Studies on single step formation of undoped and doped zinc oxide nanowire thin films for optoelectronic, sensing and self cleaning applications

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by

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То

My parents and teachers

DECLARATION

I, Ummar Pasha Shaik, hereby declare that the thesis entitled "Studies on single step formation of undoped and doped zinc oxide nanowire thin films for optoelectronic, sensing and self cleaning applications" submitted by me under the supervision of Prof. M. Ghanashyam Krishna is a bonafide research work which is also free from plagiarism. I also declare that it has not been submitted previously in part or in full in this university or any other University or Institution for the award of any degree or diploma. I hereby agree that my thesis can be deposited in Shodganga/INFLIBNET.

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Chapter 1. Introduction	1
11 Background	5
1.1 Dackground	
1.2 Metal oxide based nanostructured materials	5
1.3 Synthesis of nanostructured materials	6
1.3.1 Liquid phase techniques	9
1.3.2 Vapour phase growth process	10
1.3.3 Physical vapour deposition based techniques	14
1.4 Metal oxide nanostructures	15
1.4.1 Zinc oxide	16
1.4.2 Properties of ZnO	16
1.5 Surface enhanced Raman spectroscopy application of ZnO	19
1.5.1 Mechanism of enhancement in SERS	21
1.6 Wettability, self cleaning applications	23
1.7 Objective and importance of the thesis	25
Chapter 2. Experimental and Characterization Techniques	27
2.1 Thin film deposition techniques	31
2.1.1 PVD processes	
2.1.1.1 Thermal evaporation	32
2.1.1.2 Ion beam sputter deposition	
2.1.1.2.1 Parameters used for IBSD in this study	

Contents

2.2 Characterization	37
2.2.1. Thickness measurement	37
2.3. Structural characterization3	37
2.3.1 X-ray diffraction	37
2.3.2 Crystallite size, lattice parameter and strain calculations	39
2.4 Transmission electron microscopy	£0
2.4.1 Selected area electron diffraction4	1
2.4.2 Microstructural characterization4	12
2.4.3 Field emission scanning electron microscopy4	13
2.4.4 Atomic force microscopy4	14
2.5 Chemical composition	19
2.5.1 Energy dispersive x-ray spectroscopy4	19
2.6 Optical characterization	50
2.6.1 Ultra violet-visible-near infrared spectrophotometer	50
2.6.2 Raman spectroscopy and Photoluminescence spectroscopy 5	52
2.7. Nanoindentation	54
2.8 Contact angle goniometry	57
2.8.1 Pendant drop method5	59
2.8.2 Contact angle hysteresis:5	59
2.9 Summary	51

Chapter 3. Growth, Mechanical and Photoluminescence properties of
ZnO nanowire thin films63
3.1 Introduction
3.2 Experimental
3.3 Results and discussion
3.3.1 Growth of ZnO nanowire thin film
3.3.1.1 Structure
3.3.1.2 Microstructure
3.3.1.3 Cross-sectional FESEM76
3.3.1.4 Transmission electron microscopy77
3.3.1.5 Mechanism of nanowire growth78
3.3.1.6 Mechanical properties80
3.3.2 Photoluminescence study of ZnO nanowires with Zn residue 84
3.3.2.1 Optical transmittance
3.3.2.2 Photoluminescence
3.3.2.3 Photoluminescence excitation
3.3.3 Raman scattering93
3.4 Summary
Chapter 4. Morphology dependent non-linear optical response of ZnO
thin films
4.1 Introduction

4.2 Experimental	102
4.3 Results and discussion	104
4.3.1 Structure	104
4.3.2 Microstructure	105
4.3.3 Optical properties	107
4.3.4 Photoluminescence	108
4.3.5 Raman spectra	110
4.3.6 Energy level diagram	111
4.3.7 NLO properties	112
4.4 Summary	123
Chapter 5. Optical properties of Indium and Tin doped ZnO nan	owire
Chapter 5. Optical properties of Indium and Tin doped ZnO nan thin films	owire 125
Chapter 5. Optical properties of Indium and Tin doped ZnO nan thin films 5.1 Introduction	owire 125 129
Chapter 5. Optical properties of Indium and Tin doped ZnO nan thin films 5.1 Introduction 5.2 Experimental	owire 125 129 129
Chapter 5. Optical properties of Indium and Tin doped ZnO nan thin films 5.1 Introduction 5.2 Experimental 5.3. Results and discussion	owire 125 129 129 130
Chapter 5. Optical properties of Indium and Tin doped ZnO nan thin films	owire 125 129 129 130 130
Chapter 5. Optical properties of Indium and Tin doped ZnO nan thin films	owire 125 129 129 130 130 137
Chapter 5. Optical properties of Indium and Tin doped ZnO nan thin films	owire 125 129 129 130 130 137 145
Chapter 5. Optical properties of Indium and Tin doped ZnO nan thin films	owire 125 129 129 130 130 137 145 149
Chapter 5. Optical properties of Indium and Tin doped ZnO nan thin films 5.1 Introduction 5.2 Experimental 5.3. Results and discussion 5.3.1 Microstructure and structure 5.3.2 Compositional analysis 5.3.3 Optical properties 5.4. Summary Chapter 6. Applications of ZnO nanowire thin film	owire 125 129 129 130 130 137 145 149 151

6.2 Experimental	156
6.3 Results and discussion	158
6.3.1 Explosive detection by using surface enhanced I	Raman
spectroscopy technique	158
6.3.1.1 Morphology	158
6.3.1.2 Structure	162
6.3.1.3 SERS studies	166
6.3.2 Wettability studies	176
6.3.2.1 Structural	176
6.3.2.2 Microstructure	178
6.3.2.3 Wettability studies	179
6.4 Summary	188
Chapter 7. Conclusions and scope for future work	189
7.1 Conclusions	191
7.2 Scope for future work	194
References	195
List of publications	213

List of figures

- **Figure 1.1** Schematic representation of the building up of nanostructures [50].
- **Figure 1.2** Overview of various growth techniques for 1D nanomaterials. (tubes, wires, rods) from the gas phase and solution (scheme adopted from [87]).
- Figure 1.3 Growth of silicon nanowires by VLS [88].
- Figure 1.4 Crystal structure of ZnO.
- Figure 1.5 Schematic of electromagnetic enhancement and chemical enhancement in SERS studies.
- Figure 2.1 (a) Schematic diagram of ion beam sputter deposition system.
- **Figure 2.1(b)** View of the 16 inch dia UHV chamber with capability to sputter 3 targets without breaking vacuum (c) Kaufman type ion source (DC25 of Oxford Applied Research, UK) (d) Full view of ion beam sputter deposition coating unit and (e) the inner view of the chamber during sputter deposition.
- Figure 2.2 Illustration of stylus profilometry to measure film thickness.
- **Figure 2.3** Diffraction of X-rays by a periodically arranged of atoms in a crystalline material.
- Figure 2.4 Photograph of the Transmission electron microscope.
- Figure 2.5 Schematic diagram of atomic force microscopy.
- Figure 2.6 Positions of tip and cantilever before scanning.
- Figure 2.7 Interaction between two tip and surface from Lennard Jones Potential curve.
- **Figure 2.8** Nature of forces in the Contact and Non-contact mode of AFM operation [192].
- Figure 2.9 Photograph of the SPA-400 atomic force microscopy.
- **Figure 2.10** Photograph of field-emission scanning electron microscopy attached with INCA EDAX detector, used in the present work to determine microstructure and composition of the films.
- Figure 2.11 Schematic diagram of UV-VIS-NIR spectrophotometer [194].

- Figure 2.12 Example of nanoindentation load-displacement curve obtained from Berkovich indenter during loading and unloading.
- **Figure 2.13** photograph of the Hysitron (Triboindentor-900) nanomechanical test system.
- Figure 2.14 Drop profile over a solid substrate.
- Figure 2.15 Photograph of contact angle goniometer.
- **Figure 3.1** X-ray diffraction of the as-deposited Zn film and the films annealed at 200, 400 and 500 °C.
- **Figure 3.2** X-ray diffraction patterns of (a) as deposited and (b) Zn films annealed at 500 °C.
- **Figure 3.3** XRD patterns of (a) as-deposited, (b) 430 °C and (c) 500 °C annealed Zn thin films, # indicates Zn phase.
- **Figure 3.4** FE-SEM images of the (a) as deposited Zn films on BSG substrates and annealed to, (b) 200, (c) 400 and (d) 500 °C; (e) and (f) show the expanded view of the films annealed to 500 °C.
- **Figure 3.5.** FESEM images of Zn film deposited over (a) BSG (b) Quartz (c) YSZ (d) LAO and (e) ALO.
- **Figure 3.6** FESEM images of Zn films annealed at 500 °C over (a) BSG (b) Quartz (c) YSZ (d) LAO and (e) ALO.
- **Figure 3.7** Distribution of ZnO nanowires over BSG, Quartz, YSZ, LAO and ALO substrates.
- **Figure 3.8.** Cross-sectional FESEM images of ZnO thin films deposited on (a) ALO and (b) LAO substrates.
- **Figure 3.9** TEM images of Zn film annealed at 500 °C (a) bright field image, (b) selected area electron diffraction pattern and (c) high resolution TEM image.
- **Figure 3.10** A schematic representation of mechanism of nanowire/rod growth.

- **Figure 3.11** Typical load-displacement curves for the (a) asdeposited Zn film on different substrates and (b) ZnO nanowires on different substrates.
- **Figure 3.12** Optical transmission spectrums of (a) ZnO/Zn and (b) ZnO and (c) reflection spectrum for Zn thin film.
- **Figure 3.13** Photoluminescence spectrum of (a) ZnO/Zn and (b) ZnO thin films excited (340 nm) above bandgap energy of ZnO.
- Figure 3.14 Photoluminescence spectrum of (a) ZnO/Zn and (b) ZnO thin films excited (400 nm) near SP resonance of Zn.
- **Figure 3.15** Photoluminescence excitation spectrum of (a) ZnO/Zn and (b) ZnO thin films monitoring green and red emission respectively.
- **Figure 3.16** Photoluminescence excitation spectrum of (a) ZnO/Zn and (b) ZnO thin films monitoring blue emission.
- Figure 3.17 Raman spectrum of (a) ZnO/Zn and (b) ZnO thin films.
- **Figure 4.1** XRD pattern of thin films of (a) ZnO1 (b) ZnO2 (c) ZnO3 and (d) ZnO4.
- **Figure 4.2** FE-SEM images of (a), (e) ZnO1 (b), (f) ZnO2 (c), (g) ZnO3 (d), (h) ZnO4. (a)-(d) are in 1µm scale and (e)-(h) are in 200nm scale.
- Figure 4.3 (a) Absorption spectra of ZnO1, ZnO2, ZnO3, and ZnO4 thin films. Substrate absorption spectrum (solid line) is also included. (b)-(e) Tauc plots for ZnO1-ZnO4; Red (solid line) indicates the band gap, blue (dotted) line represents the presence of defect states.
- **Figure 4.4** PL spectra of (a) ZnO1 (b) ZnO2 (c) ZnO3 and (d) ZnO4 thin films excited with above band gap energy (355 nm) of ZnO.
- Figure 4.5 Raman spectra of ZnO1, ZnO2, ZnO3 and ZnO4.
- **Figure 4.6** Typical energy level diagram of ZnO films studied. Zni and Oi are the Zn and Oxygen interstitials, Vzn and Vo are the Zn and Oxygen vacancies.

- Figure 4.7 Fs open aperture Z-scan data of (a) ZnO1 (open triangles) (b)
 ZnO2 (open diamonds) (c) ZnO3 (open circles). Peak intensity used was ~0.21 GW/cm². Closed aperture Z-scan data of (d) ZnO1 (open triangles) (e) ZnO2 (open diamonds)
 (f) ZnO3 (open circles). Peak intensity used was ~0.034 GW/cm². Solid lines (red) in all graphs represent theoretical fits.
- Figure 4.8 Open aperture data of ZnO1 using 1 kHz chopper (open circles) recorded at peak intensity 0.21 GW/cm². Solid line (green) represents the 2PA theoretical fit. Closed aperture data of ZnO1 (open squares) recorded at peak intensity of 0.034 GW/cm². Solid line (red) represents the theoretical fit.
- Figure 4.9 Open aperture Z-scan data of (a) ZnO1 (open squares) at ~100 GW/cm² (b) ZnO2 (open diamonds) at ~119 GW/cm² (c) ZnO3 (open circles) recorded at ~144 GW/cm² (d) ZnO4 (open triangles) at ~152 GW/cm². Closed aperture Z-scan data of (e) ZnO1 (open squares) (f) ZnO2 (open diamonds) (g) ZnO3 (open circles) (h) ZnO4 (open triangles). Peak intensity used was ~28 GW/cm². Solid lines (red) in all graphs represent the theoretical fit.
- Figure 4.10 (a) Optical limiting data of ZnO1 (open circles) using ~2 ps pulses. Solid line (red) represents the theoretical fit
 (b) Optical limiting data of ZnO1 (open triangles) using ~140 fs pulses. Solid line (red) represents the theoretical fit.
- **Figure 5.1** FESEM images of In films (a) as deposited and (b)-(d) annealed at150, 200 and 250 °C.
- **Figure 5.2** FESEM images of Sn films (a) as deposited and (b)-(d) annealed at 230, 300 and 350 °C.
- Figure 5.3 X-ray diffraction patterns of the (a) In as deposited and annealed at 250 °C , (b) Sn as deposited and annealed at 350 °C and (c) Zn as deposited and annealed at 500 °C.

- **Figure 5.4** FESEM images of In-Zn, Zn-In, Sn-Zn and Zn-Sn films (a)-(d) as deposited, and (e)-(h) annealed at 500 °C.
- **Figure 5.5** EDS spectra of In-Zn, Zn-In, Sn-Zn and Zn-Sn films (a)-(d) as deposited, and (e)-(h) annealed at 500 °C.
- **Figure 5.6 (a)** X-ray diffraction patterns of the as deposited In-Zn, Zn-In, Sn-Zn and Zn-Sn films respectively.
- **Figure 5.6 (b)** X-ray diffraction patterns of In-Zn, Zn-In, Sn-Zn and Zn-Sn films annealed at 500 °C respectively.
- **Figure 5.7** Crystal structure (*P63mc*) of (a) pure ZnO, (b) In doped ZnO and (c) Sn doped ZnO.
- **Figure 5.8** Cross-sectional FESEM images of (a) In-Zn (b) Sn-Zn films annealed at 500 °C.
- **Figure 5.9 (a)** Transmittance and **(b)** Reflectance spectrum of as deposited Zn (blue), In (red) and Sn (green) films.
- **Figure 5.10 (a)** Transmittance and **(b)** Reflectance spectrum of Zn (blue), In (red) and Sn (green) films annealed at 500 °C.
- **Figure 5.11 (a)** Transmittance, **(b)** Reflectance spectrum of In-Zn as deposited (red), In-Zn 500 °C (black), Zn-In as deposited (blue), Zn-In 500 °C (green).
- **Figure 5.12 (a)** Transmittance, **(b)** Reflectance spectrum of Sn-Zn as deposited (red), Sn-Zn 500 °C (black), Zn-Sn as deposited (green), Zn-Sn 500 °C (blue).
- Figure 6.1 Schematic representation of experimental procedure for preparing ZnO films. (a) BSG substrate (b) microstructure of 1500 nm Zn film deposited by thermal evaporation (c) ZnO nanostructure, after subjecting a rapid annealing at 500 °C (d) Ag nanoparticles decorated on ZnO nanostructure (e) FESEM image of a selected region of figure (d) along with analyte detection (f) Raman spectra of the detected analyte (ANTA).
- **Figure 6.2** FESEM images of Zn films annealed at 500 °C for different morphologies A (a); B (b); C (c); D (d); E (e) and F (f).

- **Figure 6.3** Atomic force micrographs of Zn films annealed at 500 °C for different morphologies A (a); B (b); C (c); D (d); E (e) and F (f)
- **Figure 6.4** FESEM micrograph of BSG/Ag discontinuous film deposited by Ion beam sputtering unit.
- **Figure 6.5** Characterization of ZnO nanostructure: (a) XRD pattern and (b) Raman spectra of Zn/BSG films as deposited and morphology C sample. (c) Bright field image, (d) SAED pattern (e) HRTEM image of ZnO/BSG morphology C.
- **Figure 6.6** X-ray diffraction patterns of Zn film annealed at 500 °C for different morphologiesA, B, C, D, E and F.
- **Figure 6.7** (a) EDS spectra of Ag/ZnO nanostructure (b) Variation in the ratio of XRD peak intensity Zn (101) and ZnO (101) as a function of different morphology samples.
- Figure 6.8 SERS spectra of a) R6G and b) ANTA molecule adsorbed on Ag decorated ZnO films (Morphologies A, B, C, D, E and F).
 Figure 6.9 (a) SERS spectra of ANTA analyte and its (b) Enhancement factor, collected at 20 different sites over Ag/ZnO morphology C sample.
- Figure 6.10 Langmuir adsorption isotherm plots of R6G and ANTA molecules which were adsorbed on Ag decorated ZnO nanostructure.
- **Figure 6.11** Langmuir adsorption isotherm plots of CL20 and FOX 7 molecules which were adsorbed on Ag decorated ZnO.
- **Figure 6.12** SERS spectra of a) FOX-7 and b) CL20 molecule adsorbed on Ag decorated ZnOfilms (Morphologies A, B, C, D, E and F).
- **Figure 6.13** Enhancement factor for different Ag/ZnO probes (Morphologies A, B, C, D, E and F) along with Ag/BSG for (a) R6G, (b) ANTA, (c) FOX-7 and (d) CL-20.
- **Figure 6.14** A quantitative comparison of Enhancement factor for different analytes with roughness of the ZnO film.

- **Figure 6.15** XRD patterns of Zn films of thickness 500 nm (a) asdeposited and (b) annealed at 500 °C.
- **Figure 6.16** XRD patterns of Zn films of different thickness (a) asdeposited and (b)-(d) annealed at 500 °C.
- **Figure 6.17** FESEM images of Zn film of thickness 500 nm (a) asdeposited and (b) annealed at 500 °C on quartz substrate.
- **Figure 6.18** FESEM images (a)-(c) as deposited and (d)-(f) annealed at 500 °C of Zn films of thickness 2, 3 and 4µm respectively.
- **Figure 6.19** Schematic representation of (a) Wenzel's (b) Cassie-Baxter state of wetting.
- **Figure 6.20** AFM images of 500 nm thick Zn films (a), (b) as deposited and (C), (d) annealed at 500 °C deposited on BSG and quartz substrates respectively.
- **Figure 6.21** AFM images of Zn films (a)-(c) as deposited and (d)-(f) annealed at 500 °C of thickness 2, 3 and 4 μm respectively on BSG substrate.
- **Figure 6.22** Advancing and receding contact angle studies of different thickness of ZnO films deposited on BSG substrate.

List of tables

- **Table 1.1** A summary of the methods and mechanisms forsemiconducting oxide nanowires growth [95]
- Table 1.2 Properties of ZnO
- Table 1.3 Classification of wetting
- **Table 3.1** Hardness and Young's modulus of Zn films as-deposited andannealed at 500 °C.
- **Table 4.1** Estimated NLO coefficients β , n₂, χ ⁽³⁾ of ZnO films in the fs regime. Negative sign indicates negative nonlinearity. Some of the recent works are also highlighted.
- **Table 4.2** Estimated NLO coefficients β , n₂, χ ⁽³⁾ of ZnO films in the ps regime. Negative sign indicates negative nonlinearity. Some of the recent works are also highlighted.
- Table 5.1 Compositional analysis of In and Sn doped ZnO samples.
- **Table 5.2** Intensity ratios and unitcell volume of pure ZnO, In-Zn and Sn-Zn annealed at 500 °C.
- **Table 6.1** Binding equilibrium constant (*K*), initial concentration at saturation level (C_o) and adsorption factor (η) of different analytes.
- **Table 6.2** Contact angles of as deposited Zn films and films annealed to500 °C on BSG and quartz substrates.
- **Table 6.3** Contact angles and RMS roughness of as deposited Zn films ofdifferent thickness deposited on BSG substrate.
- **Table 6.4** Contact angles and RMS roughness of Zn films of differentthickness annealed at 500 °C deposited on BSG substrate.

Chapter

1

Introduction

Abstract

This chapter presents the various applications, physical and chemical properties of ZnO thin films. From the literature study, different methods to prepare metal oxide nanostructures and their applications are discussed. Objectives and the importance of the thesis and then finally the structure of the thesis are presented.

Chapter 1

1.1 Background

In recent years the study of nanostructured materials has become one of the most fascinating and exciting fields in physics, chemistry, engineering and biology [1-2]. Depending on dimensions, nanomaterials are typically classified into four groups: 0-dimensional, 1-dimensional, 2-dimensional and 3-dimensional [3]. 0-dimensional nanostructures with an aspect ratio near unity are called quantum dots or nanoparticles [4]. One-dimensional (1D) semiconductor nanostructures such as nanowires, nanorods, nanofibres, nanobelts, and nanotubes are of interest because of their potential as building blocks for other structures [5]. 1D nanostructures are useful materials as they enable investigation of the dependence of electrical, thermal transport, mechanical properties etc on dimensionality [1-2, 6]. Electronic, optoelectronic, electrochemical, and electromechanical nanodevices in the form of 1D nanostructures play an important role as both interconnects and functional units [7]. Thin films are 2- dimensional (2D) nanomaterials, which are applied widely in optical coatings, corrosion protection, and semiconductor thin film 3-dimensional (3D) nanostructures have attracted a lot of devices. attention because of their unique properties and potential applications [8-20].

1.2 Metal oxide based nanostructured materials

Metal oxides play an important role in many areas of research in chemistry, physics and materials science [21-26]. Metal oxides are an important class of materials that are used in diverse fields, such as catalysis, electronics, energy storage and conversion, biomedicine and

Introduction

sensors etc [27], because of their unique electrical, mechanical and optical properties. Nanostructured metal oxides are particularly important because materials of different shapes and sizes with special properties in comparison to those of bulk species can be synthesized easily [28-32].

As a consequence of their interesting structural, physical and chemical properties and functionalities, metal oxide nanostructures are the most widely investigated group of semiconductor nanostructure materials. The technological applications of these materials is very wide due to their unique and tunable properties such as optical, optoelectronic, magnetic, electrical, mechanical, thermal, catalytic, photochemical etc. Some of the more commonly synthesized metal oxide nanostructures are based on zinc oxide (ZnO) [33-35], copper oxide (CuO) [36-38], nickel oxide (NiO) [39-41], Iron oxide (Fe₃O₄) and Tin oxide (SnO₂) [42-43] etc. These nanostructures have been prepared by different methods, such as thermal evaporation [44-46] chemical vapour deposition, [47] and chemical synthesis, [34, 48-49].

1.3 Synthesis of nanostructured materials

There are two main approaches to synthesis nanomaterials; (1) Bottom up approach and (2) Top down approach.

(1) Bottom up approach: In this approach the energy of the process is used to realize nanostructures. It also relies on the natural ability of chemical and bio molecules to self assemble and self organize in the form of nanostructures. (2) Top down approach: In this approach the bulk solid is used as a precursor and brought to the nanoscale by a series of processing steps. These steps depend on the initial form of the solid. In the case of thin films the steps involve use of lithography and etching. However, when the solid is in the form of powder or crystal steps such as milling are involved as shown in figure 1.1.



Figure 1.1 Schematic representation of the building up of nanostructures [50].

The synthesis of nanostructured materials with desired morphology and composition is one of the most important challenges in the top down approach. Depending on the application many techniques for the

Introduction

fabrication of precursor materials in the top down approach such as thermal evaporation [51-68] metal organic and chemical vapor deposition [69-74], hydrothermal synthesis [75-81] template-based synthesis [82] can be used. Post processing of these materials result in different kinds of nanostructures such as nanoparticles, nanorods, nanowires, nanobelts, nanorings, nanoflowers, nanosheets, nanotubes, nanocombs, nanosprings, nano spirals [83-86]. The present thesis focusses on 1D nanowires due to the large range of applications in optoelectronics, electronics, solar cells and sensors.

Nanowire synthesis methods can be classified into two broad categories: liquid or solution based techniques and vapour based techniques. Liquid or solution based techniques include methods such as sol-gel synthesis, hydrothermal processes and electrodeposition. Chemical vapour deposition (CVD) using catalyst metals, reactive vapour transport, chemical vapour transport, laser ablation, carbothermal reduction, chemical beam epitaxy (CBE), thermal evaporation and thermal decomposition, and plasma-and currentinduced methods are classified under vapour based techniques [87]. A broad overview of these techniques is given in figure 1.2.

8



Figure 1.2 Overview of various growth techniques for 1D nanomaterials (tubes, wires, rods) from the gas phase and solution (scheme adopted from [87]).

1.3.1 Liquid phase techniques

The synthesis of nanowires using liquid phase techniques can be sub divided into two categories: (a) template based and (b) template free approaches.

(a) Template based methods:

These methods require the use of a basic template to guide the growth of 1D nanostructures. The templates can be positive, negative or surface step types [87]. Some of the common template based techniques are electro chemical and sol-gel methods.

(b) Template free methods:

In the template free methods the processing environment and parameters are exploited to realize 1D nanostructure. Examples of template free liquid phase methods include hydrothermal and sonochemical growth.

9

1.3.2 Vapour phase growth process

Two techniques have been explored for the formation of metal oxide nanostructures based on vapour phase growth techniques: (a) Vapour-Liquid-Solid (VLS) and (b) Vapour-Solid (VS) process.

(a) Vapour-liquid-solid technique

The VLS mechanism was first proposed in 1964 [88] to understand the unidirectional growth of silicon single crystals. It is proposed that a nanoscale particle which can form liquid solution catalyzes the nanowire growth and the initial nucleation event and the eventual nanowire diameter are critically dependent on the catalyst particle size. The nanowire is nucleated when the nanoscale liquid droplet becomes supersaturated and subsequent growth occurs by adding reactant selectively to this nanoscale droplet [88]. The orientation of the nanowire is determined by the epitaxial relation between nanomaterial and the substrate on which it is grown [89]. Figure 1.3 illustrates the growth of a silicon nanowire by VLS.



Figure 1.3 Growth of silicon nanowires by VLS [88].

The phase diagram can be used to select parameters such as catalyst composition, nanowire material, and temperature of growth for different nanowire materials and enables control of nanowire diameter and length [88]. Nanowires of important metal oxides like ZnO, MgO, CdO, TiO₂, SnO₂, In₂O₃, WO₃ [43, 51-57] have been synthesized by this technique.

(b) Solution-liquid-solid technique

The solution-liquid-solid (SLS) mechanism which is quite similar to VLS growth uses the solution phase in the SLS reaction. This is in contrast to the VLS mechanism wherein the reaction occurs in the vapour phase. This method has been employed to synthesize InP, InAs and GaAs nanowires. It has been reported that the diameter of nanowires was smaller than the diameter of the precursor catalyst nanoparticle [90]. However, in VLS growth the diameter of nanowires is

Introduction

similar or greater than the diameters of the catalyst nanoparticles [88-91]. This is attributed to the high reaction temperature of VLS (> 500 °C) which increases the size of the catalyst nanoparticle prior to nanowire growth. The smaller nanowire diameters in SLS method is attributed to the low-temperature used [91].

(c) Vapour-solid technique

The VS mechanism is another important mechanism for the formation of nanostructures that occurs in many catalysts free growth processes. In this process, control of supersaturation leads to the growth of 1D nanostructures. The steps are direct vaporization of the solid at a higher temperature followed by deposition of the nanowires at a lower temperature on solid substrates. This simple method has been widely used to synthesize a large number of semiconducting oxide nanowires [92-94] including ZnO, Ga₂O₃, SnO₂, MgO, WO₃, CdO, TiO₂, etc [43, 58-68].

Table 1.1 A summary of the methods and mechanisms for semiconducting oxide nanowires growth [95].

Materials (nanowire)	Growth method	Growth mechanism
ZnO	Direct evaporation	VS
Cd -ZnO	Thermal evaporation	VS
SnO ₂	Laser ablation	VLS
SnO ₂	Thermal evaporation	VLS
Sb-SnO ₂	Thermal evaporation	VLS
Sb-SnO ₂	Vapor-transport	VLS
Ta-SnO ₂	Vapor-transport	VLS
In ₂ O ₃	Laser ablation	VLS
Sn-In ₂ O ₃	Vapor-transport	VLS
Sn/Mo-In ₂ O ₃	Vapor-transport	VLS
Vertically aligned Sn-In ₂ O ₃	Thermal evaporation	VLS
β-Ga2O3	Chemical vapor deposition	VLS
ZnGa2O4	Chemical vapor deposition	VLS

1.3.3 Physical vapour deposition (PVD) based techniques

Thin films deposited by thermal evaporation, sputtering process, pulsed laser deposition (PLD), arc discharge method etc, have been transformed into nanowires by a variety of post processing methods.

(a) Thermal evaporation process

In thermal evaporation, the evaporated flux from the desired material source condenses on a substrate. This deposition method is performed in high vacuum without a gas atmosphere [96]. The property and characteristics of the films depend on the rate of deposition, substrate temperature, ambient pressure etc. A large number of nanostructured materials have been grown by this method [6, 34, 43, 51-68].

(b) Sputtering technique

Sputtering is a very useful technique for the deposition of compounds and alloys, (which cannot be evaporated easily) since the composition of the target can be retained in the film [97]. Recently this method has been used for the fabrication of variety of nanostructures of materials like ZnO, W, Si, B, CN, etc. [98-100].

(c) Pulsed laser deposition process (PLD)

In this technique a pulsed laser is used to vaporize a material that is tightly confined, both spatially and temporally, to produce small amount of nanoparticles [101, 102]. Significantly laser ablation can vaporize materials that cannot be evaporated [103]. PLD has been

14

significantly used to produce nanoparticles of Si, Si:H, TiO₂ and magnetic oxides [104-107].

(d) Spark discharge generation

The spark discharge technique is another method in which the source material is vaporized in the presence of inert gas by applying a bias across two metal electrodes until the break down voltage is reached. The arc (spark) formed across the electrodes then vaporizes the source material to produce small amount of nanoparticles [102]. This method can be used to produce elemental nanoparticles in the presence of inert gas and compound nanoparticles such as oxides and nitrides in the presence of the corresponding reactive gas [108, 109].

(e) Chemical vapour deposition

Chemical vapour deposition (CVD) has been used to fabricate both organic and inorganic thin film materials. In CVD process the source materials are gases that react and condense to form thin film. The precursors can be solid, liquid or gas at ambient conditions, but are delivered to the reactor as a vapour (from a bubbler or sublimation source, as necessary). Under favourable conditions, nanoparticles form due to the gas phase reactions.

