# **Effect of Aliovalent Ion Doping on Structural, Optoelectronic and Sensing Properties of ZnO**

Ph.D. Thesis

By

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## DISCIPLINE OF METALLURGY ENGINEERING AND MATERIAL SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE

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# **Effect of Aliovalent Ion Doping on Structural, Optoelectronic and Sensing Properties of ZnO**

### A THESIS

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

by TULIKA SRIVASTAVA



DISCIPLINE OF METALLURGY ENGINEERING AND MATERIAL SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE April, 2018



### **INDIAN INSTITUTE OF TECHNOLOGY INDORE**

### **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled "Effect of Aliovalent Ion Doping on Structural, Optoelectronic and Sensing Properties of ZnO" 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 MATERIAL SCIENCE, Indian Institute of Technology Indore is an authentic record of my own work carried out during the time period from July 2014 to January 2018 under the supervision of Dr. Somaditya Sen, Associate Professor, Discipline of Physics, IIT Indore and Dr. Parasharam M. Shirage, Associate Professor, Discipline of Metallurgy Engineering and Material Science, IIT Indore.

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 Tulika Srivastava

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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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Signature of Head of Discipline Date:			

## **Dedicated to Lord Krishna**

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### LIST OF PUBLICATIONS

#### 1. From Thesis work: Journal Publications

- I. Tulika Srivastava, E. G. Rini, Ashutosh Joshi, Parasharam Shirage, and Somaditya Sen, "Structural Distortion and Bandgap Increment in Nanocrystalline Wurtzite Si Substituted ZnO" Journal of Nanoscience and Nanotechnology, 16, 1–4, 2016.
- II. Tulika Srivastava, Sunil Kumar, Parasharam Shirage, Somaditya Sen, "Reduction of O2– related defect states related to increased bandgap in Si<sup>4+</sup> substituted ZnO" Scripta Materialia, 124, 11–14, 2016.
- III. **Tulika Srivastava**, Gaurav Bajpai, Nidhi Tiwari, Dibyendu Bhattacharya, S. N. Jha, Sunil Kumar, Sajal Biring, and Somaditya Sen, "Opto-electronic properties of  $Zn_{(1-x)}$  V<sub>x</sub>O: Green emission enhancement due to V<sup>4+</sup> state" Journal of Applied Physics 122, 025106, 2017.
- IV. Tulika Srivastava, Aswin Sadanandan, Gaurav Bajpai, Saurabh Tiwari, Ruhul Amin, Mohd. Nasir, Sunil Kumar, Parasharam M. Shirage, Sajal Biring, Somaditya Sen, "Zn<sub>1-x</sub>Si<sub>x</sub>O: Improved optical transmission and electrical conductivity" Ceramics International, 43, 5668–5673, 2017.
- V. Tulika Srivastava, Gaurav Bajpai, Gyanendra Rathore, Sajal Biring, Somaditya Sen, "Vanadium substitution: a simple and efficient way to improve UV sensing in ZnO" Journal of Applied Physics, 123, 161407, 2018.
- VI. Tulika Srivastava, Gaurav Bajpai, Shun Wei Liu, Sajal Biring, Somaditya Sen, "Zn<sub>1-x</sub>Si<sub>x</sub>O: Reduced photosensitivity, improved stability and enhanced conductivity" Scripta Materialia, 150, 42-44, 2018.

#### 2. From other work: Journal Publications

- I. Gaurav Bajpai, Tulika Srivastava, Mohd Nasir, Saurabh Tiwari, Shubhra Bajpai, EG Rini, Sajal Biring, Somaditya Sen, "A comprehensive theoretical and experimental study on structural and mechanical properties of Si doped ZnO", Scripta Materialia, 135, 1-4, 2017.
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- III. Gaurav Bajpai, Tulika Srivastava, Faizan Husian, Sunil Kumar, Sajal Biring, Somaditya Sen, "Enhanced red emission from Fe/Si co-doped ZnO nano-particles" Scripta Materialia, 144, 27–30, 2018.
- IV. Gaurav Bajpai, Tulika Srivastava, Faizan Husian, Shubhra Bajpai, sajal biring, "Effect of crystal radius compensated Zn<sub>(1-x)</sub> Fe<sub>(39x/50)</sub>Na<sub>(11x/50)</sub>O on structural, electronic and photoluminescence properties" submitted in Journal of Luminescence.

#### 3. <u>Conference proceedings/ Poster presentation:</u>

- I. Tulika srivastava, Gaurav Bajpai, Sunil Kumar, Parashram Shirage, Somaditya sen, "Effect of Si doping on optical & electrical property of ZnO" 13th International Conference on Fiber Optics and Photonics, IIT Kanpur, 4<sup>th</sup> -8<sup>th</sup> December, 2016[Poster Presentation and publication in Optical Society of America, 2016, paper W3A.88].
- II. Gaurav Bajpai, Tulika Srivastava, Sunil Kumar, Parasharam Shirage and Somaditya Sen, "Structure, Electronic and Photoluminescence study of Si doped ZnO nanoparticles"

IConAMMA, Amrita University,14<sup>th</sup>-16<sup>th</sup> July, 2016[Oral Presentation and IOP Conference seriesproceedings].

- III. Tulika Srivastava, Parasharam Shirage and Somaditya Sen, "Synthesis, Characterization & Device fabrication based on doped ZnO nanoparticle and film", Indian Nanoelectronics User Programs, IISc Bangalore, 20<sup>th</sup>-22<sup>th</sup> July,2015[Workshop and Poster Presentation].
- IV. Tulika Srivastava, Parasharam Shirage and Somaditya Sen, "Synthesis and Characterization of Si doped ZnO nanoparticle", Ramanujan Conclave, IIT Indore, 22<sup>nd</sup>-23<sup>rd</sup> December 2015 [Poster presentation].
- V. Tulika Srivastava, Gaurav Bajpai, Somaditya Sen, "Suppression and enhancement of deep level emission of ZnO on Si<sup>4+</sup>& V<sup>5+</sup> substitution" Applied Nanotechnology and Nanoscience International Conference (ANNIC), Rome, Italy, 18-20 October 2017 [Oral presentation and IOP conference series proceedings].
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### **TABLE OF CONTENTS**

# Contents

Acknowledgement	i
List of Publication	v
List of Figures	XV
List of Tables	xxiii
List of Abbreviations	XXV

Chapter 1: Introduction	1-28
1.1 Crystal structure	1-4
1.1.1 Physical Property	2
1.1.2Opto-electronic Property	3
1.1.3Optical Property	3
1.1.4Electrical Property	3
1.1.5 Mechanical Property	4
1.1.6Magnetic Property	4
1.2 ZnO Nanostructure	4-6
1.3 Synthesis Technique	6-9
1.3.1 Sol-gel synthesis route	7-8
1.3.2 Citrate	8-9
1.4 Defect Physics and Chemistry in ZnO	9-17
1.4.1 Oxygen Vacancies (V <sub>o</sub> )	9-13
1.4.2 Zinc Vacancies (V <sub>zn</sub> )	12-13
1.4.3 Zinc Interstitial (Zn <sub>i</sub> )	13-14
1.4.4 Oxygen Interstitial (O <sub>i</sub> )	14-15

1.4.5 Zinc antisites (Zn <sub>o</sub> )	15-16
1.4.6 Oxygen antisites (O <sub>zn</sub> )	16-17
1.5 Photoluminescence	17-20
1.5.1 Photoluminescence of ZnO	18-20
1.6 Doping in ZnO	20-21
1.7 Different functionality of modified ZnO	21-26
1.7.1 Transparent conductive oxides	21-22
1.7.2 Electron Transport Layer	22-24
1.7.3 Humidity Sensor	24-25
1.7.4 UV Sensors	25-27
Chapter Details	27-28
Chapter 2: Experimental Details	29-54
2.1 Synthesis Process	
2.1.1 Doped Sample Preparation	31-33
2.1.2 Denitrification and Decarbonization	33-34
of synthesized pure ZnO	
2.2 Characterization Techniques	34-50
2.2.1 X-Ray Diffraction	34-36
2.2.2 X-ray absorption spectroscopy (XAS)	36-41
2.2.3 Field Emission Scanning Electron	41-44
Microscope	
2.2.4 Raman spectroscopy	44-46
2.2.5 Photoluminescence spectrometer	46-48
2.2.6 UV-Vis Absorption Spectroscopy and Diffuse	48-50
Reflectance Spectroscopy	
2.2.7 Hall Set Up	50-51
2.3 Setup for Functionalities	
2.3.1 Humidity Sensing set up	51-52
2.3.2 Light Sensing set up	53-54

Chapter 3: Structural properties of Pure and	55-84
Modified ZnO	
3.1 Effect of Si <sup>4+</sup> doping on structural properties	56-64
of ZnO	
3.2 Effect of Si <sup>4+</sup> /Na <sup>1+</sup> doping on structural	64-71
properties of ZnO	
3.3 Effect of V <sup>4+/5+</sup> doping on structural	71-82
properties of ZnO	
3.4 Conclusion	82-84

<b>Chapter 4: Opto-electrics Properties of Pure and</b>	85-114
Modified ZnO	
4.1. Bandgap and defect state investigation of	85-98
undoped and Silicon doped ZnO	
4.1.1 Bandgap Analysis	86-89
4.1.2 Photoluminescence study	89-95
4.1.3 Electrical measurements of undoped and	95-98
Si <sup>4+</sup> doped ZnO	
4.2 Bandgap and defect state investigation of	99-105
undoped and Si <sup>4+</sup> /Na <sup>1+</sup> co-doped ZnO	
4.2.1 Bandgap Analysis	99-100
4.2.3 Photoluminescence study	101-104
4.2.4 Electrical measurements of undoped	105
and Si <sup>4+</sup> /Na <sup>1+</sup> co-doped ZnO	
4.3 Bandgap and Defect state investigation of	105-108
undoped and Vanadium (4+/5+) doped ZnO	
4.3.1 Bandgap Variation with V (4+&5+)	105-108
concentration	
4.3.2 Photoluminescence study	108-112

Chapter 5: Multifunctional applications of	115-134
synthesized materials	
5.1 Moisture Resistant property of pure and Si	116-119
substituted ZnO	
5.1.1 Sample Preparation	116
5.1.2 Experimental Set Up	116-118
5.1.3 Mechanism behind moisture	118-119
resistant property	
5.2 Effect of different wavelength of light on	119-123
Pure and Si substituted ZnO	
5.2.1 Sample preparation	120
5.2.2 Experimental Set Up	121-122
5.2.3 Mechanism behind reduced	122-123
Photosensitivity	
5.3 UV sensing property of Si/Na co-doped ZnO	123-127
5.3.1 Sample preparation	124
5.3.2 Experimental Set Up	124-126
5.3.3 Mechanism behind UV sensing	126-127
5.4 UV sensing property of Vanadium doped ZnO	127-128
5.4.1 Sample preparation	128-131
5.4.2 Experimental Set Up	131-133
5.4.3 Mechanism behind UV sensing	133-134
5.5 Conclusion	
Chapter 6: Conclusion and Future Scope	135-148
6.1 Conclusions	
6.1.1 Synthesis and Solubility limit	136-137
6.1.2 Structural properties	137- 141

6.1.3 Opto-electronic properties 1	141-144
6.1.4 Sensing properties of modified ZnO	144-146
6.2 Future Scope	146-148
References	149-175
Appendix	176-179

### List of Figures

<b>Figure 1.1:</b> Alternating planes of Zn2+ and O2- in wurtzite structure of ZnO	2
Figure 1.2: Various morphologies of ZnO Nanostructures	5
Figure 1.3: Schematic diagram of sol-gel synthesis route	6
Figure 1.4: Defect structure and its related color emission	9
<b>Figure 1.5:</b> Geometry of Oxygen vacancy in 2+ charge state (Vo <sup>2+</sup> )	10
<b>Figure 1.6:</b> Geometry of Zinc vacancy in -2 charge state (VZn <sup>2-</sup> )	12
<b>Figure 1.7:</b> Geometry of Zinc interstitial in +2 charge state (Zni <sup>2+</sup> )	12
<b>Figure 1.8:</b> Geometry of Oxygen interstitial in -2 charge state (Oi <sup>2-</sup> )	14
<b>Figure 1.9:</b> Geometry of Zinc antisites in +2 charge state (Zno <sup>2+</sup> )	15
<b>Figure 1.10:</b> Geometry of Oxygen antisites in -2 charge state (OZn <sup>2-</sup> )	16
Figure 1.11:SchematicofPhotoluminescenceSpectroscopy	17
Figure 1.12: Typical PL spectra of ZnO nanostructures	18
<b>Figure 1.13:</b> Schematic of OPVs using ZnO as Electron Transport Layer (ETL)	22
<b>Figure 1.14:</b> Humidity sensing mechanism in ZnO showing two different process depending upon particle size	24

<b>Figure 1.15:</b> UV sensing mechanism in ZnO showing adsorption/ desorption under dark/ light condition	25
<b>Figure 2.1:</b> (a) Schematic diagram of Sol-gel synthesis route (b) Step by step experimental pictures for Nano powder synthesis using sol-gel technique.	31
<b>Figure 2.2:</b> Thermogravimetric analysis of pure ZnO in temperature range of 0°C to 700°C showing loss of adsorbed water, nitrates and carbonates	33
<b>Figure 2.3:</b> Diffraction of X-rays through lattice/atomic planes of a crystal (indicating Bragg's law)	35
<b>Figure 2.4:</b> Schematic of XRD setup with different angles of rotation	36
<b>Figure 2.5:</b> The photoelectric effect; an x-ray is absorbed and a core level electron is promoted out of the atom. Inset shows schematic for x-ray absorption measurements: An incident beam of monochromatic x-rays of intensity I0 passes through a sample of thickness t, and the transmitted beam has intensity I.	37
<b>Figure 2.6:</b> Decay of the excited state: (a) x-ray fluorescence and (b) the Auger effect. In both cases, the probability of emission (x-ray or electron) is directly proportional to the absorption probability	40
<b>Figure-2.7:</b> Schematic of XAFS/XANES setup in fluorescence mode; fluorescence detector at a right angle with the incident x-ray beam	40
Figure 2.8: Schematic Diagram of FESEM instrument	41
Figure 2.9: Experimental set-up of Micro Raman spectroscopy	45

Figure 2.10: Schematic of experimental set up for PL	47
<b>Figure 2.11:</b> Experimental set up for diffuse reflectance measurement (a) Carry 60 UV-Vis spectrometer, (b) an integrating sphere attachment to detect diffuse reflectance	50
Figure 2.12: Schematic diagram for Hall-probe measurements	51
<b>Figure 2.13:</b> Schematic of experimental set up for Humidity sensing	52
Figure 2.14: Schematic of experimental set up for Light sensing	53
<b>Figure 3.1:</b> (a) XRD reveals pure single phase of samples without the presence of any impure phases. Changes in lattice parameters are expected from XRD peak shifts. (b) Crystallite size increases as calculated from Debye-Scherer equation	57
<b>Figure 3.2:</b> SEM micrographs showing morphology of the Z0, ZS1, ZS2 and ZS3 samples. The size of the samples is observed to increase linearly with Si-substitution. Note that for substituted samples smaller particles agglomerate to for large macro-sized chunks.	58
<b>Figure 3.3:</b> (a) EDS of Z0, ZS1, ZS2 and ZS3 (inset confirms increase in Si <sup>4+</sup> content) (b)Oxygen content in Z0, ZS1, ZS2 & ZS3 (c)Oxygen content in sample increases with increase in Si <sup>4+</sup> substitution (d) Elemental mapping of Z0, ZS1, ZS2 and ZS3 showing uniform distribution of component ions.	59



Figure 3.5: Rietveld refinement using GSAS software	62
estimated variation in (a) Lattice parameter a, b & c (b) c/a	
(c) Strain with Si <sup>4+</sup> substitution.	
Figure 3.6: (a) Raman spectroscopy of Z0, ZS1, ZS2 &	63
ZS3 (b) Strain was calculated from $A_1(TO)$ vibrational	
mode which decreases with Si4+substitution. Strain from	
Raman is in agreement with strain calculated from XRD	
<b>Figure 3.7:</b> (a) XRD reveals pure single phase of samples	
without the presence of any impure phases. Changes in	65
lattice parameters are expected from XRD peak shifts. (b)	
Crystallite size increases as calculated from Debye-Scherer	
equation	
<b>Figure 3.8:</b> SEM micrographs showing morphology of the Z0, ZSN1, ZSN2 and ZSN3 samples. The size of the samples is observed to vary with Na co-doping.	66
<b>Figure 3.9:</b> (a) EDS of Z0, ZSN1, ZSN2 and ZSN3 (b)Oxygen content in Z0, ZSN1, ZSN2 & ZSN3 (c)Oxygen content in sample decreases with increase in Na1+co-doping (d) Elemental mapping of Z0, ZSN1, ZSN2 and ZSN3 showing uniform distribution of component ions.	67
<b>Figure 3.10:</b> Rietveld refinement of Z0, ZSN1, ZSN2 & ZSN3	69
<b>Figure 3.11:</b> Rietveld refinement using GSAS software estimated variation in (a) Lattice parameter a, b & c (b) Strain and Volume with $Si^{4+}/Na^{1+}$ substitution.	69
<b>Figure 3.12:</b> (a) Raman spectroscopy of Z0, ZSN1, ZSN2 & ZSN3 (b) Strain was calculated from $A_1(TO)$ vibrational mode which decreases with Si <sup>4+</sup> /Na <sup>1+</sup> co-doping. Strain	70

from Raman is in agreement with strain calculated from XRD.

Figure 3.13: (a) XRD reveals pure single phase of samples72without the presence of any impure phases. Changes in1lattice parameters are expected from XRD peak shifts. (b)1Crystallite size increases as calculated from Debye-Scherer1equation.1

Figure 3.14: SEM micrographs showing morphology of73the Z0, ZV1, ZV2 and ZV3 samples. The size of thesamples varies with V- doping.

**Figure 3.15:** (a) EDS of Z0, ZV1, ZV2 and ZV3 (b) 74 Oxygen content in sample increases with increase in V doping (c)Oxygen content in Z0, ZV1, ZV2 & ZV3 (d) Elemental mapping of Z0, ZV1, ZV2 and ZV3 showing uniform distribution of component ions

Figure 3.16: Rietveld refinement of Z0, ZV1, ZV2 & ZV3 75

Figure 3.17: Rietveld refinement using GSAS software76estimated variation in (a) Lattice parameter a, b & c (b)Strain and Volume with V doping.

Figure 3.18: (a) V-K edge XANES spectra of ZV1, ZV278& ZV3 (inset is calculated are under pre-edge) (b)normalized XANES spectra of ZV1, ZV2 & ZV3 andreference VOSO4 ( $V^{4+}$ ) and  $V_2O_5$  ( $V^{5+}$ ).

Figure 3.19: ATHENA fitting V-K edge XANES spectra79of samples

Figure 3.20: Variation of (a) $V^{4+}(\%)$ and $V^{5+}(\%)$ content	80
(b) Theoretical calculation indicates increase in oxygen	

content with Vanadium doping. Increase in oxygen content from XANES agrees with EDS studies.

Figure 3.21: (a) Raman spectroscopy of Z0, ZV1, ZV2 &	81
ZV3 (b) Strain was calculated from A <sub>1</sub> (TO) vibrational	
mode which decreases with V doping. Strain from Raman	
is in agreement with strain calculated from XRD	
Figure 4.1: (a) Absorbance of Z0, ZS1, ZS2 and ZS3 [inset	86
is x-intercept of the extrapolated lines to the linear portion	
of optical transmittance at the maximum slope of the $(\alpha hv)^2$	
versus hv] (b) Bandgap versus x.	
Figure 4.2: Schematic diagram for Burstein -Moss effect	87
Figure 4.3: (a) Linear fit of Urbach tail (b) Urbach energy	88
versus x (inset shows schematic diagram of Urbach tail).	
Figure 4.4: (a) PL spectra of Z0, ZS1, ZS2 and ZS3 (b)	89
Chromaticity diagram confirming red shift of DLE	
Figure 4.5: (a) Gaussian fitting of PL spectra of Z0, ZS1,	90
ZS2 and ZS3 (b) Band energy diagram with different	
defects in pure ZnO showing all possible color emissions	
due to electron transition between states	
<b>Figure 4.6:</b> Variation of (a) I <sub>NBE</sub> /I <sub>DLE</sub> (b) P <sub>NBE</sub> /P <sub>DLE</sub> (c) PN	92
with Si <sup>4+</sup> substitution	
Figure 4.7: (a) Conductivity of Z0, ZS1, ZS2 & ZS3 shows	96
increasing trend (b) Composition dependence of	
conductivity at different voltage (2V, 6V & 8V). Increase	
in conductivity indicates Si <sup>4+</sup> acts as donor in ZnO lattice.	
Figure 4.8: Schematic diagram for Hall-probe	97
measurements	

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<b>Figure 4.9:</b> Variation in carrier concentration with Si <sup>4+</sup> substitution. Increase in carrier concentration confirmed the donor behavior of Si <sup>4+</sup> dopant in ZnO.	98
<b>Figure 4.10:</b> (a) Optical absorbance of Z0, ZSN1, ZSN2 & ZSN3 (b) variation of bandgap with x.	99
<b>Figure 4.11:</b> (a) Linear fit of $\ln(\alpha hv)$ vs hv to assess Urbach tail (b) Variation of Urbach energy with x	100
<b>Figure 4.12:</b> a) Gaussian fitting of PL spectra of Z0, ZSN1, ZSN2 & ZSN3 b) Chromaticity diagram indicates red shift with Na1+co-doping.	101
<b>Figure 4.13:</b> Variation of (a) $I_{NBE}/I_{DLE}$ (b) $P_{NBE}/P_{DLE}$ (c) PN with Na <sup>1+</sup> co-doping. Na <sup>1+</sup> co-doping increases defect states of ZnO.	103
<b>Figure 4.14:</b> IV characteristics of Z0, ZSN1, ZSN2 & ZSN3 shows decreasing trend with Na <sup>1+</sup> co-doping.	104
<b>Figure 4.15:</b> (a) Absorbance of Z0, ZV1, ZV2 and ZV3 (b) Variation in Bandgap with Vanadium doping.	107
<b>Figure 4.16:</b> (a) Linear fit of Urbach tail (b) Variation of Urbach energy with x	107
<b>Figure 4.17:</b> (a) PL spectra of Z0, ZV1, ZV2 & ZV3 (b) Chromaticity diagram of Z0, ZV1, ZV2 & ZV3 indicates blue shift with vanadium doping.	109
<b>Figure 4.18:</b> (a) Gaussian fitting of Z0, ZV1, ZV2 & ZV3 (b) Band energy diagram of vanadium doped ZnO.	110
Figure 4.19: Variation of (a) $I_{NBE}/I_{DLE}$ and $P_{NBE}/P_{DLE}$ (b) $P_N$ with x	111

<b>Figure 5.1:</b> Response towards humidity of Z0, ZS1, ZS2 & ZS3	117
<b>Figure 5.2:</b> Response time, Recovery and Sensitivity changes with x	118
<b>Figure 5.3:</b> (a) % current change of Z0, ZS1, ZS2 & ZS3 at different wavelength of 300 nm, 350 nm, 360 nm, 380 nm, 390 nm, 400 nm, 450 nm, 500 nm, 550 nm, 550 nm and 650 nm (b) Variation of sensitivity with wavelength (c) Variation of sensitivity with x.	121
<b>Figure 5.4:</b> Photocurrent response of Z0, ZSN1, ZSN2 & ZSN3	124
<b>Figure 5.5:</b> Sensitivity of Z0, ZSN1, ZSN2 & ZSN3. UV sensitivity increases with Si <sup>4+</sup> /Na <sup>1+</sup> co-doping.	125
<b>Figure 5.6:</b> Response Time, Recovery Time and Sensitivity of Z0, ZSN1, ZSN2 & ZSN3. Decreased Response & Recovery time and increased sensitivity was found with Si <sup>4+</sup> /Na <sup>1+</sup> co-doping.	126
<b>Figure 5.7:</b> Photocurrent response of Z0, ZV1, ZV2 & ZV3.	128
<b>Figure 5.8:</b> (a)Sensitivity of Z0, ZV1, ZV2 & ZV3 [inset is $V^{4+}$ , $V^{5+}$ and sensitivity content with x] (b) Variation in Response & Recovery time with Vanadium content. Graph shows dependence of UV sensitivity on $V^{4+/5+}$ content.	130
<b>Figure 5.9:</b> Variation in (a) response time and (b) recovery time for 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% & 90% of current growth	131
<b>Figure 6.1:</b> Sample preparation process using Sol-gel techniques	136

Figure 6.2: Variation in lattice parameter on doping (a)	137
$Si^{4+}$ (b) $Si^{4+}/Na^{1+}$ (c) $V^{4+/5+}$ in ZnO.	

**Figure 6.3:** Variation in strain on doping (a)  $Si^{4+}$  (b) 138  $Si^{4+}/Na^{1+}$  (c)  $V^{4+/5+}$  in ZnO.

Figure 6.4: Variation in Particle Size on doping (a)  $Si^{4+}$  (b)139 $Si^{4+}/Na^{1+}$  (c)  $V^{4+/5+}$  in ZnO.

**Figure 6.5:** Variation in  $E_2^{high}$  on doping (a)  $Si^{4+}$  (b) 140  $Si^{4+/}Na^{1+}$  (c)  $V^{4+/5+}$  in ZnO.

**Figure 6.6:** Variation in Bandgap on doping (a)  $Si^{4+}$  (b) 142  $Si^{4+}/Na^{1+}$  (c)  $V4^{+/5+}$  in ZnO.

Figure 6.7: Variation in color emission related defect state143on doping (a)  $Si^{4+}$  (b)  $Si^{4+}/Na^{1+}$  (c)  $V^{4+/5+}$  in ZnO

**Figure 6.8:** Based on structural and opto-electronic 146 properties all the three systems has different functionalities (a)  $Si^{4+}doped$  ZnO has moisture resistant property which make it applicable for TCOs which can be used in high humid condition (b) $Si^{4+}/Na^{1+}doped$  ZnO shows high sensitivity in UV light with low response and recovery time (c) $V^{4+/5+}doped$  ZnO also shows god UV sensitivity but lower than Si4+/Na1+doped ZnO.

### List of Tables:

Table	1.1:	Different	types	of	gels	used	for	sol-gel	7
synthe	sis								
Table	<b>3.1:</b> (	002) peak j	positio	n an	d latti	ce par	amet	er (c) in	60
Si <sup>4+</sup> su	bstitu	ted ZnO							

<b>Table 3.2:</b> Refined parameters $R_{wp}(\%)$ , $R_P(\%)$ , $\eta^2$ and	61
Density (gm/cm <sup>3</sup> ) in Si <sup>4+</sup> doped ZnO.	
<b>Table 3.3:</b> Refinement parameters $R_{wp}$ , $R_p$ , $\eta^2$ and density in Si <sup>4+</sup> /Na <sup>1+</sup> co-doped ZnO.	68
<b>Table 3.4:</b> Peak position and FWHM of $E_2^{high}$ mode in $Si^{4+/}Na^{1+}$ co-doped ZnO	71
<b>Table 3.5:</b> Refinement parameters $R_{wp}$ , $R_p$ , $\eta^2$ and density in V <sup>4+/5+</sup> doped ZnO	76
<b>Table 3.6:</b> Athena fitting parameters $[V^{4+}, V^{5+}]$ and chi-square] of XANES spectrum	78
<b>Table 3.7:</b> Peak position of Raman mode E2high and corresponding FWHM in $V^{4+/5+}$ doped ZnO	82
Table 5.1: V <sup>4+</sup> and V <sup>5+</sup> content in V doped ZnO	129

### Abbreviations

Zinc Oxide	ZnO
Tetraethoxysilane	$(C_2H_5O)_4Si$
Vanadium Pentaoxide	$V_2O_5$
Sodium Nitrate	NaNO <sub>3</sub>
Bandgap	Eg
Urbach Energy	$E_{U}$
Oxygen Vacancies	Vo
Zinc Vacancies	$V_{Zn}$
Zinc Interstitial	Zn <sub>i</sub>
Oxygen Interstitial	O <sub>i</sub>
Zinc antisites	Zno
Oxygen antisites	O <sub>Zn</sub>
Photoluminescence	PL
Full Width at Half Maxima	FWHM
Ultra Violet	UV
Visible	Vis
Diffuse reflectance spectroscopy	DRS
X-ray absorption near edge structure	XANES
X-ray Diffraction	XRD

### **Chapter 1**

### Introduction

Zinc oxide (molecular formula : ZnO) is a multifunctional material, with its unique physical and chemical properties such as high chemical stability, high electrochemical coupling coefficient, high photo stability and broad range of radiation absorption[1,2]. It is recognised as a potential II-VI photonic semiconductor materials due to its wide band gap (~3.3 eV) and high exciton binding energy (~60 meV)[3]. It possesses considerable potential for applications in optoelectronic devices such as UV lasers, LEDs, as electrode in solar cells, gas and bio sensors etc. The last few years have witnessed tremendous efforts on understanding the physical and optical properties of ZnO with particular attention on fabrication and device applications[4]. Many synthesis routes like sol-gel, hydrothermal, co-precipitation, wet chemical method etc has been used to obtain high quality nano/microstructure ZnO material[5]. It is also well established that ZnO optoelectronic properties strongly vary depending on its defect structure based on synthesis techniques.

