work opens a new arena of research in humidity sensors to evaluate measurement errors which hasn't been investigated till now. The present study dispensed an expedient comprehension towards the appreciative sensing features of humidity sensors and exclusively for the improvement of metal oxide based humidity sensors.

6.2. Synthesis Procedure

As discussed in chapter 5, ZnSnO₃ crystallites were synthesized using wet chemical methods. The nanomaterials were designated from S-01 to S-05 depending on their variation of synthesis temperature at 25°C, 45°C, 65°C, 85°C and 100°C, respectively [**13**]. The above as-prepared samples were further thermally treated (*i.e.* annealed) at different temperatures *i.e.* at 250°C, 400°C and 500°C for 6 hours before device fabrication. For simplification, the 250°C annealed samples are marked as SA-01 to SA-05, 400°C annealed samples as SB-01 to SB-05, and 500°C annealed samples are stated as SC-01 to SC-05 for their respective as-prepared samples. In this report, this nomenclature of samples was used in suitable places.

6.3. Results and Discussions

6.3.1. Humidity Sensing Measurement

The sensing device is prepared on ITO coated glass substrate as described in our earlier chapters **[10,13]**. The desired humidity condition is obtained using saturated salt solutions as per previous literature **[46]**. The DC electrical behavior of the fabricated devices was recorded within a humidity range of 8-97% applying a constant bias voltage of 5V and by monitoring resistance *vs.* time characteristics using Keithley 2401 source meter interfaced with PC using LABVIEW[®] software [10,13]. The hysteresis curve area was calculated using the in-built Integrate function of the MATLAB[®] 2015b software package [41,42,47].

6.3.2. Sensitivity

The sensitivity of a metal oxide humidity sensor is mostly affected by geometrical heterogeneities of the reacting surface **[48]**. Geometrical rearrangements like crystallization, crystal growth, coalescence are typical mass diffusion-controlled phenomena that take place during annealing and play a major role in the interaction between micro/nano-structure and sensitivity **[49]**. Other than sensitivity experimental works have also reported the positive effect of annealing on the long-term stability of the sensor. Therefore most commercial sensors based on ceramics were preaged under optimal temperature conditions before their market presence. The most possible reason for this thermal treatment procedure can be ascribed to the fact of chemical, time-dependent rearrangement which takes place in the material aimed towards thermodynamical adjustment of concentrations of surface defects to their respective equilibrium values for maximizing the interaction of foreign analyte to be detected **[50]**.

On this basis here a chemiresistive ZnSnO₃ based humidity sensor is employed for real-time measurement at 25°C within varying relative humidity 8-97% RH. Fig.6.1 shows that annealed samples displays significant changes in resistance variation with applied relative humidity. The annealed samples exhibited a significant decrease in resistance values with an increase in annealing temperature from 250°C to 500°C with respect to its parent sample. The resistance variation with annealing can be ascribed to increased concentration of surface active sites and their amplified interaction with ambient water molecules [13].



Figure.6.1. Real-time resistance measurements by ZnSnO₃ humidity sensors annealed at different temperature 250°C (SA-05), 400°C (SB-05) and 500°C (SC-05) in comparison to as-prepared sample (S-05) within 8%-97%-8% RH level variation.

6.3.3. Hysteresis Analysis

To study hysteresis induced by the sorption/desorption process, the humidity sensors were subjected to subsequent increase and decrease RH level *i.e.* 8, 33, 43, 52, 63, 75, 86, and 97% RH for 2 minutes in each turn. A single sensor undergone repetitive assessment within the same humidity alteration is mentioned as the repeatability test and three consecutive measurements provide similar results. To enumerate the resistance variations more quantitatively, the normalized resistance relative to that of 8% RH is plotted as a function of relative humidity shown in Fig.6.2. The Fig. 6.2(a-d) displays the normalized resistance as a function of applied relative humidity arranged in the format of as-prepared (6.2(a)), 250°C annealed (6.2(b)), 400°C annealed (6.2(c)) and 500°C annealed (6.2(d))

samples collectively. For example, the normalized resistance of as-prepared sensor S-05 is 0.123 ± 0.007 , whereas the corresponding annealed counterparts showed normalized resistance 0.299 ± 0.008 (SA-05), 0.099 ± 0.008 (SB-05) and 0.102 ± 0.009 (SC-05), respectively. Whereas in Fig.6.2 (*a-d*) it is observed that the variation of normalized resistance with RH is nearly superimposable with insignificant change.