1.4 Metal oxide nanostructures

As stated earlier, among all functional materials, metal oxide nanostructures are particularly attractive candidates since they exhibit a wide range of interesting optical, electronic, magnetic, mechanical and other properties. The potential applications for metal oxide
Introduction

nanostructures include self-cleaning, molecule detection by surface enhanced Raman spectroscopy (SERS), cosmetics, catalysis medical diagnostics, magnetic and optical devices, batteries, displays and fuel cells, electronic and magnetic devices, solar cells, biomaterials, sensors, structured materials and protective coatings.

1.4.1 Zinc oxide

A number of metal oxides have been investigated extensively for applications in nanostructred devices and technologies involving nanomaterials. Among these Zinc oxide (ZnO) is one of the most important II-VI group semiconducting materials having a direct wide band gap (3.37 eV) and a large exciton binding energy (60 meV) at room temperature. These properties make ZnO as one of the most attractive materials for the fabrication of optoelectronic devices operating in the blue and ultraviolet (UV) region [110, 111]. Oxygen deficient ZnO has been applied as a transparent conducting and piezoelectric material for fabricating solar cells, electrodes, and sensors [112-114].

1.4.2 Properties of ZnO

(a) Crystal structure: ZnO exists in three polymorphs (1) hexagonal wurtzite, (2) cubic zincblende, and (3) the rarely observed cubic rocksalt. Among all the three, hexagonal wurtzite structure is most common and more stable in ambient conditions with a hexagonal unit cell and lattice parameters a = 3.25 and c = 5.2 Å. In the wurtzite structure the tetrahedral unit is formed by the oxygen anions and Zn cations and lacks a centre of symmetry. The structure of ZnO can be described as a

number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternatively along the c-axis [98-100, 108, 109, 115-121] as shown in the figure 1.4.



Figure 1.4 Crystal structure of ZnO.

(b) Mechanical and thermal properties: ZnO is a soft material compared to other oxides having a hardness value of 4.5 on the Mohs scale. It works as a ceramic material due to the high heat capacity and thermal conductivity with low thermal expansion and high melting temperatures. ZnO has one of the highest piezoelectric tensor of 1.29 C/m² [122] which makes it suitable candidate for piezoelctric applications that require a large electromechanical coupling.

(c) Electronic properties: The large band gap enables ZnO to sustain high electric fields, leading to the possibility of lower electronic noise and high temperature operation. Most of the ZnO based materials are ntype and p-type doping is difficult.

(d) Optical properties: Due to its wide band gap, ZnO exhibits luminescent properties in the near ultra violet and visible regions and excitonic emissions are also observed. Bulk and thin film ZnO exhibit three PL peaks, a UV near band-edge emission peak near 380 nm, a green emission near 510 nm and a red emission around 650 nm [123-125]. The broad green-yellow band near 505 nm is due to deep level emissions in green region, which is ascribed to oxygen vacancies, zinc interstitials or zinc vacancies [126]. The physical properties of the ZnO material are summarized in the table 1.2 below [127, 128].

Properties			
Chemical formula	ZnO		
Molar mass	81.4084g/mol		
Appearance	Amorphous white solid		
Odor	Odorless		
Density	5.606g/cm ³		
Melting point	1,975 °C		
Boiling point	2360 °C		
Solubility in water	0.16mg/100 mL		
Band gap	3.37 eV (direct)		
Refractive index	2.0		
Structure			
Crystal structure	Wurtzite		
Space group	C _{6v} ⁴ -P6 ₃ mc		
Lattice constant	a = 3.25 Å, $c = 5.2$ Å		
Coordination geometry	Tetrahedral		

Table 1.2 Properties of ZnO.

1.5 Surface enhanced Raman spectroscopy application of ZnO

Surface enhanced Raman spectroscopy (SERS) is one of the most powerful techniques for the detection of molecules at the trace level. SERS is a surface dependent spectroscopic technique, typically utilizing metal nano-structures, which allows enhancement of the Raman signal from adsorbed analyte species of very low concentration. SERS is observed primarily for analytes adsorbed onto metals like Au, Ag, Cu or alkali (Li, Na, K) metal surfaces, with the excitation wavelength near or in the visible region [129, 130].

Raman signature enhancement can be obtained when the analyte in trace amount gets in contact with the nanosized plasmonic metal surface through the excitation of surface plasmons. The oscillations of surface

Introduction

plasmons generate local field intensity enhancements under the influence of which an analyte molecule radiates more. If the excitation wavelength is closer to plasmonic absorption of metal nanomaterial resonantly enhances the Raman scattering.

The SERS effect was first observed by M. Fleishmann in 1974 for pyridine molecules adsorbed on silver electrodes. Albrecht and Creighton [131] proposed that the resonance Raman transitions from the electronic states of molecules those broadened due to the interaction of metal surface target might be responsible for Raman enhancements [132]. Single molecular (SM) detection was carried out by different groups Kneipp et al. [133], Nie et al., [134] and Emory et al. [135]. Researchers have reported that the colloidal Ag and Au NPs have demonstrated enhancement factors (E.F.s) upto 10⁷ [136-138]. Xu et al. [139] increased the E.F. up to 10¹¹ in the presence of sharper edge of disintegrated spherical NPs (nanoparticles) and also recognized that the space between the Ag NPs demonstrated huge enhancement. Moreover, the plasmonic NSs (nanostructures) such as Ag, Au and Cu, have been comprehensively used as active platforms for SERS for trace level detection of various analytes [140-145]. Similarly the plasmonic plating of silicon (Si) NMs (nanomaterials) substrates also demonstrated the SERS activity [146-149]. SERS is the proficient technique for the identification bio-molecules [150, 151], bacterial detection [152, 153] and explosive molecules in the trace level [154-156].

1.5.1 Mechanism of enhancement in SERS

In recent years many groups have demonstrated the SERS enhancement of the analytes through adsorption in colloidal Ag and Au NPs and they confirmed that the enhancement occurred under the effect of nanostructure and it is not because of surface effect [157].

There are two possible mechanisms responsible for the Raman signature enhancement in SERS process. First, number of molecules (cross-section) participating in Raman is more when these molecules are in close contact with metal NSs enables charge transfer between the NS and analyte molecule. This is known as chemical enhancement. Second, enhancement of Raman signal takes place due to local field produced through the surface plasmons excitations which is known as electromagnetic enhancement.



Figure 1.5 Schematic of electromagnetic enhancement and chemical enhancement in SERS studies.

High SERS enhancement factor practically means spatial inhomogeneity. The enormous SERS effects usually occur in the so-called 'hot sites', i.e., very small volumes in the cavities between metal nanoparticles [139, 158, 159]. Theoretical studies show that the local electromagnetic field near metal nanoparticles is strongly confined to the 'hot sites' by the surface Plasmon resonance resulting in an inhomogeneous electromagnetic energy distribution [160]. Since metallic nanoparticle arrays supply a

high density of nanocavities between particles, i.e., SERS 'hot sites', they seem to be the perfect substrates for SERS [161-165].

1.6 Wettability, self cleaning applications

Wetting of a solid by a liquid depends on many parameters specific to both liquid and substrate properties such as surface tension of the liquid and surface energy of the solid. By controlling the liquid properties it is important to control the interactions between the liquid and the surface of the substrate in many practical applications. In particular by changing the concentration of multi-component liquids the reversible switching between hydrophobicity and hydrophilicity is an attractive property [166, 167]. The wetting behaviour of a liquid on a solid substrate is determined by the difference between the cohesive interactions holding the liquid together and the adhesive interactions between the liquid and the solid. The classification of wetting in terms of liquid-liquid and solid-liquid interaction is presented in Table 1.3.

Contact angle	Degree of wetting	Solid-liquid interaction	Liquid-liquid interaction
$\theta = 0^{\circ}$	Perfect wetting	Very Strong	Very Weak
$0 < \theta < 90^{\circ}$	High wettability	Strong	Weak
$90^\circ \le \theta < 180^\circ$	Low wettability	Weak	Strong
$\theta = 180^{\circ}$	Perfect non- wetting	Very Weak	Very Strong

Table 1.3 Classification of wetting.

Surface roughness of the substrate is also influences wetting. Roughness leads to amplification in wetting properties [168]. Increase in the roughness of hydrophilic surface decreases the contact angle Introduction

whereas in case of hydrophobic surfaces increase in roughness increases the contact angle. The normal hydrophobicity of a material becomes superhydrophobic when the wetting property of the material is amplified by the roughness of the substrate. For the dust-free coatings superhydrophobicity is an important, which prevent snow sticking etc. There are two kinds of Superhydrophobic surfaces. One type provides a sticky surface on which it is difficult for liquid drops to move and the other is slippery surface where there is little resistance to drop motion. Lotus leaf is the best example of superhydrophobic surface where water molecules are not able to settle on these surfaces and the contact angle of water is more than 150° [169]. The hierarchical structure of lotus leaf provides the superhydrophobicity [170, 171]. Due to micro and nano scale order of the roughness lotus leaf shows superhydrophobicity [170]. Based on the behaviour of the lotus leaf by introducing the dual scale roughness or patterning there is an interest to study the superhydrophobicity on different surfaces [168]. Micro and nano structured substrates are known to show super-hydrophobicity [171].

Recently there is interest in solid surfaces whose wettability is reversible under ultraviolet irradiation [172, 173]. By rain water and antifogging superhydrophilic property is used for self-cleaning action [174] On the other hand superhydrophobicity is used in various industrial products for stain proof, rust resistant surfaces to increase the life of the machine [175].

Under UV irradiation some of the metal oxides such as ZnO, SnO₂ and TiO₂ change their wetting property from hydrophobic to

hydrophilic state. These kinds of metal oxides are the ideal choice for self-cleaning coating due to their high oxidation power, photo-induced hydrophilicity, and high transparency in the visible range. Due to UV irradiation surface electrons and holes will generate on the surface of these materials. Oxygen ion vacancy is created by the interaction between the holes and lattice oxygen. The interaction between electrons and metal will produce surface trapped electrons. As a consequence the binding energy between metal and oxygen atom decreases. The hydroxyl absorption takes place by the oxygen ion vacancy and as result after UV exposure the substrate becomes hydrophilic. The change in wettability is due to enhanced surface hydroxyl group which improves wetting. There is desorption of hydroxyl ion by keeping the sample in the dark as a result the substrate regains its original state of wetting. Upon UV exposure a metastable state is formed which can be changed to its original state by dark storage. Transparency of the film is also important for their use as self-cleaning surfaces.

1.7 Objective and importance of the thesis

The foregoing literature review clearly indicates the importance of nanostructured materials and devices in a variety of applications. It is also evident that ZnO is a material that possesses a wide variety of interesting physical properties. The preparation of nanostructures such as nanowires, however, remains a challenge especially in the context of developing a process that is compatible with current technology.

Introduction

The objectives of the present work are to

- 1. Develop a single step process for the preparation of ZnO nanowires.
- 2. Investigate conditions of growth that lead to formation of nanowires.
- 3. Study optical, wettability, mechanical and sensing properties of the nanowires.

The structure of the thesis is as follows: Chapter 2 reports the general experimental methodologies used in our research works. Chapter 3 deals with the growth, properties of ZnO nanostructures deposited on different substrates. Chapter 4 deals with the morphological dependent nonlinear optical properties of nanostructured ZnO thin films. Chapter 5 deals with the growth and the optical properties of nanostructured doped ZnO thin films. Chapter 6 gives the information about the SERS and self-cleaning applications of ZnO. Chapter 7 presents the general conclusions of the work reported in the thesis and some ideas on the scope for future work.

2

Experimental and Characterization Techniques

Abstract

In this chapter, a brief description of the thermal evaporation and Ion beam sputter deposition methods is provided and the importance of the process parameters in thin film deposition is discussed. Details of characterization techniques such as, x-ray diffraction, transmission electron microscopy, field emission-scanning electron microscopy, atomic force microscopy, energy dispersive x-ray spectroscopy, UV-VIS-NIR spectrophotometer, Photo Luminescence spectroscopy, Raman spectroscopy, nanoindentation and contact angle are presented in the second part.

2.1 Thin film deposition techniques

The physical and chemical properties of deposited thin films are strongly dependent on the technique used. Structurally, the deposited films may have polycrystalline, amorphous or single crystalline nature, depending on the type of substrate and the preparation technique. In general, thin film deposition techniques are broadly classified into two categories [176].

- 1. Physical methods
- 2. Chemical methods

In physical methods a thin film of material is deposited on a substrate according to the following sequence of steps: 1) the material to be deposited is taken in solid form and converted into vapor by physical means; 2) the vapor is transported across a region of low pressure from its source to the substrate; and 3) the vapor undergoes condensation on the substrate to form the thin film. This process is called as Physical Vapor Deposition (PVD).

In a chemical process, the substrate is placed inside a reactor into which a number of gases are supplied. A chemical reaction takes place between the source gases and the product of that reaction is a solid material which condenses on all surfaces inside the reactor. This process is called as Chemical Vapor Deposition (CVD). If the precursor is taken in the form of a solution then the techniques can be broadly classified under chemical solution deposition techniques including sol-gel, electroplating etc.

Experimental...

In the present study we have used PVD techniques for the deposition of thin films.

2.1.1. PVD processes

The PVD process is divided into two categories: (1) thermal evaporation and (2) sputtering. In the present study we have used thermal evaporation and Ion beam sputtering for the deposition of Zn, In, Sn, Ag, Au and Cu metal films.

2.1.1.1 Thermal evaporation

Thermal evaporation is one of the most simple and commonly used techniques for the deposition of metals, metal oxide and alloys. In this process, the evaporated flux from desired solid material source is allowed to condense on a substrate. Typically, evaporative deposition method is performed in high vacuum without a gas atmosphere [96, 177]. The quality and the characteristics of the film will depend on the rate of deposition, substrate temperature, ambient pressure etc. The thickness of the film can be varied by changing the source substrate distance and deposition time. Metals of high melting point like Tungsten, Molybdenum and Tantalum are generally used in the form of wire or boats having different shapes. The choice of heating source depends entirely on the materials to be evaporated. The primary consideration is the evaporated material does not react with the source metal at high temperatures. By using this method, under optimized conditions Zn, In and Sn metal films of desired thickness were deposited

onto borosilicate glass (BSG), quartz, lanthanum aluminate (LAO), Sapphire (ALO) and Yttria stabilized zirconia (YSZ) substrates. Thermal evaporation was carried out at high vacuum (5×10⁻⁶ mbar) and during the deposition substrates were maintained at room temperature.

2.1.1.2 Ion beam sputter deposition

There are two methods of sputter deposition (1) the electrodes are immersed in the ionized gas medium leading to techniques such as DC, RF sputtering with variants such as magnetron and reactive sputtering and (2) the ions are produced in a source and accelerated towards the sputter target leading to Ion beam sputter deposition.

The surface atoms of the target are sputtered due to exposure to the ion beam of energy between 0.1 to 2 keV and the process is called Ion Beam Sputter Deposition (IBSD). The overall magnitude of deposited energy (and therefore the number of sputtered atoms) is sensitive to the surface. The use of ion beams for processing as opposed to directly extracting ions from a plasma in which cathode and anode are immersed to bombard a sample has many advantages leading to controlled processing of materials with ion bombardment. The control parameters of ion beam include flux, energy, species, charge state and direction (and divergence). IBSD operates in the range of 1x10⁻⁵ to 1x10⁻³ Torr. This makes IBSD compatible with a number of other processes used in thin film deposition which is not possible in other plasma based sputtering techniques that work at much higher pressures. One other significant advantage attached to operation in this relatively low pressure region is the long mean free paths of both the incident ions and sputtered atoms. As a result there is little scattering due to gas phase collisions and therefore the issue of charge exchange modification of the ion flux can be neglected.

2.1.1.2.1 Parameters used for IBSD in this study

The ion beam sputter deposition system used in this work is a home built system that consists of a Kaufman type DC ion source (of Oxford Applied Research, Model DC25, 100 – 1500 eV model). This ion beam is capable of producing ion beams of 2.5 cm in diameter. The main reason for using such a low energy ion beam sputtering is to obtain self ordered nanostructured thin films. Figure 2.1(a) shows the schematic diagram of ion beam sputter deposition system used in the current work.



Figure 2.1 (a) Schematic diagram of ion beam sputter deposition system.

The ion source consists of cylindrical type chamber (anode) where cathode (tungsten filament) is mounted and surrounded by a magnet

and water cooled chamber which is attached to two grids (called screen grid and extractor grid). Ar gas is passed through the ion source itself. When current is applied to the filament, it emits electron which collide with the Ar gas that is ionized. The direction of magnetic field causes the emitted electrons to move in helical path so that they collide with more Ar gas molecules, thus enhancing the ionization process. Ions are then extracted by the extractor grid and accelerated towards the target. They bombard the target and sputter the material. The screen grid screens the electron from coming out of the ion source. Ion beam sputter deposition has many advantages over other physical vapor deposition techniques like thermal evaporation and normal glow discharge sputtering. Some of the advantages are listed below: Photographic images of the system are shown in figures. 2.1(b) to (e).



Figure 2.1 (b) View of the 16 inch dia UHV chamber with capability to sputter 3 targets without breaking vacuum (c) Kaufman type ion source (DC25 of Oxford Applied Research, UK) (d) Full view of ion beam sputter deposition coating unit and (e) the inner view of the chamber during sputter deposition.

Ion beam sputter deposition	Glow discharge system	Thermal evaporation
Can sputter at high vacuum like 10^{-4} to 10^{-5} Torr.	Sputtering takes place at pressure > 10 ⁻³ Torr.	Can evaporate at 10 ⁻⁵ Torr or lower pressure.
Can sputter metals and insulator.	Cannot sputter insulator unless RF is used.	Can evaporate metals and insulator but stoichiometry is a problem.
There is no contamination in the film as the Ar gas is passed in the ion source itself and ions are extracted.	Ar gas is filled in the chamber so there will be scattering and contamination.	Contamination due to reaction between evaporant and heat source (such as W, Ta or Mo boat).
Has independent control on energy, current density and angle of incidence of ions.	No independent control possible.	Energy and flux is related to source temperature, angle of incidence can be controlled.

In the present work, Ag, Au and Cu films were deposited with the following conditions:

Pumping unit : Rotary + turbo pump

Base pressure : 2 x 10-6Torr

Working pressure : 4.5 x 10⁻⁴Torr

Ion source to target distance : 15 cm

Target to substrate distance : 10 cm

Substrate temperature : Room temperature

Ion energy : 400 eV

Ion current : 9 mA.

Extractor voltage : - 70 V.

2.2 Characterization

2.2.1. Thickness measurement

The thickness of thin films was measured using a stylus profiler (profilometer) (Model XP-1, Ambios Technology, USA). Surface profilometer is a direct, simple and fast measurement technique for determining the physical thickness of thin films [178]. The only requirement is the existence of a step as shown in figure 2.2. In this study, the step was made by using a thin stainless steel surgical blade. This method involves loading a stylus slightly in contact with the film surface and gently dragging it across the step as shown in figure 2.2. The vertical deflection measures the change in step height (film thickness) and the trace is recorded with high accuracy. In the present study we have used a profilometer of Diamond stylus (tip) to measure the thickness of as deposited Zn films.



Figure 2.2. Illustration of stylus profilometry to measure film thickness.

2.3. Structural characterization

2.3.1 X-ray diffraction

To determine the crystal structure and lattice parameter of the crystalline material X-ray diffraction (XRD) is one of the most important techniques. Solid crystalline materials act as diffraction grating for X-

Experimental...

rays, by virtue of the regular arrangement of the atoms or molecules in space. Since the inter atomic distances are about the same order of magnitude as the wavelength of X-rays, when a beam of X-rays falls up on a crystal it is transmitted as a number of diffracted beams.

In X-ray diffraction, a collimated beam of X-rays, with wavelength 0.5-2Å, is incident on a specimen and is diffracted by the crystalline phases in the specimen according to the Bragg's law [179].



Figure 2.3 Diffraction of X-rays by a periodically arranged of atoms in a crystalline material.

In the above figure 2.3, X-ray PA is incident up on a lattice point and diffracted from it, after which it moves in the direction of AR. Similarly, incident ray QC is diffracted in the direction of CS. Thus, the path difference between the two x-rays is given by BC+CD.

Therefore,

From
$$\triangle BAC$$
, $\sin \theta = \frac{BC}{d}$

$$BC = dsin\theta$$

From $\triangle CAD$, $sin\theta = \frac{CD}{d}$
 $CD = dsin\theta$

For constructive interference the path difference (BC+CD) must be equal to the integral multiple of wavelength.

Thus, BC+CD = $n\lambda$

$$2d\sin\theta = n\lambda \tag{2.1}$$

where, n- is the order of diffraction.

d- is the interplanar spacing.

 λ –is the wavelength of the x-ray.

In the present work, x-ray diffractometer (Bruker D8 Discover) equipped with Cu K_{α} radiation (λ =1.5405Å) was used. The GI-XRD pattern was obtained with a grazing angle of 0.5°. Calibration using a Si standard was done to account for the instrumental line broadening and the value was approximately 0.10° for Bruker diffractometer. The GIXRD patterns of all films were indexed using joint committee on powder diffraction standards (JCPDS) [180, 181].

2.3.2 Crystallite size, lattice parameter and strain calculations

The crystallite sizes ware calculated from the line profile analysis of the peak broadening of diffracted peaks using Scherrer's relation [182]

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

where k=0.94, λ is the wavelength of the x-ray (Cu-K_{α} radiation, λ =1.5405Å), and β is full width at half maximum of the peak at a diffraction angle of θ .

The lattice parameters were calculated using 2θ peak position from the relation

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$
(2.3)

where,

a, c - lattice constants

d- interplanar spacing

h,*k*,*l*- miller indices

The strain developed during the growth of the films were calculated by using the following relation

$$\operatorname{strain} = \frac{d - d_{o}}{d_{o}}$$
(2.4)

where, d, is the observed interplanar distance and 'd_o' is the standard value taken from the JCPDS file (89-1397). If the strain developed is positive, the nature of strain is tensile and it is compressive if the strain developed is negative.

2.4. Transmission electron microscopy

In transmission electron microscope (TEM), a beam of electrons of very short wavelength is used as the source of illumination. An electron emitter is fixed at the top of a cylindrical column of about 2 m height. To avoid the collision of electrons with air molecules the whole system of the microscope is enclosed in vacuum. Along the column at

specific intervals, magnetic coils are placed to focus the electron beam. The magnetic coils placed at specific intervals in the column, thus acts as an electromagnetic condenser lense system. The electron beams are passes through the specimen and scattered by the internal structures [183, 184].

The emitted electrons are then accelerated by a voltage in the anode. A higher anode voltage will give the electrons a higher speed. Thus, the electrons will have a de Broglie wavelength defined according to the equation, $\lambda = h/mv$. The resolving power of a microscope is directly related to the wavelength of the irradiation, which is used to form an image. Therefore, the resolution of the microscope is increased if the accelerating voltage of the electron beam is increased. Typical acceleration voltage in a TEM ranges from 100 to 300keV. The accelerated electrons focused and transmitted through partially transparent specimen carry information about the microstructure and structure of the specimen. The image is magnified by a series of magnetic lenses and recorded using a CCD (charge-coupled device) camera. The image detected by the CCD is displayed in real time. TEM can yield information about the morphology including size, shape, arrangement of particles, crystallographic texture, composition and compounds or defects in areas as small as a few nanometers.

2.4.1 Selected area electron diffraction

Selected area electron diffraction (SAED) is a technique used to determine crystal phases of nanomaterials and crystal defects. SAED refers to area selected in the image mode, where the electron diffraction pattern is recorded. The image mode is then switched into diffraction mode when the SAED aperture is inserted into TEM beam path and can be performed in the region of 100-200 nm. The resultant pattern is recorded using a CCD camera [183].

In the present study, the crystal structure of ZnO films and the growth of ZnO nanowires were also determined using transmission electron microscope operated in the selected area electron diffraction (SAED) mode (model: FEI Tecnai G² S-Twin, FEI electron microscope operated at 200 kV using Gatan CCD camera).



Figure 2.4 Photograph of the transmission electron microscope.

2.4.2 Microstructural characterization

The microstructure of Zn, ZnO and In, Sn doped ZnO thin films were determined using field emission-scanning electron microscopy (Carl ZEISS, FEG, Ultra 55) and atomic force microscopy (Seiko Instruments, SPA-400 of 3800 probe station, Japan) respectively. The FE-SEM images were obtained at an operating voltage of 5 kV and the

working distance is 4 mm. The AFM images were registered in a contact mode with Si cantilevers of length $100\mu m$. The resonant frequency and spring constants of the cantilever is 13 kHz and 0.18 N/m respectively.

2.4.3 Field emission scanning electron microscope

Field emission scanning electron microscopy (FESEM) is used to obtain information about microstructure, morphology and chemical composition on solids. The construction is same as the TEM expect that the acceleration voltages are limited to 30keV. The two major benefits of SEM are range of magnification and depth of field in the image, giving three dimensional information of image [185, 186].

The main difference between the SEM and the FESEM is emitter type (Thermionic emitter and Field emitter, respectively). In a typical SEM, Tungsten (W) or Lanthanum hexaboride (LaB6) are used as filament materials in thermionic emitter. Thermally emitted electrons will accelerate towards the anode. In a FESEM a Field Emission Gun (FEG) in contrast is used to emit the electrons. There are two types of FEGs (1) cold cathode and (2) hot cathode [187, 188]. In the current work a hot cathode FEG is used.

When a beam of electrons is incident on a surface a number of different interactions take place which generate secondary electrons, back scattered electrons, transmitted electrons, X-rays and Auger electrons. Each of these events can be detected to obtain detailed information about the solid.

2.4.4 Atomic force microscopy

Scanning probe microscopy is powerful Non-destructive technique used to image the surface morphology of thin films. A Scanning probe microscope essentially deals with two techniques [189].

- 1. Scanning Tunneling Microscope (STM)
- 2. Atomic Force Microscope (AFM)

STM is based on the concept of tunneling in which a conductive tip is brought close to the surface to be scanned. When a potential difference is applied between the two there is tunneling of electrons between them through vacuum. The tunneling current is a function of surface undulations. The main limitation of STM is the requirement for the samples to be conductors.

In contrast, AFM does not suffer the limitation of conductivity of the sample. AFM generates images based on the modulation of inter atomic forces.

Major components of AFM are

- 1. Tip or probe
- 2. Photo detector
- 3. Piezo electric scanner
- 4. Feedback mechanism

1. AFM tip or probe:

A tip or probe is a very important component of AFM as, in some cases, it physically touches the sample surface to be scanned. The resolution of AFM is critically dependent on its dimensions. The typical 10-15 nm size of AFM tip is mounted on a cantilever whose length is 100μ m. The spring constant of the cantilever is very low to enable it to respond to minute Van der Waals forces between tip and surface. The tip senses the force and cantilever responds.

2. Photo detector

A Photo detector is a position sensitive detector (PSD) that is used to detect changes in amplitude of a laser beam incident on the rear surface of a cantilever. These variations are then correlated with the surface roughness/morphology of the sample being imaged.

3. Piezo electric scanner and feedback mechanism

The samples are placed on a piezo electric scanner whose motion in the X, Y, Z directions, as a result of the Van der waals forces, generates an image based on constant height or force detection. The schematic diagram of AFM is shown in figure 2.5.



Figure 2.5 Schematic diagram of atomic force microscopy.

Experimental...

Before scanning any sample first adjust the tip of the cantilever in such a way that laser falls at centre of quadrant photo detector (QPD) which can be confirmed by null voltage reading as shown in figure 2.6

Figure 2.6(A) depicts a perfectly aligned AFM. After alignment the tip is brought close to the sample surface and when it is sufficient close Van der Waals forces arises between tip and sample surface. This bends the AFM tip as a result of which it touches the surface. As the AFM tip bends, a corresponding deflection is observed in the QPD, as shown in figure 2.6 (B) and (C). Further movement leads to pushing the cantilever against the surface at which point the tip starts moving in the opposite direction till it reaches the set point (Green dot) as shown in figures 2.6 (D)-(F). A set Point is a predefined voltage on QPD beyond which the stepper motor does not move the cantilever. Further movement of motor can break the cantilever which is not desired.



Figure 2.6 Positions of tip and cantilever before scanning.

Entire above mentioned mechanism can be understood by using a Lennard Jones Potential curve as shown below, in figure 2.7



Figure 2.7 Interaction between two tip and surface from Lennard-Jones Potential curve.

Figure 2.7 depicts the force of interaction between two particles approaching each other. When they are far apart there is no force of attraction between each other (position A). After a certain distance (~few nanometers), as they approach closer Van der Waals forces developed between them causes attraction (position B). The force of attraction is maximum when two surfaces are closest to each other (position C), beyond which repulsive forces will develop. At a certain position the attractive forces exactly balance the repulsive forces (position D) and the cantilever starts retracting [190-192].

Two distance regimes are labeled in figure 2.8, the contact and the non-contact regime. In the contact regime, the cantilever is held at a distance of a few nm above the sample surface. At this distance the interatomic force between the cantilever and sample is repulsive [192]. In the non-contact regime, the cantilever is held about tens to hundreds of nm away from the surface (largely a result of the long-range Van der Waals interactions).



Figure 2.8 Nature of forces in the contact and non-contact mode of AFM operation [192].

Modes of operation:

There are three modes of operation of AFM: contact mode, noncontact mode and intermittent contact mode.

In the current work, the intermittent contact mode, also called the dynamic force mode has been used to acquire images of the surface. This has been done to avoid damage to the surface that may occur during contact mode operation.

In the present study Seiko SPA-400 scanning probe microscope (shown in figure 2.9) was used in the DFM mode to obtain the surface morphology of Zn and ZnO thin film samples. The AFM images were registered in a contact mode with Si cantilevers of length 100μ m. The resonant frequency and spring constants of the cantilever is 13 kHz and 0.18 N/m respectively.



Figure 2.9 Photograph of the SPA-400 atomic force microscopy.

2.5. Chemical composition

Chemical composition of Zn, ZnO and In, Sn doped ZnO thin films was determined using energy-dispersive X-ray spectroscopy (EDS or EDAX).

2.5.1 Energy dispersive x-ray spectroscopy

Energy Dispersive X-ray Spectroscopy is a chemical microanalysis technique used in conjunction with scanning electron microscopy (SEM). Electron bombardment of the sample surface induces X-ray emission. The X-ray energy is characteristic of the element from which it was emitted [193]. This can be used to characterize the elemental composition of the analyzed volume, and features or phases as small as 1 µm or less can be analyzed.



Figure 2.10 Photograph of field-emission scanning electron microscopy attached with INCA EDAX detector, used in the present work to determine microstructure and composition of the films.

In the present study, chemical composition of ZnO and In, Sn doped ZnO films was determined using energy-dispersive x-ray spectroscopy (EDAX) analysis. The EDAX spectrum is obtained in an FE-SEM equipped with an INCA EDAX system, (give detector details). The operating voltage and working distance for EDAX measurement is 20 kV and 8.0 mm respectively.