### **1.1 Crystal Structure:**

ZnO generally crystalizes in three forms: Hexagonal Wurtzite, Cubic Zinc Blende and Rocksalt structure. According to the first principle periodic Hartree-Fock linear combination of atomic orbitals theory, the hexagonal Zinc wurtzite is found to be the most thermodynamically stable form[6]. It belongs to the space group of  $P6_{3}mc$  [6,7] which has two lattice parameters; a= 3.25 Å, c= 5.20 Å and is characterized by two interconnecting sub lattices of Zn<sup>2+</sup> and O<sup>2-</sup> where each anion is surrounded by four cations at the corners of a tetrahedron with a typical *sp3* covalent bonding. The number of alternating planes of tetrahedrally coordinated O<sup>2-</sup> and Zn<sup>2+</sup> ions which are pilled alternately along c-axis (Figure 1.1) describe the Wurtzite structure of ZnO.

### Introduction

The zinc and oxide center in the wurtzite ZnO is tetrahedral and this tetrahedral symmetry plays an important role for polarity of ZnO. Piezoelectricity and pyroelectricity are the direct consequences of polar symmetry of ZnO along hexagonal axis. ZnO is generally found to be n-type structure. This n-type is due to the structural point defect (vacancies and interstitials) and extended defects (threading/planar dislocations). The presence of oxygen vacancies in ZnO lattice gives it n-type conductivity.



Figure 1.1: Alternating planes of  $Zn^{2+}$  and  $O^{2-}$  in wurtzite structure of ZnO

### **1.1.1 Physical property:**

Pure ZnO is white in colour and turns yellow on heating. Its molecular weight is 81.37. ZnO has relative density of 5.607. Under high pressure, the melting point of ZnO is 1900°C and its heat capacity is 9.62cal/deg/mole at 25°C. It is insoluble in water but soluble in acid. During the application of pressure, the lattice becomes compact. At melting temperature, there is volumetric expansion in the lattice.

Applying pressure, supresses the volumetric expansion and therefore delays the melting point.

#### **1.1.2 Opto-electronic property**:

ZnO has a large exciton binding energy around 60 meV at room temperature due to excitonic recombination[8]. This large exciton binding energy makes efficient excitonic emission in ZnO which suggests ZnO a promising material for optical devices at room temperature and higher. The process of optical absorption and emission are very much influenced transition related to dopants or defects which are usually responsible for creating mid gap discrete electronic state[8]. Many reports show that the photoluminescence of ZnO shows green emission and the intensity of green emission increases with decrease particle size and reduced nanowire diameter which gives quantum size effect. The reduction in particle size increases the binding energy and which in turn enhances the opto-electronic property of ZnO nanomaterial.

#### **1.1.3 Optical properties:**

As reported in different literature, the optical band gap of ZnO is 3.44eV at low temperature (4K) and 3.3eV at room temperature[9] which corresponds to energy of 375.75Å photons. So, zinc oxide is transparent to visible light but strongly absorbs ultra violet light below 375.75 Å. Due to this reason, ZnO is used in varieties of optoelectronic applications like Light Emitting Diode (LED's), Solar Cells, photo detectors etc. [6,10–12]. The band gap of ZnO depends upon the carrier concentration; Band gap tends to decrease as there is an increase in carrier concentration. Photoluminescence of ZnO represents a relatively sharp absorption peak at 380nm (due to band to band transitions) and a wider yellow-green emission band (due to presence of oxygen vacancies and other related defects).

### **1.1.4 Electrical Properties:**

ZnO has a wide bandgap of 3.3 eV at room temperature. This wide band gap has many advantages like higher breakdown voltage, ability to sustain large electrical fields, lower electronic noise, high temperature and high-power operation. These properties make ZnO nanomaterial fit for wide varieties of electrical applications. Electron mobility of ZnO strongly dependent on temperature and possess a maximum of ~2000 cm<sup>2</sup>/ (V·s) at 80 K.

#### **1.1.5 Mechanical Properties:**

ZnO is a relatively soft material with approximate hardness ~ 5. Its elastic constants are smaller than other materials belonging to same group. The high heat conductivity, low thermal expansion and high melting temperature of ZnO are some of the basic characteristics of ZnO nanomaterial. High thermal conductivity makes it useful in rubber industry; ZnO is added in the rubber in order to increase the thermal conductivity of tyres. ZnO exhibits high radiation hardness property which makes it useful in space or at high altitude[13,14].

### **1.1.6 Magnetic property:**

Various reports show that room temperature magnetism can be achieved by doping magnetic impurity in ZnO like Fe, Pb, Co etc. But preserving magnetism at room temperature in this material is still a challenge. Despite of many experimental results, the reason behind origin of magnetism in this material is not clear. In some cases, it is explained in terms of segregation of metallic clusters [15] while in other cases it is due to double exchange [16,17]. Double exchange occurs between ions of different oxidation state which predicts the way by which electrons are transferred between two spicies.

#### **1.2 ZnO nanostructures:**

Nanostructures possess unique physical and chemical properties due to their high surface area and nanoscale size. Their optical properties are reported to be dependent on the size, which imparts different colors due to absorption in the visible region. Their reactivity, toughness and other

#### Introduction

properties are also dependent on their unique size, shape and structure. The importance of these materials realized when researchers found that size can influence the physiochemical properties of a substance e.g. the optical properties. A 20-nm gold (Au), platinum (Pt), silver (Ag), and palladium (Pd) NPs have characteristic wine red color, yellowish gray, black and dark black colors, respectively. In fact, much of the interest in nanoscale materials arises from both an understanding of the novel physical, chemical, and size-dependent phenomena on the nanometer length scale and the development and beneficial uses of these materials in a wide-range of applications from environmental remediation and green chemistry to telecommunications and medicine.

The bandgap of the material is changed because of the discretization of the electron energy, which can be controlled by the nanometers size particles. Such quantum dots behave like atoms and become luminescent. Their emission can be continuously tuned through a large spectrum by changing their size. On decreasing the size, the electron gets confined to the particle (confinement effects) leading to increase in bandgap energy and band levels get quantized (discrete).

With reducing size of the particle the density of states becomes more quantized and the bandgap shifts to higher energies (shorter wavelengths). By changing the size of the nanoparticles the frequency of emission can be tailored.

ZnO nanostructures are of intense interest since they can be prepared by a variety of methods and in a range of different morphologies like nanorods, nanobelts, nanoflowers, nanoneedles, nanorings etc. as shown in Figure 1.2. Vapour phase synthesis method is the most extensively and commonly used method by different research group for the synthesis of 1-D nanorods or nanowires. The typical vapour phase synthesis method includes vapour liquid solid (VLS) growth, chemical vapour deposition (CVD), metal organic chemical vapour deposition (MOCVD), physical vapour deposition (PVD), molecular beam epitaxy (MBE), pulsed laser deposition (PLD), and metal organic vapour phase epitaxy (MOVPE). Nano flower and nano belts are mainly synthesized by using hydrothermal, solid state process, pyrolysis, wet chemical

### Introduction

method, precipitation process and many others methods. However, the primary motive of ZnO research is its great potential for a variety of practical applications, such as in optoelectronic devices, energy harvesting devices, electronic devices, sensors, catalysts, active compounds in sunscreens, etc.



Figure 1.2: Various morphologies of ZnO Nanostructures [18]

### **1.3 Synthesis Techniques:**

Most of the present technological applications of ZnO, such as photodetectors, varistors, transparent conductive electrodes for solar cells, piezoelectric devices and gas sensors have made use of polycrystalline material that are synthesized by a variety of techniques like chemical vapour deposition[19–29], sol–gel synthesis[30–36], Hydrothermal[37–46], co-precipitation[47–51], mechanochemical[52–57] etc. Although, range of solution based techniques have been emerged but among these sol-gel is the most versatile technique. This technique offers some advantage over other methods - It provides control over particle size and morphology, allows the use of low temperature during synthesis, reduces the cost and results in a homogenous and highly pure sample.

#### 1.3.1 Sol-gel synthesis route:

Sol-gel process is a known process since the late 1800s. The versatility of the technique has been rediscovered in the early 1970s when glass was produced without high temperature melting process [58].

Sol–gel chemistry is the preparation of inorganic polymers or ceramics from solution through a transformation from liquid precursors to a sol and finally to a network structure called a 'gel' (figure 1.3). A "sol" is a colloidal suspension of solid particles of ions in a solvent. A "gel" is a semi-rigid mass that forms when sol begins to transform into a denser form in between solid and liquid by evaporation of the solvent. Particles or ions are left behind to join together in a continuous network.



Figure 1.3: Schematic diagram of sol-gel synthesis route

Formation of metal oxides involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. After drying process, the liquid phase is removed from gel. In the sol–gel process, there are many different ways that a gel can be formed. Sometimes, the same precursors can result in very different structures with only small changes in
conditions. Generally, gel state is simply defined as a non-fluid 3D network that extends through a fluid phase.

#### 1.3.2 Citrate:

Citric acid is a small organic molecule which often used in sol–gel chemistry is citric acid. Being a weak triprotic acid with three carboxylic acid moieties which are able to dissociate. It is readily available and cheap making it an effective chelating agent. In a typical synthesis, aqueous metal salts (*e.g.* nitrates) are mixed with citric acid and the resulting solution heated to form a viscous solution or gel.

Type of gel	Bonding	Source
Colloidal[59]	Particles connected by	Metal oxide or
	Vander Waals or	hydroxide sols
	hydrogen bonding	
Metal-oxane	Inorganic polymers	Hydrolysis and
polymer[60]	interconnected via	condensation of
	covalent or	metal alkoxides
	intermolecular bonding	
Metal complex[61]	Weakly interconnected	Concentrated metal
	metal complexes	complex solution
Polymer complex I	Organic polymer	Polyesterification
insitu polymerizable	interconnected by	between
complex (Pechini	covalent and co-	polyhydroxy
method)[62]	ordinate bonding	alcohol and
		carboxylic acid
		with metal complex
Polymer complex II	Organic polymer	Co-ordinating
Co-ordinating and	interconnected by co-	polymer and metal
crosslinking	ordinate and	salt solution
polymers[63]	intermolecular bonding	

Table 1.1: Different types of gels used for sol-gel synthesis

Although there are several types of gel (Table 1.1) but citric acid sol-gel method is commonly used for the synthesis of metal oxide powders.

Conversion of 'gel' to a metal oxide is simply achieved by pyrolysis in air, with temperature depending on specific properties of the samples. Using this method, binary, ternary and quaternary metal oxides in both crystalline as well as amorphous forms can be synthesized. The key advantage of this method is the homogeneity of the starting material. As the metal–citrate 'gels' are heated, the organic component undergoes combustion at  $\sim$ 300–400 °C, depending on metal counterion and presence of additives. The organic matrix during the first stages of synthesis can signify when nucleation occurs, the sites are evenly dispersed, ensuring a small crystallite size. The matrix is can also the different metals remain mixed on an atomic scale in the case of ternary or quaternary systems. In this work, sol-gel technique has been used for synthesis of zinc oxide where citric acid is used as a chelating agent.

#### 1.4. Defect Physics and Chemistry in ZnO:

Control of defects and its engineering are most important factor for potential application of Zno in various fields. However, despite of many reports published on ZnO, the relationship between defect chemistry, processing, and properties have not received much attention [64]. Defect studies has been extensively done in the last four decades. However, ZnO is such a material that people find new surprises everyday making it an extremely flexible matter of unending research. Hence, everday people are adding new components which can modify resultant properties of materials based on ZnO. A delicate balance of various defects in ZnO, gives rise to fundamentally newer material characteristics[65–67]. Understand of defects in doped ZnO with aliovalent ions is critically important to achieve certain functionality. The concentration of defects in a lattice depends on its formation energy. If there are N atoms, the equilibrium defect concentration n is given by[68]:

$$\frac{n}{N-n} = \exp(-\frac{E^f}{K_B T})$$

Where  $E_f$  is the formation energy,  $K_B$  the Boltzmann constant and T being the temperature. This equation can be derived by considering free

energy model of the system without taking into account defect-defect interaction.

In the limit n << N, the above equation reduces to a simple form

$$n \cong Nexp(-\frac{E^f}{K_B T})$$

This equation indicates two important facts:

- The equilibrium vacancy concentration decreases with increase of temperature.
- Defects having high formation energies will occur in low concentrations.

Defects introduce levels in the band gap of semiconductors and transition from bands to these levels is responsible for green, blue, violet, yellow and orange-red emissions, but the chemical natures of the defects responsible for these emissions have not been conclusively established shown in figure 1.4. The basic native defects which are present in the ZnO are oxygen vacancies (V<sub>0</sub>), zinc Vacancies (V<sub>Zn</sub>), zinc interstitials (Zn<sub>i</sub>), Oxygen interstitials (O<sub>i</sub>), Oxygen antisite (O<sub>Zn</sub>) and zinc antisite (Zn<sub>0</sub>).



Figure 1.4: Defect structure and its related color emission

#### 1.4.1 Oxygen Vacancies (V<sub>0</sub>):

In determining the physical and chemical properties of ZnO, oxygen vacancies play crucial roles which are a common native point defect.

The oxygen vacancy is the source of unintentional n-type conductivity[69]. Although there are many controversial reports on this fact as few reports suggested that oxygen vacancy (V<sub>o</sub>) in ZnO are +2 charged near the conduction band minimum which establish the fact that oxygen vacancies are dominant donor type defect and responsible for n-type conductivity in ZnO. Other reports suggested that V<sub>o</sub> is a deep rather than shallow donor and therefore cannot contribute to the n-type conductivity. An oxygen vacancy possesses three possible charge states: the neutral oxygen vacancy (V<sub>o</sub>), the singly ionized oxygen vacancy (V<sub>o</sub><sup>•</sup>) (figure 1.5).



*Figure 1.5: Geometry of Oxygen vacancy in* 2+ *charge state*  $(V_o^{2+})$ 

First principle calculations predict that the oxygen vacancies are negative-U centers[70]. As a result, the singly ionized state is thermodynamically unstable, and therefore oxygen vacancies will be either in neutral or doubly charged state, depending on the Fermi level position. The neutral oxygen vacancies have the lowest formation energy, and thus will dominate. The green luminescence band centred around 2.4 eV (510 nm) has been attributed to O vacancies due to an excited-to-ground state transition.

In case of oxygen vacancy in ZnO, formation energy is given by[68]:

$$E^{f}(V_{0}^{q}) = E_{tot}(V_{0}^{q}) - E_{tot}(ZnO) + \mu_{0} + q(E_{F} + E_{VBM})$$

where  $E_{tot}(V_0^q)$  is the total energy of a supercell containing the oxygen vacancy in the charge state q,  $E_{tot}(ZnO)$  is the total energy of a ZnO perfect crystal in the same supercell and  $\mu_0$  is the oxygen chemical potential. Expressions similar to above equation apply to all native point defects. The chemical potential varies with the experimental conditions, which can be either Zn-rich, O-rich or in between, and is, therefore, explicitly regarded as a variable in the formalism.

Oxygen vacancies defects plays vital role in determining functionality of synthesized ZnO material.

#### 1.4.2: Zinc Vacancies (V<sub>Zn</sub>):

Electronic structure of zinc vacancies (Vzn) can be understood by removal of a Zn atom from the ZnO lattice which results in four oxygen dangling bonds and a total of six electrons[68] (figure 1.6). These four oxygen dangling bonds combine into a doubly occupied symmetric state located deep in the valence band and three almost degenerate states in the band gap, close to the valence band maxima (VBM). Only four electrons are present in these three states which therefore can accept up to two additional electrons showing acceptor behaviour of V<sub>Zn</sub> in ZnO. With increasing up Fermi level energy the formation energy of acceptortype defects decreases thereby  $V_{Zn}$  can easily be formed in n-type materials. Whereas, in case of p-type ZnO, formation energy of V<sub>Zn</sub> is very high. Concentration of V<sub>Zn</sub> should be negligible in p-type ZnO. First principle calculation revealed that  $V_{Zn}\ /V_{Zn}\ ^{-1}$  and  $V_{Zn}\ ^{-1}/V_{Zn}\ ^{-2}$ acceptor levels lies 0.1eV-0.2eV and 0.9-1.2 eV above the valence band maxima respectively. According to full potential linear muffin tin orbital potential, transition from conduction band or zinc interstitial to zinc vacancy  $(V_{Zn})$  leads to blue emission.



*Figure 1.6: Geometry of zinc vacancy in -2 charge state*  $(V_{Zn}^{2-})$ 

#### 1.4.3 Zinc Interstitials (Zni):

Zinc interstitial might be the source of n-type conductivity of ZnO. There are two main sites for Zn<sub>i</sub> in the wurtzite structure i.e., one at tetrahedral site and another at octahedral site[68]. At the tetrahedral site, Zni has one Zn and one O as nearest-neighbour atoms, at a distance of ~0.833  $d_0$  ( $d_0$  is the Zn–O bond length along the *c* axis). At the octahedral site, the Zn<sub>i</sub> has three Zn and three O atoms as nearest neighbours at a distance of ~1.07 $d_0$ .



*Figure 1.7: Geometry of zinc interstitial in* +2 *charge state* ( $Zn_i^{2+}$ )

It has been reported that octahedral site is the most stable site for  $Zn_i$ , while  $Zn_i$  at the tetrahedral site is 0.9 eV higher in energy and highly unstable.  $Zn_i$  defects induces a state with two electrons above the CBM. These two electrons are transferred to conduction-band states, stabilizing the +2-charge state ( $Zn_i^{2+}$ ) (figure 1.7). Hence,  $Zn_i$  donate electrons to the conduction band, thus acting as a shallow donor[69]. Formation energy of  $Zn_i$  in n-type ZnO, where fermi level lies near the conduction band minimum, is high. Therefore, concentration of  $Zn_i$  defect in n-type ZnO is very low and unlikely to be responsible for n-type conductivity. While formation energy of  $Zn_i^{2+}$  decreases rapidly when the Fermi level lies near the the Valence Band Minima, making Zn interstitials a potential source of compensation in p-type ZnO. According to full potential linear muffin tin orbital potential,  $Zn_i$  lies ~0.22 eV below conduction band and transition from zinc interstitial (Zn<sub>i</sub>) to valence band leads to Violet emission.

#### 1.4.4 Oxygen Interstitials (Oi):

There are two non-bonded sites for oxygen interstitial ( $O_i$ ) in the wurtzite ZnO i.e., tetrahedral site and octahedral site (figure 1.8). Density functional theory calculations revealed that  $O_i$  at tetrahedral site is unstable and relaxes into a split-interstitial configuration. The calculated O-O bond length in this case is 1.46 Å[69].  $O_i$  at the octahedral site is stable and introduces states in the band-gap that could accept two electrons, so transition levels of  $O_i/O_i^{-1}$  and  $(O_i^{-1}/O_i^{-2})$  are located at 0.5 eV and 1.4 eV above the valance-band maximum, respectively.  $O_i$  do not contribute to n-type conductivity in ZnO. DFT calculation revealed the Zn-O<sub>i</sub> distance is 2.19Å which is somewhat greater than the 1.98Å for the host Zn–O bond-length.



*Figure 1.8: Geometry of Oxygen interstitial in -2 charge state*  $(O_i^{2-})$ 

First-principles studies suggest that the O interstitial are very high in formation energy and/or electrically inactive[71]. These defects are not expected to play important roles under thermal equilibrium. According to full potential linear muffin tin orbital potential, transition from conduction band to  $O_i$  and  $Zn_i$  to  $O_i$  leads to yellow and orange-red colour emission.

#### 1.4.5 Zinc antisites (Zno):

Zinc antisites (Zn<sub>o</sub>) defect originates when zinc atom substitutes at oxygen atom site (figure 1.9). Zn<sub>O</sub> is a double donor in n-type ZnO, but its high formation energy indicates that it is an unlikely source of unintentional n-type conductivity[68]. Electronic structure of Zn<sub>O</sub> involves both deep and shallow donour levels[71]. It has shallow level of (Zn<sub>O</sub><sup>+2</sup>/Zn<sub>O</sub><sup>+1</sup>/Zn<sub>O</sub>) near the conduction band maxima and deep level of (Zn<sub>O</sub><sup>+4</sup> /Zn<sub>O</sub><sup>+3</sup>) and (Zn<sub>O</sub><sup>+3</sup>/Zn<sub>O</sub><sup>+2</sup>) levels located below the middle of the band gap.



*Figure 1.9: Geometry of zinc antisites in* +2 *charge state*  $(Zn_o^{2+})$ 

Formation energy of  $Zn_0$  is even higher than that of  $Zn_i$  under n-type condition. While formation energy of  $Zn_0$  is lower in case of p-type ZnO because of the preference of the highly positive charge states, as is seen in the case of O vacancy and Zn interstitial. Hence,  $Zn_0$  is unlikely to form at a substantial concentration in *n*-type ZnO.

#### **1.4.6 Oxygen antisites (Ozn):**

Oxygen antisites ( $O_{Zn}$ ) defect originates when oxygen atom substitutes at zinc atom site (figure 1.10). The oxygen antisite ( $O_{Zn}$ ) is an acceptortype defect having very high formation energy and electrically inactive, even under the most favourable O-rich conditions. Therefore, concentration of  $O_{Zn}$  defects are very low in ZnO at equilibrium. However,  $O_{Zn}$  could potentially be formed under non-equilibrium

conditions such as under irradiation or ion implantation. It was found that O on the ideal Zn site is unstable and spontaneously relaxes to an off-site configuration[69]. DFT calculation suggested that O–O bond length is 1.46Å in the –2 charge state and 1.42Å in the neutral charge state. The distances between  $O_{Zn}$  and other nearby oxygen atoms are ~2.0 Å, much larger than twice the oxygen covalent radius of 0.73 Å, thus indicating the absence of bonding.  $O_{Zn}$  are deep acceptors with transition levels  $O_{Zn}/O^{-1}_{Zn}$  and  $O^{-1}_{Zn}/O^{-2}_{Zn}$  at 1.52 and 1.77 eV above the VBM.



Figure 1.10: Geometry of Oxygen antisites in -2 charge state  $(O_{Zn}^{2-})$ 

#### **1.5 Photoluminescence:**

In a semiconductor, photons with energy greater than that of the band gap excite electrons from the valence band into the conduction band. In the case of photoluminescence (PL) a laser is the primary means of achieving this. Electrons in an excited state always seek to return to their lowest energy state; in this case the ground state is at the top of the valence band. The question of what happens to the energy lost when transitioning between the conduction band and the valence band is answered in several parts. In semiconductors with a direct band gap and few mid gap energy states, a favourable outcome is the production of a photon, where the energy of the photon corresponds to the band gap of the semiconductor, however energy may also be lost through phonons (vibrations) in the lattice. In a perfect semiconductor, consisting of an infinitely homogenous and isotropic lattice, every emitted photon would exhibit the exact same characteristic energy and the PL. The schematic of the physics behind the PL phenomenon is shown in Fig. 1.11. PL of a semiconductor is largely dependent on the temperature due to the thermal expansion/contraction of the lattice and changes in the electronphonon interaction[72,73].



Figure 1.11: Schematic of Photoluminescence Spectroscopy

#### 1.5.1: Photoluminescence of ZnO:

ZnO defect structure and its related colour emission (optical properties) can be studied using photoluminescence spectroscopy. The majority of reported luminescence spectra of ZnO nanostructures have been measured at room temperature. Room-temperature PL spectra of ZnO typically consist of a UV emission (near band edge) and possibly one or more visible bands due to defects and/or impurities also called deep level emission (DLE)[74]. The typical PL spectra of ZnO nanostructures grown using sol-gel technique is shown in Figure 1.12.

In room-temperature PL spectra, there is a variation in peak position for different nanostructures. Peak positions (387 nm for tetrapod, 381 nm for needles, 397 nm for nanorods, 377 nm for shells, 379 nm for faceted rods, and 385.5 nm for ribbons/combs) can be observed[74].

Since the defect density on the surface is higher than in the bulk, spectral shifts due to different defect concentrations are expected to occur in nanostructures with different sizes due to different surface-to-volume ratios. The defects could affect the position of the band-edge emission as well as the shape of the luminescence spectrum. Therefore, clarifying the origins of different defect emissions is an important issue. However, it should be noted that the ratio of the intensity of Near Band Edge (NBE) ( $I_{NBE}$ ) and Deep Level Emission (DLE) ( $I_{DLE}$ ) is dependent on the excitation density as well as the excitation area[75].





The ratio of NBE and DLE is useful in comparing the quality of different samples when the measurements are performed under identical excitation conditions. Keeping this into account, ratios of areas of NBE (P<sub>NBE</sub>) and DLE (P<sub>DLE</sub>) has also been estimated in this work for more accurate analysis. Yellow-Green emission is the most commonly observed defect emission in ZnO nanostructures similar to other forms of ZnO. Several different hypotheses have been proposed for the explanation of the origin of various deep level emissions: Green emission is often attributed to singly ionized oxygen vacancies although this assignment is highly controversial. Various transitions related to intrinsic defects, such as donor-acceptor transitions, recombination at Vo++ centres (where these centres are generated by surface trapping of photo generated holes, followed by recombination with electron in an oxygen vacancy Vo+), zinc vacancy, and surface defects. The origin of the green emission is still an open and controversial question and the identification of the exact origin of this emission requires further study. Although, green emission has not yet been conclusively identified, there is convincing evidence that it is located at the surface. It was shown that coating ZnO nanostructures with a surfactant suppressed green

emission. Polarized luminescence experiments from aligned ZnO nanorods also indicated that green emission originated from the surface of the nanorods. Also, the possible presence of  $Zn(OH)_2$  and  $OH^-$  at the surface, especially for nanostructures prepared by solution methods, could affect the emission spectra from ZnO nanostructures. Yellow emission (defect related) is very commonly reported in ZnO nanostructures represents a common feature in samples prepared from aqueous solutions of zinc nitrate hydrate and hexamethylenetetramine. This emission is typically attributed to oxygen interstitial, although a Li impurity represents another possible candidate[74]. The deep levels responsible for green and yellow emissions were found to be different; unlike the defect responsible for the green emission, the defect responsible for the yellow emission is not located at the surface[74,76]. In addition to green and yellow emissions, orange-red emissions are also observed. Orange-red emission can be attributed to oxygen interstitials. The orange-red and the yellow emissions exhibit different decay kinetics. Both the emissions involved a similar final state related to excess oxygen but with different initial states (conduction band and donor centres). It should be noted that although the majority of studies attribute red-NIR emission to excess oxygen, zinc interstitials were also proposed to explain the origin of a red emission in ZnO particles. Thus, although this emission is less controversial than the green one, further studies are needed to clarify its origin.

#### **1.6 Doping in ZnO:**

Wide bandgap semiconductors such as GaN, ZnSe, CdTe and metal oxides (like ZnO) show a pronounced doping asymmetry. The materials occur naturally as n-type or p-type and it is quite difficult to achieve stable opposite conductivity by conventional extrinsic doping methods. Impurities and deliberate doping with aliovalent (differently charged) ions have remarkable effects on the defect equilibria. Further Carriers in ZnO are introduced depending on whether the ions have a lower valence (e.g. Li<sup>1+</sup> introduces holes) or higher valence (e.g. Al<sup>3+</sup> introduces electrons) than the Zn. Element doping offers a method to tailor

electrical, optical, and magnetic properties of ZnO. For achieving n-type conductivity in ZnO, group III elements (B, Al, Ga and In), group IV elements (Si, Ge, Sn) on Zn- site and group VII elements (F,Cl) on O-site has been reported[77–81]. Although achieving p-type conductivity in ZnO is difficult but doping group I elements (Li, Na, K, Cu, Ag) on Zn-site & Zn vacancies and group V elements (N, Sb and As) on O-site has been reported to produce p-type conductivity in ZnO[82–86]. Effect of doping on ZnO is determined by three factors i.e., dopant formation energy, dopant ionization energy and dopant solubility.

Doping affects luminescence of ZnO either by modifying native defects of ZnO or by introducing new defect state in ZnO, e.g. red emission in Co doped ZnO[87], yellow-orange-red emission in Mn doped ZnO[88], blue emission in Cu doped ZnO[89], green emission in Tb doped ZnO[90], red emission in [91,92], blue emission in Ce doped ZnO[93] etc. Bandgap also gets modified by doping different materials like Cr, Ni, Cd doping decreases the band gap, whereas Mg, Co and Mn doping increases the band gap[94].

Doping in ZnO modifies carrier concentration, luminescence, electronic structure (bandgap and defects structure) and structural parameters (lattice parameter, strain, c/a etc.) and therefore determines the functionality of the modified ZnO.