Figure.6.2. Normalized resistance as a function of relative humidity that shows sorption/desorption hysteresis for (*a*) as prepared, (*b*) 250° C, (*c*) 400° C and (*d*) 500° C annealed samples.

The above-mentioned data represented in the format of (mean \pm standard deviation) among three individual sensors made in the same condition. The reproducibility of the prepared humidity sensor is defined as (Standard deviation/Mean) ×100 (%) at 97% RH [41]. From Fig. 6.3 (*a*), it is observed that the value stood around 6.08 % for S-05 whereas its corresponding annealed samples showed reproducibility of 2.69 %, 8.36 %, and 9.17 % for SA-05, SB-05, and SC-05, respectively. The figure 6.3(*b*) shows that except

SC-02 all other 500°C annealed samples exhibits the highest reproducibility than their counterparts confirming its wide applicability to prepare humidity sensors. The sensitivity (S) of the humidity sensor is defined as:

$$S = \frac{(\Delta R/R)}{\Delta RH} \qquad (7.1)$$
$$\frac{\Delta R}{R} = (R_8 - R_x) / R_8 \qquad (7.2)$$

Where ΔRH is the difference between initial and final *RH* levels. *R*₈ and *Rx* are the resistance of the device at lower humidity and change in humidity, respectively [10-13,51,52]. Fig.6.3 (*b*) shows the sensitivity variation among as-prepared samples and their annealed variants at 97% relative humidity level. It is observed that in all cases the 500°C annealed samples demonstrated the highest sensitivity in comparison to their counterparts. The as-prepared samples showed variation in sensitivity values *i.e.* 2.76 % (S-01), 3.85 % (S-02), 4.07 % (S-03), 2.54 % (S-04) and 2.63 % (S-05) with variation in their synthesis temperature. Similarly, their annealed counterparts at 500 °C *i.e.* SC-01 to SC-05 showed sensitivity values 7.54 %, 11.26 %, 8.03 %, 11.04 % and 10.12 %, respectively.

The observed variation in sensitivity values per RH level reveals the improvement of concerned sensors either based on the variation of synthesis temperature or thermal treatment temperature or both. Collectively the Fig.6.3 exhibits the fact that sensors have proportionate relation between reproducibility and sensitivity. Hence the role of high-temperature thermal treatment of ZnSnO₃ materials demonstrated as potential to reduce the hysteresis induced by sorption/desorption of water molecules for more accurate measurement of humidity. To accumulate more information on hysteresis Fig. 6.4 displays relative humidity *vs*. resistance plots of sensors made of as-prepared and annealed samples. Interestingly from Fig.6.4 (a), it is observed that S-03 to S-05 samples showed a steep decrease in resistance than other as-prepared samples conveyed the importance of synthesis temperature on humidity sensing. With the variation of synthesis

temperature from 65° C to 100° C, the decrease in resistance with an increase in relative humidity follows the trend of S-05>S-04>S-03.



Figure.6.3. (*a*) Reproducibility and (*b*) Sensitivity variation of ZnSnO₃ based sensors made out of as-prepared and their corresponding annealed samples at 97% RH level.

Also from Fig. 6.4(b-c) it is noted that the annealed analogous of S-04 and S-05 samples revealed more marked resistance variation with applied relative humidity. All the annealed samples exhibited a distinctive reduction in resistance values as a function of RH. Whereas the Fig. 6.4 (d) displayed nearly superimposable plot for SC-01and SC-02 and the variation of resistance for SC-03 and SC-04 marked only after \geq 50% RH level. The above plots of resistance of sensors against applied relative humidity confirm the widely accepted sensing mechanism. At high RH level, a steep decrease in resistance of theses sensors is with prior results [13]. It is well known that under an electric field the physisorbed water got ionized to produce hydronium and hydroxide ions ($2H_20 \rightarrow H_30^+ + 0H^-$) stimulates the observed decrease in resistance value. At high RH circumstance, the multi-layered adsorbed water molecules show the charge transport behavior due to proton hopping process which based on the Grotthuss mechanism. The mechanism describes the role of hydronium ion further which reacts with a neighbouring water molecule ($H_30^+ + H_20 \rightarrow$ $H_2O + H_3O^+$) through the creation of hydrogen bond and proton hopping

acts as a charge carrier transport mechanism and causes a reduction in resistance value with an increase in relative humidity content[**10,13**]. These results strongly suggest the encouraging role of 500°C annealed samples in humidity sensing at room temperature on the viewpoint of sensitivity.