2.6 Optical characterization

2.6.1 Ultra violet-visible-near infrared spectrophotometer

Optical properties of the Zn, ZnO and In, Sn doped ZnO thin films were studied using a JASCO V-570 Ultra violet–Visible-Near infrared (UV-VIS-NIR) double beam Spectrophotometer. The important parameters that can be obtained from the measured spectral data include absorption coefficient and optical band gap. In the present study the data were collected in the range 190 to 2500 nm, with air as reference.

The Ultra Violet -Visible-Near Infrared (UV-VIS-NIR) spectrophotometer uses two light sources, a deuterium (D₂) lamp for ultraviolet region and a halogen lamp for visible and NIR region. The light from the source lamp reflected from mirror 1 passes through slit 1 and is incident on a diffraction grating. The grating can be rotated to allow for a specific wavelength to be selected and pass through slit 2. A filter is used to remove unwanted higher order diffracted beam. The light beam is then incident on a second mirror before it is split by a beam splitter. One of the beams is allowed to pass through a reference sample (air in the present case), while the other passes through the film coated substrate. The intensities of the light beams are then measured at the end as shown in figure 2.11. The photometer (not shown) computes the ratio of the sample signal to reference signal (I/I_0) to obtain the transmittance.



Figure 2.11 Schematic diagram of UV-VIS-NIR spectrophotometer [194].
2.6.2 Raman spectroscopy and Photoluminescence spectroscopy

The Raman spectra of all the ZnO samples were recorded in air using a Nd:YAG laser at 532 nm in the back scattering geometry in a CRM spectrometer equipped with a confocal microscope and 100X objective with a CCD detector (model alpha 300 of WiTec, Germany). The PL spectra were recorded in air in the same spectrometer using a 355 nm diode laser with ~7 mW input power in reflection configuration and 40X UV objectives with a CCD detector (WiTec, Germany). The Photoluminescence (PL) spectra were also measured at room temperature using a Horiba JobinYvon model FL3-22 spectrometer.

The analyte on the ZnO nanostructures could be recognized through the in-built optical microscope (with an objective lens of 100X) and the spectrum was collected by the in-built spectrometer in the WiTec instrument simultaneously. Acquisition time for recording was 5 s and all spectra and was calibrated with Raman peak of silicon wafer at 520 cm⁻¹. In the Micro Raman spectrometer the laser beam was focused on to the substrate using an objective lens (100X) and the theoretical beam waist estimated was ~600 nm. To estimate enhancement factor, the normal Raman spectra of analyte was recorded with higher concentration which was adsorbed on a borosilicate glass substrate and compared with SERS spectra of analyte at lower concentration in the presence of ZnO nanostructures with different morphology.

When metal (Ag, Au and Cu) particle is in contact with an ntype semiconductor particle such as ZnO, the charge distribution is readjusted for equilibration of the Fermi level between the two particles,

which results in the elevation of the metal particle Fermi level and the formation of a Schottky barrier (depletion layer) at the junction between the two materials [161]. The metal deposited on the nanostructured ZnO surface is excited by an incident laser light and the photo excited electrons are injected into the conduction band of ZnO connecting with metal and/or subsequently onto the lower energy level of ZnO. They are then transferred to the lowest unoccupied molecular orbital (LUMO) energy levels of the molecules adsorbed on ZnO nanostructures, which enhances photo absorption of the charge transfer complex. These additional electrons provide ZnO with a considerable SERS effect to the adsorbed molecules. Also intrinsic charge transfer from ZnO to adsorbed molecule and adsorbed molecule to metal could occur when the energy levels of the system match with the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of adsorbed molecule under excitation.

The SERS enhancement factor (EF) was calculated using the following formula [162].

$$EF = \frac{I_{SERS}}{I_{RS}} \frac{N_{RS}}{N_{SERS}}$$
(2.5)

where, ISERS is the enhanced Raman intensity at lower concentration on SERS substrate, IRS is the normal Raman intensity at higher concentration measured over non-plasmon surface, *NSERS* is the number of molecules that giving rise to SERS from Ag decorated ZnO nanostructure, *NRS* is the number of molecules giving rise to Raman signal from non-SERS surface. *NSERS* and *NRS* are determined by the relation [163].

Experimental...

$$N_{SERS} = \eta N_A V C_{SERS} \frac{A_{laser}}{A_{SERS}} , \qquad N_{RS} = N_A V C_{RS} \frac{A_{laser}}{A_{RS}}$$
(2.6)

where η is the adsorption factor, N_A is Avogadro number, V is total volume of the solution added onto the substrate, A_{laser} is the area of the laser spot, A_{SERS} and A_{RS} are the total area of the SERS and non-SERS substrate respectively, and are the lower and higher concentration of analyte applied over SERS and non-SERS substrates respectively. The adsorption factor (η) was estimated following the Langmuir isotherm models [164, 165].

In the present study by depositing Ag nano particles on the ZnO nanowire substrate we have observed the high enhancement in SERS signal by using high energy molecule analytes. In this work so far used analytes are Rhodamine 6G (R6G) ANTA (5-amino-3-nitro-1,2,4-triazole), CL-20 (2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane), FOX-7 (1,1-diamino-2,2-dinitroethene).

2.7. Nanoindentation

Nanoindentation is a simple method that consists of hard indenter, indenting a specimen by a very small load using a high precision instrument, which records the load and displacement continuously [195]. The mechanical properties of thin films up on nanoindentation can be derived from the measured load-displacement (or loading /unloading) curve through appropriate analysis.

Hardness, H, of a material is defined as the resistance to local plastic deformation when a force is applied. The depth of penetration in the sample is measured as a function of applied load and results are

presented in the form of a load-displacement curve for the loading and unloading part of the indentation process as shown in figure 2.12



Figure 2.12 Example of nanoindentation load-displacement curve obtained from Berkovich indenter during loading and unloading.

An analysis of the unloading data provides a value for the depth of the area of contact at full load. The area of contact at full load is determined from the known angle or radius of the indenter. For Berkovich tip the total included angle on this tip is 142.3°, with a half angle of 65.35°. The hardness is derived by dividing the maximum load (P_{max}) by area of contact (A), thus [195]

$$H = \frac{P_{\text{max}}}{A(h_c)} \tag{2.7}$$

Experimental...

The slope of the linear variation of the unloading curve measures the elastic stiffness (S).

$$S = \frac{dp}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A(h_c)}$$
(2.8)

Here E_r is the reduced modulus of the material. The Youngs modulus (Es) can be calculated using the equation

$$\frac{1}{E_r} = \frac{(1 - v_i^2)}{E_i} + \frac{(1 - v_s^2)}{E_s}$$
(2.9)

In the above equation v and E are Poisson's ratio and Young modulus of indenter and sample. The subscript i and s represents the indenter and sample respectively.

In the present case, Zn and ZnO films were indented by Berkovich-type pyramidal diamond tip with a maximum load of 2000 μ N. The trapezoid load function (which includes the loading, holding and unloading segments) was used to measure the hardness of the films with a loading rate of 200 μ Ns⁻¹ and segment time of 10 see for each segment.



Figure 2.13 photograph of the Hysitron (Triboindentor-900) nanomechanical test system.

2.8 Contact angle goniometry

The wettability of a solid surface by a liquid is characterized by the contact angle θ as shown in figure 2.14.



Figure 2.14 Drop profile over a solid substrate

Surface contact angle goniometer is an instrument which is used for measuring the contact angle between the liquid and the substrate. The goniometer consists of

- (1) a Charge Coupled Device (CCD) camera
- (2) a stand fitted with a clamp to hold the goniometer micro syringe
- (3) a flat stage table to place the solid substrate
- (4) a variable fiber-optic- illuminator and
- (5) a straight needle for manual dispensing.

In the experiment, a drop of the liquid is carefully dropped on a substrate placed on the flat stage table of the goniometer. The CCD camera captures the profile of the liquid drop over the substrate and the video is presented on the screen. The contact angle is calculated by drop shape analysis of the software. The main assumptions of this analysis are as follows.

1) The drop is assumed to be symmetric about a central vertical axis. This means that it is irrelevant from which direction the drop is viewed.

Experimental...

2) The drop is not in motion and viscosity and inertia plays a role in determining its shape.

The Rame-Hart Model-250 goniometer used to measure the contact angle of a sessile drop on top of a solid substrate is shown in figure 2.15. The instrument also has an automated software-driven dispensing system with a nozzle and a piping system fitted to it for producing precise pendant and sessile drops.



Figure 2.15 Photograph of contact angle goniometer.

The goniometer is used to measure the static contact angle, advancing and receding contact angles, surface tension of liquid by pendant drop method and also the surface energy, adhesive energy of the solid substrate from measured contact angles.

Sessile drop method is the most frequently used and the most convenient contact angle measurement technique [196]. In this method, a liquid drop is placed on a solid substrate and the contact angle is measured between the solid surface and the tangent to the drop profile at the drop edge. Either the static or the dynamic sessile drop method can be used to measure the contact angle.

2.8.1 Pendant drop method

In pendant drop method a drop is allowed to suspend from the tip of an inverted syringe. The surface tension of the drop is calculated from Young-Laplace equation, which is given by equation 2.10

$$Y = \frac{\Delta \rho g R_0^2}{\beta}$$
(2.10)

where, Y is the surface tension of suspended liquid, $\Delta \rho$ is the density difference between the drop and the surrounding medium, *g* is the acceleration due to gravity, *R*₀ is the radius of curvature at the drop apex and β is the shape factor [197].

2.8.2 Contact angle hysteresis

While the static contact angle gives the information about the interfacial tensions between the solid, liquid and the fluid, various types of dynamic studies can be conducted to determine more advanced wetting properties. Experimentally when the volume of a drop is increased, the contact angle increases. The contact angle eventually reaches a maximum value, which is referred to as the "advancing contact angle" [198]. Similarly, when the drop volume is decreased, the contact angle decreases until it reaches a minimal value, which is called the "receding contact angle". The difference between the advancing and the receding contact angles is termed "the contact angle hysteresis"

Experimental...

which can be used to characterize surface heterogeneity and roughness and can be used to quantify contamination and the effect of surface treatments. The drop volume is increased or decreased by the automated dispenser attached with the goniometer.

By measuring the contact angle of different liquids over various substrates surface energies of the substrates can be calculated. The surface energies are characteristics of the solid being studied. Surface energy of a solid substrate can be calculated by using the contact angle values of different liquids (at least two) over that particular substrate.

Thomas Young described surface energy as the interaction between the forces of cohesion and the forces of adhesion which in turn dictate if wetting occurs. Contact angle can be related to the three interfacial tensions via Young's equation 2.11 (1936).

$$\cos\theta = \frac{Y_{SV} - Y_{SL}}{Y_{LV}}$$
(2.11)

where, Y_{SV} =Solid-vapor interfacial tension.

Y_{SL}=Solid-liquid interfacial tension.

Y_{LV}=Liquid-vapor interfacial tension.

From Young's equation the contact angle θ and liquid-vapor interfacial tension can be measured directly but other quantity like solid-liquid and solid-vapor interfacial tension cannot be measured directly from the experiment. Dupree (1869) modified the Young's equation by introducing the concept of adhesion which is the work done (W) to separate the two phases. The modified equation is

$$W = Y_{SV} + Y_{LV} - Y_{SL}$$
(2.12)

Comparing the above equation with Young's equation the adhesive energy is

$$W = Y_{LV}(1 + \cos \theta)$$
 (2.13)

Equation 2.13 is known as Young-Dupree equation.

2.9 Summary

In summary, in the current work, Zn thin films were deposited on various substrates by thermal evaporation. This was followed by a thermal oxidation process in which the metal films were heated to different temperatures from 200 to 500 °C. The metal and metal oxide films were characterized for microstructure, structure, optical, mechanical, wettability and Raman scattering properties.

3

Growth, Mechanical and Photoluminescence properties of ZnO nanowire thin films

Abstract

Nanostructured Zn metal films were deposited by thermal evaporation, on borosilicate glass (BSG), Quartz, sapphire (ALO), lanthanum aluminate (LAO) and yttria stabilized zirconia (YSZ) substrates. The asdeposited films are nanocrystalline and show a morphology that consists of triangular nanosheets. The films are annealed at 200, 400 and 500 °C. Thermal annealing of the films at 500 °C results in partial oxidation of Zn to ZnO. Annealing also causes transformation of the Zn nanosheets into ZnO nanowires that are polycrystalline in nature. The ZnO nanowires are in the range of 15–100 nm in diameter and about few µm long. The ZnO nanowires are much softer than the as-deposited Zn metal films, with hardness between 0.02 and 0.4 GPa and Young's modulus between 3 and 35 GPa. As a result of the Zn residue in the ZnO there is decrease in optical transmittance along with a significant variation in photoluminescence properties. The blue shift of blue emission and the red shift in the band edge absorption at photoluminescence excitation monitoring blue emission for ZnO/Zn film is correlated with charge transfer from Zn to ZnO. The photoluminescence excitation peak position at shorter wavelength monitoring blue, red and green remains unchanged, albeit band edge excitation peak shows significant red shift for ZnO/Zn thin films. This indicates that the excitation resonance at shorter wavelength is not caused by the usual electronic band to band or defect transition but by the plasmons in ZnO.

3.1 Introduction

As discussed in chapter 1, there are several methods of fabricating ZnO nanowires. Some of these techniques require catalysts while others require high temperature, in addition to catalysts. Hence one of the objectives of the present study is to examine the transformation of Zn to ZnO by single thermal oxidation step. To study this transformation, the films were heated to temperatures below the melting point (T_M) of Zn (419 °C) and also temperatures greater than T_M. The microstructural evolution is followed using FE-SEM and mechanism is probed using TEM. The metal and metal oxide films were also characterized for mechanical, photoluminescence behavior.

3.2. Experimental

Zn films were deposited onto five different substrates used are borosilicate glass (BSG), quartz, sapphire (ALO), lanthanum aluminate (LAO) and yttria stabilized zirconia (YSZ) by the thermal evaporation process in high vacuum (5×10⁻⁶ mbar). The source substrate distance was 2.5 cm and the substrates were maintained at ambient temperature during deposition. The measured thicknesses of these films are of the order of 500, 700 and 7500 nm. The as deposited films were post deposition annealed in air at 200, 400 and 500 °C for 30 mins. Growth, Mechanical ...

3.3 Results and discussion

3.3.1 Growth of ZnO nanowire thin film

3.3.1.1 Structure

The x-ray diffraction (XRD) patterns of the as deposited Zn film on the BSG substrate and the films annealed to 200, 400 and 500 °C of thickness 500 nm are shown in figure 3.1 (a) to (d). It is observed that upto an annealing temperature of 400 °C the films show peaks that can be indexed as belonging to Zn. At 400 °C there is appearance of a weak reflection at a 20 value of 31.7° that can be indexed as belonging to ZnO which suggests the initiation of oxidation of the films. At 500 °C there is complete transformation of Zn into ZnO as evidenced by the disappearance of peaks belonging to Zn metal film.



Figure 3.1 X-ray diffraction of the as-deposited Zn film and the films annealed at 200, 400 and 500 °C.

The observed peaks can be indexed as arising from the hexagonal ZnO structure, with no evidence for unreacted Zn. The behaviour on quartz substrates (not shown here) is the same. This is significantly different from the work of Li et al. [199] and Barshillia et al. [200] who have observed significant residue of elemental Zn even after oxidation of the Zn films at high temperatures. It may be noted that the melting point of Zn is 420 °C. Therefore, at 500 °C the Zn film melts. As the film melts and the Zn-Zn bonds break, the Zn atoms react with the ambient oxygen to form ZnO. Furthermore, since the annealing temperature is much greater than the melting point of elemental Zn, there is sufficient energy for the crystallization, in addition to the chemical reaction resulting in the formation of ZnO. The crystallite sizes calculated using Scherrer's formula were 120, 98, 67 and 58 nm at ambient, 200, 400 and 500 °C respectively. In addition there was decrease in thickness of the films, at 500 °C, by approximately 10% due to Zn reevaporation.

The X-ray diffraction patterns of as deposited Zn films and the Zn films annealed at 500 °C deposited on different substrates (namely BSG, Quartz, YSZ, LAO and ALO) of thickness 7500 nm are shown in figure 3.2 (a) and (b), respectively.



Figure 3.2 X-ray diffraction patterns of (a) as deposited and (b) Zn films annealed at 500 °C.

The diffraction peaks observed in the as deposited film can be assigned to the hexagonal structure of Zn (JCPDS No. 87-0713) with unit cell parameters of a = 2.67Å and c = 4.95 Å. The x-ray diffraction patterns on annealing these films to 500 °C show peaks that can be assigned to both Zn and ZnO. The weak reflections at 20 values of 38.9, 43.2, 54.3, 82.0 and 86.5° are attributed to metallic Zn film whereas the diffraction peaks at 20 values of 31.7, 34.3, 36.2, 47.4, 56.5, 62.7, 66.3, 67.8 and 69.0 correspond to the hexagonal structure of ZnO (JCPDS No. 89-1397). It can, thus, be inferred that the Zn films annealed at 500 °C are only partly oxidized with substantial residue of metallic Zn still being present. The calculated unit cell parameters for ZnO were a = 3.245Å and c = 5.206Å. Similar observation of Zn residue in ZnO films has been reported by other workers [199, 201-204]. It appears that the oxidation of Zn is thickness dependent. In case of the 500 nm thick films presented in figure 3.1 the films were completely oxide, in contrast to the 7500 nm thick films subjected to the same annealing condition.

The average crystallite sizes for Zn phase were 25 nm on sapphire, 40 nm on BSG, YSZ and Quartz substrates and 82 nm on LAO. The average crystallite size for ZnO phase is 30±2 nm on all the substrates. A qualitative understanding of the ZnO phase growth on different substrates has been derived from the ratio of the intensity of strongest peaks of ZnO and Zn. The ratio of the intensities of the two different phases is proportional to the weight fraction of the two phases [182].

$$\frac{I_{ZnO}}{I_{Zn}} \propto \frac{W_{ZnO}}{W_{Zn}}$$
(3.1)

where I_{ZnO} and I_{Zn} are the intensities of the strongest peaks of ZnO and Zn and W_{ZnO} and W_{Zn} are the weight fraction of ZnO and Zn respectively. The intensity ratio of ZnO (100) to Zn (101) is 0.7, 1.0, 1.1, 3.1, and 13.0 on BSG, YSZ, Quartz, LAO and ALO respectively. This observation suggests that ZnO shows high growth rate on the ALO substrate and it is low on BSG substrate. The strain developed during

the growth of the films on different substrate has been calculated by using the following relation

strain =
$$\frac{d - d_o}{d_o}$$
 (3.2)

where, 'd' is the observed interplanar distance and 'd_o' is the standard value taken from the JCPDS file (89-1397). It is observed that on all the substrates the strain developed is positive, which suggests that the nature of strain is tensile. The calculated strain value of as deposited and Zn films annealed at 500 °C is 5.25×10^{-4} and 6.45×10^{-4} respectively.

The XRD patterns of the as-deposited Zn film and the films annealed at 430 and 500 °C are shown in figure 3.3(a), figure 3.3(b) and figure 3.3(c) respectively. The as-deposited Zn film does not show (figure 3.3(a)) any evidence for the presence of the oxide phase.



Figure 3.3 XRD patterns of (a) as-deposited, (b) 430 °C and (c) 500 °C annealed Zn thin films, # indicates Zn phase.

As deposited Zn films exhibits diffraction at (002), (101), (102) and (103) orientations (JCPDS card No. 04-0831). The films annealed at 430 and 500 °C showed (100), (002), (101), (102), (110) and (112) orientations of the hexagonal phase of ZnO (JCPDS card No. 89-1397). However, the XRD pattern of Zn films annealed at 430 °C (figure 3.3(b)) also exhibits a very sharp (103) diffraction line at 70.38°, which indicates presence of residual Zn. The presence of small amount of untraced residual Zn in 500 °C annealed ZnO film cannot be ruled out. Incomplete oxidation of Zn may result in the formation of an intermediate Zn clusters and Zn interstitials (Zn_i). The film annealed at 430 °C is called ZnO/Zn and the film annealed at 500 °C is reffered as ZnO hereafter.

3.3.1.2 Microstructure

Evidence for the melting process is presented in the form of Field Emission Scanning Electron micrographs shown in figures 3.4(a) to (d) for the as-deposited, 200, 400 and 500 °C annealed films respectively.

The as deposited films shows densely packed aligned triangular grains (figure 3.4 (a)), which is retained even at an annealing temperature of 200 °C (figure 3.4(b)). At 400 °C the initiation of the melting process is evidenced by the smearing of the grain boundaries and loss of shape of the grains. The grains of the films are no longer separated by well-defined boundaries (figure 3.4 (c)). The transformation in morphology at 500 °C is more remarkable as seen from figure 3.4 (d). The grains merged together to form a large "ball-like" mass, which is a clear consequence of the process of melting and flowing. The ball also has several needle-like structures that project outward from the surface. Growth, Mechanical ...

Closer examination of this feature (figure 3.4 (e) and (f)) shows that it is comprised entirely of nanowires of 15-100 nm diameter and lengths of the order of few μ m. It is also seen that the film below this ball is not a continuous film but consists of nanowires. The expanded view of the film (figure 3.4(f)) below the ball confirms that the rest of the film is also comprised of nanowires. Thus, the nanowires are formed all over the BSG substrate.



Figure 3.4 FE-SEM images of the (a) as deposited Zn films on BSG substrates and annealed to, (b) 200, (c) 400 and (d) 500 °C; (e) and (f) show the expanded view of the films annealed to 500 °C.

The FESEM images of Zn and Zn film annealed at 500 °C are shown in figure 3.5 (a)-(e) and figure 3.6(a)-(e) respectively. The as deposited films (figure 3.5(a)-(e)) show triangular nanosheets on BSG, Quartz, LAO and ALO substrates but the morphology on YSZ substrate differs from others. Annealing of these films to 500 °C leads to transformation of the triangular nanosheets into nanowires, independent of the substrate (figure 3.6(a)-(e)).



Figure 3.5. FESEM images of Zn film deposited over (a) BSG (b) Quartz (c) YSZ (d) LAO and (e) ALO.



Figure 3.6 FESEM images of Zn films annealed at 500 °C over (a) BSG (b) Quartz (c) YSZ (d) LAO and (e) ALO.

The distribution of diameters of the nanowires on different substrates is shown in figure 3.7. It can be seen that the peak diameter of

Growth, Mechanical ...

the wires between 20-40 nm in all the cases with a long tail of diameters towards the higher values. The largest aspect ratio observed is 600. The maximum nanowire diameter is 140 nm on BSG and Quartz substrates whereas nanowire diameters upto 200 nm are observed on the single crystal substrates. Thus, independent of the substrates, thermal oxidation of Zn films in air at 500 °C results in the formation of ZnO nanowires.



Figure 3.7 Distribution of ZnO nanowires over BSG, Quartz, YSZ, LAO and ALO substrates.

3.3.1.3 Cross-sectional FESEM

To determine whether the nanowires are present through the entire thickness of the films, cross-sectional FESEM images were recorded and are shown in figure 3.8(a) and (b) for films deposited on ALO and LAO substrates respectively. It is evident from these images that the nanowires emerge only from the surface of the film. There are no nanowires at the film-substrate interface, suggesting that the substrate has no role to play in the formation of nanowires. It can be inferred from these results, in conjunction with XRD patterns, that only the top surface of the Zn films are oxidized and transform into nanowires.



Figure 3.8. Cross-sectional FE-SEM images of ZnO thin films deposited on (a) ALO and (b) LAO substrates.

3.3.1.4 Transmission electron microscopy

To confirm the nanowire growth, the samples were examined under a transmission electron microscopy (TEM). A typical image presented in figure 3.9 (a) clearly shows droplets of metal oxide (presumably quenched) and the dendrites emerging out of the droplet. TEM, suggests that the mechanism of growth of nanowires is selfcatalysis [205, 206].



Figure 3.9 TEM images of Zn film annealed at 500 °C (a) bright field image, (b) selected area electron diffraction pattern and (c) high resolution TEM image.

3.3.1.5 Mechanism of nanowire growth

Based on the microstructural evidence it is preposed that the mechanism of formation of nanowires is the process of self-catalysis as suggested by Dang et al. [201] and Zacharias and co-workers [202, 203]. In this process, the melting metal plays the role of reactant and catalyst simultaneously, which makes it different from the VLS mechanism of nanowire growth. As the temperature increases beyond the melting point of Zn, the metal forms molten liquid droplets (depicted schematically in figure 3.10 and shown in TEM image figure 3.9(a)). In addition, oxygen present in the ambient atmosphere first gets adsorbed and then reacts with the molten Zn on the surface to form ZnO. These ZnO droplets then act as nuclei for the formation of dendrites. Earlier workers have shown that, in the growth of nanowires by thermal oxidation, the rate of stress generation during the solid state phase

transformation is one of the main controlling parameters [205, 206]. Yuan et al. [205] have shown, in the case of CuO nanowires formed by the thermal oxidation of Cu, that the driving force for the nanowire formation is the volume change associated with the solid-state transformation at the CuO/Cu interface. This produces compressive stresses, which stimulates CuO nanowire growth to accompany the interface reaction. Li et al. [206] have grown nanowires of ZnO by thermal oxidation of Zn metal in an oxygen atmosphere, unlike the present study. However, the mechanism of formation of nanowires appears similar. They state that when the Zn powder is subjected to the oxidizing atmosphere it is covered by an oxide coating on the surface. This oxide helps to create an appropriate Zn vapor supersaturation which facilitates the formation of a ZnO buffer layer and the catalytic Zn/ZnOx liquid droplets which initiate growth of the nanowires.



Figure 3.10 A schematic representation of mechanism of nanowire/rod growth.

It may be noted that the nanowires are, in general, aligned, parallel to the surface of the substrate. Thus, the mechanism of the nanowire formation and the alignment appears to be related to the alignment of the triangular Zn grains along the plane of the substrate. Therefore, during the melting process, the reconstruction of the morphology into ZnO nanowires occurs in a direction parallel to the substrate. This is again different from other processes where the nanowires are either vertically or randomly aligned. Although nanowire formation using processes at much lower temperatures such as 95 °C are reported, the current process is very fast as compared to the 4-6 hrs required in the lower temperature process [207]. An additional advantage is that the initial film is deposited in vacuum ensuring purity of the material.

3.3.1.6 Mechanical properties

In this section the mechanical properties of Zn films deposited on BSG, quartz, ALO, YSZ and LAO substrates are presented. The change in mechanical properties due to the transformation of Zn and ZnO is also investigated. The role of substrates in determining mechanical behavior is examined.

Nanomechanical studies were performed on the as-deposited Zn and ZnO nanowire films. The effect of substrates on the nanomechanical behaviour is presented in figure 3.11(a) for the as deposited Zn and figure 3.11(b) for the ZnO nanowire films. The hardness was 5.8, 8.7, 33.1, 17.8 and 22.6 GPa respectively for the bare BSG, quartz, ALO, YSZ and LAO substrates. The lowest hardness is

observed for the as deposited films on BSG substrates while the highest hardness is achieved on the LAO substrate with the values of 0.15 and 0.8 GPa, respectively. The hardness values on the other substrates are between these two values, as shown in Table 3.1. On annealing to 500 °C, the hardness values decrease to 0.02 and 0.4 GPa on BSG and LAO, respectively. It is pertinent to note that the effect of the substrate was decoupled by limiting the indentation depths to 10% of the total thickness of the films. In the present case, this value is 750 nm as the total thickness is 7500 nm. It can be observed from figure 3.11(a) and (b) that only in the case of the annealed films on BSG and quartz substrates is the indentation depth is approximately 15% of the total thickness [208]. However, even in these cases, the calculated values of hardness are much lower than that of the bare substrate indicating that the substrate effect is negligible.

Table	3.1:	Hardness	and	Young's	modulus	of	Zn	films	as-deposited	and
anneal	ed at	t 500 ∘C .								

		Young's		Young's	
Substrate	Hardness (GPa)	modulus	Hardness (GPa)	modulus	
		GPa(±0.5)		GPa(±0.5)	
	As dep	osited	Annealed at 500 °C		
BSG	0.15 (±0.02)	18.6	0.021	3.26	
Quartz	0.31 (±0.02)	53.4	0.025	3.36	
ALO	0.29 (±0.02)	33.2	0.075 (±0.02)	9.26	
YSZ	0.66 (±0.02)	29.8	0.121 (±0.02)	16.11	
LAO	0.79 (±0.02)	87	0.417 (±0.02)	35.05	

It is evident that there is softening due to the formation of ZnO nanostructures. The difference in hardness values on different substrates can be attributed to the variations in aspect ratios of the nanowires. The higher aspect ratio nanowires (on BSG, Quartz and ALO) show low hardness and low Young's modulus whereas the low aspect ratio nanowires exhibit higher hardness and Young's modulus. The observed hardness values are lower than those reported by other workers and that for bulk ZnO (5 GPa) [209].



Figure 3.11 Typical load-displacement curves for the (a) as-deposited Zn film on different substrates and (b) ZnO nanowires on different substrates.

The contribution of buckling to the estimation of hardness of vertically aligned ZnO nanowires (NWs) has been dealt in detail by Ji et al. [210]. However, in the present case, not all the NWs are vertically aligned on the substrates to use buckling models alone to estimate the Young's modulus of the individual nanowires [210]. The NWs in the present study are aligned both vertically and horizontally. Therefore, the mechanical properties measured in this study have contributions of both buckling and plastic deformation of vertically and horizontally aligned NWs, respectively. It is difficult to isolate contributions from the buckling and plastic deformation with the available data. Therefore, the term hardness (which is a measure of the resistance to the plastic deformation) is used in this study only to show the differences in the mechanical response of as-deposited and annealed films. Furthermore, it is evident from figure 3.6 and 3.8 that most of the NWs grow horizontally, therefore the method suggested by Feng et al. [211] was used to estimate the hardness of the nanowires. The hardness values derived from this expression and those using the Oliver- Pharr method were within 10% of each other. Therefore, it is inferred that the hardness calculated for the bundle of nanowires is not very different from that of a single nanowire. The possibility of the buckling load being lower in the present case, because a few of the NWs are vertically aligned cannot be ruled out. The estimation of hardness could be affected by the presence of porosity.

Evidence for the nanowires being softer on substrates where the aspect ratio is high is seen from the occurrence of "pop-in" events in the

Growth, Mechanical ...

load-displacement curves. A pop-in is defined as a displacement burst caused by local stress fields at the interface of the film and substrate. Pop-in generally occurs when maximum shear stress generated under the indenter is of the order of theoretical shear strength [212]. This high local stress causes homogeneous nucleation of threading dislocations beneath the indenter surface, producing a sudden displacement discontinuity. The pop-in event shows up on the load-displacement graph as increase in indentation depth at constant load, which is followed by the usual increase in depth with increasing load, i.e. like a step. It is pertinent to note that buckling of vertically aligned nanowires under uniaxial compression that manifests itself as a pop-in event has been observed earlier, similar to the current study [209, 213].