#### 1.7 Different functionalities of modified ZnO:

Depending upon structural, opto-electronics, electrical and optical properties, functionalities of ZnO can be determined. Especially, modification of native defect of ZnO on doping or new defects introduced by dopants determine its application. Mechanism behind few applications (like Transparent Conductive oxides, Humidity sensing, Light sensing etc) which has been explored in this thesis is explained here:

#### **1.7.1 Transparent conductive oxide:**

Transparent conductive oxides (TCOs) are those material which are highly transparent to visible light and electrically conductive. TCOs are used as transparent electrodes in Dye sensitized solar cells (DSSC) and

flat panel displays such as liquid crystal displays (LCDs), plasma display panels, electronic paper displays, light-emitting-diodes (LEDs)[95], and touch panels[96,97]. A carrier concentration on the order of  $10^{20}$  cm<sup>-3</sup> or higher and a band-gap energy above 3 eV are usually required for high conductivity and transmittance[98]. Various TCOs material like impurity-doped SnO<sub>2</sub> (SnO<sub>2</sub>: Sb and SnO<sub>2</sub>: F), In<sub>2</sub>O<sub>3</sub> (In<sub>2</sub>O<sub>3</sub>: Sn, or ITO), and ZnO (ZnO:Al and ZnO:Ga) have been researched so far in this field [5, 6]. Among them, tin-doped indiumoxide (ITO) is the one in practical use[99,100]. But due to its high cost, scarcity of Indium, toxicity and thermal instability, alternative material is required[95].

Fortunately, ZnO may be a promising alternative to the commonly used ITO, because of being low cost, nontoxic, thermally stable, highly durable in comparison to ITO[101]. Besides, it has a more proper work function for the transparent contact cathode electrodes of transparent OLEDs[102]. Pure ZnO is resistive and absorbs visible light due to presence of defects in the lattice. Doping of appropriate material in appropriate concentration in ZnO can make it a promising candidate for TCOs. Several reports are available on doped ZnO TCOs.

Several reported elements such as B, Al, Ga, In, F etc are doped in ZnO. Among them Al-doped ZnO and Ga-doped ZnO are most studied for TCOs applications due to its high transparency, high conductivity and thermal stability. Although, Al-doped ZnO and Ga-doped ZnO have capacity to become TCOs material but they cannot withstand high humid condition. At high humid condition, they start degrading their electrical properties as suggested by few reports[103–106]. In this thesis, Silicon doped ZnO is proposed to be a strong candidate for TCOs application which can withstand high humid condition (explained in further chapters).

# **1.7.2 ZnO as electron transport layer in Organic photovoltaics/Dye sensitized solar cells:**

Organic photovoltaics (OPVs) is nowadays a promising energy technology in the field of renewable sources due to its low cost, light weight, flexibility and easy manufacturing.



*Figure 1.13: Schematic of OPVs using ZnO as Electron Transport Layer (ETL)* 

In this device configuration as shown in figure, the bottom transparent electrodes (TCOs) are modified by interlayers with low work function, which is known as electron transporting interlayers (ETLs). Photo stability of organic photovoltaic devices is a key requirement for commercialization of this technology which is major challenge nowadays due to surface defects of ETL material. A variety of solution based methods used to synthesize ETL materials have been demonstrated. Metal oxides such as zinc oxide (ZnO), titanium oxide  $(TiO_2)$  and aluminum oxide  $(Al_2O_3)$  have been widely investigated as electron extraction layers (ETL) in inverted organic solar cell devices[107]. In particular, ZnO has drawn special interest due to its appealing properties, such as excellent visible transparency, high electron mobility, environment-friendly nature, and ease of fabrication. In addition, ZnO can be synthesized in the form of nanoparticles (ZnO NPs) which can be deposited from solution generating thin films with high conductivity without the need of strong thermal treatments. The major problem with the ZnO used as an ETL in solar cells: Under dark condition, O<sub>2</sub> molecules captures electrons from the conduction band of ZnO and gets chemisorbed which reduces the conductivity of the material. This chemisorption actually occurs on the surface defects (oxygen vacancies) created during synthesis process. Under UV irradiation, oxygen molecules can be released from the ZnO layer leading to an improvement of the ZnO conductivity. Although light

irradiation could restore the conductivity of ZnO but prolonged illumination could induce irreversible degradation. Moreover, these intra-gap states which is produced due to surface defects act as recombination centres for photo generated charge carriers, causing significant photo current loss[108]. Hence, there is a need of alternative materials for ETL which shows low surface defects and low trap states and therefore do not get affected by oxygen and water molecules. Doping other element in ZnO structure, surface passivation, synthesizing under special environment etc are few reported ways to reduce/remove the surface defects.

#### 1.7.3 Humidity sensing:

Humidity sensors are very important device which are used in monitoring the environmental moisture for human comfort. Humidity sensors can also be used in automotive, medical, construction, semiconductor. meteorological and food processing industries[109,110]. Several sensing principles can be used for these purposes, but solid-state sensors are an attractive choice due to their low cost and functionality. In this field, several materials (ceramics, semiconductors and polymers) have been tested and have shown diverse results related to humidity sensing. Metal oxide semiconductors such as tin oxide (SnO2), zinc oxide (ZnO), tungsten oxide (WO3) and iron oxide (Fe2O3) are the most popular humidity sensing materials. ZnO is commonly used due to its high thermal stability, low cost, abundancy and non-toxicity. Development of an ideal humidity sensor depends on some key criteria, such as accuracy, power consumption, precision, repeatability, long-term stability, response time, size, packaging, and cost. There are two different humidity sensing mechanism depending upon the particle size and morphology shown in figure 1.14. For nanoparticle size between 2 nm to 100 nm, capillary condensation process occurs[111–114]. In this process, with increase in Relative Humidity  $(R_H)$ , water molecule gets adsorbed on the surface and forms a path. Electrons, which were earlier flowing through ZnO surface, will now flow through the water channel due to high resistivity of the surface which increases the conductivity. In this mechanism, conductivity of the ZnO increases with increase in  $R_{\rm H.}$ 



Figure 1.14: Humidity sensing mechanism in ZnO showing two different process depending upon particle size

While for particle size >100 nm (especially nanorods), inverse behavior takes place[115,116]. The hydrogen sites of water molecules are positively charged due to high electronegative nature of oxygen as compared to hydrogen. At high relative humidity, these charged hydrogen sites capture free electrons from the conduction band of ZnO and reduces the conductivity. In this mechanism, conductivity of the ZnO decreases with increase in  $R_{\rm H}$ . In order to get high humidity sensitivity, different dopant has been introduced in ZnO to create more active adsorption sites for water molecules.

#### 1.7.4: UV sensing in ZnO:

Ultraviolet detection is becoming important nowadays related to various important aspects of science/technology associated with health, environment and even space research[117,118]. Sensitive silicon based UV detectors are already available in market. But these detectors require costly visible light filters as they are sensitive to visible light. Faster, more sensitive, cost-effective UV detection is therefore an important research area. GaN, SiC and diamond are promising candidates[119–121]. But all of these are expensive materials.



Figure 1.15: UV sensing mechanism in ZnO showing adsorption/ desorption under dark/light condition

ZnO is an abundant, inexpensive, non-toxic and environmental friendly material with good thermal/chemical stability and high photoconductivity. UV sensing and response in ZnO, mainly depend on the surface reaction and therefore, surface defects, grain size and oxygen adsorption properties[122–124]. The mechanism of UV sensing is shown in figure 1.15. When the ZnO material is kept in the dark conditions, the oxygen molecules get adsorbed on the surface of the ZnO by capturing free electrons from n-type ZnO

$$O_2(g) + e^- \rightarrow O_2^-(ad)$$

Which forms a high resistance region near the surface of ZnO. The electron-hole pairs are generated

$$h\nu \rightarrow e^- + h^+$$

when the ZnO surface is illuminated UV light. The photo generated holes oxidize the adsorbed oxygen molecules

$$O_2^-(ad) + h^+ \rightarrow O2(g)$$
]

Oxygen molecules get desorbed from the surface of ZnO nanoparticles, increasing free carrier concentration and producing a large photocurrent. However, pure ZnO materials typically exhibit a relatively poor UV sensing performance due to the large n-type carrier concentration as well as fast recombination rate of photoexcited electron–hole pairs. To resolve this fundamental issue, defect engineering and doping processes have been applied to tailor certain properties of ZnO.

As discussed, the important of defect modification for achieving different functionality of ZnO. Defect engineering can be done in many ways. In this work, defect engineering has been done targeting an investigation of valence state and size of dopant. As ZnO is inherently oxygen deficient, this work relates the charge state of the dopant and related modifications. Hence, we have targeted three different series of aliovalent ion dopant to answer the importance of dopant element and its properties. In present work, Si<sup>4+</sup> (for observing the effect of higher charge of metalloid), Si<sup>4+</sup>/Na<sup>1+</sup> (for observing the effect of charge compensation) and V<sup>5+</sup> (for observing the effect of higher charge of transition metal) has been doped in ZnO lattice. The modified structural and opto-electronic properties determine functionality of ZnO material. The research work reported in present thesis has been accomplished systematically in following manner

- (i) Synthesis of pure and doped ZnO samples
- (ii) Analysis of structural properties of pure ZnO (strain. Lattice parameters etc) and its variation on doping.
- (iii) Analysis of opto-electronics properties of ZnO and its variation on doping/co-doping other elements
- (iv) Studying the co-relation between structural and optoelectronics properties.
- Investigation of functionalities of synthesized samples depending on its structural and opto-electronics properties
- (vi) Understanding of mechanism behind proposed functionalities.

The remaining chapters of thesis are summarized as follows:

#### **Chapter 2: Experimental Details:**

This chapter covers - procedure used for the synthesis of pure and doped ZnO samples, basic description of characterization techniques and description of the inhouse fabricated set up used for testing functionalities of the material. Presently used techniques includes, Lab source x-ray diffraction (XRD), x-ray absorption near edge structure (XANES), UV-Vis spectroscopy, Raman spectroscopy,

Photoluminescence etc. The basic working principle along with the schematic representation of used set-ups and attachments is discussed in detail.

#### Chapter 3: Structural properties of pure and modified ZnO;

This chapter presents an observation of effect in structural properties of ZnO on doping it with Silicon, Silicon/Sodium and Vanadium. Analysis of lattice parameters, particle size and strain has been done by Rietveld refinement using GASUS software. Oxidation state of vanadium doped in ZnO has been determined using Athena software from XANES. Deep analysis of structural properties of ZnO on doping has been done in this chapter.

#### **Chapter 4: Opto-electronics properties of pure and modified ZnO:**

This chapter provides an analysis of opto-electronic properties of ZnO and its variation on doping Silicon, Silicon/Sodium and Vanadium. Luminescence properties has been studied using Photoluminescence spectroscopy of all samples. Quantitative analysis of each defect state has been done. Co-relation between structural properties and optoelectronics properties has been analyzed and established in this chapter.

#### **Chapter 5: Multi-functional application of synthesized material.**

In this chapter, based on structural and opto-electronic properties, appropriate application of synthesized material has been determined. Functionalities like light sensing, UV sensing, humidity sensing has been carried out. Mechanism behind enhancement of functionalities on doping has been proposed.

#### **Chapter-6: Conclusions and Future Research Scope;**

This chapter summarizes the results of present research work with concluding remarks. The possible future scope of present study has also been discussed.

28

## Chapter 2

### **Experimental Details**

This chapter provides basic information about the synthesis procedure (sample preparation) and characterization techniques used in present research work. All presently studied samples have been prepared using solgel synthesis routes. As far as characterization techniques are concerned, we have performed (i) X-ray diffraction (XRD) to confirm the formation of structural phase, (ii) FESEM to study morphology and size of the material (iii) EDS to confirm chemical composition of the material (iv) Raman spectroscopy to study the changes in vibrational modes in pure and  $Si^{4+}/Na^{1+}Si^{4+}/V^{5+}$  doped ZnO (v) UV-Vis spectroscopy to study the band gap tailoring affected by the defect states generated by doping (vi) Photoluminescence spectroscopy to study the defect states and related optical properties (color emission) of the materials. (vii) XANES to estimate the oxidation state of Vanadium. Different software like GSAS, Athena, Fullproof, etc. has been used for analysis of structural and physical properties. Further, more specific details about synthesis of samples and characterization techniques are discussed accordingly in the 'experimental' section of each forthcoming chapter. The functionalities of these materials were looked into in the domains of humidity/light sensing and their utilization capabilities as transparent conductive oxides and UV sensors.

#### 2.1 Synthesis Process:

ZnO nanoparticles were synthesized by sol-gel method[58] (standard Pechini method) followed by solid state sintering. Schematic diagram and experimental steps evolved in nano powder synthesis using sol-gel technique [figure 2.1 (a, b)].

ZnO powder (Alfa Aesar, purity 99.9%) was dissolved in HNO<sub>3</sub> [*ZnO* +  $2HNO_3 \rightarrow Zn(NO_3)_2 + H_2O$ ] to form a Zn solution. A polymeric solution was formed by concentrated glycerol (Alfa Aesar, 99.9%) in de-ionized water at 70°C for 4hrs. The Zn solution was then added to the polymeric solution. This solution was stirred and heated on hot plates at ~60°C to obtain finally "gel-ready solution". The Zn ions get attached homogenously to the chains of the polymeric solution. The solution was gradually dehydrated to form gel in ~4hrs.

 $Zn(NO_3)_2 + C_6H_8O_7 + C_3H_8O_3 \rightarrow$   $----(C_2H_5-O-Zn-O-C_2H_5)_{\overline{n}} \rightarrow$   $\rightarrow ZnO + H_2O + N_2 + CO_2 \rightarrow$ 

The gel was burnt on hot plates in ambient conditions to obtain yellowish white colored powders. These resultant powders were decarbonized and denitrified by heating in air at 450°C for 6 hours to form white powders of ZnO. The powders were further annealed at 600°C for 2 hours. For electrical characterization, the obtained white powders were pelletized under 4T pressure and sintered at 1000°C for 4hr.



Figure 2.1: (a) Schematic diagram of Sol-gel synthesis route

#### **2.1.1 Doped Sample Preparation:**

For all doped samples the final "gel-ready solutions were prepared by obtaining a mixed solution of the constituent elements in the right proportions. For all doped samples the gels were burnt, decarbonized and denitrified similar to the process discussed in Section 2.1.



Figure 2.1:(b) Step by step experimental pictures for Nano powder synthesis using sol-gel technique.

Annealing temperature and time was chosen by considering solubility limit of dopant. In case of Si and Si/Na doped ZnO, annealing temperature chosen was 600°C since beyond it, secondary phase of  $Zn_2SiO_4$  is observed. While, in V doped ZnO, secondary phase of  $Zn_2V_2O_7$  (Zinc Vanadate) peaks is observed above 500°C. Annealing time chosen was 2hr for all samples since at a lower growth time, the formation of small particle is kinetically favored. The formation of small particles reduces the super saturation and hence the possibility of coalescing/agglomerating. The processes of obtaining these solutions are detailed in the following sections.

#### a) Si<sup>4+</sup> doped ZnO synthesis:

 $Zn_{(1-x)}Si_xO$  were synthesized for x=0, 0.013, 0.020 and 0.027 and named Z0, ZS1, ZS2 and ZS3 respectively. Tetraethyl Orthosilicate [(C<sub>2</sub>H<sub>5</sub>O)<sub>4</sub>Si] (Alfa Aesar (99%)) was used as a precursor for Si<sup>4+</sup>. Appropriate amount of

Si precursor was dissolved in distilled deionized water (DDIW). These Si solutions were then added to appropriate amount of Zn solution (prepared similarly as Section 2.1) to achieve Z0, ZS1, ZS2 and ZS3.

 $(C_2H_5O)_4Si + H_2O \rightarrow OH-(C_2H_5O)_3 - Si + C_2H_5OH$ 

The obtained homogenous mixtures containing Zn and Si ions were rigorously stirred for several hours to obtain the "gel-ready solutions".

$$Zn(NO_3)_2 + OH - (C_2H_5O)_3 - Si + C_6H_8O_7 + C_3H_8O_3 \rightarrow$$

$$(C_2H_5 - O - Zn - O - C_2H_5 - O - Si - O - C_2H_5)_n \rightarrow$$

$$\Rightarrow Zn_{1-x}Si_xO + H_2O + N_2 + CO_2$$

#### b)Na<sup>+1</sup>/Si<sup>4+</sup> co-doped ZnO synthesis:

 $Zn_{(1-x)}Si_{x/3}Na_{2x/3}O$  were synthesized for x=0, 0.013, 0.020 & 0.027 and named Z0, ZS1, ZSN2 and ZSN3 respectively. Sodium nitrate (NaNO<sub>3</sub>) was dissolved in DDIW and used as a precursor for sodium. Si precursor was the same as discussed in Section 2.1.1 (a). Ratio of Si<sup>4+</sup>: Na<sup>1+</sup> was maintained as 1:2.

 $(C_2H_5O)_4Si + H_2O \rightarrow OH - (C_2H_5O)_3 - Si + C_2H_5OH$ 

 $NaNO_3 + H_2O \rightarrow NaOH + HNO_3$ 

The solution of Na/Si was poured to the Zn solution in required proportions and rigorously stirred for 2h to obtain homogenous "gel-ready solutions".  $Zn(NO_3)_2 + OH - (C_2H_5O)_3 - Si + NaOH + C_6H_8O_7 + C_3H_8O_3 \rightarrow (C_2H_5 - O - Zn - O - C_2H_5 - O - Si - O - C_2H_5 - O - Na - O - C_2H_5)_n \rightarrow Zn_{1-x}Si_{x/3} Na_{2x/3}O + H_2O + N_2 + CO_2$ 

#### c) V<sup>4+/5+</sup> doped ZnO synthesis:

 $Zn_{(1-x)}V_xO$  were synthesized for x=0, 0.0078, 0.015 and 0.023, were synthesized and named Z0, ZV1, ZV2 and ZV3 respectively. Vanadium Pentoxide (V<sub>2</sub>O<sub>5</sub>) (Alfa Aesar (99%)) dissolved in ammonium hydroxide (NH<sub>4</sub>OH) was used as a precursor for vanadium.

 $V_2O_5 + 2NH_4OH \rightarrow NH_4VO_3 + H_2O$ 

This vanadium solution was then added to Zn solution (Section 2.1) to achieve Z0, ZV1, ZV2 and ZV3. The obtained homogenous mixtures containing Zn and V ions were rigorously stirred for 2h to obtain homogenous "gel-ready solutions".

$$Zn(NO_3)_2 + NH_4VO_3 + C_6H_8O_7 + C_3H_8O_3 \rightarrow$$

$$----(C_2H_5 - O - C_2H_5 - O - V - O - C_2H_5)_n \rightarrow$$

$$\Rightarrow Zn_{1-x}V_xO + H_2O + N_2 + CO_2 \rightarrow$$

#### 2.1.2. Denitrification and Decarbonization of synthesized pure ZnO:

Sol-gel processed pure ZnO powders need to be heated at a specific temperature in order to remove carbon, nitrates, moisture, and other undesirable material.



Figure 2.2: Thermogravimetric analysis of pure ZnO in temperature range of  $0^{\circ}$ C to 700°C showing loss of adsorbed water, nitrates and carbonates

The denitrification and decarbonization temperature is known as calcination temperature. Different materials have different calcination temperature

#### **Experimental Details**

which varies with synthesis condition and synthesis technique. In order to optimize the calcination temperature, thermogravimetric (TGA) analysis has been done as shown in figure 2.2. The TGA curve for ZnO shows a weight loss of ~12 % in the temperature range of 0°C to 700°C due to escape of adsorbed water molecules, nitrates, carbon and other undesirable materials. The weight of ZnO starts decreasing at 350°C and losses ~16% of weight at 400°C. The first step is in the range of 50°C to about 190°C, demonstrating the loss of surface-adsorbed water. The second step, which is a major weightlessness step, occurs in the range of 190°C to about 350°C with no further weight loss up to 700°C temperature, indicating the loss of carbonates and nitrates[125,126].

Considering the experimental evidence of removal of undesirable materials from the sample above 350°C, all synthesized undoped and doped ZnO samples in this thesis work were calcined at 450°C for 6 h.

#### **2.2 Characterization Techniques**

Structural characterization techniques are briefly discussed below.

#### 2.2.1 X-Ray Diffraction:

X-ray diffraction (XRD) is a basic and reliable probe to assess the structure and hence the phase of a material. Using the fact that interatomic distances (d-spacing) of all matter are of the same order as X-rays wavelength,  $\lambda$  (~Å), X-ray diffraction is a non-destructive method of assessing the d-spacing, and therefore the lattice constants. Strain and nano-crystalline size can also be estimated using XRD data. X-ray falls at an incidence angle,  $\theta$ , and gets diffracted by sets of atomic planes of the crystal lattice. When, d and  $\theta$ satisfy the condition that the path difference between diffracted rays generated by two parallel planes equals a multiple of  $\lambda$ , Bragg relation,  $2dsin\theta=n\lambda$  (where, n is an integer) is satisfied and a constructive interference takes place. A schematic ray diagram best explains the Bragg condition [figure 2.3]. By analyzing these constructive interference



patterns, one can calculate the d-spacing and therefore the crystal structure.

Figure 2.3: Diffraction of X-rays through lattice/atomic planes of a crystal (indicating Bragg's law)

Geometrical path difference,  $\Delta$ , between two rays, ABC and A'B'C',  $\Delta = N'B' + B'N = BB'Sin\theta + BB'Sin\theta = 2BB'Sin\theta = 2dSin\theta \dots (2.1)$ 

For constructive interference, path difference must be an integer multiple of wavelength, i.e.,

Thus, from equations 2.1 and 2.2, the Bragg's condition for constructive interference of diffracted X-rays is

 $2dSin\theta = n\lambda....(2.3)$ 

where, n is an integer.

The diffracted X-ray photons are detected and counted by a detector. Peaks arise whenever Bragg's condition is satisfied at specific  $\theta$  values corresponding to particular sets of planes. Conversion of diffraction peaks to d-spacing enables identification of the material under investigation. XRD patterns of each material are unique and are signatures of the materials' structural phase. This uniqueness of a set of d-values for a particular material identifies and validates the purity of a structural phase for given a material and provides information about the crystal structure, lattice parameters, bond angles, grain size, strain etc.



Figure 2.4: Schematic of XRD setup with different angles of rotation

Samples in powder, pellet or film forms can be probed for structural studies using XRD. Schematic of a typical x-ray diffractometer is shown in figure 2.4.  $\theta$  is the angle of incidence. Therefore,  $2\theta$  is the angle of diffraction, i.e. the angle between incident beam and diffracted beam.

#### 2.2.2 X-ray absorption spectroscopy (XAS):

X-ray absorption spectroscopy (XAS) is used to determine local geometric and/or electronic structure of matter. The experiments are usually performed at synchrotron radiation source, which provides intense and tunable X-ray beam. Wavelength of x-rays ranges from 25~0.25Å. Therefore, energy of X-rays ranges from 500eV~500 keV. The wide range of x-ray energy enables x-rays to eject electrons from different levels of an atom, including the core level. When incident x-ray energy equals the binding energy of a core shell (e.g. 1s or 2p level) of a constituent element of the material, the x-ray is absorbed and the core electron lifted to an excited level. This abrupt increase in absorption cross-section gives rise to an absorption edge in the absorption versus photon energy plot. The edges for an atom can be named according to the principle quantum number of the electron that is, K for n=1, L for n=2, M for n=3, etc.



Figure 2.5: The photoelectric effect; an x-ray is absorbed and a core level electron is promoted out of the atom. Inset shows schematic for x-ray absorption measurements: An incident beam of monochromatic x-rays of intensity I<sub>0</sub> passes through a sample of thickness t, and the transmitted beam has intensity I.

The core–electron binding energy increases with increasing atomic number, ranging from 284 eV for the C (carbon) K-edge to 115606 eV for the U (uranium) K- edge, with the L-edges at significantly lower energies than that of the corresponding K-edge. For a particular electronic core level electron to absorb the incident light, the binding energy of this core level must be less than the energy of the incident x-ray. X-ray Absorption Near Edge Structure (XANES) or Near Edge X-ray Absorption Fine Structure (NEXAFS) deals with the detailed study near the absorption edge which is rich with the information of bonding type and valence state of the composite elements. The edges carry information on the structural distortion and changes in hybridization of the bonding between the elements.

#### **Experimental Details**

On the other hand, the scattering of an incident wave by the local arrangement of elements results in a complex interference pattern in the extended range of x-ray energies beyond the edge. The full implications of this process when applied to molecules, liquids, and solids will give rise to XAFS. When discussing x-ray absorption, we are primarily concerned with the absorption coefficient  $\mu$ , which gives the probability that x-rays will be absorbed according to Beer's Law[127]:

where,  $I_0$  is the x-ray intensity incident on a sample, t is the sample thickness, and I is the intensity transmitted through the sample, as shown in the inset of Figure 2.5. The x-ray intensity is proportional to the number of x-ray photons. The absorption coefficient  $\mu$  is a smooth function of energy, with a value that depends on the sample density  $\rho$ , the atomic number Z, atomic mass A, and the x-ray energy E roughly as

$$\mu \approx \frac{\rho Z^4}{A E^3} \dots (2.5)$$

The strong dependence of  $\mu$  on both Z and E is a fundamental property of x-rays, and is the key to why x-ray absorption is useful for different applications.

In XAS, when the energy of the incident x-ray equals to that of the binding energy of a core-level electron, a sharp rise in absorption takes place; an absorption edge in  $\mu$  versus *E* curve appears corresponding to the promotion of this core level electron to the continuum. An XAFS measurement is simply a measure of the energy dependence of  $\mu$  at and above the binding energy of a known core level of a known atomic species. Since every atom has core-level electrons with well-defined binding energies, the x-ray energy can be tuned according to the absorption edge of a selected element. The edge energies vary with atomic number roughly as  $Z^2$ . Following an absorption event, the atom is said to be in an excited state, with one of the core electron levels left empty (a so-called core hole) and a photo-electron comes out (figure 2.5). The excited state will eventually decay typically

#### **Experimental Details**

within a few femto seconds of the absorption event. Note that this decay does not affect the x-ray absorption process. After an x-ray absorption event, there are two main mechanisms for the decay of the excited atomic state. The first of these is x-ray fluorescence, in which a higher energy corelevel electron fills the deeper core hole, ejecting an x-ray of well-defined energy. The fluorescence energies emitted in this way are characteristic of the atom, and can be used to identify the atoms in a system, and to quantify their concentrations. For example, an L or M shell electron dropping into the K level gives the K fluorescence line. The second process for deexcitation of the core hole is the Auger Effect, in which an electron drops from a higher electron level and a second electron is emitted into the continuum (and possibly even out of the sample).

In the hard x-ray regime (> 2 keV), x-ray fluorescence is more likely to occur than Auger emission, but for lower energy x-ray absorption, Auger processes dominate. Either of these processes can be used to measure the absorption coefficient  $\mu$ , though the use of fluorescence is somewhat more common.

XAFS/XANES can be measured either in transmission or fluorescence geometries as shown in figure 2.6. The geometry for Auger measurements is typically the same as for fluorescence, except the position of detector, as in fluorescent mode it is at a right angle to the incident beam (figure 2.7) unlike to transmission mode, where, the detector is placed in line with the beam.

39



Figure 2.6: Decay of the excited state: (a) x-ray fluorescence and (b) the Auger effect. In both cases, the probability of emission (x-ray or electron) is directly proportional to the absorption probability

The fluorescence is emitted isotropically, whereas the other scatter is actually not emitted isotropically because the x-rays from a synchrotron are polarized. The polarization means that elastic scatter is greatly suppressed at 90°, thus in fluorescence mode, detectors are normally placed at a right angle to the incident beam to the incident beam, in the horizontal plane.



*Figure-2.7: Schematic of XAFS/XANES setup in fluorescence mode; fluorescence detector at a right angle with the incident x-ray beam.* 

Eventually, the energy dependence of the absorption coefficient  $\mu(E)$  can be measured either in transmission as

 $\mu(E) = \log(I_0/I)$  .....(Eq. 2.6) or, in x-ray fluorescence mode as  $\mu(E) \propto (I_f/I_0)$  ......(Eq. 2.7) where,  $I_f$  is the monitored intensity of a fluorescence line associated with absorption process. For present research work, V K-edge XANES measurements were performed in fluorescence geometry to determine the charge state of V as the charge state determination by means of XANES is already being used[128].

#### 2.2.3 Field Emission Scanning Electron Microscope (FESEM):

Morphological study of specimen has been carried out using FESEM[129]. In this work FESEM images were recorded using Supra T M 55; Carl Zeiss.



Figure 2.8: Schematic Diagram of FESEM instrument
In FESEM, electrons are incident on the surface atoms, very similar to visible light falling on matter. Due to a much smaller size of electron as compared to visible light it can resolute much better and can thereby see the sample's surface, topography, morphology. The energized electrons sometime while interacting with the atoms are capable of knocking x-ray from the same, by analyzing the x-ray spectrum, and thereby the composition of the materials.

The interaction of electron and matter results in emission of secondary electrons (SEs), backscattered electrons (BSEs), Auger electrons, X-rays, etc. A FESEM instrument uses (i) SEs and (ii) BSEs for generation of images, x-rays for elemental analysis.

#### (a) Secondary electrons

Secondary electrons originate from the surface or near-surface region of the samples as a result of inelastic interaction between primary electron beam and the samples. They have lower energies (E < 50eV) and therefore electrons are ejected within few nanometers of the sample surface. In the work, the ejected electrons are detected by Everhart-Thornley detector.

