Surface and Interface Effect in ALD-Grown ZnO: Properties and Application in Rechargeable Batteries

Ph.D. Thesis

By DIPAYAN PAL



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A THESIS

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> by DIPAYAN PAL



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Surface and Interface Effect in ALD-Grown ZnO: Properties and Application in Rechargeable Batteries" in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July, 2014 to May, 2019 under the supervision of Dr. Sudeshna Chattopadhyay, Associate Professor, IIT Indore and Dr. Chelvam Venkatesh, Associate Professor, IIT Indore.

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

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Dedicated to my country, India

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- "Structure and morphology of magnetron sputter deposited ultrathin ZnO films on confined polymeric template", Ajaib Singh, Susanne Schipmann, Aakash Mathur, **Dipayan Pal**, Amartya Sengupta, Uwe Klemradt, Sudeshna Chattopadhyay, *Applied Surface Science* **414**, 114 (2017).
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- "Violet emission of ALD grown ZnO nanostructures on confined polymer films: Defect origins and emission control via interface engineering based on confinement of underneath polymer template", Aakash Mathur, Dipayan Pal, Ajaib Singh, Amartya Sengupta, Rinki Singh, Sudeshna Chattopadhyay, *Macromolecular Chemistry and Physics* 220, 1800435 (2019).
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Acronyms

Zinc oxide	ZnO
Atomic layer deposition	ALD
Physical vapor deposition	PVD
Chemical vapor deposition	CVD
Silicon	Si
X-ray reflectivity	XRR
X-ray diffraction	XRD
Electron density profile	EDP
Scanning electron microscopy	SEM
Atomic force microscopy	AFM
Spectroscopic ellipsometry	SE
Photoluminescence	PL
Near band-edge emission	NBE
Deep level emission	DLE
Conduction band	CB
Valence band	VB
X-ray photoelectron spectroscopy	XPS
Cyclic voltammetry	CV

Chapter 1

Introduction

Owing to its direct and wide band gap ($E_g \sim 3.37 \text{ eV}$), large exciton binding energy (60 meV) at room temperature, high thermal and chemical stability, biocompatibility, zinc oxide (ZnO) has gained intensive interest in the research community in the past few years [1-4]. Its distinct properties like wide band gap and large excitonic binding energy (60 meV, which is more than twice exciton binding energy of GaN) [5], ensure efficient excitonic emission in ZnO at room temperature and even at higher temperatures [6, 7], which makes ZnO a promising material for short-wavelength optoelectronic devices, especially for ultraviolet lightemitting diodes and laser diodes [8, 9].

ZnO can crystallize in a variety of crystal structures including wurtzite, rocksalt and zinc blende, as shown in Figure 1.1. But, in general, under ambient conditions, hexagonal wurtzite structure is found to be the most thermodynamically stable form [10, 11]. In wurtzite crystal, the structure is composed of two interconnecting hexagonal close-packed (hcp) sublattice in a hexagonal lattice, each of which consisted of one of the Zn²⁺ and O²⁻ atom along the threefold *c*-axis involving *sp*³ covalent bonding where each anion is surrounded by four cations at the corners of a tetrahedron [10]. It belongs to the space group of *P6₃mc* which has two lattice parameters; a = 3.25 Å, c = 5.20 Å [11, 12]. The tetrahedral coordination in ZnO results in non-central symmetric structure and consequently induces the characteristic piezoelectricity [12].

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Figure 1.1: Stick-and-ball representation of ZnO crystal structures: cubic rocksalt, cubic zinc blende, and hexagonal wurtzite. Shaded gray and black spheres represent Zn and O atoms, respectively [10].



Figure 1.2: Cartoon displaying various applications of ZnO.

Due to its excellent properties, ZnO has been extensively investigated in various applications such as ultraviolet light emitters [5, 13], thin film transistors [14, 15], solar cells [16, 17], electrode material in battery [18, 19], transparent conducting oxide [20, 21], gas sensors [22, 23], and nanogenerators [24, 25]. ZnO has also attracted a lot of interest for being used in hybrid solar cells because it is less toxic than many other II–VI element semiconductors and is relatively easy to synthesize in large quantities with a variety of techniques [26]. Furthermore, ZnO as an n-type semiconductor with a wide band gap and a very good optical transmittance remains a potential candidate for an efficient cathode buffer layer or a transparent electrode in the organic and hybrid solar cells [26]. The cartoon in Figure 1.2 displays various potential applications of ZnO. Consequently, there is considerable interest in studying ZnO in the form of powders, thin films, or nanostructures.

Earlier experimental studies show that within the dimensions of 20 nm or less, the quantum effect in ZnO becomes apparent [27-29]. Studies also showed that the thickness of ZnO films is a key parameter in determining the device performance, as found in case of photovoltaic devices where ZnO film thicknesses below 300 nm are of specific interest in terms of optimization of device performance [24, 30]. The quantum size effects in ZnO nanostructures, such as nanocrystals [31, 32], quantum wells [33], nanorods [34, 35], nanowires [36, 37], quantum dots [38, 39], etc., have been extensively investigated by many research groups. However, few reports are available on the thickness dependence of properties of ZnO thin films [27-29]. On account of the above facts, the systematic quantitative thickness dependent study of specific properties of ZnO thin films in this regime is highly important, and a convincing scientific explanation of the observed phenomena needs to be addressed.

In recent years, atomic layer deposition (ALD) has drawn significant interest for growing ZnO thin films using sequential, self-limiting surface

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reactions [40-44]. ALD technique was originally introduced as atomic layer epitaxy (ALE) and was first developed by T. Suntola and co-workers in Finland in 1977, for depositing ZnS for flat panel displays [45]. As further ALE processes were advanced to deposit metals and metal oxides, many materials were deposited nonepitaxially and because of that, the more general name of ALD was adopted [46]. ALD is a vapor-phase deposition technique which occurs through sequential self-limiting surface reactions [47]. Over other thin film deposition techniques, ALD offers several advantages such as excellent conformality, precise thickness control down to atomic level, pinhole-free films, and high degree of reproducibility [46, 48-50]. Also, ALD grown ZnO thin film generally shows n-type conductivity due to native crystallographic defects such as oxygen vacancies and interstitial zinc which behave as electron donors; which makes it an important candidate for use in different relevant applications [5, 41, 51].

When ZnO films and associated devices are scaled down to nanoscale regime, the surface to volume ratio increases and the surface and interface play an important role in determining the material's properties, consequently the nanoscale structures exhibit some unique properties different from their bulk counterparts [29, 32, 52]. The appropriate scientific understanding of these phenomena is essential. In this respect, the size dependence, which provides us the possibility to tune the material properties, is of great interest to be studied.

In this work, in the first part, ALD technique was employed to grow ZnO thin films of different thicknesses (ranging from ~5 nm to ~70 nm) with very low surface roughness and bulklike electron density, on two different selected substrates, silicon (Si) and fused quartz (SiO₂), to study the surface/interface effects on optical properties of ZnO [53-55]. The interface of ZnO/Si (wider-band gap ZnO deposited on narrower-band gap

Si, with staggered type band alignment) corresponds to the staggered type-II quantum well, whereas in the case of ZnO deposited on wider band gap SiO₂ corresponds to type-I quantum well [56, 57]. The real and imaginary parts of the complex dielectric function of ZnO/Si showed monotonically decreasing values with decreasing ZnO film thickness at and below a threshold of about 20 nm. The reduction of the dielectric function with film thickness was explained consistently by the Tanguy-Elliott amplitude pre-factor governing the strength of optical interband transitions [58] through the lowering of the electron-hole overlap factor at the ZnO/Si interface. In the case of ZnO/Si, a staggered type-II (spatially indirect) quantum well, holes are scattered into the Si substrate, causing a lowering of the electron-hole overlap factor and thus the reduction of excitonic absorption, consequently a decrease in the real and the imaginary parts of the dielectric function. This hypothesis was confirmed with ZnO films grown on SiO₂, where a thin type-I quantum well, consisting of a narrower-bandgap semiconductor grown on a wider-bandgap (insulator) substrate, in which both the electron and the hole are confined in the ZnO thin film, leads to an increase in the electron-hole overlap matrix element with decreasing film thickness due to confinement, resulting in enhancement of the excitonic absorption in thinner ZnO films on SiO₂ [53, 54].

As an effect of surface and interface in ZnO thin films, a blue shift of the absorption edge with decreasing film thickness at and below ~ 20 nm was also reported. Thickness dependent blue shift, energy vs. $1/d^2$ (where d represents ZnO film thickness) in two different systems, ZnO/Si and ZnO/SiO₂, showed a difference in their slopes. The observed phenomena were also consistently explained by the corresponding exciton (or carrier/s) deconfinement and confinement effects at the ZnO/Si and ZnO/SiO₂ interface respectively, where Tanguy-Elliott amplitude prefactor plays the key role through the electron-hole overlap factor at the interface.

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The optical study was conducted on two different sets of ALD grown ZnO samples, grown at two different growth temperatures, at high temperature (200 °C) and at near room temperature (35 °C), where we observed the consistent results with similar interface dependent trends in thickness dependent optical properties of ZnO.

The structure and morphology of the ZnO films were studied elaborately. The structural study showed that high quality, crystalline, smooth ZnO thin films with a preferred orientation along the <0002> direction with the c axis predominantly perpendicular to the substrate surface, was grown on both the substrates irrespective of the growth temperatures. Whereas, the growth temperature dependent variation in surface morphology of ZnO films were observed. ZnO grown at high temperature exhibited wedge-shaped grains (in-plane size along major and minor axes are ~40 and ~20 nm, respectively) in their surface morphology, and in case of near room temperature growth, a spherical/circular (~20 nm) in-plane shape was predominant [53, 54].

Application of ALD grown ZnO in a specific utility as an efficient electrode in rechargeable battery was explored in the second part of our study.

Electrochemical Energy Storage (EES) has emerged as a bottleneck technology to enable a large-scale integration of renewable energy sources, such as solar or wind energy, into the electric power grid [59]. Combined with the dwindling resources of fossil fuels, there have been tremendous research activities to develop highly efficient energy storage and recovery devices. Batteries have played a dominant role in the electrochemical energy storage field for many decades, and they have enabled a transformative change in telecommunication, mobile computing, and countless every-day tools and applications. The basics of batteries have been discussed in details in Chapter 3, section 3.3.

Zinc oxide (ZnO) has been regarded as a promising electrode material in Li-ion batteries due to its high theoretical capacity (987.8 mAh g⁻¹), high
lithium-ion diffusion coefficient, in addition to its non-toxicity, environmental friendliness and very low cost [18, 60, 61]. It is worth mentioning that for triply charged Al^{3+} ion insertion, the theoretical capacity of ZnO could reach as high as ~2960 mAh g⁻¹ [62, 63]. Hence it remains absolutely essential and worthwhile to conduct in-depth study on ZnO as a potential cathode material for rechargeable Al-ion battery application.

Due to the low cost, higher safety, low-flammability, lower reactivity, environmental friendliness and natural abundance of Al, the Al-ion battery, as new efficient electrical energy storage device, has displayed excellent prospects [62, 64, 65]. Aluminium is the third most abundant element and the most abundant metal in the earth's crust and its cost is much lower than that of most other metals used for electrochemical energy storage [64, 66]. Aluminium is attractive as a negative electrode material because it has a relatively low standard reduction potential (-1.66 V vs. standard hydrogen electrode). Aluminium also delivers high specific capacity (2,980 mAh g⁻¹) originating from its low atomic weight and the trivalent character of the ion [67]. Most significantly, the high material density ($2.70 \text{ cm}^3 \text{ g}^{-1}$) of aluminium leads to volumetric capacity of around 8,046 mAh cm⁻³, which is four times higher than that of lithium (2,062 mAh cm⁻³) [67].