Figure.6.4. Hysteresis analysis of (*a*) as-prepared (*b*) 250° C (*c*) 400° C and (*d*) 500° C annealed ZnSnO₃ samples by matching the resistance with corresponding RH level. Fitting (broken black lines) to median values (triangles) between adsorption (filled square) and desorption (circles) values used to obtain the calibration curves.

Fig.6.4 displays an exponential decrease in resistance of $ZnSnO_3$ based humidity sensors during water adsorption and desorption processes. This sort of hysteresis caused out of the sorption/desorption process is certainly one of the features that lead to an error in the humidity measurement, which needs to be addressed more systematically for a comprehensive understanding of hysteresis in a humidity sensor and its minimization. Hence, sorption/desorption induced hysteresis errors in the humidity measurement are evaluated for all humidity sensors made out of as-prepared and annealed samples. To dispense relative humidity to matching resistance value, an equation that best fits the median values between adsorption and desorption data is achieved. In Fig.6.4 (*a-d*), an exponential fitting to median values (triangles) between adsorption (filled square) and desorption (circles) is used to ascribe resistance values to reference RH values. Upon utilization of the obtained equation for humidity measurement, the measurement error is defined as the difference between the measured value and fitting value either during the adsorption or desorption process.



Figure.6.5. Sorption/desorption hysteresis induced errors of (*a*) asprepared, (*b*) 250° C, (*c*) 400° C, and (*d*) 500° C annealed ZnSnO₃ humidity sensors. The maximum error values indicated within circles for suitable interpretation.

Fig. 6.5 represents the variation of sorption/desorption hysteresis induced errors of the sensors with applied relative humidity. Amongst the measurement errors induced by hysteresis within the inspected RH scope,

the maximum absolute value is selected out all the sensors plotted together and indicated by circles. The maximum error values for as-prepared samples are shown in Fig.6.5 (a), the values for S-01, S-02, S-03, S-04 and S-05 are 1.57±0.14% RH, 1.03±0.12% RH, 0.77±0.11% RH, 2.07±0.19% RH and 1.21±0.12% RH, respectively. Interestingly all the observed maximum errors for the sensors are obtained at >50% RH level, which establishes the fact that with an increase in humidity level more water adsorption/desorption took place which on the contrary increases the measurement error. Fig. 6.5(b) displays the hysteresis induced error of 250°C annealed ZnSnO₃ based sensors where the absolute error values are 1.20±0.24% RH, 0.98±0.18% RH, 2.21±0.36% RH, 1.05±0.16% RH, and 1.11±0.13% RH for SA-01, SA-02, SA-03, SA-04, SA-05, respectively. In The Same Way the 400°C annealed samples demonstrate maximum error values of 2.23±0.20% RH, 1.12±0.18% RH, 1.28±0.24% RH, 1.28±0.20% RH and 1.54±0.30% RH for SB-01, SB-02, SB-03, SB-04, and SB-05, respectively (Fig. 6.5(c)). The hysteresis induced maximum absolute error values for SC-01, SC-02, SC-03, SC-04, and SC-05 are 1.04±0.16% RH, 1.11±0.17% RH, 0.71±0.12% RH, 1.66±0.31% RH and 1.48±0.23% RH, respectively and displayed in Fig.6.5 (d). The annealed samples of ZnSnO₃ show a distribution of maximum error either at 33 % or 75 % RH. The relative humidity within 30-70 % RH is mostly recommended for normal storage of products along with storage of crops (35-40% RH), breweries (35-45% RH), pulp and paper storage (35-45% RH), laboratory equipment's (45-60% RH), computer peripherals (50-60% RH), medicines(35-45% RH), laboratory chemicals (30-45% RH), semiconductor production environment (30-50% RH), etc. Hence annealed ZnSnO₃ sensors with less hysteresis induced measurement error within 33-70% RH range makes it as promising candidates for sensing humidity.

6.3.4. Correlation between sensitivity and hysteresis induced error



Figure.6.6. Correlation between the sensitivity and hysteresis induced maximum error in (*a*) S-01, (*b*) S-02, (*c*) S-03, (*d*) S-04, (*e*) S-05 and their corresponding annealed ZnSnO₃ humidity sensors and (*f*) humidity sensors made out of S-01 to S-05 samples synthesized at different temperature.