#### (b) Backscattered electrons

Backscattered electrons originate from broad region within the interaction volume. They generate due to elastic interaction between electrons (from electron gun) and atoms in the specimen which results in a change in electron trajectory. Backscattered electrons (BSE) consist of high-energy electrons (E > 50eV), that are reflected by the specimen interaction volume by elastic scattering interactions with specimen atoms. Solid state detectors are used to detect backscattered electrons.

#### (c) Imaging in SEM

When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption. This interaction volume extends from less than 100 nm to approximately 5  $\mu$ m into the surface. The size of the interaction volume depends on the electron's energy, the atomic

number of the specimen and the specimen's density. The energy exchange between electron beam and sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current.

#### 2.2.3.1 Construction of instrument

The SEM requires an electron probe, a specimen stage to place the specimen, a secondary-electron detector to collect secondary electrons, a solid-state detector to collect backscattered electrons, an image display unit, and an operation system to perform various operations. Schematic diagram of FESEM instrument is shown in figure 2.8.

#### (a) Electron source

The illumination system of FESEM consists of an electron source which is maintained at a negative potential. The emitted electron beam, which typically has an energy ranging from a 100 eV to 30 kev, is passed through a magnetic lens system.

#### (b) Condenser lens and objective lens

The electron beam is further focused by a condenser lens to a spot  $\sim 0.4$  - 5 nm in diameter. Two-stage lenses are located below the electron gun. The objective lens determines the final diameter of the electron probe up to 5 to 10 nm.

#### (c) Detector

A scintillator is coated on the tip of the detector and a high voltage of about 10 Kev is applied to it. The electrons hit the scintillator and generate light. Secondary electrons are detected by Everhart-Thornley detector. These electrons are accelerated towards a phosphor or scintillator positively biased to about +2,000 V. The accelerated secondary electrons are sufficiently energetic to emit flashes of light by the scintillator. A light pipe carries the photon signal from the scintillator inside the evacuated specimen chamber of the SEM to the photomultiplier outside the chamber. The amplified electrical signal output by the photomultiplier is displayed as a twodimensional intensity distribution that can be viewed and photographed on an analogue video display, or subjected to analog-to-digital.

The Everhart-Thornley detector is inefficient for the detection of backscattered electrons because it is positioned to one side of the specimen and also low positive charge cannot attract high energy electrons. Therefore, solid state detectors are normally used having a p-n junction. Electrons which escape the sample are absorbed by the detector and electron-hole pairs are generated. The number of these electron-hole pairs depends on the energy of backscattered electrons. One of the two electrodes of the p-n junction attract electrons while the other holes, thereby generating an electrical current. The value of the current is therefore proportional to number of backscattered electrons. The results are displayed on a liquidcrystal display (LCD).

#### 2.2.4 Raman spectroscopy:

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational and other low frequency phonon modes in a system[130]. It relies on inelastic scattering (Raman scattering) of monochromatic light (usually from a laser in the visible, near infrared or near ultraviolet range). The experimental set-up of Raman spectroscopy is shown in figure 2.9.



Figure 2.9: Experimental set-up of Micro Raman spectroscopy

Laser light interacts with phonons i.e. molecular vibrations in the system, resulting in modification of light. The modification gives information about the energy of the phonons of the system. The reflected light from the illuminated spot is collected with a lens and sent through a monochromator. Most of the reflected light is elastically scattered and is of the same wavelength as of the incident laser line (Rayleigh scattering). This is filtered out by either a notch filter or a band pass filter. Rest of the collected light is dispersed onto a detector. Spontaneous Raman scattering is typically very weak. Separating the weak inelastic Raman scattered light from the intense Rayleigh scattered laser light is a criticality. In this work Raman measurement was carried out on a RIR-M151 Research India micro-Raman system at room temperature, using 532 nm line of diode laser as an excitation source with 75 mW power.

#### a) Laser:

Diode laser (Research Spectra) was used as an excitation source for Raman scattering experiments. Laser emission was accompanied by many spurious spontaneous emission lines which must be eliminated to avoid interference with the Raman emissions. Therefore, a laser-filter monochromator with a band pass of 1.0 nm (and transmission of 75 %) was used to eliminate the undesired plasma lines.

#### b) Filter and microscope:

Standard microscope with three planoachromatic objectives 10X, 50X and 100X, optically adapted to the aperture of the instrument. Other objectives with lower magnification can be used without a correct aperture adaptation which might introduce some vignetting effect. With the microscope, incident and scattered optical axis are identical i.e. back scattering geometry. Notch filters are used to remove Rayleigh scattering and pass Stokes and Anti-Stokes spectra. Normal mirrors and folding mirrors are used to focus the laser towards samples.

#### c) CCD detector and recording system

For this system, Peltier cooled CCD was used, working at ~215K is selected to offer highest performance to the system. Spectrometer is controlled by Research India software. The computer controlled scan range, integration time, scan speed and different scan units are available with the software.

#### 2.2.5 Photoluminescence spectrometer

Photoluminescence spectroscopy is a contact-less, versatile, nondestructive method of probing the electronic structure of a material[73]. Typically, a laser beam in incident on a sample. The energy of light is chosen such that the light may be absorbed, i.e.,  $E \ge E_g$ . Energy absorbed by the material can be dissipated through subsequent radiative/non-radiative transition of electrons to defect states or valence bands. The radiative decay results in emission of light. Schematic diagram of photoluminescence is shown in figure 2.10.

The basic equipment setup consists of two main parts:

- (1) Light source to provide excitation
- (2) Detection system to collect/analyze photons emitted from sample.

**Experimental Details** 



Figure 2.10: Schematic of experimental set up for PL

#### a) Excitation source

Helium cadmium (He-Cd) laser is used as a source for Ultra-Violet (UVA ~325 nm) output for the photoluminescence spectrometer. He-Cd lasers have excellent beam quality. They have been used extensively for diffraction grating fabrication, spectroscopy, non-destructive testing, microlithography etc. Cadmium plays the role of lasing element. Cadmium, a metal at room temperature, needs to be evaporated from a reservoir, for lasing to occur. Cd vapor needs to be distributed uniformly, through a process called electrophoresis, down the laser bore. The construction is more complicated than other helium based lasers. The laser tube contains a reservoir for cadmium and a heater to vaporize the metal. The laser needs to sustain a higher level of internal pressure allowing the vaporized cadmium to remain in the tube. The lifetime of a specific helium cadmium laser is dictated by the amount of cadmium in the reservoir. Once the cadmium supply is exhausted, the tube must be replaced.

#### b) Luminescence collection and detection equipment:

The filters are used to separate excited and emitted wavelengths. It consists a pair of lenses, mirror, filter, monochromators, photomultiplier tube (PMT), and computer (PC). A pair of cut-off filters is required to isolate a particular wavelength from the source light. These may be either glass

#### **Experimental Details**

filters or solutions in cuvettes. This light may contain some weak contribution of frequencies close to the desired frequency. A collimating mirror is used to collimate the light to a parallel beam. This collimated beam falls on a monochromator with a diffraction grating. The desired emission wavelength is selected by the monochromator. The different frequencies disperse in different angles satisfying the gratings equation. The light from the gratings is focused on to a slit which can pick the desired frequency by changing position. The light coming out of the slit is extremely monochromatic. Photomultiplier tubes are used as detectors. Spectral response of all photomultipliers varies with wavelength, but it is sometimes necessary to determine the actual intensity of incident radiation. A suitable quantum counter which can emit same number of photons as many as it absorbs, can be employed. This capability should be over a very wide wavelength range. Thus, by measuring the output of the quantum counter at one wavelength, the number of incident quanta over a wide wavelength range can be measured. The output from the detector is amplified and displayed on a readout device which may be a meter or digital display.

## **2.2.6 UV-Vis Absorption Spectroscopy and Diffuse Reflectance Spectroscopy**

### When electromagnetic radiation (light) interacts with matter, various effects can be observed such as reflection, scattering, absorbance, transmittance and fluorescence/ phosphorescence. Total potential energy of a molecule can be represented as the sum of its electronic, rotational and vibrational energies. When energy of incident light is equal to the energy required to excite an electron from a lower energy level to higher level, the light is absorbed.

#### Working Principal:

Amount of light absorbed is the difference between the incident radiation (Io) and the reflected or transmitted radiation (I). Quantitatively absorbance is described by equation:

$$A = -\log(\frac{1}{l_{\nu}})....(\text{Eq. 2.8})$$

where, A is absorbance, T is transmittance, Io and I are the intensities of incident and transmitted light respectively at a given wavelength. A UV-VIS spectrophotometer uses a tungsten-halogen or deuterium lamp as a source. A dispersion device like a monochromator is used to select the incident wavelength. A detector, which converts UV- visible light into electrical signal is the final component of the spectrophotometer. It is easy to bandgap ( $E_g$ ) from absorption spectra, in case of solid films of known low thickness, due to low scattering properties. However, in colloidal samples, due to large surface area exposure scattering is enhanced. As dispersed light does not reach the detector it is counted as absorbed light. The technique (optical absorption) cannot distinguish between the two phenomena.

UV-Vis of powdered sample is carried out by dispersing it in the liquid medium like water, ethanol, methanol etc. For larger particle size, the particles precipitate. Thus, the spectrum is mostly due to the liquid.

Diffuse reflectance spectroscopy (DRS) enables us to obtain  $E_g$  of powder samples, which scatter in perfectly diffuse manner. DRS works on Kubelka and Munk model[131], in which diffuse reflectance R is related to Kubelka– Munk function F(R) by

$$F(R) = \frac{(1-R)^2}{2R}....(Eq. 2.9)$$

where, R denotes the percentage reflectance from the sample[131,132]. A graph between  $[F(R).hv]^2$  versus hv (in eV) can provide the  $E_g$  values of a sample with direct bandgap. An indirect bandgap can be obtained from a plot of  $[F(R).hv]^{1/2}$  versus hv. Diffuse reflectance is measured by an

integrating sphere detector. This is an attachment to an UV-Vis spectrometer (Carry 60, Agilent) (figure 2.11).



Figure 2.11: Experimental set up for diffuse reflectance measurement (a) Carry 60 UV-Vis spectrometer, (b) an integrating sphere attachment to detect diffuse reflectance

#### 2.2.7 Hall Set-up:

The Hall effect, discovered in 1879 which states that when a current carrying conductor is placed in a magnetic field, a voltage, transverse to the direction of the current density, is induced. The appearance of this transverse voltage is a consequence of the Lorentz force,

F=qE+qvXB, which acts on the charge carriers and deflects them against one side of the conductor. For a magnetic field along z-direction,  $B = B_zE_z$ , this results in a Hall resistivity  $\rho_{xy} = E_y/j_x$ , which has a linear dependence on the applied magnetic field. The discovery of the Hall effect became important for determining the density and polarity of charge carriers in nonmagnetic materials.



Figure 2.12: Schematic diagram for Hall-probe measurements.

#### **2.3 Setup for Functionalities**

#### 2.3.1 Moisture Sensing set up:

For analyzing the effect of humidity on resistance of synthesized material, homemade set was fabricated in laboratory as shown in figure 2.12.

#### a) Fabrication of set up:

A home-made setup was fabricated to measure humidity dependent resistance of pellets (of synthesized materials). Two stainless steel electrodes were positioned at a fixed separation of ~1.25 mm on the surface of the pellets. Both the electrodes were connected to Keithley meter (2401) for the collection and storage of dynamic response of the material under dry air and humid air. The arrangement containing electrodes and sample holders was enclosed inside a sealed glass chamber. The sealed chamber had one inlet connected to a two-way key and one outlet connected to a vacuum pump. The two-way key had two inlets and one outlet. One inlet was for dry air and another for moisture saturated air. The outlet was connected to a vacuum pump. A digital hygrometer (Maxtech TM-1) was placed inside this chamber to measure the Relative Humidity ( $R_H$ ).



Figure 2.13: Schematic of experimental set up for Humidity sensing

#### **b)** Sample Preparation:

The synthesized powder samples were pressed into pellets by applying 3 tons of pressure. These pallets were sintered depending upon their sintering temperature. Electrodes were made using silver paste on the sintered pallets at the distance of 1.25mm. These pellets with electrodes were again heated at  $\sim$ 80°C for one hour to remove.

#### c) Working principle:

For the first cycle, Vacuum pump is kept ON and dry air inlet of two-way key is kept closed whereas wet air inlet is connected to the beaker containing water. Vacuum pump will suck moist air from the beaker. The relative humidity (R<sub>H</sub>) is increased to its maximum limit during this cycle. For the next cycle, wet air inlet is closed whereas dry air inlet is kept open. In this case, vacuum pump will suck dry air. The change in resistance (dynamic response of the material) under moist and dry air is stored in Keithley source meter. These cycles are repeated for next 4 to 5 times to check its stability and repeatability. Relative humidity should be kept constant for all dry air as well as humid air cycles. In the present work, the relative humidity of the air when experiment carried out was 45% whereas the maximum relative humidity achieved in the set up was 75%.

#### 2.3.2 Light Sensing set up:

For analyzing the effect of different wavelength of light on the resistance/ conductivity of pellets (of synthesized samples), light sensing set up was fabricated in the laboratory.

#### a) Fabrication of set up:

A homemade set up was fabricated for analyzing the effect of different wavelength of light on the synthesized samples as shown in figure 2.13. Two stainless steel electrodes were positioned at a fixed separation of ~1.25mm on the surface of the pellets. The whole arrangement was closed in a box which was internally painted with black color to avoid the interference of outside light. Electrodes were connected to the Keithely meter (2401) for the collection and storage of dynamic response of the material under dark condition and light condition.

#### **b)** Sample Preparation:

The synthesized powder samples were pressed into pellets by applying 3 tons of pressure. These pallets were sintered depending upon their sintering temperature. Electrodes were made using silver paste on the sintered pallets at the distance of 1.25mm. These pellets with electrodes were again heated at  $\sim 80^{\circ}$ C for one hour to remove.



Figure 2.14: Schematic of experimental set up for Light sensing

#### c) Working principle:

For the first cycle, under dark condition, light source is switched OFF and the data is calculated and stored. For the next cycle, light source (ranging from UV to Visible light) is switched ON. The change in dynamic response of the material for different wavelength of light is stored in the Keithley meter. The intensity of light was kept constant for whole experiment.

This set up was used for two purposes

- a) To observe the effect of different wavelength of light on the electrical properties of ZnO.
- **b**) To carry out the UV sensing experiment.

# Chapter 3 Structural properties of Pure and Modified ZnO

ZnO generally crystalizes in three forms: hexagonal wurtzite, cubic zinc blende and rocksalt structure. According to the first principle periodic Hartree-Fock linear combination of atomic orbital theory, the hexagonal zinc oxide wurtzite is found to be the most thermodynamically stable form[133]. Structural parameters like lattice parameters, strain, size *etc.* play an important role in determining its bandgap and other optical properties. Lattice parameters mainly depend upon the following factors[134]:

- (i) Free electron concentration occupying conduction band minima
- (ii) concentration of foreign substituted/doped atoms
- (iii) defects in lattice
- (iv) difference in ionic radii of host and substituted atom
- (v) strain
- (vi) temperature.

Depending on the properties of the aliovalent ion, i.e. charge, size and electronic properties local structural changes take place. It is generally the case that a higher charged ion will be able to retain or hold more oxygen in the lattice while a lesser charged ion will retain less oxygen thereby creating oxygen deficiencies. However, as much as less oxygen may generate strain in the lattice, same may happen in case of excess oxygen. Much depends on the ionic radius of the dopant on how much oxygen can be retained or driven away from the lattice. Hence, aliovalent ion doping or substitution generally generates distortion in the lattice introducing strain and thereby defects in the lattice[135]. At some amount of substitution, the lattice can no longer sustain the internal strain and reorganize overall structure of ZnO lattice. In this chapter, we have done detailed investigation of effect of aliovalent ion doping in ZnO for three series of samples Si (4+), Si (4+)/Na (1+) and V (4+/5+) on structural properties of ZnO. The change in lattice parameters, strain, vibrational modes, size *etc.* has been studied in detail.

#### 3.1. Effect of Si<sup>4+</sup> doping on structural properties of ZnO:

Different concentrations of silicon were doped in ZnO lattice. When a Si<sup>4+</sup> ion (crystal radius ~ 0.4A) is doped in ZnO lattice, Si may go to an interstitial position due to its small size compared to both Zn<sup>2+</sup> and O<sup>2-</sup> ions (crystal radius ~ 0.74 and 1.24A respectively[136]). However, due to its +4 charge  $Si^{4+}$  will locally draw more oxygen than  $Zn^{2+}$ . To compensate charge, a tendency of reduction of positive charge is natural. Thus, incorporation of Si will decrease oxygen vacancy V<sub>0</sub>. Hence, logically a substitution scenario is more probable, where lattice will arrange itself to accommodate Si in the position of Zn, rather than an interstitial scenario. But this cannot continue for long as soon the V<sub>0</sub> type of defects will be taken care of by the excess oxygen dragged by increasing Si<sup>4+</sup> concentration. The excess oxygen will drive the lattice to locally modify to other structures. However, all these changes must modify ZnO lattice parameters, strain, vibrational modes, electronic structure etc. There are limited number of reports present on silicon doped ZnO [81,137–141]. Deep analysis of structure and opto-electronics properties of these systems needs to be done.

The calcined samples were annealed at 600°C for 2h. A dominant hexagonal wurtzite ZnO structure was revealed from XRD studies as shown in Figure 3.1 (a). No secondary phases were found related to simple or complex oxides of Zn and Si for  $x \le 0.027$ , apart from some minor reflections of zinc blend. For x > 0.027, minor Zn<sub>2</sub>SiO<sub>4</sub>-like extra reflections appear. As discussed above x = 0.027 may be the solubility limit of silicon in ZnO

where the wurtzite structure does not get distorted enough to a rearrangement of a new structure. Note that the  $SiO_2$  structure is also composed of Si-O tetrahedral arrangement in a different geometry. The  $Zn_2SiO_4$  structure is a result of such bond arrangement.



Figure 3.1: (a) XRD reveals pure single phase of samples without the presence of any impure phases. Changes in lattice parameters are expected from XRD peak shifts. (b) Crystallite size increases as calculated from Debye-Scherer equation.

Zn<sub>1-x</sub>Si<sub>x</sub>O for x= 0, 0.013, 0.020 and 0.027 (within solubility limit) have been named as Z0, ZS1, ZS2 and ZS3, respectively, and will be discussed in this work. Field Emission Scanning Electron Microscopy (FESEM) images show agglomerated particles for all samples [Figure 3.2]. From FESEM analysis it is observed that particle size increases with silicon incorporation [Figure 3.2]. Particle size (average) was estimated using Image J software. The average particle size increases from 0.7 to 1.3  $\mu$ m with silicon incorporation.

To confirm the chemical composition of all samples, Energy Dispersive X-Ray Spectroscopy (EDS) and elemental mapping has been performed. Figure 3.3 (a) shows the EDS spectrum which confirmed that the synthesized sample contains only Zn, O and Si without any impurity phase.



Figure 3.2: SEM micrographs showing morphology of the Z0, ZS1, ZS2 and ZS3 samples. The size of the samples is observed to increase linearly with Si-substitution. Note that for substituted samples smaller particles agglomerate to for large macro-sized chunks.

Pure ZnO (Z0) contains only Zn and O without any extra element whereas doped samples contain Si, Zn and O. 2D elemental scan of samples confirm homogeneity in distribution of Zn, O and Si [Figure 3.3 (d)]. The atomic percentage of silicon for ZS1, ZS2 and ZS3 was found to be 0.78%, 1.54% and 2.12% at par with the targeted concentrations (inset of figure 3.3 (a)). Due to higher charge of Si<sup>4+</sup> (in comparison to Zn<sup>2+</sup>), oxygen content in ZnO lattice increased (figure 3.3 (b, c)).

The (002) peak shifts to lower angle with  $Si^{4+}$  incorporation [Table 3.1]. This indicates enhancement of c-axis from 5.144Å to 5.163Å with increasing silicon content. Such changes in lattice parameters may take place with possible substitution of  $Zn^{2+}$  by  $Si^{4+}$  in ZnO lattice due to the



excess oxygen in the Si<sup>4+</sup> doped ZnO lattice which makes the lattice to expand.

Figure 3.3: (a) EDS of Z0, ZS1, ZS2 and ZS3 (inset confirms increase in Si<sup>4+</sup>content) (b)Oxygen content in Z0, ZS1, ZS2 & ZS3 (c)Oxygen content in sample increases with increase in Si<sup>4+</sup>substitution (d) Elemental mapping of Z0, ZS1, ZS2 and ZS3 showing uniform distribution of component ions.

This has been stated in a theoretical study as well that substitution is an energetically favored situation than interstitial formation. Average crystallite size was calculated from the XRD data using Scherer's formula.

The crystallite size increases with substitution, from 55 to 67 nm [figure 3.1 (b)]. Size estimations using XRD is consistent with FESEM analysis. However, XRD values are smaller than the values obtained from SEM studies which reveal larger agglomerated particles composed of smaller crystals.

Table	e 3.1: (002)	peak position	and lattice	e parameter (	(c) in Si <sup>e</sup>	<sup>4+</sup> substituted
ZnO						

Zn <sub>1-x</sub> Si <sub>x</sub> O	(002) Peak position	c-axis parameter		
X=	(2 <del>0</del> )°	(Å)		
0	34.24	5.144		
0.013	34.21	5.148		
0.020	34.18	5.161		
0.027	34.15	5.163		



Figure 3.4: Rietveld refinement of Z0, ZS1, ZS2 and ZS3

Rietveld refinement has been done using GSAS software to estimate changes in lattice parameters, strain and crystallite size with silicon substitution [Figure 3.4]. Pseudo-Voigt profile was chosen for the peak shape. Pseudo-Voigt function, PV(x), is expressed as a linear combination of Gaussian G(x) and Lorentzian L(x) peaks:  $PV(x) = \eta G(x) + (1-\eta)L(x)$  where,  $0 \le \eta \le 1$ ,  $\eta = 0$  for a pure Lorentzian, while  $\eta = 1$  for a pure Lorentzian which shifts the profile more towards pure Gaussian or pure Gaussian.

The background was modeled using a 6-coefficient polynomial function. Zero error, sample displacement error, lattice parameters, strain  $(L_y)$ , crystallite size  $(L_x)$ , and fractional coordinates of various samples were refined for several iterative cycles.

Table 3.2: Refined parameters  $R_{wp}(\%)$ ,  $R_P(\%)$ ,  $\chi^2$  and Density  $(gm/cm^3)$  in  $Si^{4+}doped$  ZnO.

Silicon	$R_{wp}(\%)$	$R_p(\%)$	$\chi^2$	Density
concentration				(gm/cm <sup>3</sup> )
(x=)				
0 (Z0)	10.84	7.53	2.50	5.67
0.013 (ZS1)	8.83	6.13	1.83	5.65
0.020 (ZS2)	8.71	6.12	1.82	5.61
0.027 (ZS3)	9.28	6.91	1.98	5.60

Lowest achievable values of expected R factor,  $R_p$ , weighted profile R-factor,  $R_{wp}$ , and goodness-of-fit,  $\chi^2$ , confirmed the appropriateness of refinement. The refined data is plotted in Figure 3.4 and refined parameters are tabulated in Table 3.2.

Variation of lattice parameters with doping is shown in figure 3.5 (a). The c/a ratio is directly related to strain in the lattice[142–144]. The ideal value of c/a strain-free single crystal ZnO is 1.63. From figure 3.5 (b), it is observed that c/a ratio of synthesized pure ZnO (Z0) is ~1.58. With increasing substitution, the c/a ratio approaches to 1.63 (in ZS3), the ideal value, hinting at reducing strain or disorderness in the lattice with Si doping.

Strain (S) was calculated from refinement parameters using formula equation:

 $S = 100\% \frac{\pi}{18000} L_y....eq (3.1)$ 

where Ly is Lorentzian strain broadening term and was found to reduce with substitution [Figure 3.5 (c)] confirming our analogy from c/a ratio enhancement.



Figure 3.5: Rietveld refinement using GSAS software estimated variation in (a) Lattice parameter a, b & c (b) c/a (c) Strain with  $Si^{4+}$  substitution.

Oxygen vacancies (V<sub>o</sub>) are predominant defects found in ZnO due to which it shows n-type conductivity. The presence of V<sub>o</sub> defect in ZnO at room temperature produce strain in the lattice[145]. Substitution of Si<sup>4+</sup> at Zn<sup>2+</sup> site reduces this defect due to higher charge of Si<sup>4+</sup>in comparison to Zn<sup>2+.</sup> Higher charge attracts more oxygen in the lattice (evident in EDS studies) and reduces oxygen vacancies, thereby reducing strain in ZnO lattice.

Raman vibrational modes were studied in detail [Figure 3.6 (a)]. In hexagonal structures with  $C_{6v}^4$  symmetry, group theory predicts eight sets of phonon normal modes, namely,  $2A_1+2E_1+2B_1+2E_2$ . Among them, one set of  $A_1$  and  $E_1$  mode are acoustic, while the remaining six modes, namely,  $A_1+E_1+2B_1+2E_2$ , are optical modes[133]. The  $A_1$  and  $E_1$  branches are both Raman and infrared active, the two nonpolar  $E_2$  branches are Raman active only, and B1 branches are inactive. Raman phonon modes were also observed at ~201 cm<sup>-1</sup>, 325 cm<sup>-1</sup>, 435 cm<sup>-1</sup> and 576 cm<sup>-1</sup> respectively. The non-polar  $E_2^{high}$  and  $E_2^{low}$  modes are due to relative vibrations of oxygen and zinc sub-lattices in two different orientations along c-axis. Intensity of  $E_2^{high}$  mode increases with substitution which reflects good crystallinity of wurtzite ZnO[146]. Hence, structural regularity improves with substitution. There is a red shift of  $E_2^{high}$  mode in the doped samples compared to pure ZnO (Z0). Generally, three possible mechanisms may be responsible for the observed phonon shifts in Raman spectra. These are: (1) Spatial confinement within the nanostructure boundaries. (2) Phonon localization by defects such as oxygen vacancies, zinc interstitials etc. (3) Laser induced heating in nanostructures ensembles.



Figure 3.6: (a) Raman spectroscopy of Z0, ZS1, ZS2 & ZS3 (b) Strain was calculated from A1(TO) vibrational mode which decreases with Si<sup>4+</sup>substitution. Strain from Raman is in agreement with strain calculated from XRD.

On the other hand, a weak E1(LO) mode is related to oxygen/zinc vacancies. E1(LO) mode weakens implying less oxygen defects and thereby less defected lattice with Si substitution. The detailed defect state analysis was done using photoluminescence studies discussed later in the next chapter.

A similar strain analysis was done using Raman spectra as in XRD [Figure 3.6 (b)]. A1(TO) mode is related to strength of polar lattice bonds. The strain free A1(TO)frequency,  $\omega_0$ , for a ZnO single crystal is supposed to be at 379 cm<sup>-1</sup>. A weak peak appears at ~382 cm<sup>-1</sup> (ZS3) ~384 cm<sup>-1</sup> (ZO) corresponding to A1(TO) mode. Note that the energy of the mode is blue shifted in Z0 as compared to single crystal ZnO, but is red shifted thereafter in ZS3. The quantitative estimation of strain along a and b axes ( $\varepsilon_{xx}$  and  $\varepsilon_{yy}$ ) was done using formula[147]:

$$\epsilon_{xx} = \epsilon_{yy} = \frac{\Delta \omega \cdot c_{33}}{2(aC_{33} - bC_{13})}$$
.....eq (3.2)

where,  $\Delta \omega = \omega - \omega_0$ , deformation potential constants,  $a = -774 \text{ cm}^{-1}$  and  $b = -375 \text{ cm}^{-1}$ , elastic stiffness constants,  $C_{33} = 216$  GPa and  $C_{13} = 104$  GPa. The calculated strain from Raman analysis decreases with Si incorporation in agreement with XRD results.

Lattice strain generally varies inversely to particle size[148]. In case of nanoparticles one can expect enhanced oxygen defect states. These missing oxygen ions generate strain in the lattice. The strained lattice lacks long range order and hence gets terminated at smaller sizes. However, with the incorporation of Si4+, the scenario changes, and more oxygen creeps in the lattice, thereby reducing strain and increasing long range order. This results in larger particle size.

#### 3.2 Effect of Si<sup>4+</sup>/Na<sup>1+</sup> doping on structural properties of ZnO:

Silicon doping with higher charge and lower ionic radii reduces strain and lattice disorder of ZnO. Silicon reduces oxygen vacancies and other defect in ZnO lattice and modifies its structural properties like strain, lattice parameters, size etc. Small ionic radii of Si, enables the lattice to

accommodate more oxygen atoms. If ionic radii and charge difference is compensated, then structural properties may get modified. By co-doping Sidoped ZnO, with Na<sup>+1</sup> of lesser charge and higher ionic radii (~1.13A) one can compensate the extra cationic charge and increase effective ionic to study the structural modifications of ZnO. Ratio of Si:Na chosen was 1:2 to compensate charge difference. As a result, the effective ionic radius of a cation increases by ~20%. This is a huge change and makes the analysis interesting. Note that our effort to compensate charge was made because we wanted to check whether charge alone is a responsible for changes in structure and other physical properties.