The continuous, uniform and pinhole-free, conformal nature of ALD grown thin film of active electrode material can eliminate any possibilities of interference/contribution of the current collector to the performance of the electrode in the battery. The use of ALD technique to grow the active electrode materials on current collector could be explored to achieve potential binder-free electrode to fabricate the light-weight battery, which is very important and beneficial for portable electronics applications with low power consumption [68, 69]. Moreover, ALD grown highly c-axis oriented ZnO thin films show enhanced conductivity than those with randomly oriented grains [70], which facilitates the required electrical

contact and enhanced pathways for electron/ion transfer/transport kinetics in the potential electrode. Thus, ALD grown ZnO thin film on current collector was studied to explore its potential as an efficient electrode in fabrication of light-weight binder-free battery. In this part of the work, we report for the first-time binder-free ZnO synthesized by ALD as a novel cathode material for the rechargeable Al-ion batteries.

Nanoscale ZnO, directly grown on current collector through ALD, shows high electrochemical performance as a binder-free cathode for rechargeable Al-ion batteries (AIBs). Al coin cell fabricated using binderfree ALD grown ZnO cathode (ZnO ALD-E) manifests an initial discharge capacity of 2563 mAh g⁻¹, and remains at 245 mAh g⁻¹ at a current rate of 400 mA g⁻¹ after 50 cycles with almost 95% Coulombic efficiency. Distinct and consistent plateaus in discharge/charge curves reveal the Al-ion insertion/extraction process and electrochemical stability of the battery. The delivered discharge capacity of the battery with ZnO-ALD-E cathode is significantly higher (about 10 times higher) than that of batteries fabricated using a conventional ZnO cathode composed of ZnO powder (nanoparticles or bulk) and binder with conductive carbon. Ex-situ XRD and Photoluminescence spectroscopy in different discharge/charge states of Al/ZnO ALD-E battery reveal the structural information of ZnO_ALD-E, upon Al-ion intercalation/deintercalation. Such remarkable electrochemical performance is attributed to the binder-free, well-defined textured nanostructures of ALD grown ZnO cathode with c-axis orientation along the surface normal, facilitating good electrical contact and enhanced pathways for electron/ion transfer/transport kinetics. As a result, ZnO_ALD-E turns out to be a potential candidate for being used as the electrode in fabricating high-efficiency rechargeable Al-ion battery. The present study shows a multi-faceted approach for identifying and predicting promising Al-ion insertion properties for advanced Al-ionbased energy storage material. The approach reported here is potentially applicable for other relevant electrode materials (with a large volume

change and low electric conductivity) and may suggest a new path to produce high-efficiency next generation green rechargeable batteries [71].

Objectives and scope of this work:

The work is focused towards the study of surface and interface effects in structure, morphology and properties of ALD-grown ZnO thin films and explore its application in rechargeable batteries.

Broadly, the objective can be divided into the following categories:

(i) To study the surface/interface effect in structure, morphology and optical properties of ALD-grown ZnO thin films:

- a) ZnO thin films of different film thicknesses (~5 nm to ~70 nm) were grown by ALD on different substrates at two different growth temperatures, high temperature (200 °C) and near room temperature (35 °C)
- b) Study the effect of film thickness and growth temperature on the structure and morphology of ZnO thin films
- c) Study the change in optical properties of ZnO thin films as an effect of confinement
- d) Study the effect of interface in optical properties of ZnO thin films

(ii) Applications of ALD grown ZnO thin films as a potential binder-free cathode in rechargeable Al-ion batteries.

Thesis outline:

The chapter contents of the thesis are summarized as follows:

Chapter 1: It provides an introduction and discusses the current status of the problem dealt here and defines the objectives.

Chapter 2: It deals with the details of the experimental methodology used for the experimental work carried out in the thesis and procedures for the

fabrication of the ZnO thin films/nanostructures and devices. The general background and overview of atomic layer deposition (ALD) technique are also summarized in this chapter, along with its mechanism, characteristics, and unique advantages over other thin film deposition techniques. It also summarizes various equipment used for various measurements carried out during the research work.

Chapter 3: Theoretical backgrounds of characterization techniques, such as overall X-ray scattering (X-ray reflectivity and X-ray diffraction), spectroscopic ellipsometry, UV-Vis spectroscopy, photoluminescence, X-ray photoelectron spectroscopy, Raman spectroscopy are discussed in this chapter. The basics of battery and relevant electrochemistry are also discussed in this chapter.

Chapter 4: This chapter presents the effect of film thickness (about 5 nm to 70 nm) and growth temperature on the structure and morphology of ALD-grown ZnO thin films.

Chapter 5: This chapter discusses the variation in optical properties of ZnO films as an effect of confinement. The effect of interface is explored through detailed study of optical properties of ZnO thin films grown on two different selected substrates, silicon (Si 001) and fused quartz (SiO₂). The significant effect of interface in optical properties of ZnO thin films is observed and explained by the theoretical expression / Tanguy's proposition.

Chapter 6: This chapter discusses the importance of ALD grown ZnO films as high performance, binder-free, light weight cathode material in low-cost, safer rechargeable Al-ion battery application.

Chapter 7: This chapter summarizes the results and conclusions, based on the research work reported above. This chapter also discusses possible future scope of work that can be carried out for further development in this field.

Sample Preparation and Characterization Techniques

This chapter deals with the details of the experimental methodology used for the experimental work carried out in the thesis and procedures for the fabrication of the ZnO thin films/nanostructures and devices. The general background and overview of atomic layer deposition (ALD) technique are also summarized in this chapter, along with its mechanism, characteristics, and unique advantages over other thin film deposition techniques. It also summarizes various equipments used for various measurements carried out during the research work. Furthermore, more specific details about synthesis of samples (e.g., growth parameters) and characterization techniques are discussed accordingly in the 'Experimental' section of Chapter 4, Chapter 5 and Chapter 6.

2.1 Sample Preparation

In this work, ALD technique was employed to grow ZnO thin films on different substrates at different process temperatures (i.e., growth temperatures).

The fundamentals of atomic layer deposition technique, i.e., the basic principle, characteristics, and instrumentation of the ALD technique is discussed here.

2.1.1 Atomic Layer Deposition (ALD) Technique

2.1.1.1 A briefing on traditional thin film deposition techniques

Before we discuss atomic layer deposition (ALD) technique, it is necessary to know the other thin film deposition techniques, such as physical vapor deposition (PVD) and chemical vapor deposition (CVD). Physical vapor deposition (PVD) refers to a variety of vacuum deposition methods which can be used to produce thin films and coatings [72, 73]. PVD is divided into two main categories, i.e., evaporation and sputtering. In PVD process, atoms or small clusters of atoms are removed from a source and those atoms are traveling in a vacuum chamber reaching a substrate to form a thin film. The nucleation and the growth of thin films generally happen via condensation of individual atoms or polyatomic species striking the substrate surface. The rate of deposition depends principally on system pressure, source to substrate distance and substrate temperature.

On the other hand, in a CVD process, a solid material is deposited onto a heated substrate surface as a result of chemical reactions in gas phase inside the reactor [74]. Basically, the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired coating.

Both PVD and CVD have been widely applied to deposit a broad variety of thin films. However, these two commonly suffer from some drawbacks. Both these processes are source-controlled in which films are deposited continuously. For these processes, pinholes are inevitable and precise thickness control cannot be done [50]. Both of them have trouble to achieve uniform coating on the surface with high aspect ratio feature. Over these deposition techniques, ALD offers several advantages such as excellent conformality, precise thickness control down to atomic level, pinhole-free films, and high degree of reproducibility [48], as will be discussed in the following sections.

2.1.1.2 Fundamentals of ALD

Atomic layer deposition (ALD) is a technique capable of depositing a variety of thin film materials from the vapor phase [46]. In recent years, ALD has shown great potential in emerging semiconductor and energy conversion technologies. As device requirements push toward smaller and more spatially demanding structures, ALD has demonstrated potential advantages over alternative deposition methods, due to its excellent conformality, and control over materials thickness and composition [46, 75]. These unique characteristics originate from the cyclic, self-saturating nature of the ALD process.

(a) Mechanisms

A schematic of general ALD process is shown in Figure 2.1. A typical ALD process consists of sequential alternating pulses of gaseous chemical precursors that react with the substrate surface. These gas-surface reactions are known as 'half-reactions'. First, precursor A is pulsed into the reactor chamber under vacuum for a chosen period of time to allow the precursor for fully reacting with the substrate surface via a self-limiting process. Afterward, the chamber is purged with an inert carrier gas (usually N_2 or Ar) for removing any unreacted precursor or unwanted reaction by-products. This is then followed by the counter-reactant precursor (precursor B) pulse and inert gas purge, creating up to one layer of the desired material. This process is repeated until the desired film thickness has been achieved.



Figure 2.1: Schematic of the sequential ALD process. (i) Functionalized substrate, (ii) Precursor A is pulsed into the ALD chamber and it reacts with the substrate surface, (iii) Excess precursor and reaction by-products are purged with the inert carrier gas, (iv) Precursor B is pulsed into the ALD chamber, (v) Excess precursor and reaction by-products are purged with the inert carrier gas, and (vi) Steps ii–v are repeated until the desired film thickness is achieved.

The surface reactions in ALD differ significantly from other deposition techniques due to the sequential supply of the reactive precursor gases. To demonstrate the surface chemistry of the ALD process in detail, we illustrate in Figure 2.2, a schematic of ALD deposition of zinc oxide (ALD-ZnO). The most successful ALD process of ZnO (ALD-ZnO) uses diethylzinc (DEZ, Zn (C_2H_5)₂) and water (H_2O) as precursors, as displayed in Figure 2.2. The principle of ALD-ZnO growth from DEZ and H_2O is subjected to the two self-terminating reactions as follows [76, 77]:

$$ZnOH^* + Zn(CH_2CH_3)_2 \rightarrow ZnO - ZnCH_2CH_3^* + CH_3CH_3$$
(2.1)

$$ZnCH_2CH_3^* + H_2O \rightarrow ZnOH^* + CH_3CH_3$$
(2.2)



Figure 2.2: Schematic representation of ALD-ZnO growth.

It should be noted that, for an ALD process, there are three key parameters which jointly determine the deposition features. These are deposition temperature, precursors and purging time. First of all, deposition temperature is one of the crucial factors for sustaining ALD characteristics. As already discussed, ALD performs in a self-limiting manner and therefore it needs the adsorption of precursors to be chemisorption rather than physisorption [78]. Therefore, the lowest temperature acceptable for ALD should be able to minimize physisorbed ligands. In addition, a suitable ALD temperature should not decompose any precursor. Otherwise, the deposition will proceed in a CVD manner rather than an ALD one. Contrary to CVD, ALD typically proceeds at much lower temperatures, even down to room temperature (RT) [78].