3.3.2 Photoluminescence study of ZnO nanowires with Zn residue

The application of ZnO in photoluminescent devices is well documented. However, the role of Zn residue in determining the photoluminescence (PL) behavior of ZnO has not been investigated in detail. Hence in this study Zn films deposited on fused silica substrate and annealed at 430 and 500 °C are studied.

3.3.2.1 Optical transmittance

The optical transmittance spectra, in the wavelength range from 250 to 2500 nm, of the films annealed at 430 and 500 °C for the ZnO/Zn and ZnO films is shown in figure 3.12(a) and (b), respectively.



Figure 3.12 Optical transmission spectrums of (a) ZnO/Zn and (b) ZnO and (c) reflection spectrum for Zn thin film.

The as-deposited Zn film was completely opaque. The overall transmittance is strongly suppressed for ZnO/Zn thin films (figure 3.12(a)) whereas the ZnO films (figure 3.12(b)) show high transmission and a sharp absorption edge in the UV region. In the Zn-ZnO composite, the Zn interface gives off its free electrons to the conductive band of ZnO [214] leading to bleaching of the excitonic feature due to the accumulation of electrons in the conduction band of ZnO [215, 216]. Furthermore, the interface between Zn and ZnO forms a dipole which is a potential trap for electrons and increases the absorptivity to both ultraviolet and far infrared light as seen in transmission spectrum (figure 3.12(a)). Significantly, similar light trapping in organic semiconductors

has been reported very recently [217]. Hence, the accumulation of electrons in the conduction band and formation of dipole layer [218] between the Zn and ZnO interface may also be responsible for "effective *n*-type" doping. In addition, significant charge distribution at the Zn-ZnO interface which leads to band bending for alignment of the Fermi levels can also be expected. Similar band bending is reported by Jarrett [219], in the context of measured density of states at a TiO₂-electrolyte interface by a photo-electrochemical technique. As will be discussed later, excess *n*-type charge carriers in ZnO/Zn films can also be responsible for the modification of band edge transition properties observed in PL and PLE measurements. It is noteworthy that the reflectance measurement performed on Zn thin films showed strong SPR features in visible (410 nm) [220] and IR (~1000 nm) [221] region which were identified to be originate from Zn nanostructures.

3.3.2.2 Photoluminescence

The PL spectra of ZnO/Zn and ZnO thin films excited at a photon energy of 3.64 eV (340 nm), presented in figures 3.13(a) and (b) respectively, are composed of two peaks, i.e. the ultraviolet (UV) peak originating from the near band edge emission and defect related visible emission. It should be stressed that band edge emission (figure 3.13(b)) for ZnO films is split into two peaks. This can be attributed to better crystallinity of the ZnO nanowires grown at high temperature, in agreement with the XRD data. A dominant near band edge emission peak at 374 nm is ascribed to the exciton-exciton scattering process from the n=1 state to the exciton-continuum state (P-line) while other

emissions observed at longer wavelength (383 nm) and at intervals of ~72 meV might correspond to first order longitudinal-optical phonon replicas of the P-line [222].



Figure 3.13 Photoluminescence spectrum of (a) ZnO/Zn and (b) ZnO thin films excited (340 nm) above bandgap energy of ZnO.

For ZnO/Zn films, however, only a single near band edge emission peak that is red-shifted (from 374 to 378 nm) relative to those of the ZnO films was observed. The red-shift of the band edge emission by 4 nm (35 meV) is attributed to the Burstein-Moss band filling effect or a band gap shrinkage due to charge transfer from unreacted Zn to ZnO, as discussed earlier. Broad visible bands can be observed for both thin films. The green emission centered at 525 nm is assigned to the oxygen vacancies (V_o) [223, 224] while the red emission centered at 645 nm is assigned to Zn_i [225] for ZnO and ZnO/Zn films, respectively.

In conventional PL measurements, electron-hole pairs are usually generated with excitation above band gap energy (as discussed above). The emission spectrum is recorded during the relaxation of the charge carriers. The presence of the Zn residue necessitated the excitation of the films with sub-band gap energy (site selective excitation) in order to observe the PL due to the unoxidized Zn metal. This was accomplished by exciting films with energy of 3.1 eV (400 nm). This excitation energy was selected since the reflectivity measurement (figure 3.12(c)) performed on Zn metal film showed strong SP absorption at around 410 nm. The PL spectra of the ZnO and ZnO/Zn films excited with sub band gap energy of 3.1 eV (400 nm) is compared in figure 3.14.



Figure 3.14 Photoluminescence spectrum of (a) ZnO/Zn and (b) ZnO thin films excited (400 nm) near SP resonance of Zn.
It is pointed out that in the present study, the typical sub-band gap excitation does not yield emission from unreacted Zn. The PL spectra exhibit emission in the blue region accompanied by a weak and broad defect band in the long wavelength range. The blue emission peak centred at 455 and 449 nm were observed for ZnO and ZnO/Zn films respectively. It is generally accepted that the blue emission is related to the oxygen vacancies or Zn_i [226] which probably originate from radiative recombination of an electron occupying shallow donor level and a hole in the top of valence band. It is observed that for ZnO/Zn films, although the PL spectral peak is blue-shifted (from 455 to 449 nm) relative to those of the ZnO films, the integrated PL intensity is not significantly affected. This can be understood by the band-filling effect where at a sufficiently high carrier concentration, electrons fill the shallow donor states just below conduction band causing a shift in the apparent position of the blue emission to higher energies [227].

3.3.2.3 Photoluminescence excitation

The photoluminescence excitation (PLE) spectra of ZnO/Zn and ZnO thin films recorded by fixing the emission wavelength to detect red and green emission, respectively is shown in figure 3.15(a) and (b) respectively. As seen from figure 3.15(a), the PLE spectrum of ZnO/Zn films shows a near band edge excitation peak around 362 nm attributed to the free exciton (F_x) transition. This is different from the earlier report of He et al. [228] in which the peak at 362 nm (3.425 eV) was ascribed to the C exciton or the first excited state of F_x of ZnO for PL carried out at 8 K. In the present case, however, the thermal energy (kT) is higher and

therefore the transitions corresponding to C exciton or the first excited states of Fx cannot be resolved. Therefore, the transition at 362 nm is a combined effect of Fx, C-exciton and the first excited states of Fx. For ZnO thin films, the band edge excitation (figure 3.15(b)) peak is also observed around 362 nm followed by series of excitation features around 338 and 316 nm. In wurtzite ZnO, due to the influence of crystal-field and spin-orbit interactions, valence band (p-like state) splits into three bands, whereas the conduction band is mainly constructed from the slike state (τ_7^c symmetry) [229]. It should be noted that these transitions were reported between 369 and 376 nm [230]. The A and B Fx lines are usually separated by 15 meV [231, 232], in contrast to the present study. It indicates that the short wavelength PLE resonance cannot be explained by the usual transition between the spin-orbit coupling split states and the conduction band. Therefore, it is inferred that an additional excitation mechanism may also be contributing to the effect. A charge transfer process or collective charge oscillation can be the possible origin of the short wavelength resonance. To investigate this possibility, PLE measurements by monitoring blue emission were also carried out.



Figure 3.15 Photoluminescence excitation spectrum of (a) ZnO/Zn and (b) ZnO thin films monitoring green and red emission respectively.

A relative red shift is observed (figure 3.16) for near band edge excitation peak in case of ZnO/Zn thin films. In contrast, the excitation features at shorter wavelength (338 and 316 nm) are rather unperturbed for both thin films. These results indicate that there are two different processes which contribute to the PLE resonance. Since these short wavelength peaks are observed in both ZnO and ZnO/Zn films when PLE is carried out to monitor green, red and blue emission, the possibility that the bands originated from unreacted bulk Zn can be excluded. Note that for all PLE experiments, the energy separation between the series of short wavelength resonance peaks is found to be almost constant (253 ± 3 meV). The energy difference is substantially

larger than that of the optical phonon energy (72 meV) of ZnO and hence cannot be attributed to phonon related modes. Furthermore, SP resonance in different kinds of ZnO has been reported over a very large energy range of 200 meV to 16 eV [232-234]. Thus, it is tentatively assumed that these resonant features are due to excitation of surface plasmons in ZnO, may be related with Zn nanoclusters.



Figure 3.16 Photoluminescence excitation spectrum of (a) ZnO/Zn and (b) ZnO thin films monitoring blue emission.

The PLE absorption spectra recorded by monitoring blue emission for ZnO/Zn and ZnO films in figure 3.16 (a) and (b), respectively, shows that the PLE peak of the ZnO/Zn films is significantly red-shifted from 362 to 370 nm. However, such a shift is not observed for PLE measurement while monitoring defect related

green and red emission in ZnO and ZnO/Zn films respectively. This is understood by the fact that the green (defect) band transition is competing with the *Fx* transition [235]. Therefore, it is reasonable to assume that the both (Fx and green) transitions must originate from same absorption process. On the other hand, blue emission originates from completely different absorption process. When the а semiconductor is excited with energies lesser than band gap energy, defects can play a variety of electronically active roles that affect the electrical and optical properties of a semiconductor [236]. The PLE recorded by monitoring blue emission shows a resonance at 370 nm which indicates that when the light of this energy (370 nm) shines on nanaowires, electrons are excited to a level which arises from lowering the energy of the P-line of ZnO caused by the Burstein-Moss band filling effect (as stated in the PL analysis). The excited electrons hop to the defect donor level then relax into the deep acceptor level, which gives rise to blue emission.

3.3.3 Raman scattering

To provide additional information on the effect of Zn residue on vibrational properties of the ZnO thin films, Raman scattering analysis was carried out. The room-temperature Raman spectra of the ZnO/Zn and ZnO thin films are shown in figure 3.17(a) and (b), respectively. The strongest peak positioned at 437 cm⁻¹ is attributed to the E_{2H} mode of ZnO. The peak positions in the present case are similar to that reported for bulk ZnO [237]. The similarity of the results suggests that the nanowires are almost stress-free. The peaks at 332, 381 and 580 cm⁻¹ are

assigned to the A₁, A₁(TO) and E₁(LO) modes of ZnO respectively [237] while the peak around 491 cm⁻¹ can be attributed to surface optical phonon [238].



Figure 3.17 Raman spectrum of (a) ZnO/Zn and (b) ZnO thin films.

It is interesting to note that the Raman characteristics of the ZnO/Zn film are very different. The red-shift to 432 cm⁻¹ and 561 cm⁻¹ of E₂H and E₁ (LO) modes were recorded, respectively. The exchange interaction between phonon-plasmon in electron rich ZnO/Zn films and stressinduced effects due to lattice mismatch with the unreacted Zn may be responsible for the observed red-shift of phonon energies [238].

The intensity ratio of the E_1 (LO) to E_2 increases for ZnO/Zn films compared with the ZnO thin film. The presence of static electric field is the most widely accepted origin for enhancement of Raman scattering from the longitudinal optical (LO) phonon in semiconductors, arising from the long range interaction of phonon with charged (electrons) carriers [239]. Therefore, the enhancement of LO phonon scattering is attributed to the effect of electric field induced Raman scattering in the Zn-ZnO composite. The enhanced electric field due to excess charge carrier may also lead to band gap shrinkage which was anticipated by transmittance and PL measurement.

3.4 Summary

The growth of ZnO nanowires over different substrates was successfully demonstrated. The mechanism of ZnO nanowire growth was diagrammatically explained. The as grown nanowires are polycrystalline and having the diameter 20-100nm and lengths up to few micro meters. These nanowies are spread over the entire area of the substare. Mechanical properties of the ZnO nanowire thin films were studied. The as grown ZnO nanowires are softer and having low hardness values. Photoluminescence and Raman spectra of ZnO nanowires with Zn residue were studied.

4

Morphology dependent non-linear optical response of ZnO thin films

Abstract

ZnO thin films with different micro-/nano-structured morphologies that ranged from dense grains to nanorods and nanowires were fabricated. Photoluminescence studies revealed two emission peaks in these films, one in the UV region due to exciton emission while the other in the visible spectral region due to Zn or Oxygen vacancies/defects. The effect of these different micro-/nano-structures on the third-order nonlinear optical (NLO) response has been scrutinized using Z-scan technique with femtosecond (fs), MHz and picosecond (ps), kHz pulses at a wavelength of 800 nm. Various NLO coefficients such as two-photon absorption (β), nonlinear refractive index (n₂), Re $[\chi^{(3)}]$, Im $[\chi^{(3)}]$ and $\chi^{(3)}$ were evaluated. The obtained $\chi^{(3)}$ values were ~10⁻⁷ e.s.u. in the fs regime and $\sim 10^{-10}$ e.s.u. in the ps regime. Optical limiting studies of these films were also performed and limiting thresholds were estimated to be 15-130 $\mu J/cm^2$ in the fs regime while in ps regime the corresponding values were 1-3 J/cm². The NLO data clearly indicates strong nonlinearities in these ZnO thin films with possible applications in photonics.

4.1 Introduction

The dependence of linear and non-linear optical (NLO) properties of ZnO on stoichiometry and morphology is known [240]. As already demonstrated, thermal evaporation of ZnO can result in a large variety of microstructure and different morphologies. In this chapter, the manipulation of morphology of ZnO leading to interesting linear and NLO is demonstrated. NLO properties of a variety of ZnO films and nanostructures grown using different techniques and growth conditions have recently been reported [241-262]. Chan et al. [242] studied ZnO thin films and observed two-photon absorption (2PA, β) values of 10⁻⁶-10⁻⁷ cmW⁻¹ in the wavelength range of 390–420 nm using 82 MHz, 100 fs pulses. Han et al. [243] have reported ZnO thin films data with β of 10⁻⁶-10⁻⁷ cmW⁻¹at 790 nm using 76 MHz, ~140 fs pulses. Irimpan et al. [247-250] have reported NLO properties of nanostructured ZnO thin films with 2PA coefficients of ~10⁻⁴-10⁻⁹ cmW⁻¹ and $\chi^{(3)}$ of ~10⁻⁶-10⁻¹⁰ e.s.u. with ns pulses. Ouyang et al. [255] studied the 2PA and optical limiting properties of graphene/ZnO composites in organic glasses and reported a NLO coefficient (α_2) of 1530 cm/GW. Lee et al. [259] synthesized ZnOnanorods with different rod diameters (50,110, 240 nm) and investigated their fs NLO properties and time response of the nonlinearity. However, most of the studies were performed using (a) single (ns/ps/fs) pulse excitation (b) MHz, fs pulse excitation and very few of them attempted investigating exhaustive structure-property relationship. Furthermore, with MHz excitation one expects thermal contribution to the observed nonlinearities. The objective of current

work was to fabricate ZnO films with different micro-/nano-structures and investigate the NLO response keeping crystallographic details same in all cases. We have performed both femtosecond (fs) NLO studies with MHz/kHz repetition rate in conjunction with picosecond (ps) NLO studies with kHz repetition rate for all the fabricated films. It is demonstrated that the NLO response of ZnO films can be controlled by manipulating their microstructures. Our earlier studies on such ZnO films investigated the wettability, Raman, and Photoluminescence (PL) properties in detail in chapter 3.

4.2 Experimental

To achieve different morphologies, ZnO films were grown by thermal evaporation technique on borosilicate glass (BSG) substrates by four different annealing approaches. ZnO films were prepared by two different routes to achieve different micro-/nano-structures. In the first process deposition of ZnO film was achieved using Zinc Oxide powder as the source material followed by annealing at 150 °C in air (sample named as ZnO-film; ZnO1). The second process involved thermal oxidation of metallic Zn films in air or oxygen atmosphere at 500 °C. Three different types of thermal oxidation routes were followed: 1) annealing of Zn film at 500 °C maintaining a heating rate of 5 °C/min followed by soaking time of 30 min at the same temperature [sample named as ZnO-Air; ZnO2] 2) same as 1 except the annealing is carried out in an oxygen rich atmosphere [sample named as ZnO-Oxygen; ZnO3] 3) Zn film was rapid annealed at 500 °C in air atmosphere. i.e., initially the furnace was heated to 500 °C at the rate of 10 °C/min and

102

then sample was loaded and maintained at the same temperature for 30 minutes followed by natural cooling in normal furnace atmosphere [sample named as ZnO4]. Post annealing, the thickness of films were ~250 nm, ~980 nm, ~670 nm and ~1500 nm for ZnO1, ZnO2, ZnO3, and ZnO4, respectively.

NLO characterization was accomplished using the Z-scan technique [263]. In the fs regime, a Ti: sapphire oscillator (Chameleon Ultra II, Coherent) producing ~140 fs pulses with a repetition 80 MHz at 800 nm was used. The sample was scanned along the Z-direction through the focus of a 100-mm focal length lens. The input beam was spatially filtered to obtain a pure Gaussian profile in the far field. The sample was placed on a 10 μ m resolution translation stage and data was collected manually using the detector (Field-Max). The transmitted intensity was recorded as a function of the sample position. The beam waist (ω_{0}) estimated at the focus was ~25 µm with a corresponding Rayleigh range of ~2.54 mm. In the ps regime, studies were performed by using Ti: sapphire amplifier delivering ~2 ps, 1 kHz pulses at 800 nm. The amplifier was seeded with ~15 fs pulses from an oscillator (MICRA, Coherent, 1 W, 80 MHz, 800 nm). The average power from amplifier was \sim 2 W. The laser beam was focused by a 200 mm focal length lens. The output transmittance was recorded by using a photodiode in combination with a lock-in amplifier. Complete details of the ps experiments have been reported in our earlier works [264-267]. The NLO studies were performed on all the samples with linear transmittance of ~60-75% at 800 nm. All the closed aperture scans were performed at lower peak intensities so as to avoid any contribution from higher order nonlinear effects (the value of $\Delta \varphi$ estimated in all the cases was < π). The experiments were repeated more than once and the average nonlinear optical coefficients were retrieved from the theoretical fits to experimental data.

4.3 Results and discussion

4.3.1 Structure

The XRD data of ZnO1, ZnO2, ZnO3, and ZnO4 are shown in figure 4.1. The diffraction peaks of all samples exactly coincided with that of hexagonal ZnO structure and the peaks were indexed according to JCPDS No. 89-1397. We did not observe any significant Zn residue from the XRD patterns of ZnO2, ZnO3 and ZnO4 [figure 4.1(b)-1(d)], which confirmed that there was a complete phase transition from hexagonal Zn (as deposited) to hexagonal ZnO at 500 °C annealing temperature.



Figure 4.1 XRD pattern of thin films of (a) ZnO1 (b) ZnO2 (c) ZnO3 and (d) ZnO4

104

The hexagonal ZnO unit cell parameters were calculated from the XRD patterns and were independent of oxidation history of the samples. The calculated unit cell parameters were, $a = 3.2\pm0.2$ Å and c = 5.2 ± 0.2 Å. The average crystallite sizes were calculated from FHWM of ZnO peaks using Scherrer's formula [182] and the obtained value was 36 ± 2 nm for the three films of ZnO2, ZnO3, and ZnO4 and independent of different oxidation approaches used. However, ZnO1 had a crystallite size of 8 ± 2 nm. The lower value of the crystallite size in case of ZnO1 can be attributed to the lower annealing temperature as well as the lower thickness of this film.

4.3.2 Microstructure

The morphology of ZnO1 is displayed in figure 4.2(a). The SEM data revealed a dense microstructure with flakes emerging out of the surface. Closer examination revealed that there were pores in the film which were randomly distributed. Morphology of ZnO2 [depicted in figure 4.2(b)] also resulted in dense microstructure but there was evidence for formation of aggregates on the surface which rendered the surface rough. The microstructure of ZnO3 [data presented in figure 4.2(c)] depicts formation of micro/nanorods that grew along the plane of However, the most drastic change occurred in the film surface. microstructure of ZnO4, shown in figure 4.2(d). There was transformation into nanowires with diameters of ~15-100 nm and lengths extending to a few μ m emerging from the film surface. From these images it is evident that the annealing route had significant effect on the surface morphology of ZnO films. The microstructures ranged

105

Morphology

from dense films to slightly porous microstructures, micro/nano rods and nanowires. Hence, these samples provided good examples for investigating the effect of differing microstructures on NLO properties of resulting ZnO surfaces.



Figure 4.2 FE-SEM images of (a), (e) ZnO1 (b), (f) ZnO2 (c), (g) ZnO3 (d), (h) ZnO4. (a)-(d) are in 1µm scale and (e)-(h) are in 200nm scale.

4.3.3 Optical properties

The absorption coefficient α is related to incident photon energy 'hv' by the Tauc's relation [268] (α hv) = (const) (hv-E_g)ⁿ. n=1/2 and n=2 for the direct and indirect transitions in crystalline semiconductors, respectively. Optical band gap Eg was calculated by linear extrapolating the plot of $(\alpha hv)^{1/n}$ vs hv and finding the intersection with abscissa [269]. The optical band gap values (Eg) of ZnO thin films were calculated from absorption spectra presented in figure 4.3 (a). The E_g values of ZnO1, ZnO2, ZnO3, and ZnO4 determined from the Tauc plots shown in figures 4.3 (b) to (e) were 3.69 eV, 3.53 eV, 3.50 eV, and 3.15 eV, respectively. It is to be noted that the large difference in thickness of ZnO1 (250nm), ZnO2 (980 nm) and ZnO3 (670 nm) samples has a very negligible effect on the band gap. The lower value of the optical band gap, 3.15 eV, of the ZnO4 sample (which consists of nanowires) is due to the partial oxidation of the sample leading to oxygen non-stoichiometry. However, in all the cases there is clear evidence for the presence of defect states in the range of 2.5-3.1 eV range [see figures. 4.3 (b)-(e)] which manifests itself as the UV peak in the PL spectra (see discussion below) and the 2PA data (see discussion below).



Figure 4.3 (a) Absorption spectra of ZnO1, ZnO2, ZnO3, and ZnO4 thin films. Substrate absorption spectrum (solid line) is also included. **(b)-(e)** Tauc plots for ZnO1-ZnO4; Red (solid line) indicates the band gap, blue (dotted) line represents the presence of defect states.

4.3.4 Photoluminescence

PL spectra of ZnO1, ZnO2, ZnO3 and ZnO4 thin films excited at a photon energy of 3.49 eV (355 nm) are presented in figure 4.4. It is well established that bulk and thin film ZnO exhibit three PL peaks, a UV near band-edge emission peak near 380 nm, a green emission near 510 nm and a red emission around 650 nm [123-125]. In our earlier work on similar films, the dominant near band edge emission peak in 370-380 nm spectral region has been ascribed to exciton-exciton scattering process from the n=1 state to the exciton continuum state (P-line) while the broad emission observed near 550 nm is assigned to oxygen vacancies (V_o). The broad green-yellow band near 505 nm is due to deep level emissions in green region, which is ascribed to oxygen vacancies, zinc interstitials or zinc vacancies [126]. In the present study we have observed UV near band edge emission peak in the 383 -394 nm range and visible emission in the 489 -543 nm range from the films. These two peaks are frequently originating luminescent peaks reported in all ZnO samples. Thus, the results of the present study are in excellent agreement with earlier reports on thin films and bulk ZnO [125, 270-274]. It should be noted that the appearance of sharp, narrow UV emission splitting into two is an indication of better crystallinity and good quality of ZnO nanowires growth [275] which is in excellent agreement with XRD and FE-SEM results. We repeated the PL measurements for ZnO1 and ZnO4 samples after four months and did not find any significant changes in the recorded spectrum. This suggested that the samples were stable and devoid of any aging effects.



Figure 4.4 PL spectra of (a) ZnO1 (b) ZnO2 (c) ZnO3 and (d) ZnO4 thin films excited with above band gap energy (355 nm) of ZnO.

4.3.5 Raman spectra

Wurtzite ZnO belongs to C_{6V} (P63mc) space group for which the possible vibrational modes [276] are

$$U_{opt} = A_1 + 2B_1 + E_1 + 2E_2$$

where, A₁, E₁, and E₂ are Raman active and B₁ is Raman forbidden. The room temperature Raman spectra of ZnO thin films are shown in figure 4.5. The first order optical modes of ZnO at 380.8 cm⁻¹ and 437.5cm⁻¹are assigned to the A₁ [Transverse Optical (TO)] and E₂ high, optical phonons, respectively [237, 276, 277].



Figure 4.5 Raman spectra of ZnO1, ZnO2, ZnO3 and ZnO4.

The most intense peak at 437.5cm⁻¹ is the characteristic peak of ZnO wurtzite phase and can be attributed to the E₂ High mode. The peaks at 299.8 cm⁻¹, 329.7 cm⁻¹, 550.6 cm⁻¹and 674.6 cm⁻¹ have earlier been observed in bulk ZnO by other workers and assigned to B₁ low, E_{2H}-E_{2L}, B₁ high and Transverse Acoustic (TA) + Longitudinal Acoustic (LA)

modes, respectively [272, 278, 279]. The peak at 486.9cm⁻¹ has been attributed to surface optical phonons earlier [277]. The peak at 270.7 cm⁻¹ is the laser plasma line [60] while the peak at 583.8 cm⁻¹ assigned to E₁ (LO) has been inferred to arise from the formation of defects of oxygen vacancies [276, 280, 281].

4.3.6 Energy level diagram

Evidently both the Raman and PL spectra demonstrated the presence of oxygen related defects/vacancies. The corresponding energy level diagram inferred from these spectra is displayed in figure 4.6. From this energy level diagram and the calculated band gaps, it is expected that all the films would exhibit two-photon absorption (2PA) in the nonlinear absorption studies performed with ps and fs pulses.



Figure 4.6 Typical energy level diagram of ZnO films studied. Zn_i and O_i are the Zn and Oxygen interstitials, V_{Zn} and V₀ are the Zn and Oxygen vacancies.

4.3.7 NLO properties

In the fs regime, Z-scan data was recorded for ZnO1, ZnO2, and ZnO3 at 800 nm. The signatures are shown in figure 4.7 and corresponding NLO coefficients obtained from the fits to experimental data are presented in table 4.1. As stated earlier (based on the PL and Raman data) 2PA was observed for all films. We obtained β values of 0.99-1.3×10⁻⁴ cmW⁻¹ for data recorded with peak intensities of 0.2-0.3 GW/cm². The values of nonlinear refractive index, n_2 , were ~14-27×10⁻¹⁰ cm² W⁻¹ obtained with peak intensity of ~0.034 GW/cm². These values represent one of the highest reported values for ZnO nanostructures in literature. There could be contributions from various sources to the including nonlinear refractive index electronic, molecular, electrostriction, and excited state absorption population. In the fs (MHz) regime ZnO1 and ZnO3 depicted negative nonlinearity (self de-focusing type) as evident from the peak-valley signature while ZnO2 depicted positive nonlinearity (self-focusing type) as evident from the valley-peak signature. The peak valley distance (~4.4 mm) was ~1.7×Z₀in the case of ZnO1 and ZnO3 which confirms the presence of Kerr (purely electronic) type of nonlinearity. Earlier studies suggest bound electrons being responsible for negative n_2 in ZnO single crystals [253]. In the case of ZnO2 there could be contribution from thermal or excited state population [253, 254]. The reason for this discrepancy requires further detailed investigation. The Z-scan data for ZnO1 was also examined using a 1 kHz optical chopper (original repetition rate was 80 MHz) and



the data is shown in figure 4.8. We observed that there were no significant changes in the order of magnitude of NLO coefficients.

Figure 4.7 Fs open aperture Z-scan data of **(a)** ZnO1 (open triangles) **(b)** ZnO2 (open diamonds) **(c)** ZnO3 (open circles). Peak intensity used was ~0.21 GW/cm². Closed aperture Z-scan data of **(d)** ZnO1 (open triangles) **(e)** ZnO2 (open diamonds) **(f)** ZnO3 (open circles). Peak intensity used was ~0.034 GW/cm². Solid lines (red) in all graphs represent theoretical fits.

Morphology

Sample	β (cm/MW)	n2 (cm²/GW)	Im χ ⁽³⁾ ×10 ⁻⁷ (e.s.u.)	Re χ ⁽³⁾ ×10 ⁻⁷ (e.s.u.)	Total χ ⁽³⁾ ×10 ⁻⁷ (e.s.u.)	Reference
ZnO1 fs MHz pulses	99.0	-2.70	0.55	-2.43	2.49	This work
ZnO2 fs MHz pulses	12.5	1.40	0.07	1.21	1.21	This work
ZnO3 fs MHz pulses	130	-1.74	0.72	-1.51	1.67	This work
ZnO1 fs kHz pulses	175	-3.70	0.96	-3.20	3.30	This work
ZnO nanorods fs MHz pulses	-0.6-5.6	0.056-0.31	-	-	-	[259]
ZnO films fs MHz pulses	120-1100 ×10 ⁻³	-	-	-	-	[243]
ZnO films fs MHz pulses	91-681 ×10 ⁻³	1.35-2.65 ×10 ⁻²	-	-	-	[284]
ZnO nanoholes fs MHz pulses	180×10 ⁻³	-	-	_	-	[251]
ZnO/ graphene ns pulses	1.56	-	-	-	-	[255]

Table 4.1 Estimated NLO coefficients β , n₂, χ ⁽³⁾ of ZnO films in the fs regime. Negative sign indicates negative nonlinearity. Some of the recent works are also highlighted.



Figure 4.8 Open aperture data of ZnO1 using 1 kHz chopper (open circles) recorded at peak intensity 0.21 GW/cm². Solid line (green) represents the 2PA theoretical fit. Closed aperture data of ZnO1 (open squares) recorded at peak intensity of 0.034 GW/cm². Solid line (red) represents the theoretical fit.

In the ps regime, Z-scan data was recorded for ZnO1, ZnO2, ZnO3 and ZnO4 at 800 nm and the data is presented in figure 4.9. We again observed 2PA behavior in all the films. β values retrieved from the fits were ~1.15-9.5×10⁻⁸ cm W⁻¹achieved with peak intensities of ~100-152 GW/cm² while the n₂values were 6.8-39×10⁻¹³ cm² W⁻¹ achieved with a peak intensity of ~28 GW/cm². Interestingly ZnO1 and ZnO3 demonstrated positive nonlinearity (self de-focusing, valley-peak signature) while ZnO2 and ZnO4 exhibited negative nonlinearity (self-focusing, peak-valley signature). The peak-valley distance was ~1.7×Z₀

Morphology

in the case of ZnO2 and ZnO4 which confirms the presence of Kerr (purely electronic) type of nonlinearity. In the case of ZnO3 and ZnO4 the switchover of sign could possibly be related to their band gaps and/or excited state population resulting from 2PA. The excitation was with 1.55 eV photons in all the cases. Earlier studies [259] indicated that the local field enhancements through size- and structure-dependent interfacial interactions influence the magnitude of n₂. The Z-scan data was fitted using standard equations reported in literature [282]. The NLO coefficients retrieved from ps data are summarized in table 4.2. All the coefficients were estimated with ±15% uncertainty arising from errors in beam waist measurements and calibration of filters. Tables 4.1 and 4.2 also present some of the recently reported NLO coefficients of ZnO films and composites by various groups.