Figure 3.7: (a) XRD reveals pure single phase of samples without the presence of any impure phases. Changes in lattice parameters are expected from XRD peak shifts. (b) Crystallite size increases as calculated from Debye-Scherer equation.

 $Zn_{1-x}Si_{x/3}Na_{2x/3}O$  for x= 0, 0.013, 0.020 and 0.027 (within solubility limit) are named Z0, ZSN1, ZSN2 and ZSN3, respectively, and will be discussed in this work. A dominant hexagonal wurtzite ZnO structure was revealed from XRD studies as shown in [Figure 3.7 (a)]. No secondary phases were

found related to simple or complex oxides of Zn, Si and Na for  $x \le 0.027$ . Average crystallite size was calculated using the Scherer formula[149] and shown in inset of [Figure 3.7 (b)].

Field Emission Scanning Electron Microscopy (FESEM) images show agglomerated particles for all samples [Figure 3.8]. Particle size (average) was estimated using Image J software. The average particle size first decreases from 0.7 to 0.148 $\mu$ m and again increases to 0.3  $\mu$ m shown in figure 3.8. This observation is consistent with the XRD crystallite size analysis. However, XRD values are smaller than the values obtained from SEM studies which reveal larger agglomerated particles composed of smaller crystals.



Figure 3.8: SEM micrographs showing morphology of the Z0, ZSN1, ZSN2 and ZSN3 samples. The size of the samples is observed to vary with Na codoping.

To confirm the chemical composition of all samples, Energy Dispersive X-Ray Spectroscopy (EDS) and elemental mapping has been performed. Figure 3.9 (a) shows the EDS spectrum which confirmed that the synthesized sample contains only Zn, O, Na and Si without any impurity phase. A 2D elemental scans of ZSN1, ZSN2 and ZSN3 samples over the same area reveal uniform distribution of Zn, O, Na and Si only [figure 3.9 (d)]. The atomic percentage of Na & Si was found to be 0.71% & 0.37%, 1.12% & 0.5% and 1.5% & 0.81% for ZSN1, ZSN2 and ZSN3 % at par with targeted concentrations.



Figure 3.9: (a) EDS of Z0, ZSN1, ZSN2 and ZSN3 (b)Oxygen content in Z0, ZSN1, ZSN2 & ZSN3 (c)Oxygen content in sample decreases with increase in Na<sup>1+</sup>co-doping (d) Elemental mapping of Z0, ZSN1, ZSN2 and ZSN3 showing uniform distribution of component ions.

EDS spectrum confirmed the reduction of oxygen content with Na<sup>1+</sup> codoping in Si<sup>4+</sup> doped ZnO (figure 3.9 (b, c)). Similar to Si<sup>4+</sup>doped ZnO, Rietveld refinement has been done using GSAS software to estimate changes in lattice parameters, strain and crystallite size in Si<sup>4+</sup>/Na<sup>1+</sup> codoped ZnO [Figure 3.10]. Pseudo-Voigt profile was chosen for the peak shape similar to Si-doped samples.

Similar to the Si-doped samples the background was modeled using a 6coefficient polynomial function. Zero error, sample displacement error, lattice parameters, strain (L<sub>y</sub>), crystallite size (L<sub>x</sub>), and fractional coordinates of various samples were refined for several iterative cycles. Lowest achievable values of expected R factor, R<sub>p</sub>, weighted profile Rfactor, R<sub>wp</sub>, and goodness-of-fit,  $\chi^2$ , confirmed the appropriateness of refinement. The refined parameters are tabulated in Table 3.3.

Table 3.3: Refinement parameters  $R_{wp}$ ,  $R_p$ ,  $\chi^2$  and density in Si<sup>4+</sup>/Na<sup>1+</sup> codoped ZnO

Zn <sub>1-x</sub> Si <sub>x/3</sub> Na <sub>2x/3</sub> O	R <sub>wp</sub>	R <sub>p</sub>	$\chi^2$	Density
x=	(%)	(%)		(gm/cm <sup>3</sup> )
0 (Z0)	10.84	7.53	2.50	5.672
0.013 (ZSN1)	9.63	7.28	2.73	5.649
0.020 (ZSN2)	9.83	6.83	2.37	5.592
0.027 (ZSN3)	11.11	8.20	3.73	5.440

Variation of lattice parameter, strain and volume variation with Si<sup>4+</sup>/Na<sup>1+</sup> co-doping is shown in Figure 3.11 (a, b). It is observed that lattice parameter first decreases with nominal doping of ZSN1 but increases later for higher doping. Strain (S) was calculated from refinement parameters using Eq 3.1. For lower doping (ZNS1), strain increases but further reduces for higher doping. Increased strain inhibits the particle growth and reduces particle size. For higher doping reduction in strain increases the size.



Figure 3.10: Rietveld refinement of Z0, ZSN1, ZSN2 & ZSN3



Figure 3.11: Rietveld refinement using GSAS software estimated variation in (a) Lattice parameter a, b & c (b) Strain and Volume with  $Si^{4+}/Na^{1+}$  substitution.

Reports on Na doped ZnO suggested that Na prefers to occupy interstitial sites whereas higher doping leads to increase in substitutional site [84,150–152]. Similar trend is observed in the synthesized samples. With minimal  $Si^{4+}/Na^{1+}$  doping (ZSN1), Na prefers to occupy interstitial sites which

pressurizes lattice, reduces lattice parameters and thereby enhances lattice strain of the system. For higher doping, substitution increase due to proper rearrangement and coupling of Na and Si in the lattice, reducing strain. Due to higher ionic radii of Na, volume as well as lattice parameter increases. Raman vibrational modes were studied in detail [Figure 3.12 (a)]. Similar to pure ZnO Raman phonon modes were observed at ~201 cm<sup>-1</sup>, 325 cm<sup>-1</sup>, 435 cm<sup>-1</sup> and 576 cm<sup>-1</sup> respectively.

 $E_2^{high}$  is the predominant peak which is attributed to crystalline nature and phase orientation. It is well known that  $E_2^{high}$  mode at 442 cm<sup>-1</sup> in pure ZnO (Z0) is related to lattice vibration of oxygen atoms and indicates the wurtzite phase of ZnO. Co-doping of Si/Na leads to blue shift of  $E_2^{high}$  mode in comparison to Z0.



Figure 3.12: (a) Raman spectroscopy of Z0, ZSN1, ZSN2 & ZSN3 (b) Strain was calculated from  $A_1(TO)$  vibrational mode which decreases with  $Si^{4+}/Na^{1+}co$ -doping. Strain from Raman is in agreement with strain calculated from XRD.

Sample	Peak Position $(E^{2}_{high})$	FWHM
	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
ZO	429.88	16.90
ZSN1	437.00	17.86
ZSN2	439.03	17.25
ZSN3	439.50	17.42

Table 3.4 shows peak position and FWHM of  $E_2^{high}$  mode in  $Si^{4+}/Na^{1+}$  codoped ZnO.

The increased FWHM [Table 3.4] and reduced intensity of this peak shows lattice distortion and low crystalline nature with Na/Si doping in ZnO. The peak  $E_2^{high}$ - $E_2^{low}$  at 334cm<sup>-1</sup> is attributed to second order or multiple phonon scattering in ZnO. Low intensity peak at 380 cm<sup>-1</sup> is assigned to A<sub>1</sub>(TO) mode. A<sub>1</sub>(TO) peak is related to the strength of polar lattice bonds[146]. Strain has been calculated from the shifting of A<sub>1</sub>(TO) mode by using formula using equation 3.2. Strain calculated from Raman is in agreement with strain calculated from XRD [Figure 3.12 (b)]. E<sub>1</sub>(LO) mode at 576cm<sup>-1</sup> signifies the presence of oxygen/zinc vacancies in the lattice. It is observed that intensity of this mode in Z0 is low which increases with increase in doping. We noticed that Si doping reduces intensity of  $E_1(LO)$  peak. Whereas, Na co-doping leads to increase of  $E_1(LO)$ , i.e. in oxygen vacancies in ZnO lattice. This might be due to the doping of lower charge Na<sup>+1</sup> in comparison to the host Zn<sup>2+</sup>. Effect on oxygen vacancies and other defect state will be studied in detail in next chapter.

#### **3.3** Effect of V<sup>4+/5+</sup> doping on structural properties of ZnO:

Effect of higher charge of  $Si^{4+}$  and charge compensated  $Si^{4+}/Na^+$  was discussed. To confirm whether the effects of carrier enhancement was only due to charge state of the ions of dopants in ZnO, vanadium substitution with 5+/4+ charge state (higher/equivalent to silicon) has been studied.

Transition metal vanadium doping in ZnO has several contradictory reports. 5% vanadium doping in ZnO was reported to have reduced the bandgap by Toloman et al.,[153] whereas Mhamdi et al.[154] reported an increase in the bandgap with 5% vanadium doping. Similarly, some reports claim an increase in bandgap and a reduction in defect states,[155–160] whereas others report a decrease in bandgap and an increase in defect states[161–164]. There are few reports, which show an increase or a decrease in both bandgap and defect states simultaneously[153,165]. But no explanation is provided for such an unsystematic behavior. We have tried to synthesize and study this uncertainty if it exists and propose a mechanism behind from a structural and opto-electronic point of view of V doped ZnO.

The calcined samples were annealed at 500°C for 2h for studying its structural properties. Vanadium doping brings down sintering temperatures of doped ZnO. Therefore, vanadium doped ZnO samples were annealed at low temperature (500°C).



Figure 3.13: (a) XRD reveals pure single phase of samples without the presence of any impure phases. Changes in lattice parameters are expected from XRD peak shifts. (b) Crystallite size increases as calculated from Debye-Scherer equation.

XRD patterns revealed a dominant hexagonal wurtzite ZnO structure with some minor reflections similar to zinc blend as shown in Figure 3.13 (a). No secondary phases are found related to simple or complex oxides of Zn and V for all samples (with vanadium doping from x=0 to x =0.023) heat treated at 500°C. Higher doping (above ZV3) is not reported due to presence of impurity complex oxide phases.

FESEM images show agglomerated particles for all samples [Figure 3.14]. Particle size (average) was estimated using Image J software. Average particle size first decreases for ZV1 from 0.6 to 0.11  $\mu$ m and thereafter increases to 0.51  $\mu$ m shown in Figure 3.14. This observation is consistent with the XRD crystallite size analysis. However, XRD values are smaller than the values obtained from SEM studies which points to larger agglomerated particles composed of smaller crystals.

To confirm the chemical composition of the samples, EDS and elemental mapping has been performed.



*Figure 3.14: SEM micrographs showing morphology of the Z0, ZV1, ZV2 and ZV3 samples. The size of the samples varies with V- doping.* 

EDS spectrum [Figure 3.15 (a)] confirms that the synthesized samples contains only Zn, O and V without any impurity phase.



Figure 3.15: (a) EDS of Z0, ZV1, ZV2 and ZV3 (b)Oxygen content in sample increases with increase in V doping (c)Oxygen content in Z0, ZV1, ZV2 & ZV3 (d) Elemental mapping of Z0, ZV1, ZV2 and ZV3 showing uniform distribution of component ions.

Pure ZnO (Z0) do not contain any extra element except Zn and O whereas vanadium doped ZnO contain V, Zn and O. A 2D elemental scan of the sample over the same area reveals uniform distribution of Zn, V and O [figure 3.15 (d)]. The atomic percentage of V was found to be 0.67%, 1.12% and 1.71% for ZV1, ZV2 and ZV3 respectively as per targeted concentrations. Similar to Si<sup>4+</sup> doping, V<sup>5+</sup> with higher charge than Zn<sup>2+</sup> increases oxygen content in ZnO lattice (figure 3.15 (b, c)). Rietveld refinement [Figure 3.15] has been done using GSAS software with

a Pseudo-Voigt profile and a 6-coefficient polynomial function background, similar to the previous refinements.



Figure 3.16: Rietveld refinement of Z0, ZV1, ZV2 & ZV3

Table 3.5:	Refinement	parameters	$R_{wp}$ ,	$R_p$ ,	$\chi^2$ an	d densit	y in	$V^{4+/5+}$	doped	
ZnO										

Vanadium	<b>R</b> wp(%)	<b>R</b> <sub>p</sub> (%)	X <sup>2</sup>	Density
concentration (x =)				(gm/cm <sup>3</sup> )
0 (Z0)	7.68	5.52	2.20	5.671
0.0078 (ZV1)	8.01	5.60	1.94	5.647
0.015 (ZV2)	6.73	5.08	2.54	5.660
0.023 (ZV3)	11.09	8.76	3.42	5.660

Lowest achievable values of expected R factor,  $R_p$ , weighted profile R-factor,  $R_{wp}$ , and goodness-of-fit,  $\chi^2$ , confirmed the appropriateness of refinement. The refined parameters are tabulated in Table 3.5.

Variation of lattice parameter and volume with Vanadium doping is shown in figure 3.17 (a, b). It was observed that lattice parameters and the volume increase at first for ZV1 and then decrease for higher doping concentration (i.e., for ZV2 and ZV3). Lattice strain was calculated using formula equation 3.1. The lattice strain also follows lattice parameter and volume change. Average crystallite size was calculated using the Scherer formula and shown in Figure 3.13 (b). The crystallite size varies inversely to the strain.



*Figure 3.17: Rietveld refinement using GSAS software estimated variation in (a) Lattice parameter a, b & c (b) Strain and Volume with V doping.* 

The ionic radius of V<sup>4+</sup>(IV) ion is ~0.6Å, while that of V<sup>5+</sup>(IV) ion is ~0.495Å; both smaller than that of Zn<sup>2+</sup>(IV) ion ~0.745Å. The considerable ionic size difference, extra and variable charge of vanadium, as compared to zinc should change the ZnO lattice. Such factors can project vanadium doping to tailor the strain/distortion in the lattice. With minimal doping (ZV1), lattice strain, volume and lattice parameters increase noticeably and thereafter decreases with higher doping.

Naturally occurring oxygen vacancies in pure ZnO makes the material n type. With vanadium incorporation (more positively charged than zinc), the lattice will attract more oxygen. Even a small amount of doping of vanadium (as in ZV1) should result in increased oxygen content. To accommodate these oxygen ions, the lattice should expand. But at the same time, due to smaller ionic radii of vanadium, a lattice contraction is also expected with substitution. Hence, a competition between expansion and contraction of lattice is expected. The smaller size of vanadium enables the lattice to absorb more oxygen. However, initial small amount of doping of vanadium (ZV1) may lead to partial interstitial site occupation. This will introduce oxygen without actual substitution of zinc by vanadium, leading to enlargement of the unit cell. On top of that the extra vanadium will pressurize the lattice generating strain. Hence, in spite of substitution an increase of lattice parameters, strain and volume is observed. But for higher doping (ZV2 & ZV3) when interstitial vanadium ions can no longer be accommodated proper substitution at Zn<sup>2+</sup>site happens, enabling contraction of lattice and reduction in strain.

Transition metal dopant like vanadium has variable oxidation state. Variable oxidation states greatly affect structural as well as opto-electronic properties of lattice. X-ray near edge spectroscopy (XANES) at vanadium K-edge was performed to understand the oxidation state of vanadium and estimate oxygen content in all the samples [Figure 3.18 (a)]. The normalized XANES spectra of ZV1, ZV2, and ZV3 are shown in Figure 3.18 (b). Calibration was done using a spectrum of vanadium metal foil. Three
different standards representatives of three valence states were used: V metal foil (+0), VOSO<sub>4</sub> (4+), and V<sub>2</sub>O<sub>5</sub> (5+). Two features appear in the XANES data. An edge, assigned to dipole  $1s \rightarrow 4p$  transition, is preceded by a pre-edge, arising due to V  $1s \rightarrow V$  3d transition. A derivative of the absorption data hints at a mixed 4+/5+ valence state of vanadium in the doped materials [Figure 3.16 (b)]. However, the 4+ state seems to be predominant than the 5+ ones.

Table 3.6: Athena fitting parameters  $[V^{4+}, V^{5+} and chi-square]$  of XANES spectrum

Sample Name	$V^{4+}$	V <sup>5+</sup>	Chi-square
ZV1	76.6%	23.4%	0.1206
ZV2	80%	20%	0.1209
ZV3	72.6%	27.4%	0.2040



Figure 3.18: (a) V-K edge XANES spectra of ZV1, ZV2 & ZV3 (inset is calculated are under pre-edge) (b) normalized XANES spectra of ZV1, ZV2 & ZV3 and reference  $VOSO_4$  ( $V^{4+}$ ) and  $V_2O_5$  ( $V^{5+}$ ).

To find out the exact ratio of 4+ and 5+ states in all samples, fitting a linear combination was performed using Athena software. Fitting of the experimental data using Athena has been shown in Figure 3.19. Table 3.6 shows the fitting parameters. The proportion of  $V^{4+}/V^{5+}$  approximately remains invariant with small fluctuations as of 77/23, 80/20, and 73/27 in ZV1, ZV2, and ZV3, respectively [Figure. 3.20 (a)]. The pre-edge also reveals the dominance of the V<sup>4+</sup> state.

Chaurand et al.[128] mentioned that to evaluate charge state of vanadium ions, area and position of pre-edges play the most important factor. It is observed that position of pre-edge is dominantly matching withVOSO<sub>4</sub> preedge, i.e.,  $V^{4+}$  state. However, area first increases for ZV2 than ZV1 and thereafter decreases for ZV3. This supports XANES analysis [inset of figure 3.18 (a)], a double confirmation of the feature. This may be related to the decrease of interstitials in ZV2 compared to ZV1. A V<sup>5+</sup> ion is smaller in size than a V<sup>4+</sup> ion. Hence, for interstitial vanadium, a V<sup>5+</sup> state is preferable.



Figure 3.19: ATHENA fitting V-K edge XANES spectra of samples

However, when the system goes for a proper substitution, the state can afford to go to a  $V^{4+}$  state which is at a comparable 2+ state of Zn in the lattice in terms of radius and charge. Note that  $V^{5+}$  population increases with

further substitution from ZV2 to ZV3. Increasing oxygen volume in the system may pressurize the vanadium ions to shift to a smaller  $V^{5+}$  state. Hence, most probably the ZV3 sample is a chemical solution of the most oxygenated system, beyond which the system is forced to generate impurity complex oxides of Zn and V.

Variation of V<sup>4+</sup>and V<sup>5+</sup> concentrations will affect oxygen content of the lattice. Theoretical increase in oxygen content ( $\delta$ ) for  $Zn^{2+}_{(1-x)}V^{4+}_{x(y)}V^{5+}_{x(1-y)}O^{2+}_{1\pm\delta}$  was estimated using these ratios and an equation 3.3:

 $2(1-x) + 4(y)x + 5(1-y)x = 2(1 \pm \delta)$  $\Rightarrow \delta = \frac{x}{2}(3-y)....eq (3.3)$ 

where, x is the vanadium doping concentration, and y is the vanadium 4+ content in the sample estimated from the XANES fitting. We observe that  $\delta$  is approximately linearly increasing from 0.009 for ZV1 to 0.026 for ZV3 in spite of fluctuations in the 4+/5+ charge [shown in figure 3.20 (b)].



Figure 3.20: Variation of (a)  $V^{4+}(\%)$  and  $V^{5+}(\%)$  content (b) Theoretical calculation indicates increase in oxygen content with Vanadium doping. Increase in oxygen content from XANES agrees with EDS studies.

Increase in oxygen content from XANES studies agrees well with EDS studies. Increase in oxygen content signifies reduced oxygen vacancies with vanadium doping.

Raman vibrational modes were studied in detail [Figure 3.21 (a)]. Similar to pure ZnO and other doped Raman phonon modes were observed at  $\sim$ 201 cm<sup>-1</sup>, 325 cm<sup>-1</sup>, 435 cm<sup>-1</sup> and 576 cm<sup>-1</sup> respectively.

Vanadium doping leads to red shift of  $E_2^{high}$  mode in comparison to Z0. Table 3.7 shows peak position and FWHM of  $E_2^{high}$  mode. Atomic mass of zinc, vanadium and oxygen are 65.38, 50.94 and 15.99 respectively. For ZV1, oxygen content increases, increasing number of oscillators, and thereby effective mass of oscillators. This leads to red shift of  $E_2^{high}$  mode in ZV1. For higher doping, although oxygen content has increased, due to more vanadium incorporation at Zn sites, effective mass of the metal site reduces which leads to blue shift. The increased FWHM shows lattice distortion and low crystalline nature with vanadium doping in ZnO.



Figure 3.21: (a) Raman spectroscopy of Z0, ZV1, ZV2 & ZV3 (b) Strain was calculated from  $A_1(TO)$  vibrational mode which decreases with V doping. Strain from Raman is in agreement with strain calculated from XRD.

The strain free A<sub>1</sub>(TO)frequency,  $\omega_0$ , for a ZnO single crystal is at 379 cm<sup>-1</sup>. The estimation of strain along a and b axes ( $\varepsilon_{xx}$  and  $\varepsilon_{yy}$ ) was done using formula. Strain calculated from Raman using equation 3.2 is in agreement with strain calculated from XRD shown in figure 3.21 (b).

Sample Name	Peak position ( $E^{2}_{high}$ )	FWHM
	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
Z0	441	15.94
ZV1	433	25.37
ZV2	434	25.03
ZV3	437	24.05

*Table 3.7: Peak position of Raman mode*  $E_2^{high}$  and corresponding FWHM in  $V^{4+/5+}$  doped ZnO

Raman mode at 580 cm<sup>-1</sup> is assigned to  $E_1(LO)$  mode which is due to the presence of defects in the lattice like oxygen vacancies. The intensity of this peak is high in Z0 which confirms that pure ZnO has predominant oxygen vacancy defects. On doping vanadium, intensity of this peak reduces which states that oxygen vacancy decreases. This result is in agreement with XANES analysis.

## **3.4 Conclusions:**

In this chapter:

- Effect of Si, Si/Na and V doping has been observed on the structural properties of ZnO.
- Charge of aliovalent ion dopant has huge impact on defect structure of ZnO.
- Dopants are well incorporated in host ZnO lattice which is confirmed by EDS measurements. The atomic percentage of dopant is close to the actual doping percentage. Uniform incorporation of dopant was clearly observed in elemental mapping. For further

verification, TEM-EDS of 2.7% Si doped ZnO has been done and shown in appendix. The consistent variation in lattice parameter and strain with doping also signifies the incorporation of dopant in ZnO lattice.

- Si<sup>4+</sup> substitute Zn<sup>2+</sup> site and extra charge of Si<sup>4+</sup> (in comparison to Zn<sup>2+</sup>) results into reduction in oxygen vacancies defect which decreases strain of the lattice. c/a ratio tending towards ideal value with silicon substitution represents reduction in lattice disorder.
- Effect of charge compensation on ZnO defect structure is observed by co-doping Na<sup>1+</sup> in Si<sup>4+</sup> doped ZnO in 2:1 (Na:Si) ratio. Charge compensation leads to major modification in defect structure. Nominal doping increases interstitial defects which enhances strain of the lattice. Further doping increases substitution and thereby reduces strain.
- To understand effect of similar or higher charge than silicon (4+), vanadium (4+/5+) has been doped. Vanadium doping increases strain for lower doping and again decreases for further doping which might me due to competition between strain enhancement due to excess oxygen content (due to higher charge V<sup>5+</sup>) and strain relaxation due to lower ionic radii of substituted vanadium ion. Volume and lattice parameter also varies.
- In next chapter, effect of aliovalent ion doping on the optoelectronic/electronic structure of ZnO has been studied. Correlation between structural and opto-electronics properties has been investigated.

# Chapter 4 Opto-electronics properties of Pure and Modified ZnO

Zinc oxide (ZnO) is recognized as a II-VI photonic semiconductor materials with a wide band gap ( $\sim 3.37 \text{ eV}$ ) and high exciton binding energy  $(\sim 60 \text{ meV})[4]$ . It is a potential material for applications in optoelectronic devices such as UV lasers, gas and bio sensors. Wide range of properties of doped ZnO[64] depends on defects and associated charge carriers that are possible in these materials. By controlling these parameters can result in extremely important applications. Impurities created by intentional doping with aliovalent (differently charged) ions have marked effects, especially when nanostructures are grown. These impurities help modify electrical, optical and magnetic properties of ZnO particles, thus leading to important applications. There are several reports on Sn[77], As[166], Ga[167], In[80] doping of ZnO with prospects of transparent conductive oxides with high conductivity and high transparency to visible light (defect reduction). Other dopants like Al[168], V[164] etc. have introduced more defects and make it appropriate material for sensing applications. Here we will detail the effect of aliovalent dopants Si(4+), Si(4+)/Na(1+) and V(4+/5+) on opto-electronics properties of ZnO.

# 4.1 Bandgap and defect state investigation of undoped and Silicon doped ZnO:

In order to understand the effect of Si<sup>4+</sup> doping on opto-electronic properties of ZnO, bandgap and defect state modification has been investigated. Quantitative analysis of each defect state in pure and Si<sup>4+</sup> doped ZnO has been analyzed. Possible mechanisms behind these defect modifications has

also been discussed.

#### 4.1.1 Bandgap Analysis:

Electrical bandgap was estimated using UV-Vis spectroscopy. Bandgap was calculated [Figure 4.1(a)] by plotting Tauc plot[169,170] using Tauc equation:

 $(\alpha h\nu)^2 = C(h\nu - Eg) \dots eq 4.1$ 

where,  $\alpha$  is absorption coefficient,  $\lambda$  is the wavelength, C is proportionality constant, v is the frequency of light and E<sub>g</sub> is the bandgap energy. The xaxis intercept of the extrapolated linear part of this graph [( $\alpha$ hv)<sup>2</sup> versus hv] gives value of bandgap. Band gap was found to increase from 3.12 eV in Z0 steadily to 3.18 eV in ZS3 [Figure 4.1(b)].



Figure 4.1: (a) Absorbance of Z0, ZS1, ZS2 and ZS3 [inset is x-intercept of the extrapolated lines to the linear portion of optical transmittance at the maximum slope of the  $(\alpha hv)$ 2 versus hv] (b) Bandgap versus x

This increment in bandgap can be explained by:

#### a) Burstein -Moss effect:

The Burstein-Moss effect mainly happens in degenerate doped semiconductors[171]. This effect occurs when electron carrier concentration exceeds conduction band edge density of states [Figure 4.2].



Figure 4.2: Schematic diagram for Burstein -Moss effect

Pure ZnO semiconductors are generally of n-type due to inherent defects. Fermi levels shift below conduction band for pure n-type ZnO. Silicon  $(Si^{4+})$  acts as potential donor. Si gives two electrons to conduction band. These electrons populate states inside conduction band thus increasing the carrier concentration available for conduction. It will be shown in a later part that Hall measurement confirms increase in carrier concentration with silicon doping. Fermi level is shifted towards higher energy and enters conduction band. States in the conduction band below Fermi level are occupied by excess carriers. Hence, transitions of electrons from valence band to these states are no longer possible. The valence band electrons can only be excited to the conduction band above Fermi level. This makes the bandgap appear to be higher by  $\Delta E$  than the pure ZnO. This is Burstein-Moss effect. A blue shift of bandgap in doped ZnO is observed which may be related to the high carrier concentration as a result of silicon.

## b) Urbach Energy:

Appearance of Urbach tail is due to structural disorder and strain, caused by structural defects due to vacancies, dopants. ZnO lattice, naturally, have lots of vacancies and defects. These may contribute to structural disorders. These disordered states can be observed as band tails in the UV-vis absorption edge for energy, hv < Eg (inset of figure 4.3 (b)). Urbach energy has been calculated using the empirical Urbach relation[172]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_U}\right).\dots \exp\left(\frac{4.2}{E_U}\right)$$

where,  $\alpha_0$  is a constant,  $E_U$  is the Urbach energy. Slope of a ln ( $\alpha$ ) versus hv plot provides estimation of  $E_U$  (figure 4.3 (a))



Figure 4.3: (a) Linear fit of Urbach tail (b) Urbach energy versus x (inset shows schematic diagram of Urbach tail).

The composition dependence of Urbach energy was estimated and is observed to reduce with increasing Si content [Figure 4.3 (b)]. Urbach energy (E<sub>U</sub>) decreases from 83 meV in Z0 to 78 meV in ZS3. This reduction in Urbach tail width, (E<sub>U</sub>), actually reduces the states near the band edges thereby effectively increases bandgap. Interestingly, E<sub>U</sub> changes inversely with optical band gap (E<sub>g</sub>). Thus, estimation of E<sub>U</sub> not only relates increase of bandgap but also relates to reduction of structural disorder of ZnO and lattice strain with increasing Si<sup>4+</sup> concentration. Hence, silicon substitution improves crystallinity of Si-substituted ZnO material. Improvement in lattice order, i.e. reduction of lattice strain with silicon substitution is also confirmed from XRD and Raman spectra as discussed in chapter 3. Photoluminescence studies confirms reduction of defects states with silicon doping thereby relating to improved lattice regularity and reduced with silicon doping.

#### **4.1.2: Photoluminescence study:**

Room temperature photoluminescence (PL) was studied using Dongwoo Optron DM 500i spectrometer. To understand the effect of  $Si^{4+}$  ion on defects in ZnO [Figure 4.4 (a)] powders were pasted on carbon tapes and used for PL investigation. A relatively sharper near band edge (NBE) centered at ~390 nm in comparison to a wider and broader deep level emission (DLE) from 450 nm to 750 nm is observed in all samples. Note that the DLE of Z0 is centered at 518 nm. However, for other doped samples DLE regions are centered at ~620 nm. Hence a red shift in the substituted samples is observed.