There may exist a temperature range in which the growth rate of ALD is comparatively constant, referred to as the 'ALD temperature window'. Secondly, ALD precursors should provide sufficient vapors, and their concentrations in the gaseous phase must exceed a threshold value to saturate all the adsorption sites on a substrate in order to reach continuous monolayer coverage [79]. Furthermore, complete purging of excess precursors and reaction by-products is also required for avoiding continuous processes (e.g., CVD and PVD) and for accurately controlling the ALD growth per cycle (GPC). Hence, the purging time must be sufficiently enough to completely remove the excess precursors and reaction by-products, or the purges need to be elongated.

(b) Characteristics

The unique reaction mechanisms and operation of ALD bestows several distinct advantages over its vapor-phase counterparts (e.g., Chemical vapor deposition, CVD and Physical vapor deposition, PVD) and also solution-based methods, as mentioned below.

(i) Excellent uniformity and conformality

One of the main advantages of ALD is the excellent uniformity and conformality of the deposited films in comparison to those generated by CVD, PVD, and solution-based methods [78]. From atomic force microscopy (AFM), it is revealed that ALD-Al₂O₃ on flat substrates presents a surface roughness of 1-3 Å for a deposition in the range 200-560 Å [79-81]. The surface roughness of ALD grown films are very low compared to that of CVD and PVD. Apart from the uniformity, ALD offers highly conformal films on non-planar substrates as well. No other deposition technique can coat high aspect ratio structures as uniform and conformal as ALD does. Additionally, the ALD grown films are very sharp interfaces.

(ii) Precise control at atomic scale and stoichiometric deposition

Due to the layer-by-layer self-limitation, the precise control of the deposited films at the atomic scale has been achieved [75]. This feature makes ALD superior to CVD, PVD, and solution-based methods. Generally, the growth rates of ALD are at the order of magnitude of angstroms (typically less than 2 Å per cycle), jointly determined by the deposition temperature and substrate. For example, the growth rate for ALD-ZnO by using DEZ and water precursors is around ~ 0.8-2 Å/cycle depending upon the growth temperature in the range between room temperature to 240 °C [5, 82]. Also, the growth rate for ALD-Al₂O₃ by using trimethylaluminum (TMA) and water precursors is around ~1.1-1.3 Å/cycle in the temperature range 33-177 °C [83]. In addition to the control on growth rates, ALD is also capable of stoichiometrically tuning the compositions of deposited materials. The ALD-grown films stoichiometry is close to their theoretic values, but deposition temperatures may play some role [78]. For example, E. Guziewicz et al. demonstrated that the O/Zn ratios in ALD-ZnO varied from 0.9 to 1.01 in the temperature range 100-300 °C [84].

(iii) Low growth temperature

Another distinct advantage of ALD, especially in comparison to CVD, is its much lower growth temperature (typically less than 300 °C, versus 600–1000 °C for CVD) [46, 78]. In particular, ALD is capable of depositing many materials at temperatures below 100 °C, even down to room temperature. The metal oxides deposited by ALD at or around room temperature include Al₂O₃ [83, 85], ZnO [86], TiO₂ [85], ZrO₂ [87], and SnO₂ [88] etc. Additionally, some metals such as Cu [89] and Pd [90] were also deposited by ALD at a temperature below 100 °C. The interest in low-temperature ALD processes has been gradually increasing in the past few years. Film deposition at low temperatures enables us to use temperature-sensitive substrates such as polymers and biological materials, which could be destroyed at conventional process temperatures

[82]. ALD coated polymers and biomaterials have potential applications in different fields such as flexible electronics and food packaging [82].

2.1.1.3 Experimental set up of ALD:

The experimental set up of our ALD system is shown in Figure 2.3. BENEQ TFS-200 ALD reactor is used in this work.



Figure 2.3: ALD system used in the present research work.

Figure 2.4 shows the simplified schematic of the ALD reactor used in our research work.



Figure 2.4: Simplified schematic of the ALD reactor used in the present research work.

The precursors were alternately pulsed into the reactor chamber under vacuum (typically less than 5 mbar) using their intrinsic vapor pressures from external containers, i.e., bubbler cylinder. For the deposition of ZnO thin films, diethyl zinc [DEZ, Zn (C_2H_5)₂, Sigma-Aldrich] and deionized (DI) water were used respectively as precursors for zinc and oxygen. High purity Nitrogen gas (N_2 , 99.999% purity) was used both as a carrier and purging gas. One ALD reaction cycle consisted of pulsing of DEZ precursor, followed by a N_2 purge, then pulsing of H₂O precursor, and then another N_2 purge. The number of ALD cycles has been chosen until the desired film thickness has been achieved.

2.2 Physical Characterization Techniques

2.2.1 X-ray Scattering

X-ray scattering techniques, e.g., X-ray reflectivity (XRR) and X-ray diffraction (XRD) have been used in the present study. Thickness, surface and interface roughness and electron density profile (EDP) of the ZnO films were obtained by using X-ray reflectivity (XRR) measurements. The crystalline structures of the ZnO films were investigated by X-ray diffraction (XRD). The theoretical background of X-ray scattering has been discussed in details in Chapter 3, section 3.1.

Experimental set up:

XRR and XRD measurements were performed using Rigaku SmartLab automated multipurpose X-ray diffractometer with CuK_{α} radiation ($\lambda = 1.54$ Å).

X-ray diffractometer generally consists of three basic elements:

- (i) X-ray source
- (ii) Sample stage
- (iii) X-ray detector

X-rays for research purposes are produced in a standard way: by accelerating electrons with a high voltage and allowing them to collide with a metal target. X-rays are produced when these electrons are suddenly decelerated upon collision with the metal target; these x-rays are called brehmsstrahlung or "braking radiation". If the bombarding electrons have sufficient energy, they can knock an electron out from the inner shells of the target metal atoms. Then electrons from higher states drop down to fill the vacancy, emitting x-ray photons with precise energies determined by the electron energy levels. Those x-rays are called characteristic x-rays. Characteristic x-rays are used for the investigation of crystal structures by x-ray diffraction. Copper is the most common target material for X-ray diffraction, with CuK_a radiation ($\lambda = 1.54$ Å).

These X-rays are collimated and directed onto the sample. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as computer monitor. The experimental set-up is shown in Figure 2.5.



Figure 2.5: X-ray diffractometer used in the present research work.

2.2.2 Scanning Electron Microscopy

A scanning electron microscope (SEM) uses a beam of electrons to image the samples by scanning the surface in a raster scan pattern. SEM is one of the most widely used microscopes in the research community because of its extremely high magnification, higher resolution, larger depth of focus and ease of sample observation [91, 92].

Working principle:

Scanning electron microscope uses a beam of electrons to image the samples. An SEM consists of the following components: (i) an electron gun, (ii) electromagnetic lens system, (iii) detectors and (iv) sample holder. The electron gun delivers an intense beam of high energy electrons. There are two types of electron guns, which are thermionic gun and field emission gun. The thermionic gun uses a heated filament to overcome the work function of the filament material, so that the electron can escape from the material itself. Whereas, the field emission gun uses a large electrical potential gradient across the filament to pull out the electrons. The electron beam follows a vertical path through the column of the microscope. It passes through the electromagnetic lenses which focus and direct the beam down towards the sample. Figure 2.6 shows the schematic of a field emission scanning electron microscope (FESEM) instrument.

The high energy electrons upon interaction with the samples undergo either inelastic scattering with the atomic electrons or elastic scattering with the atomic nucleus. As a result of electron and sample interaction, backscattered electrons (BSEs), secondary electrons (SEs), and characteristics X-rays are produced. Several detectors are employed to detect these BSEs, SEs, and X-rays. The secondary electrons produce the most detailed image of the surface of an object, while BSEs image can provide atomic number contrast in addition to topographic contrast. X-ray detectors give information on the material composition.



Figure 2.6: Schematic of the field emission scanning electron microscope (FESEM) instrument.

The sample stage holds the sample on a small stainless steel circular plate called 'stub' (size $\sim 8 \times 8$ mm). In this work, the surface morphologies of ZnO films were examined by field emission scanning electron microscopy (FESEM, JEOL JSM-7600 F).

2.2.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is one of the most versatile and powerful microscopy technologies for studying the samples at nanoscale [93]. AFM is a kind of scanning probe microscope in which a topographical image of the sample surface can be obtained based on the interactions between a tip

and a sample surface. The atomic force microscope was invented by Gerd Binning *et al.* in 1986 at IBM Zurich [94].

Working Principle:

A typical AFM consists of a microcantilever with a small tip (probe) at its free end, a laser, a four-sectional photodiode, and a piezoelectric scanner. Figure 2.7 shows a schematic of the experimental set up of AFM.



Figure 2.7: Schematic of the AFM setup.

In AFM, a tip is used for imaging the sample. The tip is generally made of silicon or silicon nitride (Si_3N_4) material. It approaches the sample in a range of interatomic distances (~ 10 Å). It is attached to the end of the spring cantilever. When the tip comes very close to the sample surface, due to the interactions between the tip and the sample surface, attractive and repulsive forces act and cause a negative or positive bending of the cantilever. This bending is detected by the help of a laser beam. The

cantilever can be thought of like a spring. The generated force between the tip and the surface depends on the spring constant of the cantilever and the distance between the tip and the surface. This force can be described with Hooke's Law:

$$F = -k.x \tag{2.3}$$

Where F is the force, k is the spring constant and x is the cantilever deflection.

As the tip travels across the sample surface, it moves up and down according to the surface properties of the sample (i.e., topography). These fluctuations are sourced by the interactions (i.e., electrostatic, magnetic, capillary, Van der Waals) between the tip and the sample. The displacement of the tip is then measured and a topographical image is obtained.

Generally, the AFM probe does not move. Instead of its motion, the sample is moved in the x, y, z directions by a piezoelectric material. When a voltage is applied, the piezoelectric materials can enlarge or shrink. By this approach, very precise movements in the x, y, z directions can be possible. A laser beam is focused onto the back of the cantilever. It can be reflected back to a four-sectional photodiode detector. By the help of this position sensitive photodiode, the bending of the cantilever can be measured precisely. The cantilever deflects according to the atomic force variations between tip and the sample and thereby the detector measures the deflection. The created image is a topographical illustration of the sample surface.

The AFM can be operated in three modes, depending on the application. These three modes are classified, according to the nature of the tip motion: (i) contact mode, also called static mode; (ii) tapping mode, also called intermittent contact; and (iii) non-contact mode. In this work, AFM measurements of the ZnO films were performed in the tapping mode using a Bruker Dimension icon with ScanAsyst (Bruker, Santa Barbara, CA).

2.2.4 Spectroscopic Ellipsometry

Spectroscopic Ellipsometry (SE) is a versatile thin film characterization technique that has applications in many diverse fields. The main advantages of the SE technique are its precision and nondestructiveness [95, 96] and, particularly, the ability to measure simultaneously the thicknesses and the optical constants of the system [96].

Spectroscopic Ellipsometry uses the fact that light undergoes some change in polarization when it is reflected off the surface of a material. The polarization state of the light wave is changed from linearly polarized to elliptical polarized, thereby the name "ellipsometry". The polarization change is characteristic of the surface structure of the sample and we can obtain various information about the material, such as, optical properties, film thickness, surface-interface roughness, simply by analyzing the reflected light beam. The detailed theory and data analysis of spectroscopic ellipsometry have been discussed in Chapter 3, section 3.2.1.

Experimental set up:

A general ellipsometer configuration is depicted in Figure 2.8. As can be seen from Figure 2.8, the light source emits unpolarized light, which is linearly polarized by the polarizer. After reflection at the sample surface, the polarization state of the light wave is changed from linearly polarized to elliptical polarized. The analyzer is rotated and the light intensity is measured at different rotational azimuth angles of the analyzer. Finally, the detector measures the intensity of the light from the analyzer.