Figure 4.9 Open aperture Z-scan data of **(a)** ZnO1 (open squares) at ~100 GW/cm² **(b)** ZnO2 (open diamonds) at ~119 GW/cm² **(c)** ZnO3 (open circles) recorded at ~144 GW/cm² **(d)** ZnO4 (open triangles) at ~152 GW/cm². Closed aperture Z-scan data of **(e)** ZnO1 (open squares) **(f)** ZnO2 (open diamonds) **(g)** ZnO3 (open circles) **(h)** ZnO4 (open triangles). Peak intensity used was ~28 GW/cm². Solid lines (red) in all graphs represent the theoretical fit.

Morphology

Table 4.2 Estimated NLO coefficients β , n₂, $\chi^{(3)}$ of ZnO films in the ps regime. Negative sign indicates negative nonlinearity. Some of the recent works are also highlighted.

Sample	β (cm/GW)	n2 (cm²/TW)	Im χ ⁽³⁾ ×10 ⁻¹⁰ (e.s.u.)	Re χ ⁽³⁾ ×10 ⁻¹⁰ (e.s.u.)	Total χ ⁽³⁾ ×10 ⁻¹⁰ (e.s.u.)	Reference
ZnO1 ps, 1 kHz	95.0	3.9	0.530	3.38	3.43	This work
ZnO2 ps, 1 kHz	30.0	-2.2	0.160	-1.89	1.90	This work
ZnO3 ps, 1 kHz	19.5	3.0	0.110	2.59	2.60	This work
ZnO4 ps, 1 kHz	11.5	-0.7	0.064	-0.60	0.60	This work
ZnO-PS ns pulses	0.082- 0.281	0.43-1.33	-	-	5.71-14 ×10 ⁻⁵	[258]
ZnO films ps pulses	-4.75 ×10 ³	7.1×10 ⁻³	-	-	0.0123	[254]
ZnO films ns pulses	2.9-103.7 ×10 ³	-	-	-	2.3-13.4 ×10 ⁴	[249]
ZnO nanocones ns pulses	18, 4.6	-	-	-	-	[260]

A survey of literature shows that the values of β and n_2 are strongly dependent on the processing technique leading to a large scatter in the values of these parameters. This is also a consequence of the fact that microstructural evolution of thin films is, in general, process

dependent. Therefore, not surprisingly, the values of β and n₂ for our samples (ZnO1-ZnO4) are slightly different to that of the values reported earlier [283]. For example, Chan et al. [283] studied fs NLO absorption of ZnO thin films grown by laser molecular beam epitaxy and obtained β values of 3000 cm/GW at 390 nm (or 3 cm/MW) which was much larger than that of ZnO bulk measured at 532 nm. In contrast, Lee et al. [259] synthesized vertically aligned ZnO nanorods with different rod diameters (50 nm, 110 nm, 240 nm) and investigated their fs (MHz) NLO properties. They obtained NLO coefficients (β) with magnitudes of 2.91×10⁻⁶ cm/W to 5.61×10⁻⁶ cm/W (i.e. 2.91-5.61 cm/MW) at 815 nm. They argue that the high 2PA values may have originated from the large residual absorption at the fundamental and TPA wavelengths and the band-edge local field enhancement due to surface trapped states. They further convey that 2PA-induced thermal nonlinearity could not be fully excluded because of the large absorption at TPA wavelength. In our case too we observe residual absorption at two photon wavelength of 400 nm (Z-scan excitation at 800 nm). They also reported n₂ values of $0.92-3.11 \times 10^{-10}$ cm²/W (i.e. 0.092-0.311 cm²/GW) whereas we observed values in the range of 1.4-3.7 cm²/GW in our case. However, in their case the rod diameters (vertically aligned) were 50 nm, 110 nm, and 240 nm whereas in our case the films morphology was completely different. Lee et al. [259] further summarize that the geometric arrangement of nanostructures strongly varies with the sample thickness and is one of the crucial factors contributing to the observed overall optical

Morphology

nonlinearity, confirming our observation morphology dependent NLO properties.

Porosity is the property of materials which affects the nonlinear optical response at nanoscale. Earlier studies have indicated that nanoporous Si [284], aluminum oxide nanostructures [285] exhibited large $\chi^{(3)}$ values depending on the pore structure, size, and density. In the case of our samples ZnO1 had well sorted pores, compared to others, probably resulting in a higher $\chi^{(3)}$ for ZnO1 and ZnO3 compared to that of ZnO2. The porosity was highest in ZnO1 films, which leads to the inference that largest $\chi^{(3)}$ value observed for ZnO1 in ps/fs measurements is, possibly, a consequence of its denser microstructure. Similar results were obtained in porous Al oxide nanostructures [285] wherein they demonstrated that the local electric field enhancement was due to pore size, pore shape, and surface state effects which in turn enhanced the nonlinearity [284]. Han et al. [243] reported β values of 1.1 cm/MW for ZnO films annealed at 950-1050 °C and attributed the increased nonlinearity due to the interfacial state enhancement. Trejo et al. [254] prepared nanostructured ZnO thin solid films by electro deposition of hydrothermal sol–gel solutions and obtained a β value of 4750 cm/GW but measured at 532 nm and using 180 ps pulses (as against a value of 95 cm/GW in our case measured at 800 nm and ~2 ps pulses). The higher value obtained in their case can be attributed to (a) different wavelength and (b) longer duration pulses. The $\chi^{(3)}$ values obtained in the present studies (10⁻⁷ esu) are similar to that that of $\chi^{(3)}$ values of ZnO microcrystallite thin films [286] studied near the excitonic resonance at

various temperatures using fs degenerate four-wave-mixing technique. Further detailed studies are necessary to exactly identify the mechanism for superior nonlinearities in our case. The values of β and n₂ for pure ZnO thin films measured with fs MHz pulse excitation were ~10⁻⁶ cm/W and ~10⁻¹¹ cm²/W, respectively [259]. The values of β and n₂ for bulk ZnO measured using 25 ps, 532 nm excitation were found to be ~4.2 cm/GW and ~9×10⁻¹⁵ cm²/W, respectively [252, 253]. The NLO coefficients β and n₂ of NLO crystals such as KDP and BBO are ~0.9 cm/GWand 5-6×10⁻¹⁶ cm²/W [287, 288].

Optical limiting (OL) behavior [256, 257] of ZnO thin films in the fs and ps time domains was evaluated and the data is presented in figure 4.10(a) and figure 4.10(b), respectively. OL threshold values in fs domain were estimated to be 15-130 μ J/cm², while in ps regime the values were 1-3 J/cm². Such small limiting threshold values in the fs regime could find practical applications in OL devices. Though many earlier OL studies on pure ZnO films and composites were confined to the ns regime it also imperative to identify materials for OL in the ultrafast (ps/fs) time domain since the detectors/sensors usually are equally prone to laser induced damage with those pulses associated with large peak intensities. In the fs case the threshold for OL was lower since the magnitude of nonlinearities was large due to thermal contribution. In the ps regime the measurements were performed with kHz pulses and, therefore, the thermal contribution could be negligible

Morphology



Figure 4.10 (a) Optical limiting data of ZnO1 (open circles) using ~2 ps pulses. Solid line (red) represents the theoretical fit **(b)** Optical limiting data of ZnO1 (open triangles) using ~140 fs pulses. Solid line (red) represents the theoretical fit.

We have also evaluated the contribution of thermal effects [283] for data recorded with MHz repetition rate has also been reported. Thermo-optical nonlinearity is an important parameter while calculating the nonlinear index of refraction. In particular, thermo-optic contribution is added by non-local nonlinearity while using ultrashort laser pulses. For some materials this contribution becomes significant. It depends on the thermal characteristic time and thermo-optic coefficient. In the first case contribution is significant, if thermal characteristic time τ_c is longer than the time period of the laser. Thermal characteristic time τ_c was calculated using the parameters of beam waist (ω_0), density (ϱ), specific heat (c_p), and thermal conductivity (k) [283]

$$\tau_c = \frac{\omega_o^2 \rho c_p}{4k}.....(4.1)$$

The estimated τ_c was ~8.3×10⁻⁶ s for the fs data. The thermo-optic coefficient values for ZnO1, ZnO2, and ZnO3 in the fs regime were calculated using the relation

$$\Delta n_0 = \frac{\alpha F_0}{2\rho c_v} \frac{dn}{dT}.....(4.2)$$

F₀ is the fluence, ϱ is the density, c_v is the specific heat, and $\frac{1}{2}$ denotes the fluence averaging factor. Thermo-optic coefficient $\left[\frac{dn}{dT}\right]$ values estimated were (a) ZnO1: 2.14×10⁻⁴ K⁻¹ (b) ZnO2: 2.41×10⁻⁴ K⁻¹ (c) ZnO3: 2.01×10⁻⁴ K⁻¹. In the ps regime we performed the measurements with 1 kHz pulses (1 ms time between consecutive pulses) and, therefore, we expect minimal thermal contributions to the observed nonlinearity and predominantly has electronic contributions.

4.4 Summary

NLO characterization in the fs and ps regimes has been performed on ZnO thin films fabricated with different morphologies. All the films exhibited 2PA at 800 nm in both the regimes with magnitudes of ~10⁴ cm/W, ~10⁻⁸ cm/W in fs, ps regimes, respectively. The n₂ values were ~10⁻⁹ cm²/W in ps and ~10⁻¹² cm²/W in fs regimes. Third order nonlinearity [$\chi^{(3)}$] values were also estimated. Very low limiting threshold values (15-130 µJ/cm²) were recorded with fs pulses.It is demonstrated that NLO response of ZnO films can be controlled by manipulating their microstructures.

5

Optical properties of Indium and Tin doped ZnO nanowire thin films
Abstract

Single step transformation of Indium-Zinc and Tin-Zinc films into doped ZnO nanowires is demonstrated. In and Sn doped ZnO nanowires are formed by the annealing of In-Zn and Sn-Zn bilayer films to 500 °C in air. Independent of processing conditions all the nanostructures are polycrystalline as evidenced from X-ray diffraction patterns. The optical transmission, reflectance and absorption, in the wavelength range between 200 to 2500 nm, have been measured as a function of annealing temperature. It is shown that all the bilayers and the In and Sn doped nanowires can be used as solar absorber materials due to their high absorption, low transmittance and reflectance, in this region of the spectrum. In certain cases, the nanowires exhibit high transmittance and very low reflectance making them very attractive for use as antireflection coatings.

Chapter 5

5.1 Introduction

The ability to produce doped ZnO nanowires is very important for a large variety of applications [289-291]. Among the many dopants, In and Sn doped ZnO nanowires have been the subject of recent interest [292-302]. These reports mainly concentrate on transport and gas sensing behavior of In and Sn doped ZnO nanowires. However, there are very few reports on the effect of In and Sn doping on the linear optical properties of ZnO nanowires (NWs).

In the current work, doping of ZnO nanowires with In and Sn by the same single step thermal oxidation method used in the undoped case is demonstrated. The process involves he deposition of bilayers of the corresponding metal layers followed by a rapid heating process in air at 500 °C. The morphological evolution is characterized using scanning electron microscopy whereas the structure is investigated by Xray diffraction. The nanowire thin films are then characterized for their optical response in the wavelength range of 190-2500 nm. In this study it is demonstrated that these materials can be used for solar absorber and anti-reflective coatings in photovoltaic cells.

5.2 Experimental

Pure In, Sn and Zn-In, In-Zn, Zn-Sn and Sn-Zn bilayer metal films were deposited on borosilicate glass (BSG) substrate by the thermal evaporation process in high vacuum (5×10⁻⁶ mbar). High purity metals (99.99%) were used as the source and the source-substrate distance was Optical properties ...

of the order of 10 cms. Two geometries of bilayers were used. In the first geometry, Zn was deposited first and was followed by the dopant metal (In or Sn) deposition. In the second geometry, the dopant metal (In or Sn) was first deposited which was then followed by the deposition of Zn. The substrates were maintained at ambient temperature during deposition. The as-deposited In and Sn metal films were post-deposition annealed at different temperatures, while the bilayer metal films were post deposition annealed in air at 500 °C for 30 min.

5.3. Results and discussion

5.3.1 Microstructure and structure

It was shown in chapter 3 that annealing of Zn metal films at temperature greater than its melting point results in the formation of nanowires. Since the main condition for formation of ZnO nanowires is that the temperature should be greater than the melting point, it was expected that similar conditions would lead to the growth of In and Sn oxide nanowires.



Figure 5.1 FESEM images of In films (a) as deposited and (b)-(d) annealed at 150, 200 and 250 °C.

Chapter 5

The FESEM images of In films as deposited and annealed at 150, 200 and 250 °C are shown in figure. 5.1(a) to (d). The melting point of In is ~156 °C and hence the temperatures were selected as being below, approximately equal to and above the melting point. The asdeposited films exhibit an island like structure with discontinuities and irregular shapes with lateral dimensions of 200-250 nm. On annealing the films to temperatures approximately equal to and slightly greater than the melting point, no significant changes are observed. The islands are still irregularly shaped with lateral dimensions of the order of 200-250 nm. At 250 °C, however, the islands break up into smaller nearly spherical particles with a peak size of 80 nm. This is, evidently, a consequence of the melting of Indium between 200 and 250 °C. Due to surface tension of the liquid droplets of In that form on melting, they breakup into smaller droplets as the temperature exceeds the melting point. Since the annealing process is carried out rapidly, the quenching results in freezing of droplets at the point of contact with the substrate. So, contrary to the expected behavior that the In particles would melt, flow, completely wet the substrate and form nanowires or continuous film at these temperatures, there is evidence for dewetting. Solid-solid dewetting has been observed in other film-substrate systems [303]. It is known that dewetting occurs at pre-existing holes or film edges when the free energy barrier to form a continuous film is high for a particular film-substrate system and is strongly temperature dependent. Evidently, this is the case for the In-BSG interface.



Figure 5.2 FESEM images of Sn films (a) as deposited and (b)-(d) annealed at230, 300 and 350 °C.

The Sn films were also annealed at different temperatures, using the same selection criterion as that for In. The FESEM images of the as-deposited films and those annealed at 230, 300 and 350 °C are shown in figure 5.2(a)-(d). In contrast to the In films, the Sn films are continuous and exhibit large sub-micron pebble shaped particles. The dimensions in this case are 300-400 nm for the as deposited films that increases to 500 nm for the films annealed at 230 °C (melting point) and 300 °C (slightly greater than melting point). At 350 °C, there is evidence for flow of the large pebbles and the formation of much larger grains.

The microstructural evolution of the three metal films (Zn, In and Sn) is, thus, different even though all the three were heated to temperatures much greater than their melting points. In the case of In and Sn nanowire formation is not observed whereas Zn forms nanowires on annealing. To further examine the origin of these differences, the X-ray diffraction patterns of the In, Sn and Zn films annealed at different temperatures are presented in figure 5.3(a), (b) and (c), respectively.



Figure 5.3 X-ray diffraction patterns of the (a) In as deposited and annealed at 250 °C , (b) Sn as deposited and annealed at 350 °C and (c) Zn as deposited and annealed at 500 °C.

It is seen that in all three cases there is transformation of metal into the corresponding oxide at elevated temperatures. In the case of In, peaks due to In₂O₃ appear at 150 °C whereas for Sn, low intensity peaks due to SnO appear at 230 °C, indicating onset of oxidation at temperatures close to the melting point. It may be noted that these temperatures (150, 200 and 400 °C) are just below the melting point of

Optical properties ...

the respective metals, In, Sn and Zn. Clearly, although annealing in air leads to oxidation of all the metals, the extent of oxidation is different. While it is complete in the case of In, oxidation is partial in the case of Sn and Zn. This can be attributed to the differences in melting points of the metals. In being the lowest melting point (at 156.4 °C) metal oxidizes faster than both Sn (230 °C) and Zn (419.6 °C) because of their higher melting points.

In previous chapters, the formation of ZnO nanowires by the adsorption of oxygen through thermal oxidation of metallic Zn films was discussed in detail. Thus, even though there is oxygen adsorption, not all metals act as nuclei for the formation of dendrites at the same temperature and therefore do not form nanowires. As a consequence, for a given metal there is only a small window of temperatures and rates of heating over which nanowire growth takes place. Evidently the conditions for growth of In₂O₃ and SnO₂ nanowires do not fall within the window of parameters favourable for nanowire growth. This result is in conformity with reports that In₂O₃ and SnO₂ nanowires tend to form at temperatures > 600 °C using the VLS approach [304, 305].

One of the issues that needed to be addressed is the role of the substrate in the formation of nanowires *i.e.* whether the glass substrate catalyzes the growth of nanowires. This question was resolved by depositing Zn film on different substrates and examining the microstructural evolution under thermal oxidation. Indeed, it was found that independent of substrate, (fused silica, single crystal sapphire,

Chapter 5

lanthanum aluminate and yttria stabilized zirconia) nanowires were formed by this process as reported in chapter 3.

The formation of alloy films exploiting the inter diffusion in thin film bilayers and multilayers annealed at elevated temperatures has been studied over many years [306, 307]. It is of particular importance in semiconductor devices to create electrical contacts. In the current work, the phenomenon of inter diffusion has been used to realize In and Sn doped ZnO nanowires. For this purpose, two different bilayer geometries were studied: (1) In-Zn metallic bilayers subjected to thermal oxidation with In as the overlayer in one case and In as the underlayer in the other case and (2) Sn-Zn metallic bilayers subjected to thermal oxidation with Sn as the overlayer in one case and Sn as the underlayer in the other case. Thermal oxidation in all cases was carried out at 500 °C, a temperature which is higher than the melting point of all three metals.

In the following section the top metal layer is mentioned first *i.e.* In-Zn would mean In is on the top and Zn at the bottom, whereas Zn-In would mean that Zn is at the top.

The morphology of as deposited In-Zn, Sn-Zn, Zn-In and Zn-Sn films is shown in figure 5.4 (a) to (d). In the In-Zn case, the morphology is similar to that of the pure In except that Zn particles appear to bind to the periphery of the In islands forming "nano-feet" with an In base and Zn fingers. The bases of the nano-feet are between 100-200 nm and the Zn fingers are approximately 20-30 nm in size. In the case of Sn-Zn films

Optical properties ...

there is a more drastic change in the microstructure with the formation of three-dimensional hexagonal micro-cubes. A closer examination of these shapes and comparison with the micro-pebbles in the single layer Sn film suggests that these emerge from the pebble-like microstructure exhibited by the pure Sn films. The height of the cubes is of the order of 400-500 nm with side ranging from 100-300 nm. Significantly, the cubes consist of a highly dense three dimensional array of uniformly packed spherical particles of 20-25 nm diameters. The origin of the selforganized structure is not very clear. Remarkably, when Zn films are on top, in both cases, the morphology replicates that observed in the case of pure Zn films deposited directly on glass substrates.



Figure 5.4 FESEM images of In-Zn, Zn-In, Sn-Zn and Zn-Sn films (a)-(d) as deposited, and (e)-(h) annealed at 500 °C.

The FESEM images in figure 5.4(e) to (h) show that, on annealing to 500 °C, all the films form nanowires and nanoneedles independent of the location of Zn prior to annealing. The as-deposited microstructure is completely destroyed due to the melting and thermal oxidation process. In the Zn-In and Zn-Sn cases the microstructure bears resemblance to that observed for pure Zn films annealed to 500 °C. It is observed in the In-Zn and Sn-Zn cases that the nanoneedles emerge out of the underlying thin films at various places. However, the fraction of that is converted into nanowires when In or Sn are at the top in the asdeposited state, is lower. This is attributed to the fact that, as stated earlier, the formation of nanowires depends strongly on the ability of the metal to adsorb and react with oxygen. The heats of formation of indium, tin, and and zinc oxides are -925.8, -577.6 and -350.5 kJmol⁻¹ respectively [308]. In addition, lattice energies of In₂O₃ SnO₂ and ZnO 13928, 11807 and 4142 kJmol⁻¹, respectively. These values clearly indicate that Zn will oxidize more readily than In or Sn. Thus, when In or Sn are at the top in the as deposited state, they act as diffusion barriers for oxygen in to Zn, thereby inhibiting the oxygen controlled diffusion process that is necessary for the formation of nanowires, as stated earlier.

5.3.2 Compositional analysis

Compositional analysis of In and Sn doped ZnO samples were characterized using energy dispersive X-ray spectroscopy (EDS). We have identified In, Zn and Oxygen from the In-Zn, Zn-In and Sn, Zn and Optical properties ...

Oxygen were identified from the EDS spectra of Sn-Zn and Zn-Sn asdeposited and annealed at 500 °C samples. We have also observed the small at.% 5-10% of Oxygen in the case of as deposited samples which is due to the partial oxidation of surfaces. The quantitative analyses of these elements were shown in table 5.1. The unidentified peaks from the EDS spectra were correspond to the elements of the substrate and the peaks corresponding to Au which is used for the conductive coating.



Figure 5.5 EDS spectra of In-Zn, Zn-In, Sn-Zn and Zn-Sn films (a)-(d) as deposited, and (e)-(h) annealed at 500 °C.

Sample	Atomic % of the elements (as deposited)					
Jumple	In	Sn	Zn	О		
In-Zn	11.14		82.86	6.01		
Zn-In	4.36		85.50	10.13		
Sn-Zn		0.73	92.74	6.53		
Zn-Sn		0.48	93.74	5.78		
Atomic % of the elements (annealed at 500 °C)						
In-Zn	1.06		50.63	48.30		
Zn-In	2.49		47.13	49.58		
Sn-Zn		0.42	52.93	62.61		
Zn-Sn		0.32	65.82	36.83		

Table 5.1 Compositional analysis of In and Sn doped ZnO samples.

X-ray diffraction patterns of the as deposited In-Zn, Zn-In, Sn-Zn and Zn-Sn films are presented in figure 5.6(a). In the as deposited case, independent of whether Zn is on the top or at the bottom, evidence for the crystallization of both metals is present. For example, in the In-Zn and Zn-In cases the peak at 2θ value of 32.9° is assigned to the (101) plane of In while the remaining peaks correspond to that of the hexagonal structure of Zn. In the Sn-Zn and Zn-Sn cases all the diffraction peaks are indexed based on hexagonal structure of Zn. It should be noted that there is overlap in the diffraction peaks of In and Zn and therefore, some of the peaks (such as those at 36.34, 39.17, 43.5 and 54.46°) can also be assigned to In. Similarly, there is overlapping of diffraction peaks of Sn and Zn for the 2θ value of 36, 39.2 and 54.4°;

Optical properties ...

therefore these peaks can also be assigned to Sn The large width of the peak as well as the shift in its position indicates that both metals contribute to the peak. As in the case of In, the peaks due to Zn dominate over that of Sn due to its higher thickness. It can be inferred from these X-ray diffraction patterns that both metals are present in the films, i.e. In and Zn in one case and Sn and Zn in the other case.



Figure 5.6 (a) X-ray diffraction patterns of the as deposited In-Zn, Zn-In, Sn-Zn and Zn-Sn films respectively.

All these films were annealed at 500 °C and their X-ray diffraction patterns are displayed in figure 5.6(b). The X-ray diffraction patterns present clear evidence for oxidation of Zn in all the cases, but the extent of oxidation differs depending on the location of Zn in the as

deposited state. In the In-Zn and Zn-In cases there is complete oxidation of Zn into ZnO. However, there is no evidence for the crystallization of Indium oxide or any Zn residue. All the observed peaks can be indexed as belonging to the hexagonal structure of ZnO. In the Sn-Zn and Zn-Sn cases, similar to the Indium case, although there are peaks that can be assigned to ZnO, there are no peaks due to the crystallization of tin oxide.



Figure 5.6 (b) X-ray diffraction patterns of In-Zn, Zn-In, Sn-Zn and Zn-Sn films annealed at 500 °C respectively.

The ionic radii of Zn, In and Sn in tetrahedral coordination system are 0.6, 0.62 and 0.55Å respectively. Since the ionic radius of Zn^{2+} (0.6 Å) is less than that of In^{3+} (0.62 Å) and is greater than that of Sn^{2+} (0.55 Å), it would be expected that when In is doped the unit cell volume

increases where as in case of the Sn doped system, the unit cell volume should decrease. As shown in table 5.2, the unit cell volume indeed increases for In and decreases for Sn doped ZnO. However, due to the very small difference (0.02 Å) between ionic radii of Zn²⁺ and In³⁺ the increase in unit cell volume is only marginal, in contrast to the Sn²⁺ doped ZnO when compared to that of pure ZnO. From figure 5.6(b) the intensity ratios of I(101)/I(100) and I(101)/I(002) for In-Zn and Sn-Zn annealed at 500 °C were calculated and compared with that of pure ZnO as shown in table 5.2.

Table 5.2 Intensity ratios and unitcell volume of pure ZnO, In-Zn and Sn-Zn annealed at 500 °C.

Sample	I(101)/I(100)	I(101)/I(002)	V=a ² c* sin60 (Å ³)
Zn 500 °C	3.2	9.3	47.545
In-Zn 500 °C	1.1	1.2	47.568
Sn-Zn 500 °C	2.2	1.3	47.439

Intensity ratios of In and Sn doped samples decreases in comparison with that of pure ZnO. This is clear evidence that the dopant metal (In^{3+}/Sn^{2+}) occupies the a/c plane of hexagonal structure of ZnO, which is shown in figure 5.7 (b)&(c).



Figure 5.7 Crystal structure (*P63mc*) of (a) pure ZnO, (b) In doped ZnO and (c) Sn doped ZnO.

To verify that In and Sn were indeed present in the annealed films, EDX measurements were carried out which confirmed the presence of these elements at approximately 3-5 wt%. It is thus inferred that ZnO was doped with In and Sn on annealing.

The volume fraction of Zn converted to oxide depends on the thickness of the films. When the thickness is of the films is of the order of 500 nm, it was reported in chapter 3 that, there is no Zn residue. However, in the current case the thickness of the films is much higher, ~3000nm. Hence, the fraction of Zn that converts into ZnO is much smaller leading to the presence of metal residue. This is also evident from the X-ray diffraction patterns shown in previous sections. It should be noted that X-ray diffraction patterns are obtained at angle of incidence of 0.5°, which would indicate that X-rays do not penetrate the

Optical properties ...

whole thickness. The presence of Zn residue is also confirmed in the cross-sectional FESEM image displayed in figure 5.8(a) and (b) for In-Zn and Sn-Zn films. The FESEM images clearly show nanowires emerging from an underlayer, which on examination using EDS, showed only Zn. The EDS carried out at interface between the film and the substrate does not indicate the occurrence of interdiffusion between the film and substrate.



Figure 5.8 Cross-sectional FESEM images of (a) In-Zn (b) Sn-Zn films annealed at 500 °C.

A significant difference between the In-Zn and the Sn-Zn cases is the presence of Zn residue. The X-ray diffraction patterns clearly indicate that there is unreacted Zn independent of whether Sn is on the top or at the bottom in the as-deposited state. The effect is more pronounced when the Sn layer is initially on top. Evidently majority of the Zn remains unreacted indicating that Sn acts as an oxygen diffusion barrier. It can also be inferred that oxygen preferentially seeks Zn atoms which then get oxidized and act as nuclei for the outward diffusion in the form of nanowires and nanoneedles. In the process, In or Sn also diffuse in to ZnO_x structures to form In or Sn doped ZnO. Thus, a single step rapid annealing process to realize In and Sn doped ZnO nanowires is demonstrated. It is expected that the process can also be extended to other metals.

5.3.3 Optical properties

The linear optical response of the undoped and doped ZnO nanowires was investigated to determine possible optical applications. The optical transmittance and specular reflectance of the materials was recorded in the wavelength region between 200-2500 nm (figures 5.9 and 5.10).



Figure 5.9 (a) Transmittance and **(b)** Reflectance spectrum of as deposited Zn (blue), In (red) and Sn (green) films.

The optical transmittance of the as deposited Zn films shows that the transmittance is <2% between 250-2500nm. The reflectance of the samples is also less than 8% in the visible region indicating that more than 90% of the light is absorbed (calculated by subtracting the sum of reflected and transmitted intensities from the incident intensity. i.e. if 100 is the incident intensity then absorption A% = 100 –(transmittance% + reflectance%) in the medium. When these films are annealed at 500 °C, the transmission increases and reaches a maximum of 80% at 2000 nm, due to oxidation (figure 5.10(a)).



Figure 5.10 (a) Transmittance and **(b)** Reflectance spectrum of Zn (blue), In (red) and Sn (green) films annealed at 500 °C.

The reflectance, in contrast remains low (<5%) in the entire measured region of the spectrum. This indicates that the absorption is low and the ZnO nanowire films can be used as anti-reflection coatings. The band gap of the films is ~2.5eV which is much less than the bulk value of 3.37 eV and can be attributed to the partial oxidation of Zn which confirms the observation of Zn residue by X-ray diffraction shown in figure 5.6(b).

The measured optical transmittance and specular reflectance of the In-Zn and Zn-In films (as-deposited and annealed at 500 °C), shown in figure 5.11(a) and (b) reveal that the transmission is low (<2%) in all cases except the Zn-In film annealed at 500 °C. It may be noted that this film had Zn as the top layer initially and X-ray diffraction showed that the film had completely oxidized. However, when In is at the top, both transmittance and reflectance continue to be low even after annealing at 500 °C.



Figure 5.11 (a) Transmittance, **(b)** Reflectance spectrum of In-Zn as deposited (red), In-Zn 500 °C (black), Zn-In as deposited (blue), Zn-In 500 °C (green).

The In-Zn and Zn-In films both show high reflectance in the as deposited state, which decreases to <2% on annealing at 500 °C. The absorption is >60% in the as deposited In-Zn and Zn-In cases and >90% in the In-Zn film annealed at 500 °C, making them suitable for application as solar absorber coating.

The measured optical transmittance and specular reflectance of the Sn-Zn and Zn-Sn films (as-deposited and annealed at 500 $^{\circ}$ C) is shown in figure 5.12 (a) and (b).



Figure 5.12 (a) Transmittance, **(b)** Reflectance spectrum of Sn-Zn as deposited (red), Sn-Zn 500 °C (black), Zn-Sn as deposited (green), Zn-Sn 500 °C (blue).

In contrast to the previous case, it is evident that the transmission is low (<15%) in all cases, independent of whether the samples are in the as-deposited or annealed state. In addition, all the samples show reflectance <10% indicating that the absorption is >75% for the Zn-Sn film annealed at 500 °C and 90% for the as deposited and annealed Sn-Zn and the as deposited Zn-Sn film, making them suitable for application as solar absorber coatings.

To better understand these optical responses, the role of the individual In and Sn layers was also examined. It was observed that in both cases with increase in annealing temperature the films became more transparent and less reflecting leading to lower absorption. It may also be recalled that the as-deposited Zn metal film showed low transmission and low reflectance. However, on annealing the transmission increased and the total absorption decreased. Thus, the individual layers do not behave in the same way as the as deposited and annealed bilayers. From these observations it can be inferred the optical response of the doped ZnO nanowires is different due to the presence of metal residue (either Zn itself or In/Sn as the case maybe). This observation also confirms the X-ray diffraction observation of the presence of metal residue. Thus, by controlling the metal residue in the nanowires they can be suitable for use either as anti-reflection coatings or solar absorber coatings. It is to be noted that the anti-reflection properties are strongly dependent on the surface morphology, roughness and microstructure of the films. The observed optical behavior, thus, only indicates the potential for application and more detailed studies are required to produce device quality films.