Fig. 6.6 shows the correlation between sensitivity and the maximum absolute error are prompted by hysteresis due to sorption/desorption in ZnSnO₃ based chemi-resistive humidity sensors. Fig.6.6 (*a-e*) displays the effect of annealing on the correlation between sensitivity and maximum measurement error, where the individual as-prepared samples along with their respective annealed ones are placed in the same plot. It is noticed that in the case of S-01 and S-03 series there is an increase in sensitivity with a decrease in hysteresis induced error for their respective $500^{\circ}C$ annealed

samples. Fig. 6.6 (b & d) pointed that S-02 and S-04 series have a trade-off connection between the properties where the hysteresis induced error can be negotiated with the sacrifice of the sensitivity of the sensor. Whereas, for the S-05 series it is observed that sensitivity decreases with a rise in hysteresis induced error. Collectively based on results from Fig.6.6 (a-e) we can conclude that with annealing the sensitivity shows an increment with a reduction in hysteresis induced errors concerned to their as-prepared analogous. This result can theorize a significant positive role of post thermal treatment as an improved measurement technique for metal oxide-based humidity sensors. The improvement of thermally treated sensors can be assigned to the surface functionalization and reduction of hydrophilic nature of functionalized surface-active sites. Fig.6.6 (f) showed the relation between maximum measurement error and sensitivity in as-prepared ZnSnO₃ sensors prepared at varied synthesis temperature. Even though there is no linear relation between the two factors still then it is observed that with an increase in synthesis temperature from 25°C to 65°C the measurement error goes down from S01 to S-03 (i.e. from 1.57 (S-01), 1.11 (S-02) and 0.77(S-03)) and then suddenly increases for S-04 (2.07) and S-05 (1.21). The samples indicate initially a decrease and then an increase in sensitivity values for the as-prepared samples *i.e.* S-01(0.67), S-02 (2.46), S-03 (0.87), S-04 (1.95), and S-05 (2.01). This discrepancy in values of sensitivity and the maximum error of as-prepared samples can be related to the concentration of surface-active sites available during the growth of nanomaterials which basically varies with synthesis temperature. In nutshell, variation in synthesis temperature followed by annealing improvises the implementation of ZnSnO₃ based chemiresistive humidity sensors with an inverse proportionate relation between sensitivity and error induced by hysteresis. This finding in metal oxide-based humidity sensors has not yet been revealed to the best of our knowledge. These systematic studies will be decisive in choosing optimal synthesis and annealing

temperature of various nanomaterials for the augmentation of new humidity sensors.



6.3.5. Principal Component Analysis (PCA)

Figure.6.7. (*a*) 2D canonical score plot of all as-prepared and annealed (250°C, 400°C and 500°C) ZnSnO₃ samples for distribution of maximum hysteresis induced errors obtained within 8-97% RH, and (*b*) loading plot showing the distribution of RH levels.

The electrical data were processed by principal component analysis (PCA). PCA is a simple and efficient unsupervised statistical method that uses an orthogonal transformation technique for the reduction of variables from a higher dimensional space to lower-dimensional. In this process, the original data matrix converts to smaller matrixes *i.e.* the score, the loading, *etc.* to generate 2D or 3D spaces, where the sensor response occupies a different region of the PC-space [53]. The score matrix is regarded as the position of samples in the data space, where scores located at close positions refer to samples of similar features, whereas the loading matrix describes the weights for each original variable when calculating the principal component. In practical terms, the loadings here refer to our sensors and the weight they impart to the scores. The similarity of the data from the same analytes led to the data clustering in the PCA plot.

We used PCA to study the distribution of maximum hysteresis induced errors of the as-prepared and annealed samples with subjected RH level.

The score plot (Fig. 6.7(a)) showed that the first two principal components (PC1 and PC2) contribute 89.92% and 4.64% variance. The score PCA plot depicted the distinctive arrangement for S-01 and annealed samples (1st quadrant), S-05 and annealed samples (2nd quadrant), S-04 (4th quadrant) whereas the S-02 and S-03 samples along with their annealed analogous were placed in 3rd quadrant. The samples are grouped with their annealed ones based on their maximum hysteresis induced error values obtained at a specific RH level. In Fig.6.7 (b), the loading plot confirms the significance of RH levels (43%, 52%, 86%, and 97% RH) which are clustered in the same quadrant shares similar error distribution among the humidity sensors. Whereas it is observed that the 33%, 63%, and 75% RH level shows the maximum distinctiveness than other RH levels. It is observed experimentally that with an application of thermal treatment the maximum hysteresis induced errors for sensors associated with higher RH i.e. 75% and 86% RH level are declining towards 33% RH. These statistical facts are in close relation with experimental results suggesting that the maximum variation of measurement error is in either 33% or 75% RH level and confirms the linear working domain of ZnSnO₃ samples within 33-75% RH. This comparison between experimental and statistical results confirms the substantial role of thermal treatment on both sensitivity and reduction in measurement error towards more accuracy in the collection of humidity sensing results.