Figure 2.8: Schematic of the ellipsometry setup.

In this work, spectroscopic ellipsometry measurements were performed on ZnO thin films deposited on Si substrates with an ellipsometer (J.A. Woollam, Co., Lincoln, NE, Model: VASE) in the photon energy range of 0.8–6.5 eV at three incident angles of 60°, 65°, and 70°. Ellipsometry techniques have been extensively used to explore the optical properties of the ZnO films, namely, complex dielectric function, absorption coefficient, and band gap along with the film thickness and surface roughness, using the WVASE (J.A. Woollam, Co.) software.

2.2.5 UV-Visible Spectroscopy

Ultraviolet-visible (UV-Vis) spectroscopy refers to absorption or reflection spectroscopy in UV-Vis spectral region. When irradiated, molecules in a sample absorb light in the ultraviolet and visible part of the electromagnetic spectrum and undergo electronic transitions which give rise to UV-Vis spectra. UV-Vis spectroscopy is a reliable analytical tool for the qualitative and quantitative analyses of samples [97, 98]. The detailed theory of UV-Vis spectroscopy has been discussed in Chapter 3, section 3.2.2.

Experimental set up:

The basic parts of the spectrophotometer are a light source, a diffraction grating in a monochromator, and a detector (see Figure 2.9). The light source consists of two lamps: deuterium arc lamp (or D_2 lamp), which is in the range of 190 nm to 370 nm, used for UV region; and tungsten lamp (320-1100 nm) used for visible region.



Figure 2.9: Schematic of the UV-Visible spectrophotometer.

The scanning monochromator allows the diffraction grating to "step through" each wavelength so that its intensity may be measured as a function of wavelength. This spectrophotometer is basically a doublebeam instrument. The light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% transmission (or 0 absorbance), and the measurement displayed is the ratio of the two beam intensities. The output of the detector is a plot of intensity versus wavelength which contains information about the sample. The detectors employed are typically photomultiplier tube, a photodiode or charged coupled devices.

In this work, UV-Vis absorption spectra of ZnO films, deposited on fused quartz substrates (SiO₂), were measured using a UV-VIS spectrophotometer in transmission mode (Perkin Elmer, lambda-35) in the wavelength (λ) range of 190–1100 nm.

2.2.6 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a very efficient and important tool for the investigation of the optoelectronic properties of materials [99, 100]. When electron-hole pairs are generated in a semiconductor, or when carriers are excited into higher energy levels from which they fall to their equilibrium states, light can be given off by the material [101]. Many of the semiconductors are well suited for light emission, particularly the compound semiconductors with direct band gaps [101]. The general property of light emission is called luminescence. If carriers are excited by the absorption of photons, the radiation resulting from the recombination of the excited carriers is called photoluminescence. The detailed theory of Photoluminescence spectroscopy has been discussed in Chapter 3, section 3.2.3.

Experimental set up:

A typical schematic representation of PL spectrometer is shown in Figure 2.10. The basic equipment setup contains two main parts: (i) light source to provide excitation, and (ii) detection system to collect and analyze photons emitted from the sample.



Figure 2.10: Schematic of PL spectrometer setup.

In this work, the photoluminescence (PL) emission from the ZnO films was measured at room temperature using a PL spectrometer (Dongwoo Optron DM 500i) having an excitation source consisting of a continuous wave He-Cd laser (excitation wavelength, 325 nm, PMT detector).

2.2.7 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition, chemical state and electronic state of the elements that exist within a material [102, 103]. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material being analyzed. XPS can be used to analyze the surface chemistry of a material in its as-received state, or after some treatment. The detailed theory of XPS has been discussed in Chapter 3, section 3.2.4.

Experimental set up:

As Figure 2.11 illustrates, X-rays are directed onto the sample and the resulting photoelectrons are then focused onto the entrance slit of a concentric hemispherical analyzer. Here a negative and positive potential is applied to the outer and inner cylinders, respectively, such that the central line between the cylinders is a line of zero potential. Scanning the potentials allows control of the energy of electrons that are allowed to pass through the analyzer and onto the detector, usually a channel electron multiplier (channeltron).



Figure 2.11: Schematic of the XPS instrument setup.

In this work, the X-ray photoelectron spectroscopy (XPS) was tested with AXIS Supra photoelectron spectrometer (Kratos Analytical, A SHIMADZU Group Company) with Al K_{α} radiation (1486.6 eV).

2.2.8 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational and other low-frequency phonon modes in a system [104, 105]. It is based on inelastic scattering of monochromatic light,

usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman effect. This shift provides information about vibrational, rotational and other low-frequency transitions in molecules. Raman spectroscopy can be used to study solid, liquid and gaseous samples. The detailed theory of Raman spectroscopy has been discussed in Chapter 3, section 3.2.5.

Experimental set up:

Figure 2.12 shows the schematic of the experimental set-up of the Raman spectrometer. A Raman system typically consists of four major components: (i) excitation source (i.e., laser), (ii) sample illumination system and light collection optics, (iii) wavelength selector (filter or spectrophotometer), and (iv) detector (photodiode array, CCD or PMT).



Figure 2.12: Schematic diagram of the Raman spectrometer.

In this work, Raman spectra were obtained using a Raman spectrometer (LabRAM HR Evolution, HORIBA Scientific) with a 633 nm He-Ne laser focused to a spot of size $\approx 0.8 \ \mu m$ diameter on the samples.

2.3 Electrochemical Characterization Techniques

2.3.1 Fabrication of CR 2032 coin cells

To investigate the electrochemical performance of the ALD grown ZnO thin film (ZnO_ALD-E) in Al-ion batteries, the prototype CR 2032 coin cells were assembled inside an Argon-filled glove box (MBRAUN UNIlab Plus, Germany). The photograph of the glove box used in this thesis work is shown in Figure 2.13.



Figure 2.13: Photograph of argon-filled glove box used for the fabrication of batteries.

The schematic of the coin cell assembly has been shown in Figure 2.14.



Figure 2.14: Schematic for the coin cell assembly.

The fabricated CR 2032 coin cell performances have been evaluated through the following studies:

- (i) Cyclic voltammetry
- (ii) Galvanostatic charge-discharge studies

2.3.2 Cyclic Voltammetry

Cyclic voltammetry (CV) is a powerful and popular electrochemical technique commonly employed to investigate the reduction and oxidation processes of molecular species [106]. It is the most widely used technique for obtaining qualitative information about electrochemical reactions [107]. The power of cyclic voltammetry results from its ability to provide considerable information on the thermodynamics of redox processes, on the kinetics of electron-transfer reactions, and coupled chemical reactions or adsorption processes. It has been used extensively to characterize the performance of various electrical energy storage devices such as batteries, supercapacitors and fuel cells.

Basic Principle:

Cyclic voltammetry consists of scanning linearly the potential of a working electrode versus time. The working electrode potential is scanned using a triangular waveform shown in Figure 2.15. In this case the voltage

is swept between two values at a fixed rate, starting from $E_{initial}$; when the voltage reaches E_{final} the scan is reversed and swept back to $E_{initial}$. During this potential sweep, the potentiostat measures the current resulting from the applied potential. The resulting plot of current versus potential is termed a cyclic voltammogram (see Figure 2.16).



Figure 2.15: Potential-time signal in the cyclic voltammetric experiment.



Figure 2.16: Typical cyclic voltammogram for a reversible redox process [106].

2.3.3 Galvanostatic Charge-Discharge Techniques

The galvanostatic charge-discharge is a reliable method to evaluate the electrochemical performance of a battery under controlled current conditions [108, 109]. This technique is also termed as chronopotentiometry. It is the study of the variation of the potential of a working electrode with time upon imposition of a controlled current. In this technique, the controlled current will be applied between the working and counter electrodes using a galvanostat and the potential of the working electrode versus reference electrode will be monitored/measured simultaneously. The potential against time will be plotted as response and the plot is called as chronopotentiogram. In particular, chronopotentiometry technique is used to estimate the specific capacity and to evaluate the cycling stability of the battery.

In this work, Galvanostatic charge-discharge and cyclic voltammetry studies of the prepared coin cells were performed using battery testing system (CH Instruments, CHI423B). The photograph of the battery tester is shown in Figure 2.17.



Figure 2.17: Photograph of battery tester used in this work.

Theoretical Background

In this chapter, I would present the theoretical background necessary for an elucidation of the analysis of data which is acquired through experimental techniques in Chapter 2 and whose implications are discussed in Chapter 4, Chapter 5 and Chapter 6.

Theoretical backgrounds of characterization techniques, such as overall Xray scattering (X-ray reflectivity and X-ray diffraction), spectroscopic ellipsometry, UV-Vis spectroscopy, photoluminescence, X-ray photoelectron spectroscopy, Raman spectroscopy are discussed in this chapter. The basics of battery and relevant electrochemistry are also discussed in this chapter.

3.1 A Theoretical Background of X-ray Scattering

X-ray scattering techniques are a family of non-destructive analytical techniques revealing information about the crystal structure, chemical composition, and physical properties of the materials and thin films [110, 111]. X-ray scattering is a probe to investigate surfaces on angstrom scales. This technique is non-destructive and the specimen does not require special conditioning and measurements can be done under ambient conditions.



Figure 3.1: Schematic showing the generalized scattering geometry.

Figure 3.1 shows the schematic for scattering geometry in the general case of a surface experiment. The plane of incidence contains the incident wave-vector \mathbf{k}_i , and the normal to the surface. If \mathbf{k}_f is the scattered wave vector, then the momentum transfer vector \mathbf{q} is given by

$$\boldsymbol{q} = \boldsymbol{k}_f - \boldsymbol{k}_i \tag{3.1}$$

The components of q in x, y and z directions are given by

$$q_x = k_0 (\cos \theta_f \cos \psi - \cos \theta_i)$$
(3.2)

$$q_{\nu} = k_0 (\cos \theta_f \sin \psi) \tag{3.3}$$

$$q_z = k_0 \left(\sin\theta_f + \sin\theta_i\right) \tag{3.4}$$

Where the components of **q**, parallel to the sample surface are q_x , q_y and perpendicular to the sample surface is q_z .

Where $k_0 = 2\pi/\lambda$, λ being the wavelength of the incident radiation. In a reflectivity experiment, we work in the plane of incidence and thus have the in-plane angle $\psi = 0$. In specular reflectivity, incident angle (θ_i) and the scattered angle (θ_f) are kept equal. This gives information about the thickness and electron density profile of the individual layers and the interfacial roughness [112, 113]. Off-specular diffuse scattering ($\theta_i \neq \theta_f$) provides better understanding about the in-plane correlation and also the

correlation between the interfaces [112, 114]. Specular reflectivity technique is discussed below in detail.

3.1.1 X-ray Reflectivity

In X-ray reflectivity measurements, a well collimated monochromatic xray beam is made to be incident on the sample surface at a grazing angle θ_i (starting from few milli-radians) and the reflected intensity is recorded in the plane of incidence at an angle θ_f . If the angle of incidence of impinging x-rays is sufficiently small, the penetration depth and the scattering is limited to the near surface region.

X-ray reflectivity (XRR) is an important nondestructive characterization technique to study the structure and the organization of the thin films grown at the nanometric scales [111, 115]. The XRR technique has the following characteristics: (i) it can be used to measure film thickness precisely from few nm to 100 nm, (ii) it can be used to determine the surface and interface roughness and electron density of thin films, and (iii) it can be used to determine the layer structure of multilayer film.