Figure 4.4: (a) PL spectra of Z0, ZS1, ZS2 and ZS3 (b) Chromaticity diagram confirming red shift of DLE

This was further confirmed by calculating and plotting the chromaticity coordinates of PL data (on 1931 standard). The calculation of the CIE chromaticity coordinates for a given colored object requires the multiplication of its spectral power at each wavelength times the weighting factor from each of the three color matching functions. Summing up these contributions gives three values called the tristimulus values, from which the chromaticity coordinates are derived. The calculated chromaticity coordinates from Z0, ZS1, ZS2 and ZS3 are (0.32, 0.46), (0.42, 0.41), (0.45, 0.41) and (0.43, 0.41) respectively [Figure 4.4 (b)]. These coordinates clearly indicate enhancement of orange-red emission and quenching of green emission in the samples with Si<sup>4+</sup> substitution. It is observed that the relative intensity of NBE keeps on increasing with substitution while that of DLE decreases. As per conventional understanding, the intensity ratio between NBE and DLE (I<sub>NBE</sub>/I<sub>DLE</sub>) gives an indication of crystal quality and estimation of defects present in the material [173].



Figure 4.5: (a) Gaussian fitting of PL spectra of Z0, ZS1, ZS2 and ZS3 (b) Band energy diagram with different defects in pure ZnO showing all possible color emissions due to electron transition between states.

A marked increase in  $I_{(NBE)}/I_{(DLE)}$  ratio from 0.6 in Z0 to 2.5 in ZS3 is observed, gradually increasing with increasing silicon substitution [Figure 4.6 (a)]. Generally, it is believed that such an increase is related to reduction of surface traps and improvement in optical transparency of the ZnO nanoparticles.

Deep level emission of materials corresponds to defect related emission. Different electronic states in the bandgap (in between conduction band (CB) and valence band (VB)), corresponding to various defects like vacancies, interstitials and antisites of both Zn and O in the ZnO lattice, have been reported [Figure 4.5 (b)]. These major defect centres are represented as zinc interstitials ( $Zn_i$ ), oxygen vacancies ( $V_0$ ), oxygen interstitials ( $O_i$ ), and zinc vacancies  $(V_{Zn})$ , zinc antisites  $(Zn_0)$  and oxygen antisites  $(O_{zn})$ . The antisites defects are formed in non-equilibrium conditions for example by irradiation, ion beam implantation etc. Other defects like  $Zn_i$ , Vo,  $O_i$  and  $V_{Zn}$ are located at ~0.22 eV, ~2.5 eV, ~2.28 eV, and ~2.85 eV lower than the CB respectively. Thus, transitions take place from both CB and Zn<sub>i</sub> levels to VB, V<sub>0</sub>, O<sub>i</sub> and V<sub>Zn</sub> levels giving rise to several possibilities of different color emissions such as UV (CB  $\rightarrow$  VB:  $\Delta E \sim 3.3 \text{ eV}$ )[174], violet (Zn<sub>i</sub>  $\rightarrow$ VB:  $\Delta E \sim 3 \text{ eV}$ )[174], blue (CB  $\rightarrow V_{Zn}$ :  $\Delta E \sim 2.85 \text{ eV}$ )[175], green (CB  $\rightarrow$  $V_0: \Delta E \sim 2.46 \text{ eV} \& Zn_i \rightarrow V_0: \Delta E \sim 2.24 \text{ eV})[174,175], \text{ yellow (CB} \rightarrow O_i:$  $\Delta E \sim 2.1 \text{ eV}$  [176] and orange-red emissions (CB  $\rightarrow$  O<sub>i</sub>:  $\Delta E \sim 2.28 \text{ eV} \& Zn_i$  $\rightarrow$  Oi:  $\Delta E \sim 2.06 \text{ eV}$ )[177].

The broad DLE can be decomposed into combinations of multiple peaks corresponding to UV (>3.1 eV), violet (3–3.1 eV), blue (2.50–2.75 eV), green (2.17–2.50 eV), yellow (2.10–2.17 eV) and orange-red (<2.1 eV) color ranges. To quantify the specific defect states, the broad DLE spectrum as well as the NBE was de-convoluted into several Gaussian peaks in these color ranges [Figure 4.5(a)]. The intensities of individual component peaks vary from sample to sample depending upon type and amount of defect. The color of light emitted is a resultant of mixture of such colors.

NBE of pure ZnO (Z0) is de-convoluted into three peaks located at 3.05 eV, 3.16 eV and 3.25 eV corresponding to violet emission, donor acceptor pair and free excitons (FX), respectively. DLE of Z0 is de-convoluted into 9 peaks located at 2.69 eV (blue emission), 2.25 eV, 2.4 eV, & 2.54 eV (Green emission), 2.08 eV & 2.15 eV (yellow emission) and 1.85 eV, 1.95 eV & 2.02 eV (orange-red emission).



Figure 4.6: Variation of (a)  $I_{NBE}/I_{DLE}$  (b)  $P_{NBE}/P_{DLE}$  (c)  $P_N$  with  $Si^{4+}$  substitution

Similarly, for substituted samples each color range is composed of a set of peaks contributing to:

UV (ZS1/ZS2/ZS3: 3.25 eV & 3.16 eV)

Violet (ZS1/ZS2/ZS3: 3.05 eV)

Green (ZS1/ZS2/ZS3: 2.22 eV, 2.33 eV & 2.45 eV)

Yellow (ZS1/ZS2/ZS3: 2.11 eV, 2.15 eV & 2.15 eV)

Orange-red (ZS1: 1.73 eV, 1.85 eV, 1.95 eV, 1.98 eV, 2.05 eV; ZS2: 1.75

eV, 1.77 eV, 1.82 eV, 1.89 eV, 1.98 eV, 2.05 eV; ZS3: 1.81 eV, 1.84 eV, 1.90 eV, 1.96 eV, 2.02 eV, 2.09 eV).

Number of peaks needed to fit the spectra varies in different color ranges. Actually, width and area of the fitted peaks also peaks vary. Hence, each type of deformation or defect varies in quality and amount with changing Si content. Thus, it is our belief, that instead of intensity an analysis based on area should be a better factor to quantify defects.

Areas of each de-convoluted peak were calculated. The peaks were bundled in six color ranges, UV, violet, blue, green, yellow and orange-red respectively. For each color bundle areas of constituent peaks are added and are represented by  $A_{UV}$ ,  $A_V$ ,  $A_B$ ,  $A_G$ ,  $A_Y$  and  $A_{O-R}$  for the corresponding color. To estimate contributions of each color in the entire spectrum, the color fraction,  $P_{color}$ , is calculated, given by:

$$P_{colour} = \frac{A_{colour}}{A_{total}} \dots eq (4.3)$$

where,  $A_{total} = \Sigma A_{color}$ , the total area under the spectrum. Hence,  $\Sigma P_{color} = 1$  for each sample. The color fraction,  $P_{color}$  provides a quantitative relative estimate of different defect states in the sample. The inset of Figure 4.6 (c) shows the variation of each color with increasing Si content. It appears that the green emission has decreased but the orange-red emission has increased. However, from the PL spectra it is observed that compared to the UV contribution which arises from the CB $\rightarrow$ VB transition, the orange-red contribution has not changed much, while green emission has drastically reduced. This is because  $A_{total}$  is not constant for all compositions. Although samples were prepared with utmost care, minute differences may still arise out of several factors (like amount of powder involved, angle of incidence, etc.). These minute differences may result in differences in total intensity of PL spectrum. Hence, a standard is required to normalize sample preparatory factors.

Bandgaps of doped and pure ZnO do not change remarkably. Hence the transition probability of electrons undergoing  $CB \rightarrow VB$  transition should not change much. With this assumption, entire PL spectrum was normalized with the UV contribution which corresponds to the  $CB \rightarrow VB$ transition. The new fraction after normalization is named PNcolor, given by

 $P_{N\text{-color}} = P_{color} / P_{UV} \dots eq \ 4.4$ 

Note that PN-color provides a more logistic analysis which matches the observed spectrum and also fits our expectations [Figure 4.6 (c)].

NBE contribution,  $P_{NBE}$ , was estimated by clubbing all  $P_{color}$  belonging to NBE. Similarly,  $P_{DLE}$  was estimated for DLE.  $P_{NBE}/P_{DLE}$  followed a similar trend as  $I_{NBE}/I_{DLE}$ , increasing from 0.1 to 0.4. The DLE in ZS3 decreased to 25% of Z0. This implies enormous reduction in defect states with silicon incorporation [Figure 4.6 (b)] i.e. the bandgap becomes less defective.

As seen from composition dependent  $P_{N-color}$  plots [Figure 4.6 (c)], undoped samples has very high green emission. This indicates the presence of large amount of oxygen vacancies, V<sub>0</sub>, in Z0. V<sub>0</sub> has reduced drastically on silicon substitution. Extra charge of Si<sup>4+</sup> (in comparison to Zn<sup>2+</sup>) attracts more oxygen in ZnO lattice reducing oxygen vacancies. Other emissions are lower in comparison to green emission in pure ZnO (Z0). The finite intensity of yellow emission indicates the presence of O interstitials which also get reduced with Si<sup>4+</sup> doping. Blue emission is found only in pure Z0 sample. In all the substituted samples, we do not find any blue emission suggesting that Zn vacancies ( $V_{zn}$ ) seize to exist after Si incorporation. Violet emission reduces in ZS1 but increases uniformly in ZS2 and ZS3 and is higher than the pure Z0. This indicates that Zn<sub>i</sub> decrease in ZS1 nominally but with more substitution due to localized lattice distortion an enhanced component of Zn<sub>i</sub> sites are probably generated.

Orange-red emission which is also due to  $O_i$ , reduces with silicon incorporation. Nevertheless, a significant orange-red emission exists in ZS1, ZS2 and ZS3 on chromatography index. Visible spectrum contains three primary colors red, green and blue. In the  $P_{N-color}$  vs x plots, it can be clearly seen that green emission decreases drastically while blue emission vanishes in doped samples. Thus, the red shift can be explained by the drastic reduction of green contribution and not due to enhancement of the orange contribution. Decrease in overall defects mainly oxygen vacancies  $(V_o)$  with Si<sup>4+</sup> substitution creates a more regular ZnO lattice with less defects. Increase in bandgap and reduction in Urbach tail width in doped samples is also due to the reduction of defect states. The modified ZnO material with lower defect and orange-red emission can be one of the potential candidate for photonics application.

# 4.1.3 Electrical measurements of undoped and Si<sup>4+</sup> doped ZnO:

For electrical measurements, all the powders annealed at 600°C were pressed (2 tons) into pellets and sintered at 1000°C for 2 hrs. Density of pellets were around 85% for all samples. High temperature sintering at 1000°C was done to reduce porosity and remove moisture from the sample. The phase was tested by XRD and Raman spectroscopy. There were no impurity peaks present but the XRD peaks were sharper indicating larger crystallite size. SEM studies reveal the size of these particles to be more than a micron. Porosity of the pellets of different samples was more or less comparable to each other.

#### a) Current- Voltage (I-V) characteristics:

Pellets of uniform diameter (10mm) and thickness (1mm) were prepared. Silver paste was uniformly coated on both sides of pellets and cured at the curing temperature of the silver paste ~150°C. I-V characteristics were measured in sandwich / capacitance mode [Figure 4.7] between -6V to 6V. A rough estimation of DC conductivity could be measured by this method to analyze the effect of silicon doping on electrical properties of ZnO. Consistent and precise results were only obtainable for low voltages, most probably because Ohm's law is valid for low-voltage intrinsic regime of lowconductive materials.



Figure 4.7: (a) Conductivity of Z0, ZS1, ZS2 & ZS3 shows increasing trend
(b) Composition dependence of conductivity at different voltage (2V, 6V &
8V). Increase in conductivity indicates Si<sup>4+</sup> acts as donor in ZnO lattice.

DC conductivity was calculated from the I-V curve using relation:  $\sigma(dc) = IL/VA$ , where I is the current, V is the voltage applied, L is the pellet thickness and A is the electrode area of the pellets (figure 4.7 (a)). The data reveals that silicon incorporation increases conductivity of ZnO, especially for applied voltages greater than 1V.

 ${
m Si}^{4+}$  acts as a donor and provides extra electrons to ZnO lattice which enhances carrier concentration. In ZS3, DC conductivity drastically enhances by a factor of ~10<sup>4</sup>. Hall measurement was done (shown later in next section) to confirm carrier concentration.

The composition dependence of conductance at different voltages (2V, 6V & 8V) was plotted [Figure 4.7 (b)]. It is observed that for ZS1 the change is minor for Z0 but thereafter increases linearly with silicon doping. This linear enhancement hints at a proportional relation between Si content with carrier concentration and mobility.

While Hall measurements were carried out to estimate carrier concentration, mobility was expected to increase with silicon doping due to reduced oxygen vacancies,  $V_0$ . Electrons are scattered by  $V_0$  centers to reduce mobility. Note that  $V_0$  center concentration drop with minimal Si addition for ZS1 and remain constant for all Si doped samples (as seen in photoluminescence studies). Hence, mobility is indeed a factor of conductivity enhancement resulting out of increased regularity of the lattice, but carrier concentration is more likely to be the decisive factor for linear enhancement of the conductance.



Figure 4.8: Schematic diagram for Hall-probe measurements.

#### a) Hall measurements:

Rectangular pellets were prepared by pressing nanocrystalline powder of Z0, ZS1, ZS2 & ZS3 at 3 Ton pressure in air atmosphere (figure 4.8). Four-point contacts were made at four sides using silver paste.



Figure 4.9: Variation in carrier concentration with  $Si^{4+}$  substitution. Increase in carrier concentration confirmed the donor behavior of  $Si^{4+}$  dopant in ZnO.

An immediate increase of carrier concentration from Z0  $(1.7 \times 10^{19}/\text{cc})$  to ZS1 followed by a gradual increase for ZS2 and ZS3  $(1.11 \times 10^{21}/\text{cc})$  was observed. The percentage change in carrier concentration from Z0 to ZS3 is ~1.5%. The number of donors in the Zn lattice increases due to the higher charge of Si<sup>4+</sup> which increases the carrier concentration (figure 4.9).

Higher charged and lesser ionic radii of Si<sup>4+</sup> decreases oxygen/zinc vacancy-related defects in ZnO lattice which improves optical transmission in the visible region. Reduction in defects also reduces strain in lattice and therefore c/a ratio increases and approaches towards ideal value. Improvement in optical transmission and reduction in strain increases bandgap with silicon doping. Si<sup>4+</sup> acts as a donor and provides extra electrons to ZnO lattice which enhances carrier concentration and therefore DC conductivity drastically increases by a factor of ~10<sup>4</sup>. The better optical transparency and high conductivity makes  $Zn_{1-x}Si_xO$  material fairly competent as transparent conductive oxides (TCO).

# 4.2 Bandgap and Defect state investigation of undoped and Si<sup>4+</sup>/Na<sup>1+</sup> co-doped ZnO:

Having discussed effect of silicon doping in ZnO, confirming silicon's role in suppressing defects due to its extra charge, we now focus on effect of extra charge of Si being compensated by addition of lesser charged Na<sup>+</sup> ions. The charge compensation should restrict reduction of V<sub>0</sub> and bring changes in electronic properties. A combination of Na<sup>+</sup><sub>2</sub>/Si<sup>4+</sup> co-doping is equivalent to Zn<sup>2+</sup>.

# 4.2.1 Bandgap Analysis:

Band gap was calculated using equation 4.1 which was found to be decreasing from 3.12eV in Z0 to 3.11eV in ZSN1 and then increases for higher doping [Figure 4.10].



*Figure 4.10: (a) Optical absorbance of Z0, ZSN1, ZSN2 & ZSN3 (b) variation of bandgap with x* 

As in Si doping, bandgap changes may be related to structural disorder, i.e. Urbach energy. A plot of  $ln(\alpha)$  against photon energy has been plotted and a linear fitting was done on linear part of the curve [Figure 4.11 (a)]. The composition dependence of Urbach energy was estimated from the fit using equation 4.2. Urbach energy (E<sub>U</sub>) increases from 83 meV in Z0 to 125 meV in ZSN1 and then decreases to 60 meV for ZSN3 [Figure 4.11 (b)]. These changes in Urbach energy (structural disorder) effectively modify the bandgap accordingly.



Figure 4.11: (a) Linear fit of  $\ln(\alpha)$  vs hv to assess Urbach tail (b) Variation of Urbach energy with x

It is evident from graph that  $E_U$  values change inversely with optical band gap ( $E_g$ ). The variation in bandgap might be due to the changes in Urbach tail width. The increase/decrease of  $E_U$  suggests the enhancement/reduction in atomic structural disorder of ZnO, related to decrease/increase of optical bandgap respectively with increasing Na<sup>1+</sup>/Si<sup>4+</sup> concentration. Changes in lattice disorder is also confirmed by strain variation with Na<sup>+1</sup>/Si<sup>4+</sup> co-doping as calculated from XRD and Raman spectra. The variation in lattice irregularity and strain hints modification of defects state which is later confirmed from photoluminescence studies.

## 4.2.2: Photoluminescence study:

Room temperature PL of the samples was studied in order to understand the effect of  $Na^{+1}/Si^{4+}$  co-doping on optical properties of ZnO. A relatively sharper near band edge (NBE) centered at ~390 nm in comparison to a wider and broader deep level emission (DLE) extending laterally from 450 nm to 750 nm is observed in all samples. However, the magnitude of DLE does not decrease with respect to the NBE as was the situation with Si-doping. On the contrary it becomes stronger. Note that the DLE of Z0 is centered at 518 nm whereas other doped samples are centered at ~600 nm: a clear red shift in the substituted samples similar to the Si-doped samples. To further confirm this, chromaticity coordinates have been calculated and plotted on 1931 standard chromaticity diagram.

The calculated coordinates are (0.32, 0.46), (0.47, 0.45), (0.44, 0.46), and (0.41, 0.45) for Z0, ZSN1, ZSN2, and ZSN3, respectively which indicates an enhancement of orange-red emission [Figure 4.12 (b)]. It confirms the shifting of color emission from green region to orange-red-yellow region with Na/Si co-doping.



*Figure 4.12: a)* Gaussian fitting of PL spectra of Z0, ZSN1, ZSN2 & ZSN3 *b)* Chromaticity diagram indicates red shift with Na<sup>1+</sup>co-doping.

Similar to Si-doped sample DLE is a broad spectrum composed of multiple peaks corresponding to UV (>3.1 eV), violet (3–3.1 eV), blue (2.50–2.75 eV), green (2.17–2.50 eV), yellow (2.10–2.17 eV) and orange-red (<2.1 eV) color ranges. Similar analysis was performed using Gaussian fittings [figure 4.12 (a)]. It was observed that the DLE region has a larger intensity than NBE in the doped samples. This is in contrast to the Si-doped samples where DLE decreased with doping.

NBE spectra are de-convoluted into two peaks for each sample: Z0 (3.16 eV & 3.24 eV); ZSN1 (3.18 eV & 3.26 eV), ZSN2 (3.18 eV & 3.27 eV) and ZSN3 (3.16 eV & 3.24 eV) respectively. The first peak is due to donor acceptor pair and the second peak is due to free excitons.

DLE of Z0 is de-convoluted into 9 peaks located at 2.69 eV (blue emission), 2.25 eV, 2.4 eV, & 2.54 eV (Green emission), 2.08 eV & 2.15 eV (yellow emission) and 1.85 eV, 1.95 eV & 2.02 eV (orange-red emission). Similarly, for the substituted samples each color range is composed of a set of peaks contributing to the same:

Blue: (ZSN2: 2.63 ZSN3: 2.71 eV)

Green (ZSN1: 2.28, 2.42, 2.48; ZSN2: 2.42, 2.23; ZSN3: 2.5, 2.35, 2.20) Yellow (ZSN1: 2.14 eV, 2.15 eV & 2.15 eV)

Orange-red (ZSN1: 1.64, 1.70, 1.78, 1.84 & 1.98; ZSN2: 1.63 eV, 1.74 eV, 1.93, 1.84 & 2.06 eV; ZSN3: 1.98 eV, 2.05 eV; ZS2: 1.75 eV, 1.77 eV, 1.82 eV, 1.89 eV, 1.98 eV, 2.05 eV; ZS3: 1.81 eV, 1.84 eV, 1.90 eV, 1.96 eV, 2.02 eV, 2.09 eV)

The marked decrease in the intensity ratio of  $I_{NBE}/I_{DLE}$  from Z0 (0.6) and ZSN1 (0.35) and then increase for ZV2 and ZV3 signify the enhancement in defect states with minimal co-doping of Na/Si and followed by a reduction [Figure 4.13 (a)]. P<sub>NBE</sub>/P<sub>DLE</sub> was calculated and was found to follow the same trend as  $I_{NBE}/I_{DLE}$  [Figure 4.13 (b)]. These trends exactly follow the strain (calculated in structural studies) and Urbach energy which indicates that defect state created by Na in ZSN1 is responsible for strain and lattice disorder. For higher doping ZSN2 & ZSN3, silicon dominates

and reduces overall defects.

The color fraction  $P_{color}$  of each color was calculated by using equation 4.3. Similar to Si-doped samples we have used UV as the reference contribution. The total UV emission is normalized to one, for all samples since there is very small change in bandgap with doping. Contribution of all colors arising from other transitions ( $P_N$ ) can be calculated by using equation 4.4. Green emission steadily increases from undoped samples to highly doped samples. This indicates that oxygen vacancy increases with Na<sup>1+</sup> co-doping [Figure 4.13 (c)]. The oxygen vacancies (responsible for green emission) which was reducing on silicon doping (in previous section) increases with Na co-doping. This indicates that charge compensation is incapable of reducing oxygen vacancies.



Figure 4.13: Variation of (a)  $I_{NBE}/I_{DLE}$  (b)  $P_{NBE}/P_{DLE}$  (c)  $P_N$  with  $Na^{1+}co$ doping.  $Na^{1+}co$ -doping increases defect states of ZnO.

On the other hand, the larger size of  $Na^{1+}$  creates strain in the lattice. This introduces oxygen defects. Although oxygen vacancies enhance, it changes insignificantly in higher doped sample. It might be due to the competitive effect of Si and Na in ZnO lattice; where Si reduce and Na enhance  $V_o$  concentration.

Orange-red emission has enhanced significantly for lower doping and then decreased for higher doping. This trend clearly follows strain calculated in previous chapter.

For lower doping, Na enters into interstitial sites (Na<sup>i</sup>). Na<sup>i</sup> sites also increase strain in the system (calculated in previous chapter). Structural disorder might have produced oxygen interstitials which enhances orangered emission. For higher doping, with increased amount of Si more lattice space is created due to the extremely small size of Si. Na and Si rearrange positions leading to management of space. This reduces O<sub>i</sub> defects in the lattice. Yellow emission, another signature of O<sub>i</sub>, follows similar trend as orange-red emission. This further confirms the proposed mechanism. Violet and blue emission is approximately invariant compared to other colors. This indicates minimal presence of Zn<sub>i</sub> and V<sub>Zn</sub> defects.



Figure 4.14: IV characteristics of Z0, ZSN1, ZSN2 & ZSN3 shows decreasing trend with  $Na^{1+}co$ -doping.

# 4.2.3: Electrical measurements of undoped and Si<sup>4+</sup> /Na<sup>1+</sup> co-doped ZnO

DC conductivity was using I-V measurements similar to Si-substituted samples [Figure 4.14]. Noisy data of the I-V characteristics is due to the extremely high resistance  $\sim 10^9$ - $10^{11}$  ohms. Limitations of Keithley meter 2401 restrict reliable measurements in this range. Si/Na co-doping decreases conductivity of ZnO material. Consistent decrease in conductivity may be related to increase in V<sub>0</sub> which reduces mobility by scattering electrons. Hence Na/Si modified ZnO cannot be used as a TCO but may find applications in UV sensing (explained in next chapter).

# 4.3 Bandgap and Defect state investigation of undoped and Vanadium (4+/5+) doped ZnO:

#### 4.3.1 Bandgap Variation with V (4+&5+) concentration:

It was shown that Si cleans off the defect states in the bandgap. However, Na incorporation in Si-substituted samples indeed leads to charge compensation but also leads to structural distortion, which retains and generates more defect states. Hence, higher charge substitution has been proved instrumental in removing absorption of light by decreasing defect states and donating charge carriers for transport. In this section it is to be verified whether only ionic valence is the main criteria for increasing conductivity. To verify this  $V^{4+/5+}$  ion substitution is targeted.

Optical absorbance data (using an Agilent UV–vis spectrometer (model Carry 60)) [Figure 4.15 (a)] revealed that band gap nominally increased from 3.16 eV as in Z0 to 3.20 eV for ZV1 and ZV2 (calculated using equation 4.1). For ZV3, there is again a nominal reduction to 3.19 eV [Figure 4.15 (b)]. The composition dependence of Urbach energy,  $E_U$  was estimated using equation 4.2 (figure 4.16 (a)).  $E_U$  increases from 0.082 eV in Z0 to 0.1 eV in ZV1, thereafter decreasing to 0.092 eV and 0.085 eV for ZV2 and ZV3, respectively [Figure 4.16 (b)].



Figure 4.15: (a) Absorbance of Z0, ZV1, ZV2 and ZV3 (b) Variation in Bandgap with Vanadium doping.

It was discussed that  $V^{4+}$  content increases in ZV1 and ZV2 but decreases for ZV3. Similar trend was seen for bandgap too.

Band Anti-Crossing (BAC) model[178] (equations 4.5) can be employed to model changes in band gap with vanadium incorporation. BAC model is used to describe the electronic structure in terms of interaction between localized d levels of doped vanadium and extended state of host ZnO.

$$E \pm = \frac{1}{2} [E_C + E_d \pm \{(E_C - E_d)^2 + 4x. c^2\}]^{\frac{1}{2}} \qquad \dots \text{eq 4.5}$$
  
where,  $E_c \sim \text{conduction band}$ ,  $E_d \sim V$  d-level energy,  $x \sim V$  content and  $C \sim$   
matrix element describing coupling between localized and extended states.

Neglecting E- ~  $E_V^{18}$ , the above equation transforms to,

$$E + = \left[E_C + \frac{x.c^2}{E_C - E_d}\right] \qquad \dots \dots \dots \text{ eq } 4.6$$

Conduction band shifts can be represented by equation 4.6.

When vanadium is doped into ZnO,  $V^{5+}$  creates state above valence band whereas  $V^{4+}$  creates state above  $V^{5+}$  state (comparatively closer to conduction band) [179]. According to equation 4.6, when  $E_c$ - $E_d$  is lower, conduction band shifts to higher energy and vice versa. In case of  $V^{4+}$ ,  $E_c$ - $E_d$  will be lower since  $V^{4+}$  state is comparatively near conduction band. Therefore, conduction band shift will be higher. In case of  $V^{5+}$ ,  $E_c$ - $E_d$  will be higher since  $V^{5+}$  state also is near valence band which reduces conduction band shift.



*Figure 4.16: (a) Linear fit of Urbach tail (b) Variation of Urbach energy with x* 

XANES studies (discussed in chapter 2) confirmed that  $V^{4+}$  concentration increases up to ZV2 and reduces for ZV3. This theoretical calculation exactly matches with our experimental results. With increase in  $V^{4+}$  content till ZV2, bandgap increases. For ZV3, as  $V^{4+}$  content reduces, bandgap also decreases. This confirms that band gap is dependent on vanadium oxidation state.

It is also observed in Si and Si/Na doped ZnO that reduction of Urbach energy is related to an increase of bandgap. This is because with regularization of lattice, band tails vanish and the gap increases between valence and conduction bands. However, in V doped ZnO, contrary to Si doping, bandgap does not have a monotonous nature of variation. Bandgap and  $E_U$  both change according to changes in the V<sup>4+/5+</sup> ratio [Figure 4.15 (b) and 4.16 (b)]. Contradictory results are observed where Urbach energy doesn't affect bandgap of ZnO. But, it was observed that  $E_U$  follows lattice strain (calculated from XRD and Raman). As discussed in previous chapter lower doping (ZV1) leads to interstitial sites. Lattice is disordered in this scenario and hence tail in the bands is expected, leading to an enhanced  $E_U$ . But for higher doping (ZV2 & ZV3), lattice gets relaxed due to substitution of smaller size vanadium ion, which reduces strain and thereby reduces  $E_U$ .

### 4.3.2 Photoluminescence study:

Room temperature PL spectrum of vanadium substituted samples revealed excessive increase of DLE region (extending from 450nm to 750nm) with nominal amount of introduction of  $V^{(4+/ \text{ or } 5+)}$  ions in the lattice. This reduces a little in ZV2 and ZV3 but still is of considerable amount. A relatively sharper NBE centered at ~380 nm is much nominal compared to the DLE is observed in all samples similar to Si & Si/Na doped ZnO. The DLE of Z0 is centered at 2.13 eV whereas with Vanadium doping, shifting is observed:  $ZV1 \rightarrow 2.25 \text{ eV}, ZV2 \rightarrow 2.27 \text{ eV} \& ZV3 \rightarrow 2.22 \text{ eV}$ . All three substituted samples show a blue shift [Figure 4.17 (a)]. Chromaticity coordinates have been calculated and plotted (1931 standard) to quantify and confirm the blue shift. Calculated coordinates are (0.44, 0.47), (0.39, 0.48), (0.38, 0.48), and (0.40, 0.47) for Z0, ZV1, ZV2, and ZV3, respectively which confirms enhancement of green and blue emission and reduction of red emission due to vanadium substitution [Figure 4.17 (b)]. Contrary to silicon doping, vanadium doping even with a higher charge shows enhancement in green emission.