5.4 Summary

The growth of In and Sn doped ZnO nanowires by thermal oxidation of metallic bilayer thin films was successfully demonstrated. Optical properties of the In and Sn doped ZnO nanowire thin films were studied.

Chapter

6

Applications of ZnO nanowire thin films

Abstract

The detection of secondary explosive molecules (e.g. ANTA, FOX-7 and CL-20) using Ag decorated ZnO nanostructures as surface enhanced Raman scattering probes is demonstrated. ZnO nanostructures were grown on borosilicate glass substrates by rapid thermal oxidation of metallic Zn films at 500 °C. The oxide nanostructures, including nanosheets and nanowires emerge over the surface of the Zn film leaving behind the metal residue. It is shown that concentrations as low as 10 µM, of the three explosive molecules ANTA, FOX-7 and CL-20 over Ag/ZnO nanostructures, resulted in 10^7 , 10^7 and 10^4 times enhancement in the SERS signal respectively. This demonstrates the high sensitivity of detection of explosive molecules using Ag decorated ZnO nanostructures as SERS substrates. The Zn metal residue and conditions of annealing play an important role in determining the detection sensitivity. The ZnO nanowires are superhydrophobic with contact angles between 153° and 162° , contact angle hysteresis between $5^{\circ}-8^{\circ}$ and exhibit a reversible superhydrophobic-superhydrophilic transition under UV irradiation.

Chapter 6

6.1 Introduction

Surface Enhanced Raman Spectroscopy (SERS) has attracted wide attention in the past decade as a powerful spectroscopic tool in various fields of applications. The extremely strong local electric field at the metal-dielectric interface has made it possible to improve the aman scattering cross-sections. This, in turn, has been applied in trace level molecular identification and sensing applications [309-311]. Explosive detection is one of the heightened priorities in the modern day world due to the illicit use of explosive materials. Surface plasmon resonance behavior of noble metal (Au, Ag and Cu) nanoparticles have been extensively studied in literature and it has been reported that, along with the dimensions, geometry and dielectric constant of the metal nanoparticles, the surrounding dielectric medium also influence the absorption and scattering cross sections at the metal-dielectric interface [309-311]. The dielectric surrounding the metal nanoparticles can be used to tune the SPR behavior. In the present chapter, the application of Ag/ZnO interface in the trace level explosive molecule detection is explored. The application of Ag/ZnO surface in the detection of 5amiano-3-nitro-1H-1,2,4-triazole (ANTA), 1,1-Diamino-2,2 dinitroethene (FOX-7) and 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) explosive molecules without functionalizing the surface is demonstrated.

There has been recent interest in application of ZnO nanowires as water repellant surfaces. Switching of these surfaces from

Applications ...

superhydrophobic to superhydrophillic conditions, under UV irradiation, is of interest in self cleaning applications. Hence, in this work, the possibility of applying the fabricated ZnO nanowire surfaces for self-cleaning application is also investigated.

6.2 Experimental

The detailed experimental procedure for fabrication of SERS substrates is schematically illustrated in figure 1. The Zn metal film of 1500 nm thickness was deposited on a borosilicate glass (BSG) substrate [figure 6.1(a)] by thermal evaporation using high purity Zn metal granules (Aldrich, 99.99%). The as deposited metal Zn films [figure 6.1(b)] were loaded into a furnace preheated to a temperature of 500 °C and maintained at this temperature for dwell times of 5, 10, 15, 20, 25 and 30 min (Morphology A, B, C, D, E and F respectively). The furnace was then switched off and allowed to return to room temperature. This resulted in the formation of various complex nanostructures of ZnO/Zn with different metal residue [figure 6.1(c)]. Further details of deposition annealing treatments are described in chapter 3. These and nanostructures were decorated with Ag nanoparticles deposited by ion beam sputter deposition [figure 6.1(d)] using a Kaufman type ion source (DC25 of Oxford Applied Research, UK) with argon ions of energy 400 eV and beam currents of 9 mA bombarding the Ag (99.99% purity) target. The Ag target-substrate distance was 10 cms. The combination of low energy, low flux and large substrate distances resulted in extremely good control over the microstructural evolution of the Ag films [312].

Chapter 6

The Ag deposition was carried out at a rate of 1nm/min to obtain thin films of approximately 10 nm thickness. The Ag film was deposited simultaneously on the BSG substrate coated with ZnO nanostructures as well as the bare substrate under the same deposition conditions. The Ag/ZnO/BSG nanostructures are referred to as Ag decorated ZnO nanostructures and Ag/ZnO in the rest of the chapter. The Ag/BSG nanostructure has been used as a reference to compare the enhancement of SERS signal recorded over Ag/ZnO/BSG nanostructure. SERS experiments were performed in a confocal mirco-Raman spectrometer (Alpha 300 of Witec, Germany) equipped with a second harmonic Nd-YAG laser excitation source of 532nm wavelength. The following conditions were maintained for all the SERS experiments; minimum power, 100× objective, integration time of 1s and all other instrument optics. A drop of liquid (typically 10 µL volume) was ipette out on to the Ag/ZnO surface to form a thin layer of explosive molecule under investigation [figure 6.1(e)]. Raman spectra were collected at different points on the surface and the average of five spectra has been used as a reference for comparison in the analysis [figure 6.1(f)]. All ZnO nanostructure decorated with Ag was investigated with Rhodamine 6G as the control sample followed by the explosive molecules ANTA, FOX-7 and CL-20.The static and dynamic (advancing and receding) water contact angles were measured with Rame-Hart contact angle Goniometer (model 250) equipped with a CCD camera.

157

Applications ...



Figure 6.1 Schematic representation of experimental procedure for preparing ZnO films. (a) BSG substrate (b) microstructure of 1500 nm Zn film deposited by thermal evaporation (c) ZnO nanostructure, after subjecting a rapid annealing at 500 °C (d) Ag nanoparticles decorated on ZnO nanostructure (e) FESEM image of a selected region of figure (d) along with analyte detection (f) Raman spectra of the detected analyte (ANTA).

6.3 Results and discussion

6.3.1 Explosive detection by using surface enhanced Raman spectroscopy technique

6.3.1.1 Morphology

The as-deposited Zn metal film has highly dense, crack free and triangular grain morphology, as observed and is reported in chapter 3 (figure 3.4). Different microstructure achieved by varying annealing treatment is displayed in figure 6.2(a)-(f) along with the morphology of the Ag decorated ZnO film in the inset of figure 6.2(c).The morphology A of the Zn film in figure 6.2(a) shows smearing of the grain boundaries indicating the onset of grain melting. A completely transformed grain shape evidenced for morphology B of Zn film in figure 6.2(b) indicates the complete melting of the as-deposited film surface. The microstructures of the morphology C to F are comprised of ZnO nanowires of diameter 10-200nm and length of few micrometers [figure 6.2(c)-(f)].



Figure 6.2 FESEM images of Zn films annealed at 500 °C for different morphologies A (a); B (b); C (c); D (d); E (e) and F (f).

More detailed information about the morphology was extracted from atomic force microscopy (AFM) measurements of the above samples. The diverse microstructure of ZnO films achieved by subjecting the metallic Zn films to different annealing treatments is presented in figure 6.3(a)-(f). The line profile was drawn across the horizontal

Applications ...

direction of about 20µm length on each AFM image. Morphology A in figure 6.3(a) shows uniform spherical grain distribution across the surface of the film. The line profile shows maximum peak to peak height (PPH) of 130nm. Morphology B shown in figure 6.3(b) has mixed regions of smooth morphology and rough surface comprised of distorted spherical grains of varying dimensions with a PPH of 180nm. Morphology C has completely lost the smooth spherical grain regions and relatively elongated grains of diverse dimensions are grown as observed in figure 6.3(c). A similar morphological flip is evident in the FESEM images of Morphology C sample. This is accompanied by a rise in the PPH value to 520nm. Further roughening of the surface is evidenced in the morphology D with a PPH of 620nm (figure 6.3(d)). The enhanced elongation in grain shape is attributed to the presence of nanorods observed in FESEM images. A completely different morphology with high roughness and PPH value of 1420 nm is observed in the morphology E (figure 6.3(e)). The microstructure has separated fringes like structures along with the highly rough region spread over the each fringe. Large nanorods with no residual grains, observed in FESEM image, of morphology E is expected to be the reason behind such fringe like structure. Morphology F is much similar like Morphology D with almost same peak to peak cross sectional roughness (figure 6.3(f)).



Figure 6.3 Atomic force micrographs of Zn films annealed at 500 °C for different morphologies A (a); B (b); C (c); D (d); E (e) and F (f)

The microstructure of the Ag/ZnO film, shown in the inset of figure 6.2(c) reveals a homogeneous distribution of spherical Ag nanoparticles (~50nm diameter) decorating the ZnO nanowires. Due to their complex hierarchy, the Ag decorated ZnO nanostructures encompass a large number of plasmon fields which in turn lead to a large number of hot-spots. The microstructure of Ag/BSG films is presented in figure 6.4.



Figure 6.4 FESEM micrograph of BSG/Ag discontinuous film deposited by Ion beam sputtering unit.

Applications ...

The microstructure has ellipsoidal particles with approximate dimensions of the order of 15-20nm over the entire surface. Closer examination of the microstructure, higher at magnification, demonstrates that the film has discontinuous morphology with relatively larger particles size of the order of 15-20 nm separated by nanoparticles. The growth of such isolated nanostructures is due to the low rate of deposition which is possible in ion beam sputtering technique. The combination of low energy, low flux and large substrate distances has led to good control over the nanostructural evolution of the Ag film. Ultra-low ion energy sputter deposition results in very low rates of deposition which in turn leads to the Ag particles condensing on the substrate with an energy which is much lower than the activation energy barrier for surface diffusion at room temperature [312]. This results in the freezing of the particles without diffusion across the substrate forming discontinuous nanostructured films.

6.3.1.2 Structure

Further characterizations of the ZnO nanostructures have been carried out by XRD, Raman spectroscopy and TEM and are depicted in figure 6.5. The XRD pattern of two Zn/BSG films, as deposited and morphology C samples, are compared in figure 6.5(a). The as deposited film has a diffraction pattern wherein all the peaks can be assigned to hexagonal metallic Zn (indexed according to JCPDS No 87-0713). No signature of oxidation is recorded in the as deposited film. The Zn/BSG film morphology C exhibits a set of XRD peaks which are different from those observed in the diffraction pattern of as deposited film (metallic Zn peaks are designated by asterisk (*) in the figure 6.5(a)). These new XRD peaks are identified as belonging to hexagonal ZnO (indexed according to JCPDS No-89-1397). From this study it is confirmed that the as deposited film is metallic Zn whereas the film annealed at 500 °C (morphology C) is a composite of metallic Zn and ZnO. Similar inferences are drawn from the Raman spectra presented in figure 6.5(b). The Raman spectrum of morphology C Zn/BSG film has strong Raman shift at 438 cm⁻¹, which is characteristic peak of the wurtzite phase of ZnO (E₂ mode). There are additional weak peaks at 324 cm⁻¹, 577 cm⁻¹ and 675 cm⁻¹ which are attributed to the $E_{2H}-E_{2L}$, $E_1(LO)$, $B_1(TA+LA)$ modes of wurtzite ZnO phase respectively [237, 276]. The typical TEM bright field image of morphology C Zn/BSG film is presented in figure 6.5 (c).The bright field image has two ZnO nanorods with different diameter. The selected area diffraction (SAED) pattern of this region shows that the diffraction spots are due to hexagonal ZnO. The diffraction spots designated by A, B and C in figure 6.5(d) have d values of 0.26nm, 0.26nm and 0.16 nm respectively, corresponding to the (100), (010) and (110) planes of hexagonal ZnO (according to JCPDS No-89-1397). No signature of diffraction spot from metallic Zn is observed in the SAED pattern. This observation confirms that the nano rods are pure ZnO with no metallic Zn residue. The high resolution TEM image presented in figure 6.5(e) has lattice pattern with d=0.25nm, which further confirms the (100) planes of the ZnO nano rods.


Figure 6.5 Characterization of ZnO nanostructure: (a) XRD pattern and (b) Raman spectra of Zn/BSG films as deposited and morphology C sample. (c) Bright field image, (d) SAED pattern (e) HRTEM image of ZnO/BSG morphology C.

The X-ray diffraction pattern of Zn film annealed at 500 °C for different morphology (A-F) followed by 10nm Ag film decoration is shown in figure 6.6. The XRD pattern shows that the films are polycrystalline in nature and there are contributions from both hexagonal ZnO and metallic Zn (confirmed from JCPDS card nos. 89-1397 and 87-0713, respectively). Significantly, no diffraction peaks from metallic Ag are observed.



Figure 6.6 X-ray diffraction patterns of Zn film annealed at 500 °C for different morphologiesA, B, C, D, E and F.

However, the presence of Ag is confirmed through EDS, as shown in figure 6.7(a). It is evident from a calculation of the ratio of the area under the strong XRD peaks of Zn (101) and metallic ZnO (101), that the Zn residue content decreases from morphology A to F as shown in figure 6.7(b) [313].



Figure 6.7 (a) EDS spectra of Ag/ZnO nanostructure (b) Variation in the ratio of XRD peak intensity Zn (101) and ZnO (101) as a function of different morphology samples.

6.3.1.3 SERS studies

The SERS spectra of R6G and ANTA molecules collected over the Ag decorated ZnO nanostructures for different kind of morphologies (A-F) are displayed in figure 6.8(a) and (b), respectively. The Ag decorated ZnO nanostructures were able to detect a highly diluted (1nM) R6G molecule in methanol solvent [figure 6.8(a)]. In contrast, the minimum concentration of R6G that Ag nanostructures deposited over BSG substrate could detect was 0.1 M as shown in figure 6.8(a)]. The Raman bands identified in the SERS spectra of R6G molecule at 611, 773 and 1182 cm⁻¹can be assigned to C–C–C ring in-plane bending, xanthene skeleton out-of-plane bending motion of the hydrogen atoms and C-C stretching vibrations, respectively. The bands at 1360, 1506 and 1647 cm⁻¹ are attributed to the aromatic C-C stretching vibrations of R6G molecules [314]. The area under the Raman peak centered around 1362 cm⁻¹ has been chosen for EF calculation of Ag/ZnO samples annealed at 500 °C for different morphologies (A to F) and the calculated values are 5×10⁸, 1.5×10⁹, 9.7×10⁸, 3.1×10⁹, 2.2×10⁹ and 4.7×10⁸ respectively. The corresponding EF values for Ag nanostructures deposited on BSG substrate is 4.6×10⁶.



Figure 6.8 SERS spectra of a) R6G and b) ANTA molecule adsorbed on Ag decorated ZnO films (Morphologies A, B, C, D, E and F).

The SERS spectra of the ANTA molecule in acetonitrile (0.1 M for non-resonant Raman and 10µM concentration for SERS) presented in figure 6.8(b) exhibit strong characteristic Raman modes at 840, 940, 1120, 1283, 1340 and 1459 cm⁻¹. These Raman modes are assigned to, NO₂ deformation + ring deformation (840 cm⁻¹), ring deformation (1067 cm⁻¹), N-N symmetric stretch (1120 cm⁻¹), ring deformation +N-H bend (1283 cm⁻¹) ,C-NO₂ symmetric stretch (1340 cm⁻¹) and C-N symmetric stretch (1459 cm⁻¹) [163]. The strong Raman peak in the vicinity of 1340 cm⁻¹ has been selected for EF calculation for ANTA molecule and the values for different morphologies (A-F) are 9.6×10⁶, 3.3×10⁷, 7.1×10⁷, 2.6×10⁷, 1.7×10⁷ and 5.4×10^7 respectively. In comparison, the EF was only 1.1×10^4 for the Ag nanostructures on BSG. Three orders higher EF is recorded for Ag/ZnO 3-D nanostructures relative to their Ag/BSG nanostructure counterparts. Reproducibility is one of the essential parameters to establish feasibility of these SERS substrates for practical applications. The SERS signal was collected from 20 different sites on the morphology

F Ag/ZnO sample, to establish reproducibility. The SERS spectra for ANTA collected from different sites along with the corresponding enhancement factor using the Raman peak at 1340 cm⁻¹ is depicted in figure 6.9 (a) and (b) respectively. The relative standard deviation (RSD) of SERS intensity for 20 different sites on the same sample is 28% whereas that for Ag/BSG substrate is 34%. The relatively smaller RSD suggests that the Ag/ZnO 3D nanostructure is more suitable as a SERS detection probe in comparison to the Ag/BSG 2D structure.



Figure 6.9 (a) SERS spectra of ANTA analyte and its (b) Enhancement factor, collected at 20 different sites over Ag/ZnO morphology C sample.

The SERS enhancement factor (EF) was calculated using the following formula [162].

$$EF = \frac{I_{SERS}}{I_{RS}} \frac{N_{RS}}{N_{SERS}}$$
(6.1)

where, *Isers* is the enhanced Raman intensity at lower concentration on SERS substrate, *Irs* is the normal Raman intensity at higher concentration measured over non-plasmon surface, *Nsers* is the number of molecules that giving rise to SERS from Ag decorated ZnO nanostructure, *Nrs* is the number of molecules giving rise to Raman signal from non-SERS surface. *N*_{SERS} and *N*_{RS} are determined by the relation [163].

$$N_{SERS} = N_A V C_{SERS} \frac{A_{laser}}{A_{SERS}} \qquad \qquad N_{RS} = N_A V C_{RS} \frac{A_{laser}}{A_{RS}}$$
(6.2)

where, η is adsorption factor, N_A is Avogadro number, V is total volume of the solution added onto the substrate, A_{laser} is the area of the laser spot, A_{SERS} and A_{RS} are the total area of the SERS and non-SERS substrate respectively, CSERS and CRS are the lower and higher concentration of analyte applied over SERS and non-SERS substrates respectively. For simplicity the area of both resonant (A_{SERS}) and non-resonant (A_{RS}) substrate are chosen equal in dimensions (5×5= 25 mm²).

Adsorption factor calculations (η)

The procedure followed was proposed by Langmuir in Langmuir isotherm and the adsorption factor calculations were adapted from earlier reports [164, 165, 315]. Accordingly, SERS spectra of different analytes for different concentrations which were adsorbed on Ag decorated ZnO nanostructure were recorded and a graph between SERS intensity and concentration was plotted.

To interpret and fit data with the equation

$$N = N_0 \left(\frac{Kc}{1 + Kc}\right) \tag{6.3}$$

where, N = number of molecules adsorbed, $N_0 =$ number of molecules adsorbed at saturation, c = concentration of analyte and K= binding equilibrium constant. Raman intensity is proportional to N at different concentrations and to N₀ at saturation level [315].



Figure 6.10 Langmuir adsorption isotherm plots of R6G and ANTA molecules which were adsorbed on Ag decorated ZnO nanostructure.



Figure 6.11 Langmuir adsorption isotherm plots of CL20 and FOX 7 molecules which were adsorbed on Ag decorated ZnO.

The critical characteristic of the Langmuir isotherm [164, 165, 315] can be expressed in the form of adsorption factor which is defined as $\eta = \frac{1}{1+Kc}$, where c_0 is the initial concentration at saturation level.

Chapter 6

Molecule	K (M ⁻¹)	C ₀ (M)	η
R6G	2.45× 10 ⁶	1 × 10 ⁻⁶	0.3
ANTA	1.62× 104	200 × 10 ⁻⁶	0.24
CL20	7.3× 104	100 × 10-6	0.12
FOX 7	8.0× 10 ³	1 × 10 ⁻³	0.11

Table 6.1 Binding equilibrium constant (*K*), initial concentration at saturation level (C_0) and adsorption factor (η) of different analytes.

The SERS spectra of two other explosive molecules, FOX-7 and CL-20, recorded using the same method over Ag/ZnO nanostructures produced by annealing the Zn film at different morphologies are compared in the figure 6.12(a) and (b), respectively. The two most prominent peaks in the SERS spectra of FOX-7, in figure 6.12(a), are assigned to the C-NO₂ bend (860 cm⁻¹) and skeletal deformation (1339 cm⁻¹) modes respectively [316]. The additional modes observed in the Raman spectra also match with previous reports [317]. EFs were calculated based on the change in area under the skeletal deformation Raman mode at 1339 cm⁻¹ for different morphology (A-F) Ag/ZnO films and the values are 7.4×10⁶, 1.0×10⁷, 1.3×10⁷, 6.2×10⁶, 5.3×10⁶ and 1.8×10⁷, respectively. In contrast, the EF value is only 1.5×10⁴ for the Ag nanostructure deposited directly on the BSG substrate. The peak in the SERS spectra of CL-20 shown in figure 6.12(b), at 832 cm⁻¹ is assigned to O-N-O bending; 904 and 1032 cm⁻¹ to NN-stretching; 1243, 1315 and 1448 cm⁻¹ to CH bend and 1603 cm⁻¹ to the asymmetric NO₂ stretching band [318, 319]. EFs are calculated for the most intense peak at 1315 cm⁻¹ and

Applications ...

the values are 3.2×10⁴, 2.6×10⁴, 3.4×10⁴, 2.3×10⁴, 1.42×10⁴ and 2.1×10⁴ for different morphology Ag decorated ZnO (A to F respectively) films produced by annealing Zn film at 500 °C respectively. The EF for the Ag nanostructure deposited directly on BSG substrate is much lower (three times).



Figure 6.12 SERS spectra of a) FOX-7 and b) CL20 molecule adsorbed on Ag decorated ZnOfilms (Morphologies A, B, C, D, E and F).

Two major observations can be made from the results presented in the previous sections: (1) there is a major change in the microstructure of the ZnO films with change in dwell times at 500 °C and (2) the Ag decorated ZnO nanostructures are more sensitive to the presence of the explosive molecules than Ag deposited directly on the BSG substrates. The enhancement factor for Ag/ZnO nanostructures of different morphology (A-F) and Ag/BSG microstructures for different SERS analytes are compared in the figure 6.13.



Figure 6.13 Enhancement factor for different Ag/ZnO probes (Morphologies A, B, C, D, E and F) along with Ag/BSG for (a) R6G, (b) ANTA, (c) FOX-7 and (d) CL-20.

It is pertinent to note that deposition of Ag on BSG and ZnO nanowires is carried out at the same time. Hence, conditions of deposition are exactly same in both cases. The reasons for the difference in sensitivity in the two cases are now examined. The increase in the sensitivity of the SERS signal detection in Ag/ZnO can, to a first approximation, can be attributed to the high density of hot spots [320] that the three dimensionally (3-D) networked nanostructure of ZnO nanowires provides. These Ag decorated 3-D nano-surfaces provide large surface area for adsorbing the probe molecules and localized surface plasmons of Ag on the spatially arranged mosaic nanostructures enhance the local electric fields to generate extremely large hot-spots

Applications ...

[321]. Furthermore, internal scattering of transmitted photons at nanovoids in the Ag decorated ZnO nanostructures leads to improved quantum yields and greater sensitivity for molecular detection by SERS [321]. Lahiri et al. have reported an enhanced SERS effect on Au/Si hetero-junctions derived from the electron transfer from semiconductor (Si) to metal (Au) through the interface [322]. In the present case the surrounding semiconductor (ZnO) has metal residue (Zn) which facilitates the electron transfer from semiconductor to Ag. The presence of Zn metal residue in the Ag/ZnO nanostructure is confirmed through XRD studies. From this it is inferred that the amount of Zn metal residue in the ZnO matrix depends on dwell times leading to varying magnitudes of electron charge transfer from the semiconductor (ZnO) to Ag, which in turn affects the SERS enhancement. Nano-dimensional semiconductor structures have been demonstrated to exhibit SERS due to a chemical shift effect [323] which is expected to be true even in the case of Ag decorated ZnO nanowires of the present study. The presence of metallic Zn is expected to enhance the chemical shift effect and there by lead to higher enhancements in SERS measurements. In chapter 3 we have demonstrated that the body of the nanowire is purely made of ZnO and the base has metallic Zn component (figure 3.8). The metallic Zn and decorating Ag nanoparticles are, thus, shielded by the semiconductor ZnO nanostructure. The dimensions of nanostructure (length, width and orientation) are expected to determine the extent of influence of metallic Zn on the chemical shift effect and semiconductor SERS effect. Dikovska et al. reported that the intensity of SERS signal drops with increasing dimensions of nanostructure due to the higher density of spatial inhomogeneities that will survive in the smallest dimension nanostructures [324]. This phenomenon is molecule and nanostructure dependent. In the present case the nanostructure formed is dwell time dependent. As a consequence, the highest EF for different molecules does not occur either at the same morphology or same concentration. The quantitative comparison of EF versus PPH for different analytes is presented in figure 6.14.



Figure 6.14 A quantitative comparison of enhancement factor for different analytes with roughness of the ZnO film.

It is observed that the EF is independent of the huge change in the morphology of the sample (from 100nm to 1450 nm). No systematic variation of EF is observed with PPH of different morphologies; A to F. On the other hand, the observed changes in EF may be solely assigned to the Zn metal residue present in the samples. From this study, we conclude that the SERS with higher detection sensitivity can be achieved by depositing Ag discontinuous layer on the ZnO mosaic microstructure.

6.3.2 Wettability studies

To study the wettability properties of Zn films of different thickness 500 nm-4 μ m were deposited on BSG and quartz substrates by thermal evaporation process at room temperature in high vacuum (5×10⁻⁶ mbar) and these films were annealed at 500 °C.

6.3.2.1 Structure

The X-ray diffraction patterns of as deposited Zn films and the Zn films annealed at 500 °C of thickness 500 nm were deposited onto BSG and quartz substrates are shown in figure 6.15(a) and (b), respectively.



Figure 6.15 XRD patterns of Zn films of thickness 500 nm (a) as-deposited and (b) annealed at 500 °C.

The diffraction peaks observed in the as deposited film can be assigned to the hexagonal structure of Zn (JCPDS No. 87-0713). The x-ray diffraction patterns on annealing these films to 500 °C show peaks that can be assigned to ZnO hexagonal structure (JCPDS No. 89-1397). It can, thus, be inferred that the Zn films annealed at 500 °C are completely oxidized without any Zn residue.

The X-ray diffraction patterns of as deposited Zn film and the Zn films annealed at 500 °C of thickness 2, 3 and 4 μ m were deposited on BSG substrate are shown in figure 6.16.



Figure 6.16 XRD patterns of Zn films of different thickness (a) as- deposited and (b)-(d) annealed at 500 °C.

The diffraction peaks observed in the as deposited film can be assigned to the hexagonal structure of Zn (JCPDS No. 87-0713). The x-ray diffraction patterns on annealing these films to 500 °C show peaks that can be assigned to both Zn and ZnO. The weak reflections at 2θ values of 36.2, 38.9, 43.2, 54.3, 70.0 and 70.6° are attributed to metallic Zn film whereas the diffraction peaks at 2θ values of 31.7, 34.3, 36.2, 47.4, 56.5, 62.7, 67.8 and 69.0° correspond to the hexagonal structure of ZnO (JCPDS No. 89-1397). It can, thus, be inferred that the Zn films annealed at 500 °C are only partly oxidized with substantial residue of metallic Zn still being present. Similar observation of Zn residue in ZnO films has been reported by other workers [199, 201-204].

6.3.2.2 Microstructure

The FESEM image of the as deposited Zn film on quartz substrate, displayed in figure 6.17(a), shows that the film (as in the case of BSG substrate shown in figure 3.4 reported in chapter 3) are comprised of triangular grains. On annealing these films to 500 °C, as observed from figure 6.17(b), there is transformation in to nanowires. Again these nanowires are uniformly spread over the entire substrate surface.



Figure 6.17 FESEM images of Zn film of thickness 500 nm (a) as- deposited and (b) annealed at 500 °C on quartz substrate.

The FESEM images of different thickness of Zn and Zn film annealed at 500 °C deposited on BSG substrate are shown in figure 6.18(a)-(c) and figure 6.18(d)-(f) respectively. The as deposited films (figure 6.18(a)-(c)) show triangular nanosheets. Annealing of these films to 500 °C leads to transformation of the triangular nanosheets into nanowires independent of the thickness of the film (figure 6.18(d)-(f)).



Figure 6.18 FESEM images (a)-(c) as deposited and (d)-(f) annealed at 500 °C of Zn films of thickness 2, 3 and 4μ m respectively.

6.3.2.3 Wettability studies

The functionality of the surfaces (as deposited and thermally oxidized) is further investigated using the phenomenon of wetting by a measurement of water contact angle on these surfaces. Wetting studies revealed that Zn films are hydrophobic which become super hydrophobic after annealing at 500 °C. The wetting of textured rough surfaces can be described either by the Wenzel [325] model for

Applications ...

homogeneous wetting or the Cassie Baxter model for heterogeneous wetting [326]. These models are valid only if the water droplet size is greater than the roughness of the surface. When a liquid is allowed to spread on a rough surface there are two possibilities: it can (1) fill the grooves (the Wenzel's state) or (2) remain suspended over them, keeping air pockets underneath (the Cassie state). Wenzel's equation predicts that the existing hydrophobic surface can be made more hydrophobic by enhancing the roughness of the substrate. A schematic representation of Wenzel's and Cassie-Baxter state of wetting is shown in figure 6.19. Wenzel's equation is assumed to work for surfaces where surface roughness is relatively low whereas the Cassie-Baxter model is used when the roughness is high.



Figure 6.19 Schematic representation of (a) Wenzel's (b) Cassie-Baxter state of wetting.

A quantitative estimate of the roughness of the as deposited and thermally oxidized Zn films is made from AFM images shown in figure 6.20 and figure 6.21. The as deposited films of thickness 500 nm show rms roughness value of 23.1 and 34 nm on BSG and quartz substrates respectively. There is a significant increase in the roughness when these films are subjected to annealing at 500 °C, which are 38.1 and 53.1 nm on BSG and quartz substrates respectively.



Figure 6.20 AFM images of 500 nm thick Zn films (a), (b) as deposited and (C), (d) annealed at 500 °C deposited on BSG and quartz substrates respectively.



Figure 6.21 AFM images of Zn films (a)-(c) as deposited and (d)-(f) annealed at $500 \circ$ C of thickness 2, 3 and 4 µm respectively on BSG substrate.

The rms roughness values of the as deposited Zn films of different thickness on BSG substrates varies from 29.2 to 37.6 nm,

whereas the rms roughness values of the Zn films of different thickness annealed at 500 °C are in the range of 71.9 to 81.2 nm. There is, thus, considerable roughening of the surfaces on annealing. However, the increase in roughness could also be attributed to the random orientation of the nanowires, *i.e.* while some are horizontal, a few nanowires are vertically aligned (as observed from the cross-section FESEM images in figure. 3.8 reported in chapter 3).