6.4. Summary

In summary, here we report the relationship between the sensitivity and sorption/desorption induced hysteresis of $ZnSnO_3$ thin film humidity sensors. These properties were represented through the resistance variation of $ZnSnO_3$ synthesized and annealed at varying temperatures are measured within a humidity range of 8-97% RH. It has been observed that the sensitivity of sensors increases with an increase in thermal treatment where it can be assigned to two important factors (i) concentration of surface

defects and (ii) enhancement in surface defects with annealing. This plausible reason shares the significant role of post-processing factors like thermal treatment in improved performance of metal oxide-based humidity sensors. The median value fitting approach helps to calculate the hysteresis induced measurement errors in as-prepared and annealed ZnSnO₃ sensors. With the implementation of synthesis temperature followed by annealing inverse affiliation between sensitivity and measurement error is observed for samples. For the 500°C annealed samples a decline in hysteresis induced error with an increase in sensitivity value is witnessed with respect to their respective as-prepared samples. The PCA statistical analysis of the results confirms experimental findings with the distribution of RH levels with maximum error values. The data clusters in PC-space show improved sensing performance of samples depending upon their variation in synthesis and annealing temperature. The present report provides significant evidence of the unnoticed association between apparently independent properties in sensors and hence can be beneficial in the progress of humidity sensors based on metal oxides.

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Chapter 7

The Conclusion and Future Scope of Research

The core basis of this thesis is to synthesize binary (ZnO) and ternary (NiCo₂O₄ and ZnSnO₃) nanostructures for their potential application in chemical (gas and humidity) sensing. Prominence is given to a low-cost wet chemical reaction method and understanding the fundamentals of their growth processes. Gas and humidity sensing properties have been investigated revealing room temperature sensor application of the metal-oxides. Efforts have been made to understand the role of doping and effect of thermal treatment on the improvement of sensing properties by an increase in sensitivity and reduction is hysteresis induced measurement error in sensors to realize highly efficient and promising materials for the development of next-generation chemical sensors.

7.1. Thesis summary

Chapter 1 describes a brief review of chemical (gas and humidity) sensor, their classifications, sensor terminology, metal oxide semiconductors, and their sensing mechanism. The sensing mechanism largely related to surface phenomena was portrayed using various adsorption/desorption models. A literature review on metal oxide sensors widely used in developing gas sensors due to the simplicity of usage, a large spectrum of detectable gases, low cost, and flexibility in production were discussed. Whereas the chapter ventured the feasibility of utilizing nanocrystalline binary and ternary metal oxides as a rugged sensor for environmental sensing in harsh environments.

Chapter 2 describes the main experimental techniques that are employed in this thesis related to the material as well as device fabrication and characterization.

Chapter 3 discussed the room temperature NH₃ sensing behavior of mesoporous flakes of NCH and NCO. Ni-Co hydroxide/oxide nanoflakes were synthesized using the simple and economical wet chemical method and their physio-chemical properties were investigated using XRD, FESEM, HRTEM, and BET. Mesoporous NCH samples demonstrate higher sensitivity, fast response/ recovery time towards low concentration of NH₃ due to the chemisorbed oxygen ions, uniform pore distribution along the higher surface of interaction. Whereas lowering of charge depletion width, increased chemisorbed oxygen ions assumed to help in reverting the major charge carriers on the surface of NCO to cause abnormal *p*-type (*i.e. n*-type) response towards NH₃ gas at room temperature. The variation of sensor response with ammonia concentration shows a Freundlich adsorption isotherm like behavior also correlates the higher sensitivity of NCH over NCO. The overall work validates Ni-Co hydroxide/oxide as potential

candidates for room temperature chemiresistive ammonia gas sensor, hence technologically important.