Basic principles and Theory of X-ray reflectivity:

X-rays are part of the electromagnetic spectrum. The most widely used Xrays in materials science have a typical wavelength, of the order of 1 Å. The interaction of X-rays with matter can be described by the index of refraction, n, which basically characterizes the change of direction of the X-ray when passing from air to a material. The index of refraction for Xrays can be written as [111]:

$$n = 1 - \delta + i\beta \tag{3.5}$$

with,
$$\delta = \frac{\lambda^2}{2\pi} r_e \rho_e$$
 (3.6)

and,
$$\beta = \frac{\lambda}{4\pi}\mu$$
 (3.7)

Where δ and β stand for the scattering and absorption of the material, respectively; $r_e = 2.82 \times 10^{-15}$ m is the classical electron radius, ρ_e is the electron density of the material, and μ is the absorption length.

For X-rays, the refractive index of a material is slightly less than unity. For X-rays, when passing from air to the reflecting material, it is possible for the beam to totally reflect from the surface, if the incident angle, θ (the angle between the incident beam and the surface of the sample) is smaller than the critical angle θ_c . This is known as the total external reflection of X-rays. Then, from Snell's law:

$$\cos\theta_c = n = 1 - \delta \tag{3.8}$$

As *n* is very close to unity, the angle θ_c is very small and a Taylor series approximation in θ_c yields:

$$\theta_c^2 = 2\delta = \frac{r_e \lambda^2}{\pi} \rho_e \tag{3.9}$$

Using the values of the typical parameters given above, θ_c is of order one milli-radian.

When an X-ray beam is incident on a flat material, part of the incident intensity is getting reflected and part of it is getting transmitted through the material. If the surface of the material is flat, the reflected intensity will be confined in a direction symmetric from the incident one and will be named as specular. The specular reflectivity is defined as:

$$R(\theta) = \frac{I_r(\theta)}{I_0} \tag{3.10}$$

Where I_0 is the incident intensity and $I_r(\theta)$ is the reflected intensity at an angle θ . The domain of validity of X-ray reflectivity is limited to small incidence angles, where it is possible to consider the electron density as continuous [115]. In this approximation, the reflection can be considered as a classical problem of reflection of an electromagnetic wave at the interface. This leads to the classical Fresnel relationship which gives the reflection coefficient in amplitude for the (s) and (p) polarization. The

reflectivity which is the modulus square of this coefficient can be formulated in the case of X-rays as:

$$R(\theta) = rr^* = \left| \frac{\theta - \sqrt{\theta^2 - \theta_c^2 - 2i\beta}}{\theta + \sqrt{\theta^2 - \theta_c^2 - 2i\beta}} \right|^2$$
(3.11)

The equation (3.11) is independent of the polarization. The X-ray reflectivity is only observed in specular conditions (i.e., incident angle is equal to the exit angle). Figure 3.2 shows the geometry for XRR in specular conditions.



Figure 3.2: Geometry for X-ray reflectivity in specular conditions.

Specular reflectivity scans, i.e., scans in the plane containing the incident beam and the normal to the sample surface, with incident angle θ_i = scattering angle θ_f , were performed with varying the incident angle. If $q = k_f - k_i$ is the momentum transfer vector and k_f and k_i being the scattered and incident X-ray wave vector respectively, then this geometry makes the components in the sample plane, $q_x = q_y = 0$, and q_z (= $(4\pi/\lambda) \sin \theta_i$), the component normal to the sample surface. The X-ray reflectivity, $R(q_z)$, calculated from any electron density profile, $\rho(z)$, is [116, 117]:

$$R(q_z) = R_F(q_z) \left| \frac{1}{\Delta \rho} \int \frac{d\rho(z)}{dz} e^{-iz\sqrt{q_z(q_z^2 - q_c^2)^{1/2}}} dz \right|^2$$
(3.12)

Where, R_F is the Fresnel reflectivity from a single ideal step-function interface, $\Delta \rho$ is the total change in electron density across the interface and q_c is the momentum transfer at the critical angle for total external reflection. Equation (3.12) can be used to calculate $R(q_z)$ from a given analytic function $\rho(z)$, but, the reverse is not simple. When $R(q_z)$ is experimental data collected over a finite range and with finite accuracy, $\rho(z)$ cannot be directly calculated from it. The general procedure to solve the inverse problems has been employed for the analysis of x-ray reflectivity data: a model $\rho(z)$, specifically a slab model, is assumed, and parameters in the model are adjusted until good fits to the data have been achieved, following the Parratt formalism [118-122].

This expression for reflectivity (Equation 3.12) valid for an ideally smooth interface, is then modified in the presence of the Gaussian interface width or 'roughness' (σ) as:

$$R^{rough}(q_z) = R(q_z) exp(-q_z^2 \sigma^2)$$

(3.13)

The extracted values of film thickness, electron density and interface width or roughness from the best fit of reflectivity data, were used to construct the electron density profiles (EDPs), i.e., the electron density as a function of film depth from the top for thin films (ZnO thin films), after convoluting the profile with the interface widths.

Figure 3.3 shows the summaries of the effect of film thickness, electron density, surface roughness, and interface roughness on the X-ray reflectivity curve of ZnO thin films deposited on Si substrate. As shown in Figure 3.3, the reflectivity profile shows oscillations caused by the interference of X-rays. Interference occurs between the X-rays reflected
from the surface of the ZnO film and the interface between the ZnO film and Si substrate. These oscillations were first observed in 1931 by Kiessig and are called Kiessig fringes [123]. The period of oscillations depends on the film thickness; the thicker the film, the shorter the period of oscillations [124]. The amplitude of the oscillation depends on the difference between the electron densities of the film and the substrate (i.e., contrast of electron density); the large the difference in the electron density, the higher the amplitude of the oscillation [124]. The effects of surface and interface roughness on the X-ray reflectivity curve are as follows: intensity of reflected X-ray decreases more rapidly with a larger surface roughness; and amplitude of oscillations decreases with increasing interface roughness [124].



Figure 3.3: Information provided by X-ray reflectivity profile: X-ray reflectivity data for ~ 9 nm ZnO film on Si.

The X-ray reflectivity data (shown in Figure 3.3) has been fitted by the Parratt formalism and Figure 3.4 shows the corresponding electron density profile (EDP) of ~ 9 nm ZnO film on Si extracted from XRR fit.



Figure 3.4: Corresponding extracted electron density (ρ) profile from XRR fit for ~ 9 nm ZnO film on Si.

3.1.2 X-ray Diffraction

X-ray diffraction (XRD) is one of the most suitable and reliable technique to probe the structure of a material as the wavelength of X-rays (of the order of Å) is comparable to the interatomic distances [125, 126]. XRD is a non-destructive method of assessing the d-spacing (spacing between successive atomic planes), and therefore the lattice constants. Strain and mean crystallite size can also be estimated from the XRD data. In XRD, X-ray is incident on the material at some incidence angle, gets diffracted through a different set of atomic planes present in the crystal structure. When, both, d (d-spacing) and θ (the angle of incidence of X-ray), satisfies the Bragg relation, $2d \sin \theta = n\lambda$ (here, d is the inter-planer distance, λ is wavelength of incident X-ray and *n* is an integer), constructive interference takes place between the diffracted waves. The diffracted X-ray photons are detected and counted by the detector. In this way, with the satisfaction of Bragg's condition, a peak, across the corresponding 2θ value appears in the intensity (I) versus angle (2θ) curve. Conversion of the diffraction peaks to d-spacing enables the identification of the material under investigation. It is worth mentioning that the XRD pattern of each element/material is unique and can be considered as a signature of its structural phase. This uniqueness enables the XRD to identify and validate the purity of a structural phase for a given material.

XRD pattern contains almost complete information about the crystal structure, like-lattice parameters, grain size, strain, phase composition, orientation etc... Schematic of the geometry for XRD set up is shown in Figure 3.5. Here, 2θ is the angle between incident beam and diffracted beam, φ is angle of rotation about a plane perpendicular to the surface, χ is angle about the line parallel to the surface, whereas, ω is the angle between incident X-ray beam and sample surface. In ' θ -2 θ ' scanning, angle ω is treated as θ . Depending upon the type of information to be extracted; XRD can be operated in different scanning modes.



Figure 3.5: Schematic of the geometry for XRD.

3.2 A Theoretical Background of Spectroscopic Analysis

3.2.1 Spectroscopic Ellipsometry

Theory:

Spectroscopic Ellipsometry does not directly measure thickness or optical constants, instead, it measures the change in light polarization expressed as ψ and Δ . ψ and Δ determine the differential changes in amplitude and phase, respectively, experienced upon reflection by the components of the electric field vector parallel and perpendicular to the plane of incidence. Spectroscopic ellipsometry measures the Jones ratio, *J*, as a function of

photon energy (*E*) and angle of incidence (ϕ), described by the equation [127-129]:

$$J(E,\phi) = \frac{r_p}{r_s} = (\tan\psi)e^{i\Delta}$$
(3.14)

Where, r_p and r_s are the complex Fresnel reflectance ratios for p and s polarized light, respectively. ψ and Δ are the ellipsometric angles corresponding to the amplitude ratio and the relative phase change, respectively [128, 130].

Ellipsometry data analysis:

Figure 3.6 summarizes the process of ellipsometry analysis. It is an indirect method. The first step is to collect the SE data in the form of ψ and Δ . After that, the sample is described using a theoretical optical model, which represents layer thicknesses and optical constants for each material. Reference optical constant values for many materials are already available in the literature. The model optical constants are then allowed to vary to 'best match' the experimentally measured ψ and Δ data. Basically, the regression analysis is used. The unknown model parameters are varied to improve the match between model-generated curves and experimentally collected data by minimizing differences between the curves, as described by mean squared error (MSE) value. The model can be modified, in a further attempt to improve the match between models predicted data and measurement. SE measurements are commonly used to determine thin film thickness, surface-interface roughness and optical properties.



Figure 3.6: Schematic for spectroscopic ellipsometry measurements and data analysis.

There is a correlation between the experimentally measured ψ and Δ with the optical constants through the following equation [130]:

$$\langle \tilde{\mathbf{n}} \rangle^2 = \sin^2 \phi \left[1 + \tan^2 \phi \cdot \left(\frac{1-J}{1+J} \right)^2 \right]$$
(3.15)

Where, \tilde{n} is complex refractive index, *J* is the Jones ratio as described in Equation (3.14) and ϕ is the angle of incidence in ellipsometry measurement.

The optical properties of the ZnO thin films, namely, complex dielectric function (ε), complex refractive index (\tilde{n}), absorption coefficient (α), and band gap were determined using ellipsometry.

Complex dielectric function has been defined as:

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \tag{3.16}$$

Where, ε_1 and ε_2 are the real and imaginary part of the complex dielectric function, respectively.

Complex refractive index has been defined as:

$$\tilde{\mathbf{n}} = \mathbf{n} + i\mathbf{k} \tag{3.17}$$

Where, n and k are refractive index and extinction coefficient, respectively.