Table 6.2 Contact angles of as deposited Zn films and films annealed to 500 °Con BSG and quartz substrates.

Sample	Drop profile Contact angle (0) Before UV irradiation	Drop profile Contact angle (θ) After UV irradiation
	112.5°	106.8°
Zn BSG as deposited		
	122.2°	6.7°
Zn BSG 500°C		
	142.5°	122.7°
Zn Quartz as deposited	0	0
	153.0°	8.8°
Zn Quartz 500°C	0	

The contact angle, to water, of the as deposited Zn films of thickness 500 nm on BSG showed of contact angle 112.5° while the Zn films deposited on quartz displayed contact angle of 142.5° . The experimental error in measurement of contact angle is $\pm 2^{\circ}$, over about 10 measurements, and the changes beyond this range are attributed to

Chapter 6

the difference in morphology over the film. On annealing at 500 °C, while Zn films over BSG did not show a significant change in contact angle (increases from 112.5–122.2°). The contact angle of water on ZnO films over quartz showed a value of 153°. Significantly the films annealed at 500 °C also exhibited a wettability reversal under UV irradiation going from a superhydrophobic (contact angle >150°) to superhydrophillic (contact angle <10°) for exposure of about 1 h, that makes these films particularly suitable for self-cleaning and photocatalytic applications. Contact angles of as deposited Zn films and films annealed to 500 °C on BSG and quartz substrates shown in table 6.2. The differences in contact angles on BSG and quartz are attributed to the differences in roughness of the films on these substrates.

The water contact angle shows values between 115.7-121.7° on the as deposited films of different thickness which correlates with the roughness values. This is a significant observation since it indicates that the as deposited metallic thin films are hydrophobic. Although, hydrophobic metallic surfaces have been reported earlier, there are no other reports that Zn metal films can be hydrophobic [327-330]. There is a transition from the hydrophobic to superhydrophobic state on annealing the films to 500 °C exhibiting water contact angles between 160.1 and 161.7°. Nanostructuring of ZnO films leading to superhydrophobicity has been reported by several workers and the without chemical modification, and the values reported here compare quite favourably with literature [331-335]. In contrast to the as deposited films, the annealed films do not exhibit a roughness dependent variation

Applications ...

in the contact angle. This is inferred from the fact that the variation in roughness from 71.9 to 81.2 nm results in less than \approx 2% change in the contact angle.

It is desired that superhydrophobic surfaces should have high contact angle, low contact angle hysteresis and the water droplets should be able to roll off easily for self-cleaning applications. Thus, to observe the hysteresis and to estimate the Wenzels and Cassie-Baxter state of wetting, the advancing and receding contact angle were measured on ZnO deposited over BSG substrate with different thickness and are shown in figure 6.22.



Figure 6.22 Advancing and receding contact angle studies of different thickness of ZnO films deposited on BSG substrate.

Chapter 6

Advancing and receding contact angles were studied by adding and withdrawing water from the drop, respectively using a microsyringe attached with an automated dispenser. It has been observed that contact angle hysteresis (θ_{A} - θ_{R}), *i.e.* the difference between advancing and receding contact angle are 6.5, 7.2, and 5.0° on 2, 3 and 4µm thick substrates respectively. As matter of fact, water does not penetrate the roughness grooves and sit on the surface asperities [336]. Due to the composite interface, the area of contact between the water and substrates decreases which leads to increase in contact angle. Thus, rolling of droplet over those substrates is due to low adhesion which is a consequence of small water-solid contact area and thereby the Cassie-Baxter regime is generated. As a consequence, water droplets readily roll off on those surfaces. It has been observed that the water droplet used to roll-off on those substrates without tilting the base of the substrates.



Figure 6.23 Contact angle variation of (a) as deposited Zn film and (b) Zn films annealed at 500 °C on different thick surfaces as a function of UV irradiation time.

Applications ...

The wettability behaviour further investigated by measuring the contact angle after UV irradiation for the as deposited Zn and nanowired ZnO films is presented in figure 6.23 (a) and (b) respectively. It is evident that there is a change in the contact angle of the as deposited Zn films when subjected to UV irradiation is in the range of 33-38°. In contrast, the ZnO nanowire films that were superhydrophobic prior to UV irradiation transformed to the superhydrophilic state after 50 min of irradiation. There is monotonic decrease in contact angle under UV irradiation for annealed film. The observed effects can be attributed to the surface hydroxylation of ZnO film. Contact angles and RMS roughness values of as deposited Zn films and Zn films annealed to 500 °C of different thickness deposited on BSG substrate are shown in table 6.3 and table 6. 4.

 Table 6.3 Contact angles and RMS roughness of as deposited Zn films of

 different thickness deposited on BSG substrate.

Sample	Contact angle (0) Before UV irradiation	Contact angle (0) After UV irradiation	RMS Roughness (nm)
Zn 2µM	121.7•	84.4°	29.2
Zn 3µM	120.5*	86.6*	35_9
Zn 4µM	115.7*	80.6°	37.6

Sample	Contact angle (0) Before UV irradiation	Contact angle (8) After UV irradiation	RMS Roughness (nm)
ZnO 2µM	160.9*	7.8°	76.5
ZnO 3µM	160.1*	6.7°	81.2
ZnO 4µM	161.7•	7_4•	71.9

Table 6.4 Contact angles and RMS roughness of Zn films of different thickness annealed at 500 °C deposited on BSG substrate.

Further, upon storing the film in the dark, ZnO films recover their original hydrophobic state after 72 hours. The decrease in contact angle in case of ZnO film under UV irradiation is attributed to the structural changes of ZnO, forming a metastable state which can absorb hydroxyl group [337] Thus, UV irradiation changes the chemical state of the substrate, which promotes water molecules to dissociatively absorb on them. The superhydrophobic-superhydrophilic conversion on ZnO film is due to surface hydroxyl group present in the ZnO surface. Thus, the growth of photo responsive moieties like ZnO with different thickness has potential to act as self cleaning surfaces because of high contact angle and low contact angle hysteresis with ability to exhibit rewritable wetting transition [338].

6.4 Summary

In conclusion, trace level detection of explosive molecules over Ag/ZnO 3D nanostructure has been demonstrated. Different ZnO nanostructures were realized by the thermal oxidation of precursor Zn films at 500 °C. The as deposited films are nanocrystalline and exhibit hydrophobic contact angles. Thermal annealing leads to the formation of ZnO nanowires that exhibit superhydrophobicity.

Chapter

7

Conclusions and scope for future work

7.1 Conclusions

Nanostructured Zn metal films were deposited by thermal evaporation, on borosilicate glass (BSG), quartz, sapphire (ALO), lanthanum aluminate (LAO) and yttria stabilized zirconia (YSZ) substrates. The as-deposited films are nanocrystalline and show a morphology that consists of triangular nanosheets. Thermal annealing of the films at 500 °C results not only in oxidation of Zn to ZnO but also transformation of the Zn nanosheets into ZnO nanowires that are polycrystalline in nature. The ZnO nanowires are in the range of 10–100 nm in diameter and about few µm long. The ZnO nanowires are much softer than the as-deposited Zn metal films, with hardness between 0.02 and 0.4 GPa and Young's modulus between 3 and 35 GPa. The extent of oxidation is dependent on thickness of the pristine Zn films. Under the same annealing conditions, at thicknesses of ~500 nm the oxidation is complete whereas at thicknesses > 500 nm, the oxidation partial leaving a Zn residue. As a result of the Zn residue, there is a decrease in optical transmittance along with a significant variation in photoluminescence properties. In the case of nanowires, the blue shift of blue emission and the red shift in the band edge absorption at photoluminescence excitation wavelength for ZnO/Zn film is correlated with charge transfer from Zn to ZnO. The photoluminescence excitation peak position at shorter wavelength remains unchanged, while the band edge excitation peak shows significant red shift for ZnO/Zn thin films. This indicates that the excitation resonance at shorter wavelength is not caused by the usual electronic band to band or defect transition but by the plasmons in

Conclusions...

ZnO/Zn. With variation in micro-/nano-structures from dense grains to nanorods and nanowires, photoluminescence studies revealed two emission peaks, one in the UV region due to exciton emission and another in the visible spectral region due to Zn or Oxygen vacancies/defects. The effect of these different micro-/nano-structures on the third-order nonlinear optical (NLO) response has been scrutinized using Z-scan technique with femtosecond (fs), MHz and picosecond (ps), kHz pulses at a wavelength of 800 nm. Various NLO coefficients such as two-photon absorption (β), nonlinear refractive index (n₂), Re [χ ⁽³⁾], Im $[\chi^{(3)}]$ and $\chi^{(3)}$ were evaluated. The obtained $\chi^{(3)}$ values were ~10⁻⁷ e.s.u. in the fs regime and ~10⁻¹⁰ e.s.u. in the ps regime. Optical limiting studies of these films was also performed and limiting thresholds were estimated to be 15-130 μ J/cm² in the fs regime while in ps regime the corresponding values were 1-3 J/cm². The NLO data clearly designates strong nonlinearities in these ZnO thin films with possible applications in photonics.

Single step transformation of Indium-Zinc and Tin-Zinc films into doped ZnO nanowires is also demonstrated. In and Sn doped ZnO nanowires are formed by the annealing of In-Zn and Sn-Zn bilayer films to 500 °C in air. Independent of processing conditions all the nanostructures are polycrystalline as evidenced from x-ray diffraction patterns. The optical transmission, reflectance and absorption, in the wavelength range between 200 to 2500 nm, have been measured as a function of annealing temperature. It is shown that all the bilayers and the In and Sn doped nanowires can be used as solar absorber materials due to their high

Chapter 7

absorption, low transmittance and reflectance, in this region of the spectrum. In certain cases, the nanowires exhibit high transmittance and very low reflectance making them very attractive for use as antireflection coatings.

The detection of secondary explosive molecules (e.g. ANTA, FOX-7 and CL-20) using Ag decorated ZnO nanostructures as surface enhanced Raman scattering substrates was also demonstrated. It is shown that concentrations as low as 10 µM, of the three explosive molecules ANTA, FOX-7 and CL-20 over Ag-ZnO nanostructures, resulted to 10⁷, 10⁷ and 10⁴ times enhancement in the SERS signal, respectively. This demonstrates the high sensitivity of detection of explosive molecules using Ag decorated ZnO nanostructures as SERS substrates. Wetting studies revealed that Zn films which are hydrophobic become super hydrophobic after annealing at 500 °C due to the formation of ZnO nanowires with contact angles between 150-160°. The wettability is reversible under UV irradiation making these films extremely suitable for self-cleaning applications.

In the thesis, thus, a single step thermal oxidation process for the formation of ZnO nanowires (undoped and doped) was developed. The nanostructures are shown to have interesting optical, mechanical, wettability and sensing properties.

193

Conclusions...

7.2 Scope for future work

Some possibilities for extending this work in the future are,

- 1. Using electron beam lithography technique to fabricate vertically aligned metal oxide nanowires and nanorods.
- To study other metal oxides nanowires such as SnO₂, In₂O₃, Fe₂O₃ and decorate them with the Ag, Au and Cu nanoparticles for use as SERS substrate for the detection of toxic chemicals and biological molecules.
- To study the sensitivity of the metal oxide nanostructures under various gases by fabricating a gas sensor.
- 4. To study the size dependent mechanical properties of different metal oxide nanowires.
- 5. (a) Recording the spectral dependence of the nonlinearities in the ps regime, (b) understanding the excited state dynamics in these thin films using ps/fs degenerate and non-degenerate pumpprobe studies and (c) estimating the figures of merit for NLO application over the entire visible spectral range using ps/fs kHz pulses.
- 6. Fabricate different dimensions of metal oxide nanostructures and to study their size dependent physical properties.

References

- C. N. R. Rao, A. Muller, A. K. Cheetham "The Chemistry of Nanomaterials: Synthesis Properties and Applications" (WILEY-VCH Verlag GmbH & Co. KGaA) (2006).
- [2] B. Bhushan, D. Luo, S. R. Schricker, W.Sigmund, S. Zauscher "Handbook of Nanomaterials Properties", (Springer, Germany) (2014).
- [3] Y. Zhang, M. K. Ram, E. K. Stefanakos, D. Y. Goswami J. Nanomater 2012 (2012) 1.
- [4] W. Liu, A. B. Greytak, J. Lee et al., J. Am. Chem. Soc. 132 (2010) 472
- [5] B. Weintraub, Z. Zhou, Y. Li, Y. Deng, J.Nanoscale, 2 (9) (2010) 1573.
- [6] Y. Xia, P. Yang, Y. Sun et al., Adv. Mater 15(5) (2003) 353.
- [7] G. C. Yi, C. Wang, W. I. Park, Semicond. Sci. Tech. 20 (2005) S22.
- [8] R. F. Service, *Science* **95** (2005) 309.
- [9] G. M. Whitesides, M. Boncheva, Proc. Natl. Acad. Sci. USA, 99 (2002) 4769.
- [10] S. Park, J. H. Lim, S. W. Chung, C. A. Mirkin, Science 303 (2004) 348.
- [11] D. H. Gracias, J. Tien, T. L. Breen, C. Hsu, G. M. Whitesides, *Science* 289 (2000) 1170.
- [12] T. L. Breen, J. Tien, S. R. J. Oliver, T. Hadzic, G. M. Whitesides, *Science* 284 (1999) 948.
- [13] M. Mo, J. C. Yu, L. Z. Zhang, S. K. A. Li, Adv. Mater 17 (2005) 756.
- [14] A. M. Cao, J. S. Hu, H. P. Liang, L. J. Wan, Angew. Chem. Int. Ed. 44 (2005) 4391.
- [15] A. C. Chen, X. S. Peng, K. Koczkur, B. Miller, *Chem. Commun.* (2004) 1964.
- [16] W. W. Chen, C. H. Tzang, J. X. Tang, M. S. Yang, S. T. Lee, *Appl. Phys. Lett.* 86 (2005) 103114.
- [17] J. S. Hu, Y. G. Guo, H. P. Liang, L. J. Wan, L. Jiang, J. Am. Chem. Soc. 127 (2005) 17 090.
- [18] J. S. Hu, L. L. Ren, Y. G. Guo, H. P. Liang, A. M. Cao, L. J. Wan, C. L. Bai, Angew. Chem. Int. Ed. 44 (2005) 1269.

- [19] S. Mann, Angew. Chem. Int. Ed. 39 (2000) 3393.
- [20] E. Dujardin, S. Mann, Adv. Mater. 14 (2002) 775.
- [21] C. Noguera, Physics and Chemistry at Oxide Surfaces; Cambridge University Press:Cambridge, UK, (1996).
- [22] H. H. Kung, Transition Metal Oxides: Surface Chemistry and Catalysis; Elsevier:Amsterdam, (1989).
- [23] V. E. Henrich, P. A. Cox, The Surface Chemistry of Metal Oxides; Cambridge University Press: Cambridge, UK, (1994).
- [24] A. F. Wells, Structural Inorganic Chemistry, 6th ed; Oxford University Press: New York, (1987).
- [25] J. A. Rodríguez, M. Fernández-García, (Eds.) Synthesis, Properties and Applications of Oxide Nanoparticles. Whiley: New Jersey, (2007).
- [26] M. Fernández-García, A. Martínez-Arias, J. C. Hanson, J. A. Rodríguez, Chem. Rev. 104 (2004) 4063.
- [27] J. Fierro, Metal oxides: chemistry and applications, CRC Press, (2006).
- [28] H. Gleiter, Nanostruct. Mater. 6 (1995) 3.
- [29] M. Valden, X. Lai, D.W. Goodman, Science 281 (1998) 1647.
- [30] J. A. Rodriguez, G. Liu, T. Jirsak, Z. Chang, J. Dvorak, A. Maiti, J. Am. Chem. Soc. 124(2002) 5247.
- [31] M. Baumer, H.-J. Freund, Progress in Surf. Sci. 61 (1999) 127.
- [32] M. L. Trudeau, J. Y. Ying, Nanostruct. Mater. 7 (1996) 245.
- [33] Z. Wang, X.-F. Qian, J. Yin, Z. Zhu, J. Solid. State. Chem. 177 (2004) 2144.
- [34] L. E. Greene, M. Law, J. Goldberger, F. Kim, J. C. Johnson, Y. Zhang,
 R. J. Saykally, P. Yang, Angew. *Chem. Int. Ed.* 42 (2003) 3031.
- [35] F. Bai, P. He, Z. Jia, X. Huang, Y. He, Mater. Lett. 59 (2005) 1687.
- [36] B. Liu, H. C. Zheng, J. Am. Chem. Soc. 126 (2004) 8124.
- [37] H. Jiang, T. Herricks, Y. Xia, Nano Lett. 2 (2002) 1333.
- [38] H. -H. Lin, C. -Y. Wang, H. C. Shih, J.-M. Chen, C.-T. Hsieh, *J. Appl. Phys.* **95** (2004) 5889.
- [39] G. Boschloo, A. Hagfeldt, J. Phys. Chem. B 105 (2001) 3039.

- [40] X. M. Liu, X. G. Zhang, Electrochim. Acta. 49 (2004) 229.
- [41] Y. -N. Nuli, S. -L. Zhao, Q. -Z. Qiu, J. Power Sources 114 (2003) 113.
- [42] G. Wang, X. Gou, J. Horvat, J. Park J. Phys. Chem. C 112 (2008) 15220.
- [43] Z. R. Dai, J. L. Gole, J. D. Stout, Z. L. Wang, J. Phys. Chem. B 106 (2002) 1274.
- [44] Y. G. Wang, A. Z. Jin, Z. Zhang, Appl. Phys. Lett. 81 (2002) 4425.
- [45] S. Papaefthimiou, G. Leftheriotis, P. Yianoulis, Ionics 4 (1998) 321.
- [46] Y. J. Xing, Z. H. Xi, X. D. Zhang, J. H. Song, R. M. Wang, J. Xu, Z. Q. Xue, D. P. Yu, *Appl. Phys. A* 80 (2005) 1527.
- [47] K. Frohlich, R. Luptak, E. Dobrocka, K. Husekova, K. Cico, A. Rosova, M. Lukosius, A. Abrutis, P. Pisecny, J. P. Espinos, *Mater. Sci. in Semicond. Proces.* 9 (2006) 1065.
- [48] D. H. Park, S. T. Lim, S. J. Hwang, Electrochim. Acta 52 (2006) 1462.
- [49] W. H. Zhang, J. S. Zhao J. Mol. Struct. 789 (2006) 177.
- [50] http://www.gitam.edu/eresource/nano/NANOTECHNOLOGY/ role_of_bottomup_and _topdown_a.htm
- [51] S. Y. Bae, H. W. Seo, J. H. Park, J. Phys. Chem. B 108 (2004) 5206.
- [52] Y. J. Chem, J. B. Li, et al, J. cryst. Growth 245 (2002) 163.
- [53] J. M. Wu, H. C. Shih, W. T. Wu, Y. K. Tseng, I. C. Chen, J. Cryst. Growth 281 (2005) 384.
- [54] L. Dai, X. L. Chen, et al., Appl. Phys. A Mater. Sci. Process. 75 (2002) 687.
- [55] P. C. Chang, Z. Y. Fan, W. Y. Tseng, A. Rajagopal, J. G. Lu, *Apply. Phys. Lett.* 87 (2005) 2221002.
- [56] X. Wen, S. Wang, Y. Ding, Z. L. Wang, S. Yang, J. Phys. Chem.B 109 (2005) 215.
- [57] J. Zhou, L. Gong, et al., Apply. Phys. Lett. 87 (2005) 223108.
- [58] A. Umar, Y. B. Hahn, nanotechnology 17 (2006) 2174.
- [59] A. Umar, Y. B. Hahn, Apply. Phys. Lett. 88 (2006) 173120.
- [60] A. Sekar, S. H. Kim, A. Umar, Y. B. Hahn, J. Crystal. Growth 277 (2005) 471.
- [61] A. Umar, S. H. Kim, Y. S. Lee, K. S. Nahm, Y. B. Hahn, J. Crystal. Growth 282 (2005) 131.

- [62] A. Umar, S. Lee, et al., J. Crystal. Growth 277 (2005) 479.
- [63] A. Umar, S. Lee, Y. H. Im, Y. B. Hahn, Nanotechnology 16 (2005) 2462.
- [64] A. Umar, S. H. Kime, Y. H. Im, Y. B. Hahn, Superlatt. Microsostruc. 39 (2006) 238.
- [65] J. Zhou, Y. Ding, et al., Adv. Mater. 17 (2005) 2107.
- [66] J. Q. Hu, X. L. Ma, et al., J. Phys. Chem. B 106 (2002) 3823.
- [67] H.W. Kim, N. H. Kim, Appl. Phys. Mater. Sci. Process. 81 (2005) 763.
- [68] Q. Zhao, X. Xu, H. Zhang, Y. Chen, J. Xu, D. Yu, *Appl. Phys. A Mater. Sci. Process.* 79 (2004) 1721.
- [69] W. I. Park, D. H. Kim, S.-W. Jung, G. C. Yi, *Appl. Phys. Lett.* 80 (2002) 4232.
- [70] B. P. Zhang, N. T. Binh, Y. Segawa, K. Wakatsuki, N. Usami, Appl. Phys. Lett. 83 (2003) 1635.
- [71] W. Lee, H. G. Sohn, J. M. Myoung, Mater. Sci. Forum 449 (2004) 1245.
- [72] J. Su, M. Gherasimova, et al., Appl. Phys. Lett. 87 (2005) 183108.
- [73] T. T. Kang, X. Liu, R. Q. Zhang, W. G. Hu, G. Cong, F. Zhao, Q. Zhu, Appl. Phys. Lett. 89 (2006) 071113.
- [74] J. B. Baxter, E. S. Aydil, Appl. Phys. Lett. 86 (2005) 053114.
- [75] B. Liu, H. C. Zeng, J. Am. Chem. Soc. 125 (2003) 4430.
- [76] M. Guo, P. Diao, S. M. Cai, J. Solid State Chem. 178 (2005) 1864.
- [77] M. H. Cao, Y. H. Wang, et al., J. Nanosci. Nanotechnol. 4 (2004) 824.
- [78] J. Zhang, Z. G. Liu, et al., J. Crystal. Growth 280 (2005) 99.
- [79] D. S. Zheng, S. X. Sun, et al., J. Phys. Chem. B 109 (2005) 16439.
- [80] K. B. Zhou, X. Wang, et al., J. Catal. 229 (2005) 206.
- [81] Z. Y. Yuan, B. L. Su, Colloids Surf. A Physicochem. Eng. Aspects 241 (2004) 173.
- [82] G. Cao, "Nanostructures & Nanomaterials: Synthesis, Properties & Applications", Imperial College Press, London (2004).
- [83] Z. L. Wang J. Phys.: Condens. Matter16 (2004) R829.
- [84] L. S. Zhong, J. S. Hu, H. P. Liang, A. M. Cao, W. G. Song, L. J. Wan Adv. Mater. 18 (2006) 2426.
- [85] A. K. Radzimska, T. Jesionowski Materials 7 (2014) 2833.
- [86] L. Znaidi*Mat. Sci. Eng. B* **174** (2010) 18.

- [87] M. Meyyappan , M. Sunkara, Inorganic Nanowires, Applications, Properties and Characterization, CRC Press, Taylor and Francis Group, Boca Raton, London, New York, (2010).
- [88] R. S. Wanger, W. C. Ellis, Applied Physics Letters 4 (1964) 89.
- [89] C. M. Lieber, MRS Bulletin, 28 (2003) 486.
- [90] C. M. Lieber, Z. Wang, MRS Bulletin, 32 (2007) 99.
- [91] Y. H. Tang, C.S. Lee, S. T. Lee, *Phys. Rev. B*, 58 (1998) R16024.
- [92] Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li, C. L. Lin, *Appl. Phys. Lett.*, 84(18) (2004) 3654.
- [93] H. Li, Q. Wan, Y. X. Liang, T. H. Wang, Appl. Phys. Lett. 84 (22) (2004) 4556.
- [94] Y. J. Chen, M. S. Cao, T. H. Wang, Q. Wan, Appl. Phys. Lett. 84 (17) (2004) 3367.
- [95] Q. Wan, J. Sun , H. Liu Semiconducting Oxide Nanowires: Growth, Doping and Device applications, Nanowires - Implementations and Applications, Dr. Abbass Hashim (Ed.), ISBN: 978-953-307-318-7, (2011).
- [96] L. I. Maissel, R. Glang, Handbook of thin film technology, McGraw-Hill (1970).
- [97] K. Wasa, M. Kitabatake, H. Adachi, "Sputtering of compound materials". William Andrew, Springer (2004)
- [98] T. Karabacak, A. Mallikarjunan, et al., *Appl. Phys. Lett.* **83** (2003) 3096.
- [99] L. M Cao, Z. Zhang et al., Adv. Mater. 13 (2001) 1701.
- [100] L. M. Cao, K. Hahn et al., Appl. Phys. Lett. 80 (2002) 4226.
- [101] H. M. Smith , A.F.Turner , Appl. Opt. 4 (1965) 147.
- [102] M. T. Swihart Curr Opin *Colloid In* **8** (2003) 127.
- [103] W. Marine, L. Patrone, B. Luk'yanchuk, M. Sentis. *Appl. Surf. Sci.* 154–155 (2000) 345.

[104] Y. Nakata, J. Muramoto, T. Okada, M. Maeda J. Appl. Phys. 91 (2002) 1640.

[105] S. R. Shinde, S. D. Kulkarni, A. G. Banpurkar, R. Nawathey-Dixit,
 S. K. Date, S. B. Ogale J. Appl. Phys. 88 (2000)1566.
- [106] A. Harano, K. Shimada, T. Okubo, M. Sadakata J. Nanoparticle. Res. 4 (2002) 215.
- [107] T. Makimura, T. Mizuta, K. Murakami. Jpn. J. Appl. Phys. 41 (2002) L144.
- [108] A. P. Weber, M. Seipenbusch, G. Kasper. J. Phys. Chem A105 (2001) 8958.
- [109] E. F. Rexer, D. B. Wilbur, J. L. Mills, R. L. DeLeon, J. F. Garvey. *Rev Sci. Instrum.* 71 (2000) 2125.
- [110] H. Cao, J. Y. Xu, D. Z. Zhang, S. H. Chang, R. P. Ho, E. W. Seelig, X. Liu, R. P. H. Chang, *Phys. Rev. Lett.* 84 (2000) 5584.
- [111] N. Saito, H. Haneda, T. Sekiguchi, N. Ohashi, I. Sekiguchi, K. Koumoto Adv. Mater. 14 (2002) 418.
- [112] M. A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, R. Noufi Prog. *Photovolt*.7 (1999) 311.
- [113] U. Rau, N. Schmidt Thin Solid Films 387 (2001) 14.
- [114] I. F. Dong, Z. I. Cui, Z. K. Zhang Nanostruct. Mater. 8 (1997) 815.
- [115] F. K. III. Urban, A. Hosseini-Tehrani, P. Griffiths, A. Khabari, Y. W. Kim, I. Petrov J. Vac. Sci. TechnolB 20 (2002) 995.
- [116] C. J. Brinker, G. W. Scherer, Sol-Gel Science, Academic Press, Inc. New York, (1990).
- [117] L. L. Hench, J. K. West, Chem. Rev. (Wash-ington, D.C.) 90 (1990) 33.
- [118] B. O'Regan, J. Moser, M. Anderson, M. Gratzel, J. Phys. Chem. 94 (1990) 8720.
- [119] R. Kaur, A. V. Singh et al., J. Non-Cryst. Solids, 32 (2006) 2565.
- [120] R. Kaur, A. V. Singh, et al., J. Chem. Phys. 123 (2005) 134701.
- [121] X. Y. Wang, X. Y. Wang, et al., J. Power Sources 140 (2005) 211.
- [122] H. J. Xiang, J. Yang, J. G. Hou, Q. Zhu Appl. Phys. Lett. 89 (2006) 223111.
- [123] R. D. Vispute et al. Appl. Phys. Lett. 73 (1998) 348.
- [124] S. Cho, J. Ma, Y. Kim, Y. Sun, G. Wong, J. B. Ketterson Appl. Phys. Lett. 75 (1999) 18.
- [125] B. K. Meyer et al. Phys. Status Solidi B 241 (2004) 231.

- [126] F. H. Leiter, H. R. Alves, A. Hofstaetter *Phys. Status Solidi B* 4 (2001) 226.
- [127] J. H. Yang, G. M. Liu, L. Jun, Y. F. Qiu, S. H. Yang, *Appl. Phys. Lett.* 90 (2007) 103109.
- [128] C. S. Rout, S. H. Krishna, et al., Chem. Phys. Lett. 418 (2006) 586.
- [129] R. L. Garrell, Anal. Chem. 61 (1989) 401A.
- [130] T. R. Jensen, M. D. Malinsky, C. L. Haynes, R. P. Van Duyne, J. Phys. Chem. B,104 (2000)10549.
- [131] A. Campion, P. Kambhampati, Chem. Soc. Rev. 27 (1998) 241.
- [132] M. G. Albrecht, J. A. Creighton, J. Am. Chem. Soc. 99(1977) 5215.
- [133] K. Kneipp. Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari, M. Feld, *Phys. Rev. Lett.* 78 (1997) 1667.
- [134] S. Nie, S. R. Emory, Science, 275 (1997) 1102.
- [135] S. R. Emory, S. Nie, Anal. Chem. 69(1997) 2631.
- [136] M. Kerker, O. Siiman, L. A. Bumm , D. S. Wang, Appl. Opt. 19 (1980) 3253.
- [137] D. S. Wang, M. Kerker, Phys. Rev.B 24 (1981) 1777.
- [138] E. J. Zeman, G. C. Schatz, J. Phys. Chem. 91(1987) 634.
- [139] H. X. Xu, J. Aizpurua, M. Kall , P. Apell, Phys. Rev. E 62 (2000) 4318.
- [140] K. Fukami, M. L. Chourou, R. Miyagawa, A.M. Noval, T. Sakka, M. Manso- Silván, R. J. Martín-Palma, Y. H. Ogata, *Materials* 4 (2011) 791.
- [141] Z. Dai, X. Xiao, L. Liao, J. Zheng, F. Mei, W. Wu, J. Ying, F. Ren, C. Jiang, Appl. Phys. Lett. 103 (2013) 041903.
- [142] B. Sharma, R. R. Frontiera, A. I. Henry, E. Ringe, R. P. Van Duyne, *Mater. Today* **15 16** (2012).
- [143] X. M. Lin, Y. Cui, Y. H. Xu, B. Ren, Z. Q. Tian, Anal. Bioanal. Chem. 394 (2009) 1729.
- [144] S. Schlucker, Angew. Chem. Int. Ed. 53 (2014) 4756.
- [145] G. McNay, D. Eustace, W. E. Smith, K. Faulds, D. Graham, Appl. Spec. 65 (2011) 825.
- [146] H. H. Lin, J. Mock, D. Smith, T. Gao, M. J. Sailor, J. Phys. Chem. B 108 (2004) 11654.