Chapter 4 demonstrated the room temperature chemiresistive humidity sensing behavior of pure and Ni-doped ZnO sensors. The sensor characteristics like highest sensitivity (~153%), negligible hysteresis error, fast response/recovery time (27s/3 s), robust stability, the lowest detection limit of 3.71% RH, *etc*, accounts Ni10ZnO as the best candidate for the humidity sensing operation. A better correlation between the sensing mechanism and Freundlich adsorption model is devised to understand the guiding adsorption phenomena within subjected RH range. The phenomena reveals two distinct water adsorption regimes due to chemisorption and physisorption in ZnO nanostructures. The fitted model bargain high adsorption capacity and adsorption strength of Ni-doped ZnO sensors supporting their potential to serve as an excellent humidity sensor at room temperature.

Chapter 5 discussed the chemi-resistive humidity sensing performance of sensors fabricated from various ZnSnO₃ nano-morphologies synthesized using facile wet chemical method combined with a subsequent annealing process. The Ostwald ripening law guided the controlled growth of ZnSnO₃ from nanospheres to nanocubes. The fabricated humidity sensors based on annealed samples exhibited low hysteresis, high sensitivity, fast response/ recovery times within 8-97% RH range at room temperature operation. The Freundlich adsorption model for ZnSnO₃ sensor provides much deeper insight into the physical significance of water vapor adsorption and the role of synthesis parameters for potential design of an excellent room temperature humidity sensor.

Chapter 6 summarizes the relationship between the sensitivity and absorption/desorption induced hysteresis of ZnSnO₃ thin film humidity

sensors within an 8-97% RH range. The increment in sensitivity value for humidity sensors with annealing can be assigned to two important factors (i) concentration of surface defects and (ii) enhancement in surface defects with annealing. An inverse relationship between sensitivity and measurement error is established for ZnSnO₃ samples. A significant decrease in measurement error with an increase in sensitivity value was witnessed for 500°C annealed samples in comparison to as-prepared samples. The principal component analysis (PCA) implied the distribution of RH levels with maximum error values for sensors depending upon their variation in synthesis and annealing temperature. The detailed analysis affords significant evidence of unnoticed nexus between apparently independent properties in sensors and hence can be beneficial in the progress of metal oxide-based humidity sensors.

Overall, it is concluded that the controlled growth of binary (ZnO) and ternary (NiCo₂O₄ and ZnSnO₃) is required for repeatable production of prototypes with stable characteristics. Although established vapor phase methods achieve the robust control and reproducibility of the nanostructures, widely acclaimed wet chemical methods are more suitable due to their low cost and great potential for scalability and compatibility. There are several aspects which are addressed in the present work. Firstly, the growth of NiCo₂O₄ nanoflakes for low concentration NH₃ gas detection at room temperature. Secondly, the controlled growth of Ni-doped ZnO and ZnSnO₃ nanostructures for humidity sensing applications in close coordination with available Freundlich isotherm model. Finally, the evaluation of the correlation between sensitivity and hysteresis induced measurement error in humidity sensors.

Thus, the verdict of the present study is a decent contribution to the inorganic semiconductor metal oxides as chemical sensors. This study also fulfill the main objectives of the thesis, and also the thesis title is quite well justified.

7.2. Outlook and Future Prospects

Accounting the benefits from the literature and taking notes from different aspects of the present study, several proposals of future work are in line. A few of them are presented briefly:

Binary and ternary metal oxide (ZnO, NiCo₂O₄ and ZnSnO₃) based sensors will be further explored for their potential towards a wide range of VOC (volatile organic compound) gases like xylene, styrene, acetylene *etc*. and common air pollutants (CO, CO₂, NO_x, H₂S *etc*.). A detailed theoretical insight into sensing mechanism will be developed based on available physical models.

With advancements of nano-sensors it becomes progressively more necessary to unravel their working potential using mathematical modeling. Hence comprehensive strategies will be developed using genetic algorithm (GA) to obtain optimal parameters. The obtained results will be implemented for machine learning, development of graphical user interface (GUI) for subsequent application and employment.

The role of discussed metal oxides in the form of wearable devices *i.e.* pressure sensor, temperature sensor, nanogenerator, *etc.* will be investigated for possible commercialization.

As metal oxides like NiO, Co₃O₄, ZnO, SnO₂ shows good biocompatibility and are of low cost, therefore it has shown recent exciting progress in the field of biomedical applications. This opens the opportunity to utilize binary (ZnO) and ternary (NiCo₂O₄ and ZnSnO₃) nanostructures presented in this thesis in the field bio-sensing and drug delivery applications.