There exists a relationship between ε and \tilde{n} , which is:

$$\varepsilon_1 = n^2 - k^2 \tag{3.18}$$

$$\varepsilon_2 = 2nk \tag{3.19}$$

3.2.2 UV-Visible Spectroscopy

Theory:

When sample molecules are irradiated with UV or visible light having an energy equivalent to the possible electronic transition within the molecule, the electrons in the molecule absorbed some of the light energy and are getting promoted to a higher energy level, which is the characteristic of the molecules. UV spectrophotometer principle follows the Beer-Lambert Law. The law relates the attenuation of light to the properties of the material through which the light is traveling. This law is expressed through the equation:

$$A = \log_{10} \left(\frac{I_0}{I} \right) = \varepsilon lc \tag{3.20}$$

Where, A stands for the absorbance, I_0 refers to the intensity of light incident to the sample, I is the intensity of light transmitted from the

sample, l stands for the length of the sample and ε refers to the molar absorptivity or molar extinction coefficient and is a measure of the probability of the electronic transition. Basing from the Beer-Lambert law, it has been established that the greater the number of the molecules that are capable of absorbing light at a certain wavelength, the greater the extent of the absorption of light.

A UV-Vis spectrophotometer records both the degree of absorption (*i.e.*, intensity) and absorption peak for each wavelength. The resulting spectrum is a graph of absorbance versus wavelength. The wavelengths of the absorption peaks represent the types of bonds present in a given molecule and are valuable in determining the electronic transition in a molecule.

UV–Vis spectroscopy is also used to explore the optical properties of thin films. The absorption coefficient α can be calculated from the Beer-Lambert's law as [131]:

$$\alpha = \frac{2.303 \cdot Abs(\lambda)}{d} \tag{3.21}$$

Where, *d* and *Abs* are the film thickness and film absorbance, respectively. The optical band gap (E_g) value can be easily determined from absorption spectra. The optical band gap of thin films (i.e., ZnO thin films in this study) has been determined using the Tauc model [132, 133] and the Davis and Mott model [134] in the high absorbance region:

$$\alpha(\nu)h\nu = B(h\nu - E_g)^n \tag{3.22}$$

Where E_g is the optical band gap, *B* is a constant, hv is the incident photon energy and $\alpha(v)$ is the absorption coefficient. For the direct band gap material, i.e., ZnO, n = 1/2 was found to be more appropriate, because it gives the best linear curve in the band-edge region,[8, 135] correspondingly, the relationship between $(\alpha hv)^2$ and hv has been plotted. The band gap energy, E_g , can be obtained by extrapolating the linear portion to $(\alpha hv)^2 = 0$ in that graph.

3.2.3 Photoluminescence Spectroscopy



Figure 3.7: Principle of photoluminescence spectroscopy.

Theory:

Photoexcitation causes electrons within the material to excite into permissible higher energy states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a non-radiative process) as shown in Figure 3.7. The energy of the emitted light is related to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. In semiconductor systems, the most common radiative transition is between states in the conduction and valence bands, with the energy difference being known as the bandgap. During a PL experiment, excitation is provided by laser light with energy much larger than the optical band gap. The photo excited carriers consist of electrons and holes, which relax toward their respective band edges and recombine by emitting light at the energy of the band gap. Radiative transitions in semiconductors may also involve localized defects or impurity levels, therefore, the analysis of the PL spectrum leads to the identification of specific defects or impurities, and the magnitude of the PL signal allows determining their concentration. Thus photoluminescence is a process of photon excitation followed by photon emission and important for determining band gap, purity, crystalline quality and impurity defect levels of semiconducting material. It also helps to understand the underlying physics of the recombination mechanism.

Photoluminescence (PL) is a very powerful technique to probe the crystallinity and defect-related information of ZnO films. In general, photoluminescence spectra of ZnO typically consist of two bands. One of these is the near band edge emission (NBE), i.e., free excitonic emission located near the energy of the band gap, i.e., in the UV region (~ 380 nm). This free excitonic PL (also called 'edge' PL) can only be seen in films of good structural quality, in which nonradiative processes are inefficient and in which carriers are not dominantly trapped by some defect centers [5, 136]. The second is the defect-related deep level emission (DLE) located in the visible region (generally green-yellow emission). The visible emission is usually considered to be related to various intrinsic defects present in ZnO [5, 136]. Native or intrinsic defects are imperfections in the crystal lattice that involve only the constituent elements. They include vacancies (missing atoms at regular lattice positions), interstitials (extra atoms occupying interstitial position in the lattice) and antisites (a Zn atom occupying an O lattice site or vice versa). Figure 3.8 shows the defect energy levels in ZnO [137, 138].



Figure 3.8: Energy level diagram showing some of the principal defect levels in ZnO. The ZnO has an assumed bandgap of 3.36 eV. Potential transitions between the various levels are color coded.

Figure 3.8 shows various shallow and deep energy levels in ZnO originated from intrinsic defects present in the crystal. V_{Zn} , Zn_i , $ex-Zn_i$, V_0 , V_0^+ , V_0^{++} , V_0^* and O_i denote zinc vacancy, zinc interstitial, extended states of zinc interstitial, oxygen vacancy, singly charged oxygen vacancy, doubly charged oxygen vacancy, neutral state of oxygen vacancy and oxide interstitial, respectively. Some of the photogenerated electrons and holes are tapped by these shallow and deep energy levels and corresponding to different visible emissions.

3.2.4 X-ray Photoelectron Spectroscopy

Theory:

XPS involves the photo-ionization and examination of the kinetic energy distribution of the emitted electrons. In XPS, soft X-rays of energy 100 - 2500 eV is usually used to study the core levels of the sample surface under ultra-high vacuum. Normally, when the sample is illuminated with

X-rays of sufficient energy, it results in the excitation of electrons in the bound states leading to ionization and emission of the core electrons as shown in Figure 3.9. The ejected photoelectrons are then collected with the help of a hemispherical electron analyzer which measures their kinetic energy. Based on the concept of the photoelectric effect, the electron analyzer produces an energy spectrum of the ejected photoelectrons versus binding energy according to the relation [139]:

$$E_b = hv - E_k - \phi \tag{3.23}$$

Where, E_b is the binding energy of the photoelectrons, hv is the photon energy, E_k is the kinetic energy of the emitted photoelectrons and ϕ is the work function.



Figure 3.9: Principle of X-ray photoelectron spectroscopy.

In XPS spectra of ZnO, Zn 2p and O 1s core level spectra are of interest. In general, there are two components in Zn 2p XPS spectra. The peak at ~1022 eV corresponds to Zn $2p_{3/2}$ and the peak at ~1045 eV corresponds to Zn $2p_{1/2}$ [140, 141]. An energy separation of ~23 eV

between two core level Zn 2p components makes out a good agreement with earlier reported literature for crystalline ZnO [140, 141]. On the other hand, there are typically two components in O 1s spectra. The 1st peak centered at ~530.4 eV is attributed to the O²⁻ ions in wurtzite structure of the hexagonal Zn²⁺ ion array, which are surrounded by zinc atoms with the full supplement of nearest-neighbor O²⁻ ions [142-144]. Therefore, the 1st peak can be attributed to the Zn–O bonds [144]. The 2nd peak centered at ~531.74 eV corresponds to oxygen-deficient regions within the ZnO matrix, which is a signature of oxygen vacancy, V₀ [145].

3.2.5 Raman Spectroscopy

Theory:

The Raman effect is based on molecular deformations in electric field *E* determined by molecular polarizability α . The laser beam can be considered as an oscillating electromagnetic wave with electric field vector *E*. Upon interaction with the sample it induces electric dipole moment, $P = \alpha E$, which deforms the molecules. Because of the periodical deformation, molecules start vibrating with characteristic frequency v_m . In other words, monochromatic laser light with frequency v_0 excites molecules and transforms them into oscillating dipoles. Such oscillating dipoles emit light of three different frequencies (see Figure 3.10) when:

(i) A molecule with no Raman-active modes absorbs a photon with the frequency v_0 . The excited molecule returns to the same basic vibrational state and emits light with the same frequency v_0 as an excitation source. This type of interaction is called an elastic Rayleigh scattering.



Figure 3.10: Energy-level diagram showing the states involved in Raman spectra.

(ii) A photon with frequency v_0 is absorbed by Raman-active molecule which at the time of interaction is in the basic vibrational state. Part of the photon's energy is transferred to the Raman-active mode with frequency v_m and the resulting frequency of scattered light is reduced to v_0-v_m . This Raman frequency is called Stokes frequency, or just 'Stokes'.

(iii) A photon with frequency v_0 is absorbed by a Raman-active molecule, which, at the time of interaction, is already in the excited vibrational state. Excessive energy of excited Raman-active mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to v_0+v_m . This Raman frequency is called Anti-Stokes frequency, or just 'Anti-Stokes'.

About 99.999% of all incident photons undergo elastic Rayleigh scattering. This type of signal is useless for practical purposes of molecular characterization. Only about 0.001% of the incident light produces inelastic Raman signal with frequencies $v_0 \pm v_m$. Spontaneous

Raman scattering is very weak and special measures should be taken to distinguish it from the predominant Rayleigh scattering. Instruments such as notch filters, tunable filters, laser stop apertures, double and triple spectrometric systems are used to reduce Rayleigh scattering and obtain high-quality Raman spectra.

Raman scattering is sensitive to the crystal lattice structure of ZnO via its vibrational properties. Raman spectroscopy is a non-destructive characterization technique, based on inelastic light scattering that provides information about the phonon vibrational and rotational mode properties of the material. Wurtzite-type ZnO belongs to the space group $C_{6\nu}^{4}$ with two formula units in the primitive cell [146, 147]. Each primitive cell of ZnO has four atoms, each occupying $C_{3\nu}$ sites, which leads to 12 phonon branches: 9 optical modes and 3 acoustic modes [148]. At the centre of the Brillouine zone (Γ point), group theory predicts the following lattice optical phonons have the following irreducible representation [146]:

$$\Gamma_{opt} = 1A_1 + 2B_1 + 1E_1 + 2E_2 \tag{3.24}$$

Where A_1 and E_1 are polar modes and they are both infrared and Raman active. E_2 modes are non-polar and only Raman active. The E_2 modes have two wave numbers, namely, E_2 (high) and E_2 (low) associated with the motion of oxygen and Zn sub lattice respectively [148]. Strong E_2 (high) mode is characteristic of the wurtzite lattice and indicates good crystallinity. The vibrations of A_1 and E_1 modes can polarize in the unit cell, which creates a long-range electrostatic field splitting the polar modes into longitudinal optical (LO) and transverse optical (TO) component. The B_1 modes are Raman and infrared inactive (silent modes).

3.3 Basics of batteries

3.3.1 Batteries vs. Fuel Cells vs. Electrochemical Capacitors

Batteries, fuel cells, and electrochemical capacitors are systems for electrochemical energy storage and conversion. Although the energy storage and conversion mechanisms are not the same, there are "electrochemical similarities" in these three systems [149]. Similarities are that the energy-providing processes take place at the electrode/electrolyte interface and that electron and ion transports are separated [149].

In batteries and fuel cells, electrical energy is generated by conversion of chemical energy through redox reactions happening at the anode and cathode. The difference between batteries and fuel cells is associated with the locations of energy storage and conversion.

Batteries are closed systems, with the anode and cathode being the charge-transfer medium and taking an active part in the redox reaction as "active masses" [149]. Basically, in batteries, energy storage and conversion happen in the same compartment.

On the other hand, fuel cells are open systems where the anode and cathode are just charge-transfer media and the active masses undertaking the redox reaction are being delivered from outside the cell, either from the environment, such as, oxygen from air, or from a tank, for example, fuels such as hydrogen and hydrocarbons [149]. Energy storage (occurring in the tank) and energy conversion (occurring in the fuel cell) are thus locally separated.