- [147] S. Chan, S. Kwon, T. W. Koo, L. P. Lee, A. A. Berlin, Adv. Mater. 15 (2003) 1595.
- [148] R. Miyagawa, K. Fukami, M. L. Chourou, T. Sakka, Y. H. Ogata, ECS Trans. 33 (2011) 109.
- [149] J. Yang, J. Li, Z. Du, Q. Gong, J. Teng, M. Hong, Sci. Rep. 4(2014) 6657.
- [150] T. M. Cotton, Surface and Interfacial Aspects of Biomedical Polymersed J Andrade (New York: Plenum), p 161 (1985).
- [151] Y. Wei, C. Cao, R. C. Jin , C. A. Mirkin, Science 297 (2002) 1536.
- [152] S. Efrima, B. V. Bronk. J. Phys. Chem. B 102 (1998) 5947.
- [153] H. Zhou, D. Yang, N. P. Ivleva, N. E. Mircescu, R. Niessner, C. Haisch, Anal. Chem. 86 (2014) 1525.
- [154] I. Talian, J. Huebner, J. Raman Spectrosc. 44(2013) 536.
- [155] F. T. Docherty, P. B. Monaghan, C. J. McHugh, D. Graham, W. E. Smith, M. J. Cooper, *IEEE Sensors Journal*, 5 (2005) 632.
- [156] L. Guerrini, D. Graham, Chem. Soc. Rev. 41 (2012) 7085.
- [157] M. Moskovits J. Chem. Phys. 69 (1978) 1459.
- [158] H. X. Xu, E. J. Bjerneld, M. Käll, L. Börjesson Phys. Rev. Lett. 83 (1999) 4357.
- [159] A. M. Michaels, J. Jiang, E. Brus J. Phys. Chem. B,104 (2000) 11965.
- [160] S. Imamova, A. Dikovska, N. Nedyalkov, P. Atanasov, M. Sawczak, R. Jenrizejewski, G. Sliwinski, M. Obara J. Optoelectron.&Adv. Mat., 12 (2010) 500.
- [161] L. Yang, X. Jiang, W. Ruan, J. Yang, B. Zhao, W. Xu, J. R. Lombardi, J. Phys. Chem.C 113 (2009) 16226.
- [162] M. A. Mohiddon, L. D. V. Sangani, M.G. Krishna, *Chem. Phys. Lett.* 588(2013) 160.
- [163] S. Hamad, G. K. Podagatlapalli, A. Mohiddon, V. R. Soma, Appl. Phys. Lett 104 (2014) 2631041.
- [164] N. Ahalya, R. Kanamdi, T. V. Ramachandra, Indian J. Chem. Technol. 13 (2006) 122.
- [165] K. R. Hall, L. C. Eagleton, A. Acrivos, T. Vermeulen, *I&EC Fundam*. 5 (1966) 212.

- [166] V. Madhurima, D. D. Purkayastha, N. V. S. Rao, Wettability, J Colloid Interf Sci. 357 (2011) 229.
- [167] K. S. Liao, H. Fu, A. Wan, J. D. Batteas, D. E. Bergbreiter, *Langmuir*. 25 (2009) 26.
- [168] Z. X. Jiang, L. Geng, Y. D. Huang, S. A. Guan, W. Dong, Zi. Y. Ma, J Colloid Interf Sci 354 (2011) 866.
- [169] Xi. Zhang, F. Shi, J. Niu, Y. Jiang, Z. Wang, J. Mater. Chem. 18 (2008) 621.
- [170] C. Mao, C. Liang, W. Luo, J. Bao, J.Shen, X. Hou, W. Zhao, J. Mater. Chem. 19 (2009) 9025.
- [171] L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu Adv. *Mater.* 14 (2002) 1857.
- [172] D. P. Subedi, D. K. Madhup, A. Sharma, U. M. Joshi, A. Huczko Int. Nano Lett., 1 (2011) 117.
- [173] C. Y. Wang, S. H. Pang, L. Qi, T. C. Ma, P. W. Wang Mater. Chem Phys. 125 (2011) 281.
- [174] M. Takeuchi, S. Dohshi, T. Eura, M. Anpo J. Phys. Chem. B., 107 (2003) 14278.
- [175] C. Neto, K. R. Joseph, W. R. Brant, Phys. Chem. Chem. Phys., 11 (2009) 9537.
- [176] <u>M. Ohring</u>, Materials Science of Thin Films, Second Edition 2nd Edition (2001).
- [177] <u>www.semicore.com/news/71-thin-film-deposition-thermal-</u> evaporation
- [178] K. Creath , A. Morales, Contact and noncontact profilers in optical shop testing, 2nd ed. Wiley, New york (1992).
- [179] C. Suryanarayana, M. Grant Norton, X-Ray Diffraction: A Practical Approach, Springer Science & Business Media (1998).
- [180] JCPDS file number 87-0713.
- [181] JCPDS file number 89-1397.
- [182] B. D. Cullity, S. R. Stock, "Elemets of X-ray diffraction" 3rd Ed prentice Hall (2001).

- [183] L. Reimer, H. Kohl, 'Transmission Electron Microscopy Physics of Image Formation', 5thEd, Springer, New York, 10013, USA (2008).
- [184] Z. L. Wang, J. Phys. Chem. B, 104 (2000)1153.
- [185] www.photometrics.net/analytical-techniques/field-emissionscanning-electron-microscopy-fesem.
- [186] Y. J. Kim, C. R. Park, Carbon Science, 2 (3&4) (2001) 202.
- [187] L. Reimer, "Scanning electron microscopy" Springer (1998).
- [188] J. M. Huggett, H. F. Shaw, Clay Minerals 32 (1997) 197.
- [189] C. Binning, C. F. Quate Phys. Rev. Lett 56 (1986) 930.
- [190] Q. Zhong, Surf. Sci. Lett., 290 (1993) L688.
- [191] J. Giessibl Franz, Review of Mod. Phys., 75 (2003) 949.
- [192] J.B. Hudson, Surface Science-An introduction, Wiley, New York (1998)
- [193] J. Goldstein, D. Newbury, D. Joy, Ch. Lyman, P. Echlin, E. Lifshin,L. Sawyer, J Michel "Scanning electron microscopy and X-ray micro analysis" Springer (2003).
- [194] O. Stenzel, The Physics of thin film Optical Spectra: an Introduction, Springer Germany (1996).
- [195] C. Anthony, F. Cripps "Nanoindentation", 3rd Ed, Springer (2011).
- [196] D. Y. Kwok, T. Gietzelt, K. Grundke, H. J. Jacobasch, A.W. Neumann, Langmuir. **13** (1997) 2880.
- [197] E. Y. Arashiro Demarquette. Mater. Res., 2(1999) 23.
- [198] A. Marmur, Soft Mater., 2 (2006) 12.
- [199] G. Li, B. Wang, Y. Liu, T. Tan, X. Song, H. Yan Appl. Surf. Sci 255 (2008) 3112.
- [200] H. C. Barshilia, K. R. S. Tej, L. M. Devi, K. S. Rajam, J. Appl. Phys. 108 (2010) 074315.
- [201] H. Y. Dang, J. Wang, S. S. Fan Nanotechnology 14 (2003) 738.
- [202 H. J. Fan, R. Scholz, F. M. Kolb, M. Zacharias, U. Gosele, F. Heyroth, et al. *Appl.Phys. A* **79** (2004)1895.
- [203] H. J. Fan, R. Scholz, F. M. Kolb, M. Zacharias Appl. Phys. Lett 85 (2004) 4142.
- [204] D. Yuvaraj, K. N. Rao, K. K. Nanda, J. Phys. D. Appl. Phys. 42 (2009)

035403.

- [205] L. Yuan, Y. Wang, R. Mema, G. Zhou, Acta. Mater. 59 (2011) 2491.
- [206] S. Li, X. Zhang, B. Yan, T. Yu, Nanotechnology 20 (2009) 495604-1.
- [207] J. Wu, J. Xia, C. Jing, W. Lei, B. P. Wang. Appl. Phys. A 105 (2011) 221.
- [208] S. Marka, Menaka, A. K. Ganguli, M. G. Krishna, Surf. Coat. Technol. 209 (2012) 23.
- [209] T. H. Fang, W. J. Chang, C. M. Lin, Mater. Sci. Eng. A 452-453 (2007) 715.
- [210] L. W. Ji, S. J. Young, T. H. Fang, C. H. Liu, *Appl. Phys. Lett.* **90** (2007) 033109.
- [211] G. Feng, W. D. Nix, Y. Yoon, C. J. Lee, J. Appl. Phys. 99 (2006) 074304.
- [212] C. A. Schuh, Mater. Today 9 (2006) 32.
- [213] M. Riaz, O. Nur, M. Willander, P. Klason, Appl. Phys. Lett. 92 (2008) 103118.
- [214] R. Wu, J. Wu, C. Xie, J. Zhang, A.Wang Mater.Sci.Eng. A 328 (2002) 196.
- [215] M. Liu, A. H. Kitai, P. Mascher, J. Lumin. 54 (1992) 35.
- [216] D. W. Hamby, D. A. Lucca, M. J. Klopfstein, G. Cantwell, J.Appl.Phys. 93 (2003) 3214.
- [217] R. B. Dunbar, H. C. Hesse, D. S. Lembke, L. Schmidt-Mende, *Phys.Rev.B* 85 (2012) 035301.
- [218] D. Wolf, S.Y ip, Materialsinterfaces:Atomic Level Structure and Properties, Springer, London (1992).
- [219] H. S. Jarrett, Phys. Rev. Lett. 54 (1985) 217.
- [220] X. Gui-Na, M. Shi-Qing, ActaChim.Sinica 68 (2010)1272.
- [221] H. Amekura, N. Umeda, K. Kono, Y. Takeda, N. Kishimoto, Ch Bucha S Mant, *Nanotechnology* 18 (2007) 395707.
- [222] S. Wakaiki, H. Ichida, K. Mizoguchi, D. Kim, Y. Kanematsu, M. Nakayama, *Phys.Status SolidiC* 8 (2011) 116.
- [223] A. Teke, U. Ozgur, S. Dogan, X. Gu, H. Morkocu, B. Nemeth, J. Nause, H. Everitt, *Phys.Rev.B* 70 (2004) 195207.

- [224] G. TekeXing, D. Wang, J. Yi, L. Yang, M. Gao, M. He, J. Yang, J. Ding, T. C. Sum, T. Wu, *Appl.Phys.Lett.* 96 (2010) 112511.
- [225] M. Gomi, N. Oohira, K. Ozaki, M. Koyano, Jpn.J.Appl.Phys. 42 (2003) 481.
- [226] W. Cheng, P. Wu, X. Zou, T. Xiao, J. Appl. Phys. 100 (2006) 054311.
- [227] M. RedfieQuillec, Materials for Optoelectronics, Springer, Norwell (1996).
- [228] H. P. He, Z. Z. Ye, S. S. Lin, H. P. Tang, Y. Z. Zhang, L. P. Zhu, J. Y. Huang, B. H. Zhao, J. Appl. Phys. 102 (2007) 013511.
- [229] A. Mang, K. ReimannSt., Solid State Commun. 94 (1995) 251.
- [230] D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, G. Cantwell, W. C. Harsch, *Phys. Rev. B* 60 (1999) 2340.
- [231] C. Boemare, T. Monteiro, M. J. Soares, J. G. Guilherme, E. Alves, *Physica B* 308– 310 (2001) 985.
- [232] K.W. Boer, Survey of Semiconductor Physics, Wiley, NewYork, (2002).
- [233] H. Fujiwara, M. Kondo, *Phys.Rev.B* 71 (2005) 075109.
- [234] J. Wang, Z. An, Q. Li, R. F. Egerton, Appl. Phys. Lett. 86 (2005) 201911.
- [235] L. J. Wang, N. C. Giles, J. Appl. Phys. 94 (2003) 973.
- [236] D. Redfield, R. H. Bube, Photo-Induced Defects in Semiconductors, Cambridge University Press, London, (2006).
- [237] T. C. Damen, S. P. S. Porto, B. Tell, Phys. Rev. 142 (1966) 570142.
- [238] P. M. Chassaing, F. Demangeot, V. Paillard, A. Zwick, N. Combe, C. Pages, M. L. Kahn, A. Maisonnat, B. Chaudret, *Appl. Phys. Lett.* 91 (2007) 053108.
- [239] W. Suetaka, J. T. Yates, Surface Infrared and Raman Spectroscopy: Methods and Applications, Springer, NewYork, (1995).
- [240] L. Castañeda, O. G. Morales-Saavedra, D. R. Acosta, A. Maldonado, M. de la L. Olvera, *phys. stat. sol. A* 203(8) (2006) 1971.
- [241] S. K. Das, M. Biswas, D. Byrne, M. Bock, E. McGlynn, M. Breusing, R. Grunwald, J.Appl. Phys. 108 (2010) 043107.

- [242] Y. -P. Chan, J. -H. Lin, C. -C. Hsu, W. -F. Hsieh, *Opt. Exp.* **16** (2008) 19900.
- [243] Y. B. Han, J. B. Han, S. Ding, D. J. Chen, Q. Q. Wang, Opt. Exp. 13 (2005) 9211.
- [244] K. V. Gurav et al. Sens Actuators B 190 (2014) 439.
- [245] K. K. Nagaraja, S. Pramodini, P. Poornesh, H. S. Nagaraja, J. Phys. D 46 (2013) 055106.
- [246] J. C. Johnson, H. Yan, R. D. Schaller, P. B. Petersen, P. Yang, R. J. Saykally, *Nano. Lett.* 2 (2002) 279.
- [247] L. Irimpan, A. Deepthy, B. Krishnan, L. M. Kukreja, V. P. N. Nampoori, P. Radhakrishnan, Opt. Commun. 281 (2008) 2938.
- [248] L. Irimpan, A. Deepthy, B. Krishnan, L. M. Kukreja, V. P. N. Nampoori, P. Radhakrishnan, *Appl. Phys. B* 90 (2008) 547.
- [249] L. Irimpan, V. P. N. Nampoori, P. Radhakrishnan, B. Krishnan, A. Deepthy, J. Appl. Phys. 103 (2008) 033118.
- [250] L. Irimpan, D. Ambika, V. Kumar, V. P. N. Nampoori, P. Radhakrishnan, J. Appl. Phys. 104 (2008) 033105.
- [251] L. -C. Zhang, G. Yang, K. Wang, M. Fu, Y. Wang, H. Long, P.-X. Lu, Opt. Commun 291 (2013) 395.
- [252] X. J. Zhang, W. Ji, S. H. Tang, J. Opt. Soc. Am. B. 14 (1997) 1951.
- [253] X. Zhang, H. Fang, S. Tang, W. Ji, Appl. Phys. B 65 (1997) 549.
- [254] M. Trejo-Valdez, C. T- Torres, J. H. C- Chacon, G. A. G- Armenta,
 C. I. G- Gil, A. V. Khomenko, *Opt. and Las. Tech.* 49 (2013) 75.
- [255] Q. -Y. Ouyang, Z. Xu, Z. Lei, H. Dong, H. Yu, L. Qi, C. Li, Y. Chen, *Carbon.* 67 (2014) 214.
- [256] R. K. Jamal, A. M. Suhail, M. T. Hussein, H. J. Kbashi, Int. J. Thin Film Sci. Tec. 1 (2012) 61.
- [257] P. C. Haripadmam, M. K. Kavitha, H. John, B. Krishnan, P. Gopinath, *Appl. Phys. Lett.* **101** (2012) 071103.
- [258] P. P. Jeeju, S. Jayalaxmi, K. Chandrasekharan, P. Sudheesh, Opt. Commun. 285 (2012) 5433.
- [259] H. W. Lee, K. M. Lee, S. Lee, K. H. Koh, J. -Y. Park, K. Kim, F. Rotermund, *Chem. Phys. Lett.* 447 (2007) 86.

- [260] P. C.Haripadmam, H. John, R. Philip, P. Gopinath, Opt. Lett. 39 (2014) 474.
- [261] R. Vinodkumar, K. J. Lethy, P. R. Arunkumar, Renju R. Krishnan, N. Venugopalan Pillai, V. P. Mahadevan Pillai, Reji Philip, *Mater. Chem. Phys.* **121** (2010) 406.
- [262] G. Vijaya Prakash, K. Pradeesh, A. Kumar, R. Kumar, S. Venugopal Rao, M. L. Markham, J. J. Baumberg, *Mater. Lett.* 62 (2008) 1183.
- [263] M. S. Bahae, A. A. Said, T. H. Wel, D. J. Hagen, E. W. Van Stryland, *IEEE J. Quant. Electron.* 26 (1990) 760.
- [264] D. Swain, P. T. Anusha, T. S. Prashant, S. P. Tewari, T. Sarma, P. K. Panda, S. Venugopal Rao, *Appl. Phys. Lett.* **100** (2012) 141109.
- [265] P. T. Anusha, P. S. Reeta, L. Giribabu, S. P. Tewari, S. Venugopal Rao, Mat. Lett. 64 (2012) 1915.
- [266] S. Hamad, S. P. Tewari, L. Giribabu, S. Venugopal Rao, J. Porphy. *Phth.* 16 (2012) 140.
- [267] K. V. Saravanan, K. C. James Raju, M. G. Krishna, S. P. Tewari, S. Venugopal Rao, *Appl. Phys. Lett.* 96 (2012) 232905.
- [268] J. Tauc, R. Grigorovichi, A. Vancu, Phys. Status Solidi B15 (1996) 627.
- [269] N. F. Mott, E. A. Davis, Electronic Processes in Non-Crystalline Materials, 2nd ed. Clarendon, Oxford, New York, (1979).
- [270] Z. Li, Y. Xiong, Y. Xie, Inor. Chem. 42 (2003) 8105.
- [271] B. Lin, Z. Fu, Y. Jia, Appl. Phys. Lett. 79 (2001) 943.
- [272] S. -H. Jeong, B. -S. Kim, B. -T. Lee Appl. Phys. Lett.82 (2003) 2625.
- [273] W. M. Kwok, A. B. Djurišić, Y. H. Leung, W. K. Chan, D. L. Phillips, *Appl. Phys. Lett.* 87 (2005) 22311.
- [274] J. Zhou, Y. Wang, F. Zhao, Y. Wang, Y. Zhang, L. Yang J. Lumin. 119-120 (2006) 248.
- [275] M. Willander, O. Nur, N. Bano, K Sultana, New J. Phys. 11 (2009) 125020.
- [276] M. Rajalakshmi, A. K. Arora, B. S. Bendre, S. Mahamuni, J. Appl. Phys. 87 (2000) 2445.
- [277] K. Samanta, A. K. Aroraand, R. S. Katiyar, J. Phys. D: Appl. Phys. 45 (2012) 185304.

- [278] R. Cusco, E. Alarcon-Llado, L. Artus, J. Ibanez, J. Jimenez, B. Wang , M. J. Callahan, *Phys. Rev. B* 75 (2007)165202.
- [279] J. Serrano, A. H. Romero, F. J. Manjo'n, R. Lauck, M. Cardona, A. Rubio, *Phys. Rev. B* 69 (2004) 094306.
- [280] G. J. Exarhos, S. K. Sharma, Thin Solid Films 27 (1995) 270.
- [281] Y. J. Xing, Z. H. Xi, Z. Q. Xue, X. D. Zhang, J. H. Song, R. M. Wang, J. Xu, Y. Song, S. L. Zhang, D. P. Yu, *Appl. Phys. Lett.* 83 (2003) 1689.
- [282] S. Venugopal Rao, T. S. Prashant, T. Sarma, P. K. Panda, D. Swain, S. P. Tewari, *Chem. Phys. Lett.* **514** (2011) 98.
- [283] J. -H. Lin, Y. -J. Chen, H. -Y. Lin, W. -F. Hsieh, J. Appl. Phys. 97 (2005) 033526.
- [284] T. Bazaru, V. I. Vlad, A. Petris, M. Miu, J. Opt. Adv. Mat. 12 (2010) 43.
- [285] H. W. Lee, J. K. Anthony, H. -D. Nguyen, S. -I. Mho, K. Kim, H. Lim, F. Rotermund, Opt. Exp. 17 (2009) 19093.
- [286] W. Zhang, H. Wang, K. S. Wong, Z. K. Tang, G. K. L. Wong, R. Jain, *Appl. Phys. Lett.* **75** (1999) 3321.
- [287] M. Divall, K. Osvay, G. Kurdi, E.J. Divall, J. Klebniczki, J. Bohus, Á. Péter, K. Polgár, Appl. Phys. B 81 (2005) 1123.
- [288] R. A. Ganeev, I. A. Kulagin, A. I. Ryasnyanskil, R. I. Tugushev, T. Usmanov, Opt. Spectrosc. 94 (2003) 561.
- [289] J. B. Cui, Appl Phys Lett.87 (2005) 133108.
- [290] Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, Appl Phys Lett. 84 (2004) 3085.
- [291] D. S.Kim, J.Fallert, A.Lotnyk, R.Scholz, E.Pippel, S.Senz, H.Kalt, U.Gosele, M. Zacharias, *Solid State Commun* 143 (2007) 570.
- [292] J. Dai, C. X. Xu, X. Y. Xu, J. T. Li, J. Y. Guo, Y. Lin, APL Mater1 (2013) 032105.
- [293] M. Ahmad, J. Zhao, J. Iqbal, W. Miao, L. Xie, R. Mo, J. Zhu, J Phys D Appl Phys 42 (2009) 165406.
- [294] M. Ahmad, J. Sun H Zhu, ACS Appl Mater Interfaces3 (2011) 1299.
- [295] L. Xu, Y. Su, Y. Chen, H. Xiao, L. Zhu, Q. Zhou, S. Li, J Phys Chem B 110(2006) 6637.

- [296] J. Jie, G. Wang, X. Han, Q. Yu, Y. Liao, G. Li, J. G. Hou, *Chem. Phys. Lett.* **387** (2004) 466.
- [297] C. Hsu, T. Tsai, J. Electrochem. Soc 158 (2)(2011) K20.
- [298] F.J. Sheini, M. A. More, S. R. Jadkar, K. R. Patil, V. K. Pillai, D. S. Joag, J Phys Chem C 114(2010) 3843.
- [299] S. Y. Li, P. Lin, C. Y. Lee, T. Y. Tseng, C. J. Huang, J Phys D Appl Phys 37 (2004) 2274.
- [300] S. Y. Bae, C. W. Na, J. H.Kang, J. Park, J Phys Chem B 109(2005) 2526.
- [301] M. Jung, S. Kim, S. Ju, Opt Mater 33 (2011) 280.
- [302] Y. Huang, Y. Zhang, Y.Guet al, J Phys Chem C 111(2007) 9039.
- [303] C. V. Thompson, Annu Rev Mater Res 42 (2012) 399.
- [304] C. Zhou, C. Li, D. Zhang, S. Han, X. Liu, T. Tang, Adv. Mater 15 (2003) 143.
- [305] M. Park, G. Wang, Y. Kang, D. Wexler, S. Dou, H. Liu, Angew. Chem. Int Ed. 46 (2007) 750.
- [306] G. Ottaviani, J Vac Sci Technol 16 (1979)1112.
- [307] K. N. Tu, Annu Rev Mater Sci 15 (1985) 147.
- [308] D. R. Ed. Lide, CRC Handbook of Chemistry and Physics, 80th ed., CRC Press, Boca Raton, FL, (2000).
- [309] C. M. Wynn, S. Palmacci, R. R. Kunz, M. Rothschild, *Lincoln Lab. J.* 17 (2008) 27.
- [310] Z. Bielecki, J. Janucki, A. Kawalec, J. Mikolajczyk, N. Palka, M. Pasternak, T. Pustelny, T. Stacewicz, J. Wojtas, *Metrol. Meas. Syst. XIX*(1) (2012)3.
- [311] A. Hakonen, P. O. Andersson, M. Stenbaek Schmidt, T. Rindzevicius, M. Käll, *Anal. Chim. Acta* **893** (2015) 1.
- [312] R. Brahma, M. G. Krishna, Phys. E 43(2011) 1192.
- [313] M. A. Mohiddon, K. L. Yadav, Adv. Appl. Ceram. 107(2008) 310.
- [314] L. Jensen, G. C. Schatz, J. Phys. Chem. A 110 (2006) 5973.
- [315] J. He, S. Hong, L. Zhang, F. Gan, H. Yuh-Shan, Fres. Env. Bul. 19 (2010) 2651.

- [316] S. Hamad, G. Krishna Podagatlapalli, M. Ahamad Mohiddon, S. Venugopal Rao, Chem. Phys. Lett. 621 (2015) 171.
- [317] D. C. Sorescu, J. a. Boatz, D. L. Thompson, J. Phys. Chem. A 105 (2001) 5010.
- [318] Y. Kholod, S. Okovytyy, G. Kuramshina, M. Qasim, L. Gorb, J. Leszczynski, J. Mol. Struct. 843 (2007) 14.
- [319] G. K. Podagatlapalli, S. Hamad, M. A. Mohiddon, S. V. Rao, *Laser Phys. Lett.* **12**(2015) 036003.
- [320] X. He, H. Wang, Q. Zhang, Z. Li, X. Wang, Eur. J. Inorg. Chem. 2014 (2014) 2432.
- [321] Y. Chen, G. Tian, K. Pan, C. Tian, J. Zhou, W. Zhou, Z. Ren, H. Fu, *Dalt. Trans.* 41 (2012) 1020.
- [322] A. Lahiri, R. Wen, S. Kuimalee, S. Kobayashi, H. Park, *Cryst Eng Comm* **14** (2012) 1241.
- [323] A. Musumeci, D. Gosztola, T. Schiller, N. M. Dimitrijevic, V. Mujica, D. Martin, T. Rajh, J. Am. Chem. Soc. 131 (2009) 6040.
- [324] A. O. Dikovska, N. N. Nedyalkov, S. E. Imamova, G. B. Atanasova, P. A. Atanasov, *Quantum Electron*. 42 (2012) 258.
- [325] R. N. Wenzel, Ind. Eng. Chem.28 (1936) 988.
- [326] A. B. D. Cassie, S.Baxter, Trans. Faraday Soc, 40 (1944) 546.
- [327] B. Radha, S. H. Lim, M. S. M. Saifullah, G. U. Kulkarni, Sci Rep, 3 (2013) 1078.
- [328] M. Tang, V. Shim, Z.Y. Pan, Y.S. Choo, M.H. Hong, J. Laser Micro/Nanoeng. 6 (2011) 6.
- [329] R. Jagdheesh, B. Pathiraj, E. Karatay, G. R. B. E. Romer, A. J. Huis int Veld, *Langmuir.* 27 (2011) 8464.
- [330] Z. Yuan, J. Bin, X. Wang, C. Peng, M. Wang, S. Xing, J. Xiao, J. Zeng, X. Xiao, X. Fu, H. Chen, *Surf. Coat. Technol.* 254 (2014) 151.
- [331] G. Hea, K. Wangb, Appl.Surf.Sci. 257 (2011) 6590.
- [332] J. Wu, J. Xia, W. Lei, B. P. Wang, Mater. Lett. 64 (2010) 1251.
- [333] C. Badre, T. Pauporte, M.Turmine, D. A. Lincot, Nanotechnology, 18 (2007) 365705.

- [334] G. Kwak, M. Seol, Y. Tak, K.Yong, J. Phys. Chem. C, 113 (2009) 12085.
- [335] M. Gong, Z. Yang, X. Xu, D. Jasion, S. Mou, H. Zhang, Y. Long, S. J. *Ren,Mater.Chem. A* 2(2014) 6180.
- [336] M. G. Krishna, V. Madhurima, D. D. Purkayastha, Eur. Phys. J. Appl. Phys. 62 (2013) 30001.
- [337] P. Suresh Kumar, J. Sundaramurthy, D. Mangalaraj, D. Nataraj, D. Rajarathnam, M. P. Srinivasan, J Colloid Interf Sci. 363 (2011) 51.
- [338] M. T. Z. Myint, G. L. Hornyak, J. Dutta, J Colloid Interf Sci. 415 (2014) 32.

List of publications

- Ummar Pasha Shaik, S. Kshirsagar, M. Ghanashyam Krishna, Surya P. Tewari, Debarun Dhar Purkayastha, V. Madhurima, *Materials Letters*, 75 (2012) 51-53.
- S. Kshirsagar, Ummar Pasha Shaik, M. Ghanashyam Krishna, Surya P. Tewari *Journal of Luminescence* 136 (2013) 26–31.
- Ummar Pasha Shaik, M. Ghanashyam Krishna, Ceram int 40 (2014) 13611.
- 4. Ummar Pasha Shaik, P. Ajay Kumar, M. Ghanashyam Krishna, S. Venugopal Rao, *Mater. Res. Express* **1** (2014) 046201.
- Ummar Pasha Shaik, M. Ghanashyam Krishna, Debarun Dhar Purkayastha, V. Madhurima, *Appl. Surf. Sci* 330 (2015) 292–299.
- Ummar Pasha Shaik, Syed Hamad, Md. AhamadMohiddon, Venugopal Rao Soma, M.GhanashyamKrishna J. Appl. Phys (Under review) (2015).

Other Publications/Conference proceedings

- S. Kshirsagar, Ummar Pasha Shaik, M. Ghanashyam Krishna, Surya P. Tewari *Appl Phys A* 111 (2013) 861–865.
- Ummar Pasha Shaik, M. Ghanashyam Krishna "Indium doped zinc oxide nanowire thin films for antireflection and solar absorber coating applications" *AIP Conference Proceedings* 1591 (2014) 405.

 Ummar Pasha Shaik, L.D. Varma Sangani, Anshu gaur, Md Ahamad Mohiddon, M.Ghanashyam Krishna "Ag-ZnO nanostructure for ANTA explosive molecule detection" *AIP Conference Proceedings* (*DAE-SSPS-2015*).

Oral/poster presentations

- Ummar pasha.Shaik, Sachin Kshirsagar, M.Ghanashyam Krishna, S.P.Tewari "Growth and properties of Zinc Oxide nanowires fabricated by the self – catalysis method" Advances in material processing and characterization, *AMPC 2013 (Oral presentation)*.
- Ummar Pasha Shaik, M. Ghanashyam Krishna "Indium doped zinc oxide nanowire thin films for antireflection and solar absorber coating applications" The 58th DAE Solid State Physics Symposium, (DAE-SSPS-2013) (Poster presentation).
- 3. Ummar Pasha Shaik, G.V. Reddy, M. Ghanashyam Krishna "Single step formation of undoped and doped Zinc oxide nanowires by thermal oxidation" Sixth International Conference on Nano Science and Technology, *ICONSAT 2014 (Poster presentation)*.
- 4. Ummar Pasha Shaik, L.D. Varma Sangani, Anshu gaur, Md Ahamad Mohiddon, M.Ghanashyam Krishna "Ag-ZnO nanostructure for ANTA explosive molecule detection" (*DAE-SSPS-2015*) (*Poster presentation*).

Studies on single step formation of undoped and doped Zinc Oxide nanowire thin films for optoelectronic, sensing and self cleaning applications

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