**Opto-electronics properties of Pure and Modified ZnO** 



*Figure 4.17: (a) PL spectra of Z0, ZV1, ZV2 & ZV3 (b) Chromaticity diagram of Z0, ZV1, ZV2 & ZV3 indicates blue shift with vanadium doping.* 

To quantify specific defect states, both NBE and DLE were de-convoluted into several peaks belonging to different colors using Gaussian fittings [Figure 4.18 (a)]. The NBE of Z0 and ZV1 is deconvoluted into two peaks 3.19 eV (due to donor acceptor pair) and 3.27 eV (due to free excitons), whereas for ZV2 and ZV3, it is deconvoluted into one peak at 3.21 eV (donor acceptor pair). Multiple peaks corresponding to UV (>3.1 eV), violet (3–3.1 eV), blue (2.50–2.75 eV), green (2.17–2.50 eV), yellow (2.10–2.17 eV) and orange-red (<2.1 eV) color ranges were used to fit the broad DLE. The color of light emitted is a resultant of mixture of such colors.



*Figure 4.18: (a) Gaussian fitting of Z0, ZV1, ZV2 & ZV3 (b) Band energy diagram of vanadium doped ZnO.* 

In these samples, DLE is deconvoluted into several peaks corresponding to different color emissions (figure 4.18 (b)):

Blue (Z0: 2.74 eV; ZV1: 2.68 eV; ZV2: 2.68 eV; ZV3: 2.68 eV); Green (Z0: 2.22 eV, 2.36 eV, 2.55 eV; ZV1: 2.19 eV, 2.28 eV, 2.36 eV, 2.44 eV, 2.55 eV; ZV2: 2.25 eV, 2.33 eV, 2.44 eV, 2.55 eV; ZV3: 2.22 eV, 2.36 eV, 2.50 eV);

**Yellow** (Z0: 2.12 eV; ZV1: 2.10 eV; ZV2: 2.17 eV; ZV3: 2.14 eV); **Orange-Red** (Z0: 1.76 eV, 1.83 eV, 1.92 eV, 2.02 eV; ZV1: 1.76 eV, 1.83 eV, 1.92 eV, 1.98 eV; ZV2: 1.80 eV, 1.84 eV, 1.92 eV, 2.04 eV; ZV3: 1.73 eV, 1.84 eV, 1.98 eV, 2.04 eV).

Similar to silicon doping, quantitative analysis of defect state has been done in vanadium doped samples.

 $P_N$  vs. x shows that green emission along with other color emissions has increased for ZV1; for ZV2, except green emission, all other color emissions have reduced, whereas for ZV3 there is a drastic reduction in green emission (figure 4.19 (b)). This variation agrees with chromaticity coordinates. The marked decrease in intensity ratio of  $I_{NBE}/I_{DLE}$  from Z0 (0.24) and ZV1 (0.03) and then increase for ZV2 and ZV3 signify enhancement in defect states with small V doping and then it reduces [Figure 4.19 (a)].  $P_{NBE}/P_{DLE}$  followed same trend as  $I_{NBE}/I_{DLE}$ , which confirms increase in overall defects with minimal doping of vanadium, whereas further doping has reduced defect states.



Figure 4.19: Variation of a)  $I_{NBE}/I_{DLE}$  and  $P_{NBE}/P_{DLE}$  b)  $P_N$  with x

Vanadium doping is known to produce different defect centers in the ZnO lattice, which enhances the DLE region. According to the Kröger-Vink notation[180],  $V^{4+}$  and  $V^{5+}$  going to interstitial sites produces  $V_i^{\dots}$  and  $V_i^{\dots}$  defect centers, respectively. When Zn<sup>2+</sup> gets substituted by  $V^{4+}$  or  $V^{5+}$ , it creates  $V_{Zn}^{\dots}$  or  $V_{Zn}^{\dots}$ , respectively.

Reports on vanadium doped ZnO shows very inconsistent variation in optical properties [153–159,162–164]. It is observed in Si-doped samples in this study, that introduction of higher charge dopant in place of  $Zn^{2+}$  leads to reduction in oxygen vacancies and therefore suppression of green emission. But this does not hold for vanadium doped sample. In spite of higher charge of vanadium there is enormous enhancement in green emission.

Oxygen vacancies in pure ZnO is known for green emission. But XANES studies [discussed in previous chapter] indicates linear increase in oxygen content which should have reduced green emission. Hence, green emission enhancement and variation in V doped samples is not due to oxygen vacancies.

Theoretical studies (density functional theory) confirmed that 3d orbitals of vanadium split into  $t_2$  and  $e_g$  orbitals in the tetrahedral field of the ZnO lattice[181,182]. The O2p orbital has  $t_2$  symmetry. Therefore, V  $t_2$  interacts with O2p state forming a new hybrid *pd* state within the bandgap (above the valence band) [178,181,182]. Transition of electrons from conduction band to this new hybrid state may leads to enhancement in green emission. But, if this would be the only reason then green emission would have monotonously enhanced with increasing Vanadium concentration.

Non-monotonous nature of increase/decrease in green emission suggests green emission must be governed by some other factors. Vanadium V<sup>5+</sup> has d<sup>0</sup> electronic configuration and therefore does not have any electrons for the internal d-d optical transition. But, V<sup>4+</sup> has d<sup>1</sup> electronic configuration and therefore it has one spin allowed internal d-d optical transition (eg  $\rightarrow$  t2g). XANES study revealed that V<sup>4+</sup> content decreases for ZV3, whereas in ZV1 and ZV2 they are comparable. Hence the d-d optical transition in V<sup>4+</sup> seems to enhance the green emission in ZV1 and ZV2. In all samples containing vanadium, both internal *d-d* optical transition and the *pd* hybrid orbital transition enhance the green emission drastically in spite of a decrease in oxygen vacancies. However, the reduction in V<sup>4+</sup>concentration. Figure 4.15 (b) shows the expected transitions in vanadium doped ZnO.

Therefore, to summarize, both absorption and emission is strongly related to oxidation states of vanadium.  $V^{4+}$  content shifts conduction band to higher energies and therefore bandgap changes according to  $V^{4+}$  content. Vanadium (4+/5+) doping also enhances the green emission which is due to the transition from new *pd* hybrid state and d-d optical transition present in 4+ valence state. Although there are several reports explaining the green emission enhancement with vanadium doping in ZnO but the mechanism behind this enhancement was not understood well. This work proposes a possible mechanism.

## **4.4 Conclusions:**

- Charge as well as electronic structure of aliovalent ion dopant plays an important role in determining opto-electronics properties as well as functionality of ZnO.
- Si<sup>4+</sup> doped ZnO reduces overall defects especially oxygen vacancies and increases carrier concentration. Reduced defect i.e., increased transparency to visible light and increased conductivity makes this material appropriate as a Transparent Conductive Oxide.
- With the motive to verify whether charge is the only factor to affect bandgap, extra charge of Si<sup>4+</sup> was compensated by co-doping Na<sup>1+</sup> in ZnO. Na, due to its large size, modifies ZnO structure by occupying interstitial positions and thereby increasing O<sub>i</sub> defects for ZSN1. Further structural modification due to Na and Si rearrangement for ZSN2 & ZSN3 leads to better substitution reducing O<sub>i</sub> and Na<sub>i</sub>. V<sub>O</sub> increases steadily due to structural distortion which leads to scattering of electrons. This reduces conductivity of ZnO. Enhanced V<sub>o</sub> helps in sensing application discussed in next chapter.
- With the intension to investigate whether all higher charged substituent can lead to a TCO, we tried vanadium substitution. Contrary to Si<sup>4+</sup> substitution, V<sup>4+/5+</sup> increase green emission. However, V<sub>0</sub> is not responsible for green emission in these samples. Transition of electrons from conduction band to *pd* hybrid state (V3d-O2p) and d-d optical transition (in case of V<sup>4+</sup>) results in green emission. Absorption and emission strongly depends on Vanadium oxidation state.
- Above analysis proved that properties of modified ZnO does not depend only on charge of modifying ion but also on electronic structure of the ion. Hence its functionalities.
# Chapter 5 Multifunctional applications of synthesized materials

ZnO is sensitive towards different stimuli. It has been found that one or the other form of ZnO is sensitive to light, gas or other agents. In this chapter sensitivity parameters will be studied of pure and modified ZnO to understand the role of charge and size of the modifying doped ion in the ZnO lattice. This work is focused on changes due to moisture and light in these materials, as moisture and light are the most important natural agents of device failures.

The sensitivity of ZnO depends on its morphology and modifying ions. Humidity sensing of modified ZnO doped with  $Pd^{2+}$ ,  $Mn^{2+}$ ,  $Cu^{2+}$ , etc [183–187] is reported. Similarly, UV sensing is reported with Mg, Al, Sb, Cu, etc[188–194].

Device materials to be used in solar cells, etc., should be less sensitive to properties like moisture and light, to sustain performance against harsh environmental conditions. Hence, electrical properties (i.e. conductivity) of these materials should be stable for better performance and high efficiency of devices when exposed to high humid atmosphere. One such material usage is for Transparent Conducting Oxide (TCO) applications. Al and Ga doped ZnO has been discussed as possible TCO materials[195,196]. But when exposed to humidity these materials degrade [103–106].

When pure ZnO is used as an electron transport layer (ETL) in organic solar cell, surface defects and inter-gap states degrade conductivity[108,197–199] making the device unstable. In this chapter, effect of humidity and light has been focussed on some modified ZnO samples.

### 5.1 Moisture Resistant property of pure and Si substituted ZnO:

In previous chapters, it has already been discussed that Silicon doping in ZnO not only improves transparency to visible light (by reducing oxygen and other defect states), but also increases conductivity of ZnO. Increased conductivity and improved transparency make these materials appropriate for TCOs, usable as electrodes in solar cells, flat panel displays etc. So far tin doped indium oxide (ITO) has been widely used as a TCO. But ITO is expensive and of toxic nature, Hence, an alternative is long due. Moisture dependent electrical properties of Si substituted ZnO has been performed as a test of good performance against humidity.

### 5.1.1: Sample Preparation:

Powder samples Z0, ZS1, ZS2 and ZS3 annealed at 600°C were pressed into pellets with 3 tons pressure. Pellets were then sintered at 1000°C for 6 hr. Silver paste was used to prepare two electrodes, separated by 1.25mm, on the surface of pellets, for electrical measurements.

### 5.1.2 Experimental Set Up:

In order to study moisture resistance properties, the dynamic humidity response of pure and modified ZnO at room temperature were tested. A homemade set up was used for this experiment. Dry and humid air were passed over the samples consecutively for periods of 60 seconds each. The entire experiment was carried out in dry normal atmospheric air,  $R_H \sim 45\%$  (environmental relative humidity at IIT Indore location, summer time, between 11 a.m. to 3 p.m.). As explained in Chapter 2, the humid air was obtained by bubbling air in water resulting  $R_H \sim 75\%$ . Hence, electrical property differences for  $\Delta R_H \sim 30\%$ , is being reported in this thesis.

Multifunctional applications of synthesized materials



Figure 5.1: Response towards humidity of Z0, ZS1, ZS2 & ZS3

Figure 5.1 shows five repeatable cycles, between ON ( $R_H > 75\%$ ) and OFF ( $R_H < 45\%$ ) states in 60s interval. The resistance of all samples increases with increase in humidity. For Z0, resistance increases from 29 K $\Omega$  to 30.5 K $\Omega$ , i.e. by 1.5 K $\Omega$  (~5.2% increase). For ZS1 (x=0.013), this change is about 4.5%. For x > 0.013, it reduces further.

Humidity sensitivity, S, was calculated using the relation,

$$S = \frac{\Delta R}{\Delta R_H} X \ 100$$

where,  $\Delta R$  is difference in resistance under humid air and dry air condition,  $\Delta R_{\rm H}$  is the difference in the maximum relative humidity achieved under humid condition (75%) and relative humidity of the day when experiment was performed (45%). Sensitivity [Figure 5.2] drastically decreases with increasing silicon substitution from 60  $\Omega$ /%RH in Z0 to 1.67  $\Omega$ /%RH in ZS3. The response time (time required to reach 90% of final value of resistance in the presence of humid air) and recovery time (time required to reduce the resistance to 10% of saturation value in the presence of dry air) were recorded [Figure 5.2]. Response time is faster than recovery time in all samples.



Figure 5.2: Response time, Recovery and Sensitivity changes with x

### 5.1.3 Mechanism behind moisture resistant property:

Pure ZnO is highly sensitive to moisture. The sensing mechanism is based upon interaction between ZnO surface and water vapour. In semiconductors, oxygen vacancies act as active adsorption sites for water molecules[200,201]. Adsorbed water molecule dissociates into oxygen vacancies. Via proton transfer to a neighbouring bridging oxygen atom the adsorbed water molecule creates two bridging hydroxyl groups per initial vacancy. We expect a similar behaviour in case of ZnO surface. The hydrogen sites of water molecules are positively charged due to high electronegative nature of oxygen as compared to hydrogen. These charged hydrogen sites arrest free electrons from the conduction band of the surface ZnO molecules. This reduces surface current density, and therefore surface conductivity. However, as because the conductivity in total increases we may infer that the bulk component is actually not affected by the water adsorption process. To be noted that there are reports [111-114,202-205]claiming decrease in resistance due to increase in relative humidity, R<sub>H</sub>. This is explained in literature due to capillary effect due to porosity of the ZnO surface. The increment in conductivity is mediated through a combination of water and ZnO molecules. This process takes place for nanoparticles of 2–100 nm where the surface to volume ratio is large. However, in case of larger ZnO samples ( > 100 nm) inverse behaviour is observed [115,116,202]. Hence it is obvious that if porosity is omitted then surface oxygen vacancies will adsorb water and increase surface transport resistance.

In case of Si-incorporated ZnO, surface porosity has been taken care of by sintering the pellets at high temperature ~ 1000°C for 6 hr. SEM images of surfaces and cross sections confirm minimal porosity and a continuous surface with joined grains without space in between. Hence any water mediated transport in these samples may be ruled out. On the other hand, photoluminescence studies indicate reduction of oxygen vacancies with increasing Si doping. This is due to better oxygen retention capability on account of extra charge of Si<sup>4+</sup> (elaborated in chapter 4). Thus, decrease in  $\Delta R$  with increasing Si is due to reducing oxygen vacancies on the surface. This is a probable reason for lesser moisture sensitivity of the Si-substituted samples making them more moisture resistant.

In comparison to other doped ZnO TCOs, Si-substituted ZnO is thereby expected to sustain higher humid conditions. Hence, we believe that  $Zn_{1-x}Si_xO$  is a potential next generation TCO with better transport properties and robust moisture resistance.

# 5.2: Effect of different wavelength of light on pure and Si substituted ZnO:

Obtaining stability of performance under illumination is an important requirement for transparent conductive oxides used in transistors and display application [206,207]. It requires the material being insensitive to different wavelengths of light. Finding an appropriate material which remains transparent to visible light wavelengths and also not get affected in terms of photosensitivity is a challenge. With major deficits, pure ZnO is not a good candidate in this search. The conductivity of ZnO is affected by chemisorbed oxygen molecules. ZnO usually contain surface and deep level defects which generates unwanted photo-current during light transmission and device operation. These surface defects adsorb oxygen molecules under dark condition and reduce conductivity of ZnO. Exposed to UV, oxygen molecules can be released from ZnO layer leading to an improvement of ZnO conductivity. But prolonged UV illumination can generate irreversible degradation. Deep level defects act as recombination centers for photo generated charge carriers. causing significant photo current loss[108,197,207]. To remove these defects state and obtain photo stability, different methods has been employed like doping other elements in ZnO structure, surface passivation, synthesis in special environment, etc.

Si-substituted ZnO has been shown to have improved conductivity than ZnO. The material was found to be moisture insensitive. Moreover, defects states were reduced. To analyse the photo stability, effect of different wavelengths of light on conductivity of  $Zn_{1-x}Si_xO$  materials has been investigated.

### 5.2.1: Sample preparation:

Powder samples Z0, ZS1, ZS2 and ZS3 annealed at 600°C were pressed into pallets with 3 Tons pressure. Pallets were then sintered at 1000°C for 6 hr. Silver paste was used to prepare electrodes on the surface of pellets. Distance between the two electrodes were 1.25 mm and kept inside set-up to avoid the interference of external light.

### 5.2.2 Experimental Set Up:

In order to study effect of different wavelength of light, dynamic photo response of pure and substituted ZnO at room temperature was recorded (figure 5.3 (a)).



Figure 5.3: (a) % current change of Z0, ZS1, ZS2 & ZS3 at different wavelength of 300 nm, 350 nm, 360 nm, 380 nm, 390 nm, 400 nm, 450 nm, 500 nm, 550 nm, 550 nm and 650 nm (b) Variation of sensitivity with wavelength (c) Variation of sensitivity with x.

The "ON" and "OFF" time for light irradiation on samples was ~5 min. Different wavelengths of light (350, 380, 390, 400, 450, 550 and 650 nm) influence conductivity of samples with different sensitivity. A sharp increase in conductivity of samples was observed during the 'ON' mode for all wavelengths. However, it takes some time to reach a maximum conductivity. For light with wavelengths corresponding to lower energies, the response is very low. A correlation of response to light with structure and defect states seems probable. Conductivity decays as soon as light is switched 'OFF' and returns to its original value in a short span of time.

The photosensitivity for all samples has been carried out using formula [Figure 5.3 (b)]:

$$P_S = \frac{\Delta I}{I_{dark}} \times 100$$

where,  $\Delta I = I_{UV}$ - $I_{dark}$ ,  $I_{UV}$  is the maximum current under UV irradiation and  $I_{dark}$  is the current under dark condition.

Pure ZnO (Z0) has high photo-sensitivity for all UV wavelengths [350 nm, 380 nm and 390 nm]. Photo-sensitivity reduces for visible wavelength but is still higher than substituted samples.

Sensitivity reduces with increasing substitution [Figure 5.3 (c)]. The trend is observed for all wavelengths of light. A quantitative analysis shows that for all substituted samples illumination of 390nm (near to bandgap of samples) generates highest sensitivity. Photosensitivity increases gradually in the order  $350 \rightarrow 380 \rightarrow 390$ nm illumination and thereafter reduces for higher wavelengths.

#### 5.2.3 Mechanism behind reduced photosensitivity:

### a) Reduced Photosensitivity under UV light:

UV sensing mainly depends upon adsorption and desorption of oxygen molecule from the surface. Electrons are captured by the oxygen atoms which get adsorbed on the ZnO particle surface which result in a negative oxygen ion. UV light with energy greater than the bandgap when incident on the particles creates electron-hole (e-h) pairs. The negative oxygen ions find it easy to react with the photo-generated holes, thereby neutralizing them, leaving the photo-generated electrons behind. Density of available electrons for conduction increases. This enhances carrier density and lowers barrier height, thereby increasing the current. This is a probable mechanism of UV photo-response in ZnO.

Defects like oxygen vacancies on surface acts as active adsorption sites for oxygen molecule. Higher charge of  $Si^{4+}$  in comparison to  $Zn^{2+}$  attracts more oxygen in the lattice and therefore reduces oxygen vacancies (discussed in previous chapters). Reduction of oxygen vacancies from surface reduces

adsorption sites for oxygen molecules and therefore photosensitivity decreases for all UV wavelengths. Hence, Si<sup>4+</sup> doping stabilizes the photosensitivity of ZnO under UV irradiation.

### b) Reduced Photosensitivity under visible light:

Photosensitivity under visible light is mainly due to presence of different defect (trap) states on the surface of ZnO. These intragap states act as recombination centers for photo generated charge carriers, causing significant photo current loss. On illumination of light these defect states de-trap electrons and contribute to the conductivity. Visible light sensing is not very prominent in ZnO since trapping and de-trapping of electrons is not very significant. Reduction in photo sensitivity with Si substitution under visible light is a double confirmation for suppression of all trap state (Zn<sub>i</sub>, O<sub>i</sub>, V<sub>zn</sub>, V<sub>O</sub>, Zn<sub>O</sub> & O<sub>zn</sub>) which make this material photostable under visible light.

Si<sup>4+</sup> doping in ZnO leads to:

- Reduction of oxygen adsorption/desorption of oxygen molecule from the ZnO surface with Silicon doping stabilizes conductivity under UV light irradiation.
- Reduced trap state with silicon doping in ZnO decreases the photocurrent losses which is evident from visible light photosensitivity.

### 5.3 UV sensing property of Si/Na co-doped ZnO:

Silicon substitution makes ZnO moisture resistant and photostable by reducing surface defects and deep level defects. Such materials can be used as TCO to be used in solar cells, display devices, etc. Na co-doping in Si doped ZnO modifies overall defect structure and opto-electronic properties as discussed in earlier chapters. Because the resistivity increases in Na/Si modified these materials cannot be used as TCO material. But, such defect modification can be utilized for UV sensing application. To analyse it, UV

sensing properties of these materials has been studied.

### 5.3.1 Sample Preparation:

Powder samples Z0, ZSN1, ZSN2 and ZSN3 annealed at 600°C were pressed into pellets with 3 Tons pressure. Pellets were then sintered at 600°C for 2 hr. The pellets were not heated to 1100oC for this characterization because we wanted the surface porosity to increase in order to increase the surface area of the materials. Silver paste was used to prepare electrodes on the surface of pellets. Distance between two electrodes were 1.25 mm and kept inside the home made set up (explained in chapter 2).

### 5.3.2 Experimental Set Up:

To study the effect of UV light, the dynamic UV response of pure and doped ZnO at room temperature was tested. Intensity of UV light used for this experiment was 260 LUX. UV light of 390 nm wavelength corresponding to bandgap of material was selected at a voltage of 8V. "ON" and "OFF" time of UV light is ~ 7.5 min. This experiment was carried out in home-made set up ensuring there is no interference of outside light [Figure 5.4].



Figure 5.4: Photocurrent response of Z0, ZSN1, ZSN2 & ZSN3.

With irradiation of light, there is a sharp increase in conductivity of all samples. As soon as light is switched "OFF", conductivity falls drastically. The photosensitivity has been calculated using formula [208,209]:

$$P_S = \frac{\Delta I}{I_{dark}} \times 100$$

where,  $\Delta I = I_{UV} - I_{dark}$ ,  $I_{UV}$  and  $I_{dark}$  represent maximum current under UV irradiation and minimum current under dark condition.

Figure 5.5 shows six repeatable cycles, between UV "ON" and UV "OFF" states in 7.5 min interval. For Z0, photosensitivity ( $P_s$ ) is ~30%. For doped sample ZSN1, ZSN2 and ZSN3, photosensitivity increases to 560%, 2500% and 4000% respectively. Figure 5.5 represents photosensitivity of all samples which shows that UV photosensitivity increases drastically with Si/Na co-doping. The response time (time required to reach 90% of final value of current in presence of UV light) and recovery time (time required to reduce the current to 10% of saturation value in dark condition, i.e., in absence of UV light) were recorded.



Figure 5.5: Sensitivity of Z0, ZSN1, ZSN2 & ZSN3. UV sensitivity increases with  $Si^{4+}/Na^{1+}co$ -doping.

Figure 5.6 represents response time, recovery time and photosensitivity. Response time and recovery time decreases with increase in Si/Na concentration. This confirms that co-doping of Si/Na helps faster response to UV light and faster revival under dark condition than the pure ZnO.



*Figure 5.6: Response Time, Recovery Time and Sensitivity of Z0, ZSN1, ZSN2 & ZSN3. Decreased Response & Recovery time and increased sensitivity was found with Si*<sup>4+</sup>/Na<sup>1+</sup>co-doping.

### 5.3.3: Mechanism behind UV sensing:

Surface oxygen vacancies in ZnO act as adsorption sites for water molecules and other gaseous molecules [200]. Under dark condition, oxygen molecules capture free electrons and get adsorbed on pellet surfaces. Oxygen molecule adsorption is directly dependent on amount of surface defects (especially oxygen vacancies) and porosity [210].

### $O_2(g) + e^- \rightarrow O_2^-(ad)$

This leads to increase in surface resistivity of the pellets. When surface is illuminated by UV light of energy (390 nm) corresponding to bandgap of material, electron-hole pairs are generated [ $hv \rightarrow e^- + h^+$ ]. Photo generated holes migrate towards surface and reacts with adsorbed oxygen.  $h^++ O_2^-$  (ad)  $\rightarrow O_2(g)$ . Therefore, oxygen molecules get desorbed from surface and increases free carrier concentration which produces large photocurrent.

 $Si^{4+}$  doping reduces oxygen vacancies due to its higher charge. On the other hand, Na co-doping increases oxygen vacancies due to lower charge of Na and enhanced structural distortion. Increased oxygen vacancies increase oxygen adsorption sites and improves photosensitivity. Na co-doping also leads to formation of Na<sub>i</sub> defects in ZnO lattice [150,211] which trap electrons under ambient condition and reduce conductivity as evident in last chapter. With UV irradiation, surface oxygen desorption and electron de-trapping from Na<sub>i</sub> participates to increase photosensitivity. ZSN3 has maximum oxygen vacancies. Hence it has highest photosensitivity and fastest response & recovery time.

Sensitivity, selectivity, signal to noise ratio, stability and repeatability are five parameters on which a sensor's performance is evaluated. Increased photosensitivity, fast response and recovery time, high stability, good reproducibility and repeatability is found with increase in Si/Na co-doping. Hence, ZSN3 is an appropriate material for UV sensors. We observed in this study that with very nominal changes there are modifications in defect states of ZnO which may lead to multifunctional applications. Si doping in ZnO reduced photoconductivity and was more appropriate for TCOs & solar cells application; but when remodified by additional Na enhances photosensitivity and can be use in UV sensing applications.

### 5.4 UV sensing property of Vanadium doped ZnO:

Similar to Si/Na co-doping, Vanadium doping in ZnO reduces conductivity of ZnO by trapping electrons in defect state formed due to V3d-O2p hybridization. Modification in defect states with vanadium addition may lead to photo sensing. UV sensing applications has been tested for all samples.

### 5.4.1 Sample Preparation:

Powder samples Z0, ZV1, ZV2 and ZV3 annealed at 500°C were pressed into pellets with 3 Tons pressure. Pellets were then sintered at 500°C for 2 hr. Silver paste was used to prepare electrodes on the surface of pellets. Distance between the two electrodes were 1.25 mm and kept inside the home made set up.

### 5.4.2 Experimental Set Up:

UV response of pure and doped ZnO at a bias voltage of 8V was tested with a homemade set up discussed in Chapter 2. The same intensity of UV light (260 LUX) used for Na/Si system was used for this experiment too. Photoresponse of current in pure and vanadium doped ZnO is shown in Figure 5.7.



Figure 5.7: Photocurrent response of Z0, ZV1, ZV2 & ZV3.

UV light of wavelength~390 nm corresponding to bandgap of material was selected. In the "ON" state, i.e. with UV light incident on sample, there is significant increase in current, I<sub>UV</sub>, in comparison to the current in "OFF" state, I<sub>Dark</sub>, when the sample is in darkness. Figure 5.7 shows five UV "ON/OFF" cycles. Cycles are similar in nature and repeatable. As discussed in Na/Si co-doped ZnO, in pure ZnO, dark current is due to electron-hole pairs generated due to applied external field. In case of vanadium modified ZnO, electrons get easily trapped by new defects states created by interactions of V3d and O2p orbitals [discussed in previous chapter]. This reduce electron transport and thereby conductivity of the material. Hence, there is decrease in dark current with vanadium doping [Figure 5.7]. However, although dark current was lesser in vanadium incorporated samples, with UV illumination, the percentage change in current was significant. UV sensitivity was defined by the formula:

### $P_S = \Delta I / I_{dark} \times 100;$

where,  $\Delta I = I_{UV}$ - $I_{dark}$ ,  $I_{UV}$  is maximum current under UV irradiation and  $I_{dark}$  is current under dark condition. Sensitivity was plotted for all samples [Figure 5.8] and was found to increase with increasing vanadium content. Overall V<sup>4+</sup> and V<sup>5+</sup> content was estimated using the formula, V4+ or 5+ content = x. N<sub>4+/5+</sub>, where, composition (x) is amount of vanadium content and N<sub>4+/5+</sub> is the ratio of V<sup>4+or5+</sup>. and N<sub>4+/5+</sub> was calculated by XANES analysis. XANES provided an estimation of ratio of V<sup>4+</sup> and V<sup>5+</sup> content discussed in chapter 3. Table shows V<sup>4+</sup> and V<sup>5+</sup> content in samples.