In electrochemical capacitors (or supercapacitors), energy may not be delivered through redox reactions and, thus the use of the terms anode and cathode may not be suitable but are in common usage. By orientation of electrolyte ions at the electrolyte/electrolyte interface, so-called electrical double layers (EDLs) are formed and released, resulting in a parallel movement of electrons in the external wire, i.e., in the energy-delivering process [149].

To compare the power and energy capabilities, a representation known as the Ragone plot or diagram has been shown in Figure 3.11. It reveals that fuel cells can be considered to be high-energy systems, while supercapacitors are considered to be high-power systems. Batteries have intermediate energy and power characteristics. There is some overlap in energy and power of supercapacitors, or fuel cells, with batteries. Indeed, batteries with thin film electrodes exhibit power characteristics similar to those of supercapacitors [149].



Figure 3.11: Ragone plot of the energy storage domains for the various electrochemical energy storage systems [149].

3.3.2 Basic definitions used in the course of discussions on batteries

The following definitions are commonly used during the course of discussions on batteries.

A *battery* is one or more electrically connected electrochemical cells having terminals or contacts for supplying electrical energy.

A *primary battery* is a cell or group of cells for the generation of electrical energy projected to be used until exhausted and then it is discarded. Primary batteries are assembled in the charged state; discharge is the primary process during operation. It can be used only once.

A *secondary battery* is a cell or group of cells for the generation of electrical energy in which the cell, after being discharged, may be restored to its original charged condition by applying an electric current flowing in the direction opposite to the flow of current when the cell was discharged. This type of battery is also called rechargeable battery. It can be used repeatedly depending upon the lifetime of the battery.

The *anode* is the negative electrode of a cell. It gives up electrons to the external circuit and is oxidized during the electrochemical (discharge) reaction.

The *cathode* is the positive electrode of a cell. It accepts electrons from the external circuit and is reduced during the electrochemical (discharge) reaction.

The *electrolyte* (the ionic conductor) provides the medium for transfer of charge as ions inside the cell between the anode and cathode. The electrolyte is typically a solvent containing dissolved chemicals providing ionic conductivity. It should be a non-conductor of electrons to avoid selfdischarge of the cell.

The *separator* electrically isolates the anode and the cathode, thereby prevents short-circuit of the cell. Separators must be permeable to the ions.

Open-circuit voltage is the voltage across the terminals of a cell or battery when no external current flows. Actually, the difference in chemical potential between the anode (μ_A) and the cathode (μ_C) is termed as the working voltage, also called as open-circuit voltage, V_{OC} [150]:

$$V_{OC} = \frac{\mu_A - \mu_C}{e}$$
(3.25)

Where, e is the magnitude of the electronic charge.

Open-circuit voltage is determined by the compatibility of the whole system, including the anode, cathode, and the electrolyte.

Battery capacity is the amount of charge stored per unit mass of the active material (cathode or anode). It is usually given in milliamp hour per gram (mAh/g).

Specific Energy (Wh/kg) is the battery energy per unit mass, also referred to as the gravimetric energy density.

Specific Power (W/kg) is the maximum power available per unit mass.

Energy Density (Wh/L) is the battery energy per unit volume, also referred to as the volumetric energy density.

Power Density (W/L) is the maximum power available per unit volume.

3.3.3 Thermodynamics of batteries

The energy storage and power characteristics of batteries follow the thermodynamic and kinetic formulations directly for chemical reactions [149]. The basic thermodynamics for a reversible electrochemical reaction is given by [149]:

$$\Delta G = \Delta H - T \Delta S \tag{3.26}$$

Where ΔG is the Gibbs free energy or the available energy in a reaction, ΔH is the enthalpy or the energy released by the reaction, ΔS is the entropy, and *T* is the absolute temperature, with $T\Delta S$ being the heat associated with the reaction. The terms ΔG , ΔH and ΔS are state functions and depend only on the identity of the electrode materials and the initial and final states of the reactions.

The free energy ΔG represents the net useful energy available from a given reaction, thus, the net available electrical energy from a reaction in a battery cell is given by [149]:

$$\Delta G = -nFE \tag{3.27}$$

Where n is the number of electrons being transferred per mole of reactants, F is the Faraday constant, and E is the voltage of the cell with

the specific chemical reaction. Equation (3.27) signifies a balance between the chemical and electric driving forces upon the ions under open circuit conditions; hence E refers to the open circuit potential of a cell where there is no current flowing. The voltage of the cell is unique for each reaction couple. In other words, if the electrolyte is a perfect filter that allows the passage of ionic species, but no electrons, the cell voltage is determined by the difference in the electrically neutral chemical compositions of the electrodes. The identity and properties of the electrolyte and the phenomena that occur at the electrode/electrolyte interfaces play no role. The amount of electricity produced, nF, is being determined by the total amount of materials available for reactions and can be thought of as a capacity factor; the voltage can be considered to be an intensity factor [149].

The change of free energy for a given species *i* defines the chemical potential. The chemical potential μ_i , for species *i* is correlated to another thermodynamic quantity, the activity a_i , by the defining relation:

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{3.28}$$

Where μ_i^0 is a constant, the value of the chemical potential of species *i* in its standard state. *R* is the gas constant, and *T* the absolute temperature. Consider an electrochemical cell in which the activity of species *i* is different in the two electrodes, a_i (–) in the negative electrode, and a_i (+) in the positive electrode. The difference between the chemical potential on the positive side and that on the negative side is written as $\mu_i(+) - \mu_i(-) =$ RT ln [a_i (+) / a_i (–)]. If this chemical potential difference is balanced by the electrostatic energy from Equation (3.27), we have

$$E = -\frac{RT}{nF} ln \left[\frac{a_i(+)}{a_i(-)} \right]$$
(3.29)

The above relation is the Nernst equation, which relates the measurable cell voltage to the chemical difference across an electrochemical cell. If the activity of species i in one of the electrodes is a standard reference value; the Nernst equation provides the relative electrical potential of the other electrode [151].

3.3.4 Kinetics of batteries

Thermodynamics describes reactions at equilibrium and the maximum energy available for a given reaction. Compared to the open circuit potential at the equilibrium state, the voltage drops off when current is drawn from the battery because of kinetic limitations of reactions. Figure 3.12 shows a typical discharge curve of a battery [149].



Figure 3.12: A typical discharge curve of a battery, showing the influence of the various types of polarization [149].

Electrochemical reaction kinetics follows the general considerations as those for bulk chemical reactions. However, the detailed mechanism of battery electrode reactions involves a series of physical, chemical and electrochemical steps, including charge-transfer and charge-transport reactions. The rates of these individual steps determine the kinetics of the electrode. In general, three different kinetics effects for polarization are considered: (i) activation polarization is related to the kinetics of the electrochemical redox (or charge-transfer) reactions taking place at the electrode/electrolyte interfaces of anode and cathode; (ii) ohmic polarization is correlated to the resistance of individual cell components and to the resistance due to contact problems between the cell components; and (iii) concentration polarization is due to mass transport limitations during cell operation [152].

Activation polarization arises from kinetics of the charge-transfer reaction happening at the electrode/electrolyte interface. This type of kinetics is best understood using transition-state theory. The current flow is described by the Butler-Volmer equation. The ohmic polarization arises from the resistance of the electrolyte, materials of constructions of the electrodes, current collectors, terminals and contact between particles of the active mass. Ohmic polarization appears or disappears instantaneously when current flows or ceases. Typically the linear Ohm's law relates the current and potential. As the redox reactions proceed, the availability of the active species at the electrode/electrolyte interface changes. Concentrations polarization arises from limited mass transport capabilities, e.g., limited diffusion of active species to and from the electrode surface to replace the reacted material to sustain the reactions. This type of polarization usually becomes the rate-limiting step at the completion of charge/discharge.

3.3.5 Theoretical capacity of a material

The capacity of a battery is mainly determined by its chemistry. The theoretical capacity of electrode materials corresponds to the number of reactive electrons and the molar weight of the designed materials, as expressed by Faraday's law [150, 153]:

$$C_{theoretical}(mAh g^{-1}) = \frac{nF}{3.6 \times M}$$
(3.30)

Where n is the number of reactive electrons per formula unit, M is the molar weight of materials (g/mol), and F is the Faraday constant (96485 Coulombs/mol). The number of electrons is correlated with the number of metal ions (e.g., Li⁺, Mg²⁺, Al³⁺ ions) accommodated in the host lattice. The equation implies that smaller molecular weight and accommodation of more electrons per formula unit can produce a higher capacity in theory.

ZnO as an electrode in Li-ion battery:

Molar weight of ZnO = 81.38 g/mol

The two-step lithiation mechanism of ZnO contains the reduction of ZnO to Zn accompanied by the formation of a Li₂O matrix (equation (3.31)) and the subsequent formation of a LiZn alloy (equation (3.32)) [154]:

$$ZnO + 2Li^+ + 2e^- \leftrightarrow Zn + Li_2O \tag{3.31}$$

$$Zn + Li^+ + e^- \leftrightarrow LiZn \tag{3.32}$$

Three Li⁺ ions (i.e., three electrons) are involved in these reactions,

so, n = 3

So, using the equation (3.30), the theoretical capacity of ZnO in Li-ion battery is 987.8 mAh g^{-1} .

ZnO as an electrode in Al-ion battery:

Similarly, in case of Al-ion battery, three Al^{3+} ions can be accommodated into ZnO (Al^{3+} has relatively smaller ionic radius, Al^{3+} 0.53 Å vs. Li^+ 0.76 Å) [155].

In such cases, three Al^{3+} ions (i.e., nine electrons) are involved, and then, n = 9.

So, using the equation (3.30), the theoretical capacity of ZnO in Al-ion battery is ~ 2961 mAh g⁻¹.

Table 3.1 gives the theoretical capacity ($C_{\text{theoretical}}$) values of some cathode materials reported in the literature [62-64, 156, 157] of Al-ion battery.

Material	Number of	Molar weight,	Theoretical	
	electrons per	M (g/mol)	capacity, C _{theoretical}	
	formula unit, n		(mAh g ⁻¹)	
V ₂ O ₅ [64]	3 (for 1Al ³⁺)	181.88	442.2	
V ₄ O ₈ [62]	$6 (for 2Al^{3+})$	331.76	484.7	
TiS ₂ [156]	3 (for 1Al ³⁺)	111.86	718.8	
Mo ₆ S ₈ [63]	6 (for 2Al ³⁺)	832.12	193.26	
TiO ₂ [157]	3 (for 1Al ³⁺)	79.86	1006.8	
ZnO (In this	9 (for 3Al ³⁺)	81.38	2961	
work)				

Table 3.1: The theoretical capacity ($C_{theoretical}$) values of some cathode materials reported in the literature [62-64, 156, 157] of Al-ion battery.