Sample name	V <sup>4+</sup> content	V <sup>5+</sup> content
ZV1	0.6	0.179
ZV2	1.2	0.3
ZV3	1.67	0.621

Table 5.1:  $V^{4+}$  and  $V^{5+}$  content in V doped ZnO

Both  $V^{4+}$  and  $V^{5+}$  contents show increasing trends similar to sensitivity as shown in inset of figure 5.8 (a). Hence, UV sensitivity must be dependent upon vanadium ( $V^{4+}$  or  $V^{5+}$ ) incorporation.



Figure 5.8: (a)Sensitivity of Z0, ZV1, ZV2 & ZV3 [inset is  $V^{4+}$ ,  $V^{5+}$  and sensitivity content with x] (b) Variation in Response & Recovery time with Vanadium content. Graph shows dependence of UV sensitivity on  $V^{4+/5+}$  content.

Response time (time required to reach 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90% of final value of current in the presence of UV light) and recovery time (time required to reduce the current to 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90% of saturation value in the absence of UV light) were calculated for each sample shown in Figure 5.8 (b).

Note that the time taken to return to basic dark current from a saturated photo-excited current is larger in case of doped samples than the pure ZnO samples. With higher substitution this rate becomes faster indicating availability of more defect states for trapping.

Response and recovery time for each percentage of current growth and current decay has been plotted. Response time was slower for pure ZnO (Z0) [Figure 5.9 (a, b)]. However, recovery time was faster for Z0 than modified samples. Note that the trend in percentage growth graphs is linear for doped samples in contrast to pure ZnO samples, clearly hinting at different mechanisms for UV sensing in these samples.



*Figure 5.9: Variation in (a) response time and (b) recovery time for 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% & 90% of current growth* 

Increased photosensitivity, faster response and recovery time, high stability, good reproducibility and repeatability are found to increase with vanadium doping. ZV3 with high photosensitivity and faster response and recovery time is found to be the most appropriate material for UV sensors.

### 5.4.3: Mechanism behind UV sensing:

Surface oxygen defects play an important role in UV-sensitivity. As discussed in Si/Na co-doped ZnO, adsorption and desorption of oxygen molecules from surface leads to UV sensitivity in ZnO[212]. In dark condition, oxygen molecules capture free electrons from the surface of pellets and get adsorbed  $[O_2(g) + e^- \rightarrow O_2^- (ad)]$ . This leads to formation of high resistive region near the surface of the pellets. When the surface is illuminated by UV light of energy (~3.18eV $\rightarrow$  390nm) corresponding to bandgap of material, electron-hole pairs are generated [hv  $\rightarrow e^- + h^+$ ]. Photo

generated holes react with adsorbed oxygen, thereby liberating oxygen from surface  $[h^++ O_2^- (ad) \rightarrow O_2(g)]$  making electrons available for surface transport. Availability of surface Vo act as active adsorption sites for oxygen molecules and therefore increases UV sensitivity. However, in vanadium doped ZnO samples due to higher valence state of vanadium, oxygen will be retained more in the lattice than pure Z0. As a result amount of V<sub>O</sub>, should reduce and zinc be replaced by  $V^{5+ \text{ or } 4+}$  sites, therefore,  $V_{zn}^{\bullet \bullet \bullet}$ or •• should increase [Kroeger and Vink notation[180]]:  $2V^{5+/4+} + 5/4O^{2-} +$  $5/4V_0^{\bullet\bullet} \rightarrow 2V_{z_0}^{\bullet\bullet\bullet/\bullet\bullet} + 5/4O_0^X$ , where,  $O_0^X$  is an oxygen ion in its site, and  $V_0^{\bullet \bullet}$  is an oxygen vacancy with two missed electrons. This reduction in oxygen vacancies was also confirmed by XANES studies. Hence, if surface oxygen defects would have been the mechanism then with reduced oxygen vacancies, sensitivity should have reduced with increased vanadium incorporation. But in contradiction, there is enhancement in sensitivity. This clearly signifies that oxygen adsorption and desorption is not the mechanism for sensitivity in vanadium doped samples.

Vanadium ( $V^{4+}$  or  $V^{5+}$ ) incorporation must be creating defect states in between valence and conduction bands of ZnO[178,181], which trap free electrons from the lattice thereby reducing dark current. While  $V^{5+}$  state is empty,  $V^{4+}$  state has one available electron. When illuminated, these  $V^{4+}$ electrons transit to conduction band and contribute to photocurrent. On the other hand, after removal of UV illumination, the excited electrons require empty  $V^{5+}$  states to transit and get trapped; i.e.  $V^{5+} + e^- \rightarrow V^{4+}$ . Trapping is easier with abundance of empty  $V^{5+}$  states. Note that with such a trapping process current decreases and gradually approach dark current. Dark current is a result of transport of available carriers in the conduction band only after trapping is saturated. Note that the time taken to return to basic dark current from a saturated photo-excited current is larger in case of doped samples than pure Z0 samples. With higher substitution response and recovery rates become faster, indicating the availability of more defect states for trapping. Photo-response is faster in vanadium doped samples than pure Z0. From this observation it may be inferred that de-trapping of electrons from V-related defect states to conduction band in V-doped ZnO is faster than adsorption/desorption rate of oxygen in Z0.

Note that the response is fastest in the ZV3 sample as compared to ZV1 and ZV2, implying that availability of more  $V^{4+}$  electrons actually contribute to promptness of photocurrent generation. Oxygen desorption and de-trapping of V d-shell electrons, in pure and doped ZnO respectively are thereby probable mechanisms behind photo response, with latter being faster.

### **5.5 Conclusions:**

The key points of this chapter are:

- Silicon doping in ZnO reduces defects and increases conductivity which makes this material appropriate for transparent conductive oxides (TCOs) application. Moreover, Si doping also helps in increasing moisture resistant property and photo-stability of ZnO. This overcomes the problems associated with other available TCOs (Ga & Al doped ZnO). Silicon substitution makes ZnO robust for adverse environmental condition.
- UV sensing has enhanced with Si/Na co-doping in ZnO. This enhanced sensing is due to two effects that occur simultaneously:
  (1) Increased oxygen vacancies due to lower charge of Na<sup>1+</sup> (in comparison to Zn<sup>2+</sup>) which increases surface oxygen vacancies and therefore adsorption sites for oxygen molecules (2) Trapping and de-trapping of electron from defect states created with Na doping (Na<sub>i</sub>).
- UV sensing has enhanced with vanadium doping in ZnO. This enhanced sensing is due to faster rate of trapping and de-trapping of electrons by V- related defects (in vanadium doped ZnO) than the adsorption and desorption of oxygen molecules from the surface (as in pure Z0).

• Photosensitivity in Si/Na doped ZnO is much higher in comparison to photosensitivity of V doped ZnO. This indicates the importance of oxygen vacancies for UV sensing application.

# **Chapter 6**

## **Conclusion and Future Scope**

### **6.1 Conclusions:**

This work started with investigations on effect of aliovalent ions on bandgap of ZnO. Si<sup>4+</sup> was chosen because Si-O bond energies are significantly higher than that of Zn-O bonds. Thus, it was expected that the bandgap will not be affected much by Si incorporation. Extra charge of Si<sup>4+</sup> was also expected to attract more oxygen into ZnO lattice thereby improving crystalline quality. To our expectations, we were not betrayed by nature, when it was observed that crystalline nature of the Si-incorporated material improved. The signatures of better crystallinity were evident from XRD, Raman, UVvis spectroscopic studies. Electronically, bandgap behaved exactly according to our expectations and defect states were reduced as was evident from PL spectroscopic studies. The reduction of defect states not only prompted us to investigate conductivity but also study optical transparency properties.

Realizing that higher ionic valence state helps to improve characteristics of ZnO as a probable TCO, we wanted to ensure that charge indeed was a responsible factor. Hence, keeping Si in the matrix, we neutralized the extra charge of Si<sup>4+</sup> by introducing Na<sup>+</sup> in the lattice. The neutralized lattice immediately became defective enough firstly due to increased amount of V<sub>0</sub> and secondly due to structural strain introduced by larger Na ion. This defective lattice offered too much scattering to electrons drastically decreasing conductivity to very low values, even lower than pure ZnO. This makes the materials imperfect as TCOs. However, in the process we realized that such highly resistive materials are better sensors to light especially in the UV range. Hence, charge did matter to improve the materials' electronic transport and electronic properties.

Next, it was important to assure that charge alone can be good enough to improve optical transparency and electronic conductivity. Hence, we tried modifying ZnO lattice with V ions which are generally in the 4+ or 5+ states. Therefore, we can expect a similar effect as Si<sup>4+</sup>. However, due to electronic defect states formed by V in the bandgap region of ZnO due to V-O hybridization, the materials become less transparent to visible light. Also, presence of defect states and distorted lattice increases scattering of electrons, which reduces conductivity. Thus, just charge of the modifying ion is not the main factor to increase conductivity but also electronic properties, involving electronic hybridizations are critical.

This work thus guides the community to work on related problems evaluating changes expected due to changes in electronic bonding along with charge to steer towards the desired functionality.

### **Major Findings and Conclusions:**

#### 6.1.1 Synthesis and Solubility limit:

All samples were prepared by low temperature sol-gel synthesis technique as shown in figure 6.1. Solubility of  $Si^{4+}$  in ZnO was 2.7% beyond which secondary phase of  $Zn_2SiO_4$  was observed.



Figure 6.1: Sample preparation process using Sol-gel techniques

To compensate charge difference of host  $(Zn^{2+})$  and dopant  $(Si^{4+})$ , Na<sup>1+</sup> of lower charge is added in appropriate amount. Ratio of Si: Na was taken 2:1. Co-doping of Na<sup>1+</sup>/Si<sup>4+</sup> in ZnO does not affect solubility limit. It remained same (2.7%) as in Si<sup>4+</sup> added ZnO. Unlike Si and Si/Na, Vanadium addition

reduces solubility limit to 2.3% due to its variable oxidation states and electronic structure. Beyond 2.3%, secondary phase of  $Zn_3V_2O_8$  was observed.

### 6.1.2 Structural properties:

### a) Lattice parameters:

Rietveld refinement (using GSAS software) has been done to estimate lattice parameters (figure 6.2). Si<sup>4+</sup> dopant with higher charge than  $Zn^{2+}$  is expected to attract excess oxygen in lattice which was confirmed from EDS studies. This excess oxygen along lower ionic radii of silicon elongates the unit cell along c-axis while shrinking it along *a* and *b* -axes. With Si<sup>4+</sup>addition, c/a ratio increases and tends towards ideal value of 1.63, which signifies reduction in lattice disorder.



Figure 6.2: Variation in lattice parameter on doping (a)  $Si^{4+}$  (b)  $Si^{4+}/Na^{1+}$  (c)  $V^{4+/5+}$  in ZnO

Charge compensation by co-doping Na<sup>1+</sup> in Si<sup>4+</sup> added ZnO modifies overall structural properties. Lattice parameters *a*, *b*, *c* reduces for nominal addition of Na<sup>1+</sup> (ZSN1) and then increases for higher Na<sup>1+</sup> content. Similarly, c/a ratio follows same trend as lattice parameters. For ZSN1, Na<sup>+1</sup> may enter as interstitials which enhances lattice disorder and reduces c/a. For higher addition (ZSN2 & ZSN3), substitutional Na<sup>+1</sup> increases which reduces lattice disorder and therefore, c/a increases and tends towards an ideal value. Vanadium addition shows inconsistent lattice parameter changes. Small amount of vanadium addition (ZV1) may lead to partial interstitial site occupation leading to increase in lattice parameters and volume. But for higher addition (ZV2 & ZV3) when interstitial vanadium ions can no longer be accommodated proper substitution at  $Zn^{2+}$ site happens, enabling contraction of lattice parameters. c/a ratio in this case does not change much.

### b) *Strain:*

Strain of all systems were estimated from refinement parameters as shown in figure 6.3.  $Si^{4+}$  addition reduces strain of ZnO due to reduction in oxygen vacancies defects (evident from EDS studies). Strain agrees well with c/a variations.

In Na<sup>1+</sup>/Si<sup>4+</sup> modified ZnO, lower addition of Na<sup>1+</sup> (ZSN1) occupies interstitial positions which increases  $O_i$  defects and therefore lattice strain enhances. For higher addition, substitution increase due to proper rearrangement and coupling of Na<sup>1+</sup> and Si<sup>4+</sup> in the lattice which reduces strain.



Figure 6.3: Variation in strain on doping (a)  $Si^{4+}(b) Si^{4+}/Na^{1+}(c) V^{4+/5+}$  in ZnO.

Like  $Na^{1+}/Si^{4+}$ , in  $V^{4+/5+}$  modified ZnO, lower addition of vanadium increases strain which indicates the occupation of interstitial sites. While

strain reduces for higher vanadium addition signifying increase in vanadium substitution at  $Zn^{2+}$  sites.

### c) Crystallite size and Particle size:

Crystallite size was calculated from XRD using Scherer formula while particle size was calculated from FESEM using image J software (figure 6.4). In all cases, particle and crystallite size follows same trend. Lattice strain generally varies inversely to particle size. With Si<sup>4+</sup> addition strain of ZnO lattice reduces and therefore, particle get relaxed and grows in size. In Na<sup>1+</sup>/Si<sup>4+</sup> modified ZnO, increase in strain for ZSN1 inhibits particle grows and therefore size reduces. Again, for higher Na<sup>1+</sup> content strain reduces because substitution predominates over interstitials. Hence, particle and crystallite size increases. Similar to Na<sup>1+</sup>/Si<sup>4+</sup>, particle size depend upon strain, reduces for lower vanadium addition (ZV1) and increases for higher addition.



Figure 6.4: Variation in Particle Size on doping (a)  $Si^{4+}$  (b)  $Si^{4+}/Na^{1+}$  (c)  $V^{4+/5+}$  in ZnO.

### d) Vibrational Modes:

Vibrational modes were studied using Raman spectroscopy (figure 6.5). In  $Si^{4+}$  modified ZnO, intensity of  $E_2^{high}$  mode increases with substitution which reflects good crystallinity of wurtzite ZnO.



Figure 6.5: Variation in  $E_2^{high}$  on doping (a)  $Si^{4+}$  (b)  $Si^{4+}/Na^{1+}$  (c)  $V^{4+/5+}$  in ZnO.

Hence, structural regularity improves with substitution which is also indicated by strain and c/a parameters. Reduction oxygen defects was evident from weak  $E_1(LO)$  mode and thereby confirms a less defected lattice with Si substitution.

In Si<sup>4+</sup>/Na<sup>1+</sup> modified ZnO, increased FWHM and reduced intensity of  $E^{2}_{high}$  peak shows lattice distortion and low crystalline nature with Na/Si addition in ZnO. The peak  $E^{2}_{high}$ - $E^{2}_{low}$  at 334cm<sup>-1</sup> is attributed to second order or multiple phonon scattering in ZnO.  $E_{1}(LO)$  mode at 576 cm<sup>-1</sup> indicates the presence of oxygen/zinc vacancies in the lattice.

Like Si<sup>4+</sup>/Na<sup>1+</sup>, in V modified ZnO increased FWHM and reduced intensity of  $E^{2}_{high}$  peak indicates lattice distortion and low crystalline nature. Vanadium addition leads to red shift of  $E_{2}^{high}$  mode in comparison to pure ZnO due to difference in atomic mass of Zn, V and O.

### e) Oxidation state:

Si<sup>4+</sup> and Na<sup>1+</sup> have stable oxidation state whereas V has variable oxidation state which affects properties of host ZnO lattice. XANES studies revealed oxidation state of vanadium is 4+ & 5+ in all samples. V<sup>4+</sup>: V<sup>5+</sup>in ZV1, ZV2 and ZV3 is 77:23, 80:20 and 73:27 respectively. Theoretical calculation shows increases in oxygen content with vanadium addition.

### f) Comparison:

 $Si^{4+}$  substitute  $Zn^{2+}$  site and extra charge of  $Si^{4+}$  (in comparison to  $Zn^{2+}$ ) results into reduction in oxygen vacancies defect which decreases strain and lattice disorder.

Increase in intensity of  $E_2^{high}$  mode with Si<sup>4+</sup> substitution also signifies good crystallinity and highly ordered lattice. In order to compensate charge difference, Na<sup>1+</sup> of appropriate amount is added in Si<sup>4+</sup> modified ZnO which leads to major modification in defect structure. Nominal addition of Na<sup>1+</sup> increases interstitial defects which enhances strain and lattice disorder. Further addition increases substitution and thereby relaxes strain to some extent. To understand effect of similar or higher charge than silicon (4+), vanadium (4+/5+) has been added. Unlike silicon, small vanadium doping increases strain which is due to interstitial defects. Higher vanadium addition further reduces strain due to occupation of substitutional sites. Structural studies indicate that not only charge of dopant but its electronic structure, solubility limit, oxidation state and other physical properties plays vital role in determining properties and functionality of ZnO.

### 6.1.3 Opto-electronic properties:

### a) Variation in Bandgap and Urbach energy:

Bandgap for all system was estimated using UV-Vis spectroscopy (figure 6.6). In Si<sup>4+</sup> modified ZnO, bandgap increases steadily with substitution while Urbach energy, which is an estimation of lattice disorder, was found to be decreasing. Reduction in Urbach tail width, suppresses states near the band edges thereby effectively increases bandgap. Similar to Si<sup>4+</sup>, in Si<sup>4+</sup>/Na<sup>1+</sup>, bandgap change is inversely proportional to Urbach energy. This indicates the dependence of bandgap on lattice disorder. Unlike above two systems, in V modified ZnO bandgap strongly depends upon interaction between d-level of variable oxidation state of vanadium and conduction band of ZnO. Urbach energy variation in all cases agrees with strain calculated in structural studies.

### **Conclusion and Future Scope**



Figure 6.6: Variation in Bandgap on doping (a)  $Si^{4+}(b) Si^{4+}/Na^{1+}(c) V^{4+/5+}$ in ZnO.

### b) Photoluminescence Studies:

In Si<sup>4+</sup> modified ZnO, Near Band Edge (NBE) is centered at 390 nm while Deep Level Emission (DLE) is red shifted with Si<sup>4+</sup> substitution from 580 nm to 620 nm. Chromaticity co-ordinates confirmed green emission in pure ZnO whereas orange-red emission in modified ZnO. Reduction in green emission confirms oxygen vacancies suppression (figure 6.7 (a)). Increase in I<sub>NBE</sub>/I<sub>DLE</sub> and P<sub>NBE</sub>/P<sub>DLE</sub> confirms the reduction of overall defects and surface traps. Decrease in overall defects mainly oxygen vacancies ( $V_0$ ) with Si<sup>4+</sup> substitution creates a more regular ZnO lattice. This analysis agrees well with reduction in strain and Urbach tail width.

Unlike Si<sup>4+</sup>, in Si<sup>4+</sup>/Na<sup>1+</sup> modified ZnO, defects state increases (figure 6.7 (b)). There is clear red shift in DLE from 518 nm as in pure to 600 nm in modified. Chromaticity co-ordinates also confirms orange-red luminescence in modified ZnO. I<sub>NBE</sub>/I<sub>DLE</sub> and P<sub>NBE</sub>/P<sub>DLE</sub> trend confirms the increase in defect state for lower Na addition (ZSN1) whereas reduces for higher concentration. This trends exactly follows strain and Urbach energy which indicates defect created by Na is responsible for lattice disorder and strain. Intense orange-red luminescence for ZSN1 shows the presence of O<sub>i</sub> defects which is created due to Na<sub>i</sub>. Whereas, with increase in Na content, substitution increases which reduces Oi and therefore, comparatively less

intense orange-red emission found.  $V_o$  increases with Na<sup>1+</sup> which is due to lower charge of Na<sup>1+</sup> (in comparison to Zn<sup>2+</sup>).



Figure 6.7: Variation in color emission related defect state on doping (a)  $Si^{4+}$  (b)  $Si^{4+}/Na^{1+}$  (c)  $V^{4+/5+}$  in ZnO.

Unlike Si<sup>4+</sup> and Si<sup>4+</sup>/Na<sup>1+</sup>, Vanadium oxidation state plays important role in determining defect structure of ZnO. Blue shift in DLE was found with V-addition which indicates the enhancement of green emission.  $I_{NBE}/I_{DLE}$  and  $P_{NBE}/P_{DLE}$  trend confirms the increase in overall defect state. XANES studies reveal increase in oxygen content, which should reduce green emission. On the contrary, enhanced green emission is found in this material (figure 6.7 (c)). Enhancement and variation in green emission is attributed to transition from conduction band to *pd* hybrid state (possible in both V<sup>4+</sup> and V<sup>5+</sup>) and d-d optical transition (possible only in V<sup>5+</sup>state).

### c) Conductivity of pure and modified ZnO:

Si<sup>4+</sup> addition leads to increase in carrier concentration which was confirmed by Hall measurement. This increase in carrier concentration increases conductivity of modified ZnO by 3 orders. Unlike Si<sup>4+</sup>, Si<sup>4+</sup>/Na<sup>1+</sup> leads to reduction in conductivity of ZnO. Increase in defect state scatters electrons which reduces mobility and therefore, conductivity decreases. Formation of new *pd* hybrid state in case of V<sup>4+/5+</sup> traps free electrons and therefore reduces conductivity of material as in case of Si<sup>4+</sup>/Na<sup>1+</sup>.

### d) Comparison:

Bandgap of Si<sup>4+</sup> and Si<sup>4+</sup>/Na<sup>1+</sup> varies inversely to Urbach energy. Higher the Urbach energy (tail width), lower is the bandgap and vice versa. Si<sup>4+</sup> addition makes ZnO lattice more regular and ordered by reducing defect especially  $V_o$  which is evident by drastic reduction in green emission. Reduction in defect reduces strain and Urbach energy which increases bandgap of the material. Unlike Si<sup>4+</sup>, lower Si<sup>4+</sup>/Na<sup>1+</sup> content increases interstitial defects (O<sub>i</sub>) by increasing interstitial sites (Na<sub>i</sub>)which is evident by intense orange-red emission. Increase in defect state increases strain and Urbach energy which eventually decreases bandgap. For higher dopant content, occupation of substitutional sites increases (reduced orange-red emission) which reduces strain and Urbach energy and thereby, bandgap increases. Steady increase in green emission signifies enhancement in  $V_o$  which is due to lower charge of Na<sup>1+</sup> in comparison to Zn<sup>2+</sup>.

Unlike above two dopants, vanadium modifies ZnO in a different manner. It introduces new *pd* (V3d-O2p) hybrid state which was not evident in other two systems. Absorption and emission strongly depends upon oxidation state of vanadium. Increase in V<sup>4+</sup> state increases green emission due transition from new hybrid state and d-d optical transitions. While d-d optical transition is not possible in V<sup>5+</sup> state due to empty d orbital, therefore green emission reduces with increases in 5+ state. Conductivity of Si<sup>4+</sup> modified ZnO increases due to increase in carrier concentration whereas it decreases for Si<sup>4+</sup>/Na<sup>1+</sup> due to reduction in mobility of electrons i.e., scattering of electrons from  $V_o$ . V<sup>4+/5+</sup> addition leads to trapping of free electrons by new hybrid state which reduces conductivity.

### 6.1.4 Sensing properties of modified ZnO:

Si<sup>4+</sup> addition reduces defect i.e., increases transparency to visible light and increases conductivity of material and make ZnO appropriate for Transparent Conductive Oxide (TCOs) applications. TCOs should be highly moisture resistant and photostable for different wavelength of light

when used in solar cells, transistors and display devices. Unlike already reported ZnO based TCOs, Si doped ZnO is highly moisture resistant and photostable. In-house set-up was fabricated to test moisture resistant and photo stable properties of Si<sup>4+</sup> modified ZnO. It was estimated that ZS3 having highest content of silicon shows best moisture resistant and photostable properties. Si<sup>4+</sup> substituted ZnO overcome the problems of existing ZnO based TCOs (figure 6.8 (a)).

Defects like  $V_o$  helps in sensing applications. Keeping this in mind, UV sensing properties of Si<sup>4+</sup>/Na<sup>1+</sup> modified ZnO materials has been tested. Enhanced UV sensing was observed with increase in Na<sup>+1</sup> content (figure 6.8 (b)). This enhanced UV sensing is attributed to increased oxygen vacancies and trapping/de-trapping of electron from defect states created with Na doping (Na<sub>i</sub>).

Although, V<sub>0</sub> reduces for V<sup>4+/5+</sup> added ZnO but enhanced defect state helps in increasing UV sensitivity (figure 6.8 (c)). Contrary to pure ZnO, UV sensing in V doped ZnO doesn't depends upon oxygen adsorption/desorption due to reduction on oxygen vacancies. In V doped ZnO, faster rate of trapping and de-trapping of electrons by V- related defects is the probable mechanism behind UV sensing. UV sensitivity in V added ZnO is lower than Si/Na added ZnO. This confirms the active role of oxygen vacancies in UV sensing application. All these three studies indicate the strong relation between defect structure and functionality of ZnO material.



Figure 6.8: Based on structural and opto-electronic properties all the three systems has different functionalities (a)  $Si^{4+}doped$  ZnO has moisture resistant property which make it applicable for TCOs which can be used in high humid condition (b) $Si^{4+}/Na^{1+}doped$  ZnO shows high sensitivity in UV light with low response and recovery time (c) $V^{4+/5+}doped$  ZnO also shows god UV sensitivity but lower than  $Si^{4+}/Na^{1+}doped$  ZnO.

### **6.2. Future Scope:**

Research work presented in this dissertation focuses on the effect of aliovalent ion i.e., Si<sup>4+</sup>, Si<sup>4+</sup>/Na<sup>1+</sup>, V<sup>4+/5+</sup> addition on defect structure, structural properties and opto-electronic properties of ZnO. Based on these properties, functionalities of these materials have been determined. All experimental characterization techniques which are required for analyzing properties of synthesized material has been carried out. This work can be a foundation for further research in two different directions. Firstly, this work definitely needs theoretical support to further confirm the findings. Theoretical analysis using density functional theory needs to be done to confirm defect modifications considering accurate models to solve energy

states with changes in lattice parameters, dopant, preparation processes. Formation energy of each defect requires to be calculated theoretically considering factors discussed above to avail better understanding of overall electronic structure of modified ZnO. Another possible major direction is in the applicability of the materials in various devices. Search of new functionalities utilizing these properties of modified ZnO like TCOs and UV/moisture sensors, etc. may lead to easier cheaper application in near future.

Apart from above, possible future scope of work can be enlisted below:

- Modifying Si-doped ZnO by co-doping K, Li etc.
- Synthesis of Ge-doped ZnO and performing a similar study to understand the difference between the two dopants
- Investigations of the role of ionic radii difference on structural and opto-electronic properties.
- Investigating effect of defect modifications by selective doping to introduce magnetic properties of ZnO.

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## **Appendix**



Figure S1: (101) peak of (a) Z0, ZS1, ZS2 and ZS3 (b) Z0, ZSN1, ZSN2 and ZSN3 (c) Z0, ZV1, ZV2 and ZV3.

Intensity of pure ZnO and doped ZnO is almost same in all cases. Therefore, we cannot comment anything about crystallinity from XRD peaks. But shifting of peaks confirms the changes in lattice parameters and strain. Shifting in 2theta is consistent with changes in lattice parameter in all cases.

## Theoretical strain Calculation from Williamson hall method:

Si doped ZnO:



Si/Na doped ZnO:



Figure S2: Strain calculation for Z0, ZSN1, ZSN2 and ZSN3

V doped ZnO:



Figure S3: Strain calculation for Z0, ZV1, ZV2 and ZV3

Theoretical calculation of strain using Williamson hall method has been done to confirm the findings from refinement parameter shown in chapter 3. Trend in strain variation estimated from Williamson hall method is similar to trend determined from refinement parameter. So, both the methods agree with each other and confirms the effect of dopant on lattice strain. Although, values are quite different which might me due to error encountered during theoretical calculation.

## **Theoretical calculation for Lattice parameters:**

Like strain, lattice parameters are also theoretically estimated using formula for hexagonal lattice:

$$\frac{1}{d^2} = \frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2}$$

Graph shows the lattice parameters of pure and doped ZnO using above formula:



Figure S4: Lattice parameter for ZSO, ZSNO and ZVO

Trend in theoretically calculated lattice parameter exactly matches with the refinement lattice parameters. This confirms the variation in lattice strain with doping.

Like strain, here also the values are quite different which is due to error encountered in the theoretical calculation.

## EDS from TEM for Si doped ZnO:



Figure S5: HRTEM image and EDS of Z0 and ZS3

To further confirm, HRTEM was performed on several individual nanoparticles of the powders. Several arbitrarily chosen particles were investigated. The HRTEM images were Fourier transformed and from these representative area diffraction patterns the interatomic distances were calculated which conforms to a ZnO structure rather than any SiO<sub>x</sub> structure. All the particles showed ZnO phase irrespective of doping. However, in case of Si doping lattice order seems to be much better than pure ZnO, in which we observe crystallographic plane tilting in the long range within the same crystal which gives rise to elongated SAED spots. Several such observations compel us to believe the role of Si in Si-doped ZnO. TEM-EDS of 2.7% Si doped sample was performed to confirm content of Si impurities. The

measured content of Si in doped samples were commensurate to the actual intended doping and was comparable to the SEM-EDS values. We believe that the respected reviewer will agree to substitution with these scientific evidences.