Structure and Morphology of ALD grown ZnO thin films: Effect of film thickness and growth temperatures

4.1 Outline of work

In this chapter, I discuss about the effect of film thickness and growth temperature on the structure and morphology of ALD-grown ZnO thin films. ZnO thin films of different film thicknesses, ranging from ~5 nm to ~70 nm, were grown by ALD on Si substrates at two different growth temperatures, high temperature (200 °C) and near room temperature (35 °C). The structure and morphology of the ZnO films were studied elaborately. The structural study showed that high quality, crystalline, smooth ZnO thin films with a preferred orientation along the <0002> direction with the c axis predominantly perpendicular to the substrate surface, was grown on Si substrates irrespective of the growth temperatures. Whereas, the growth temperature dependent variation in surface morphology of ZnO films were observed. ZnO grown at high temperature exhibited wedge-shaped grains (in-plane size along major and minor axes are ~40 and ~20 nm, respectively) in their surface morphology, and in case of near room temperature growth, a circular (~20 nm diameter)

in-plane shape was predominant. Results presented in this chapter are published in peer reviewed journals.^{$\uparrow, \ddagger, \$$}

4.2 Experimental

ALD technique was used to grow ZnO thin films on silicon [p-type doped Si (100)] substrate at two different growth temperatures (or process temperatures), high temperature (200 °C) and near room temperature (35 °C). Before loading the substrates into the ALD reactor, all the substrates were ultrasonically cleaned in acetone and ethanol in sequence for 2 min, and then kept in deionized (DI) water and finally dried in nitrogen (N₂, 99.999% purity). The precursors for zinc and oxygen were diethyl zinc [DEZ, Zn(C₂H₅)₂, Sigma-Aldrich] and DI water, respectively. Nitrogen (N₂, 99.999% purity) was used both as a carrier and the purging gas. The precursors were alternately introduced into the reactor using their intrinsic vapor pressures from external containers kept at 18 °C. ALD process parameters (e.g. pulsing time, purging time etc.) are different for different growth temperatures.

The growth parameters for process temperature (200 °C) are as follows: One ALD reaction cycle consisted of a 0.2 s exposure to DEZ, followed by a 0.75 s for N₂ purge, a 0.2 s exposure to H₂O, and then another 0.75 s N₂ purge. The reactor pressure during the growth was kept at 1.75 mbar. For the growth studies, the number of ALD cycles was varied from 30 to 410. ZnO films with different thickness (5–70 nm) were grown on Si substrates. Six representative film thicknesses (5 nm, 9 nm,

[†] Dipayan Pal, Aakash Mathur, Ajaib Singh, Jaya Singhal, Amartya Sengupta, Surjendu Dutta, Stefan Zollner, and Sudeshna Chattopadhyay*, *J. Vac. Sci. Technol. A* **35**, 01B108 (2017).

[‡] Dipayan Pal, Jaya Singhal, Aakash Mathur, Ajaib Singh, Surjendu Dutta, Stefan Zollner, and Sudeshna Chattopadhyay*, *Appl. Surf. Sci.* **421**, 341 (2017).

[§] Dipayan Pal, Aakash Mathur, Ajaib Singh, Jaya Singhal, and Sudeshna Chattopadhyay*, *Mater. Today: Proc.* **5**, 9965 (2018).

19 nm, 38 nm, 52 nm and 69 nm) have been studied. The growth rate of ZnO films on Si was about 1.6 Å per cycle (at 200 °C).

The growth parameters for process temperature (35 °C) are as follows: One ALD reaction cycle consisted of a 0.3 s exposure to DEZ, followed by a 30 s for N₂ purge, a 0.3 s exposure to H₂O, and then another 30 s N₂ purge. The relatively long purging time was used due to the extremely low deposition temperatures in order to make sure that there was only one precursor at a time in the ALD reaction chamber. The reactor pressure during the growth was kept at 2.5 mbar. For the growth studies, the number of ALD cycles ranged from 200 to 1000. ZnO films with different thickness (12–67 nm) were grown on Si substrates. Three representative film thicknesses (12 nm, 41 nm and 67 nm) had been studied. The growth rate of ZnO films on Si was about 0.7 Å per cycle (at 35 °C).

Thickness, surface and interface roughness, and electron density profile (EDP) of the ZnO films were obtained by using X-ray reflectivity (XRR) measurements. The crystalline structures of the ZnO films were investigated by X-ray diffraction (XRD). To further probe the crystallinity and defect-related information of the ZnO films, Photoluminescence (PL) spectroscopy studies were performed. The surface morphologies of the ZnO films were examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

4.3 Effect of film thickness and growth temperatures on structure and morphology of ALD grown ZnO thin films

4.3.1 ZnO films grown on Si (silicon substrates, Si (100)) at high temperature (200 °C)

As discussed in Chapter 3, section 3.1.1, XRR technique provides information about the film thickness, the electron density profile (EDP), and the surface and interface roughness of thin films.



Figure 4.1: (a) Reflectivity profiles, i.e., specular reflectivity (*R*) normalized with Fresnel reflectivity (R_F), (R/R_F) vs. normal momentum transfer q_z (in Å⁻¹) for different ZnO films grown on Si at 200 °C process temperature, with film thickness: (i) 5 nm, (ii) 9 nm, (iii) 19 nm, (iv) 38 nm, (v) 52 nm and (vi) 69 nm; R_F is the theoretical reflectivity from an ideal surface. Circles and lines represent the experimental data and theoretical fit respectively. (b) Corresponding extracted electron density (ρ) profile from XRR fits.

Figure 4.1(a) shows specular reflectivity (*R*) normalized with Fresnel reflectivity (R_F), for ZnO/Si samples with different ZnO film thickness grown at 200 °C. Circles and lines represent experimental data and theoretical fit respectively. The X-ray reflectivity data have been fitted by the well-known Parratt's exact recursive method [118-122]. X-ray reflectivity profile shows clear Kiessig fringes, and the corresponding extracted electron density indicates the formation of ZnO thin films with bulklike electron density, on silicon (Si) substrates, with very low surface and interface roughness. Figure 4.1(b) shows the representative EDPs (ρ) of the respective films extracted from XRR fits. Results show that the electron densities of ALD-grown ZnO films are close to its bulk electron density, except that at below about 10 nm film thickness, it drops slightly (by less than 7%). This signifies the formation of high quality pinhole-free ZnO films, with nearly complete surface coverage.

The thickness of our ALD-grown ZnO films ranges from about 5 to 70 nm. The growth rate of ZnO determined with XRR from the deposited films on Si was about 1.6 Å/cycle (at 200 °C), which is in agreement with previous studies of ZnO growth by ALD [158, 159]. Film thicknesses, corresponding growth parameters, surface roughness, and other relevant parameters are summarized in Table 4.1.

Figure 4.2(a) shows representative X-ray diffraction patterns of ZnO films of different thicknesses, grown on Si at 200 °C. The diffraction peaks were matched with the standard diffraction pattern of hexagonal wurtzite ZnO with a space group of P63mc (JCPDS PDF Card No. 01-079-2205), illustrated in Figure 4.2(b).

The XRD pattern of the ZnO films shows a much stronger ZnO (002) peak compared to ZnO (101), whereas the standard powder XRD pattern of bulk ZnO (hexagonal wurtzite bulk ZnO) shows the maximum intensity for the ZnO (101) peak (JCPDS PDF Card No. 01-079-2205). This clearly

indicates that the ZnO films on Si exhibited a preferred orientation along the <0002> direction with the c axis predominantly perpendicular to the substrate surface. Average grain sizes (out-of-plane) were estimated using Scherrer's formula [160]. The average grain sizes are about 20 nm for thicker ZnO films, but thin ZnO films (at and below 20 nm) show smaller grain sizes with decreasing film thickness (see Table 4.1).



Figure 4.2: (a) X-ray diffraction patterns for ALD grown ZnO films deposited at 200 °C process temperature, on Si substrate; and (b) Reference data: Standard diffraction pattern of hexagonal wurtzite ZnO with a space group of P63mc (JCPDS PDF Card No. 01-079-2205). The observed Si (200) peak at about $2\theta = 33^{\circ}$ is known as kinematically forbidden reflection (or basis-forbidden reflection) for Si (100) substrates, because such reflections can sometimes actually be present due to dynamical scattering events [161-163].

	ZnO films on Si grown at 200 °C							
No. of	ZnO film	SiO ₂	Electron	Surface	RMS of	Mean		
ALD	thickness	thickness	density	roughness	Surface	grain		
cycles	from	at ZnO/Si	of ZnO	from XRR	roughness	size		
	XRR [*]	interface	from	(Å)	from	from		
	(Å)	from	XRR		AFM (Å)	XRD		
		XRR [*] (Å)	(eÅ ⁻³)			(Å)		
30	53	0	1.39	7		< 50		
60	94	0	1.51	7	11	56		
120	194	9	1.48	15	15	123		
230	389	10	1.51	18		208		
300	515	12	1.5	19		194		
410	684	9	1.5	19	18	212		

Table 4.1: ALD grown ZnO films deposited on Si at 200 °C process temperature.

*Estimated experimental resolution for film thickness measurement through XRR technique is π/q_{max} [122], which is ~8 Å for the ZnO/Si systems [q_{max} can be obtained from Figure 4.1(a)].

To further probe the crystallinity and defect-related information of the ZnO films, Photoluminescence (PL) spectroscopy studies were carried out. Figure 4.3 shows the room temperature photoluminescence (RT-PL) spectra of the ZnO films grown on Si at process temperature, 200 °C. From Figure 4.3, it can be clearly seen that for ZnO films grown on Si, the PL spectra is dominated by strong near band edge (NBE) UV-emission originating from free exciton emission at room temperature. This intense free excitonic PL (also called 'edge' PL) can only be seen in films of good structural quality, in which nonradiative processes are inefficient and in which carriers are not dominantly trapped by some defect centers [5]. There are no prominent defect related deep level emissions (DLE) in the visible spectral region of the PL spectra. The result is consistent for all of

these ZnO films. The strong NBE and absence of DLE indicate the formation of highly crystalline ZnO films with very low density of defect states [5, 44].



Figure 4.3: Photoluminescence (PL) spectra of ZnO films with different thicknesses grown on Si at 200 °C process temperature. NBE corresponds to near band-edge emission and DLE corresponds to defect related deep level emission. The inset displays NBE peaks in log scale (to emphasize the presence of NBE in thinner ZnO films, e.g., 19 nm and 9 nm ZnO films).

On further analyses, it is found that the PL spectra of ZnO/Si samples could be well fitted by two Gaussian peaks, as shown in Figure 4.4. The peaks are assigned to free exciton (FX) and its phonon replica, FX-2LO, with detectable energy separation of 120 meV, twice the reported value of LO phonon energy of ZnO [164, 165]. The presence of FX-2LO instead of FX-1LO is indicative of high crystalline quality or less disorder [164,



166]. This also supports that at high temperature (200 °C), high quality defect free crystalline ZnO films were grown on Si substrate.

Figure 4.4: Photoluminescence (PL) spectra of ZnO films with different thicknesses grown on Si at 200 °C process temperature. The sums of the two Gaussians are indicated by the thicker solid curves as resultant fits for the experimental data (in circles).

The thickness dependent surface morphologies of ZnO films grown on Si at high temperature (200 °C) have been investigated by SEM and are shown in Figure 4.5. SEM image showed smooth and uniform surface morphology for 9 nm ZnO film. It has been observed that with the increase in film thickness, morphology changes from smooth film to wedge shaped grains. Both the 38 nm and 69 nm ZnO films showed

wedge-shaped grains in their surface morphology, which is consistent with earlier reported findings on higher temperature ALD-grown ZnO films [159]. Increase in the in-plane grain sizes have been observed with increase in film thickness from 38 nm ZnO film (in-plane size along major and minor axes are ~25 nm and ~10 nm, respectively) to 69 nm ZnO film (in-plane size along major and minor axes are ~40 nm and ~20 nm, respectively).



Figure 4.5: Thickness dependent surface morphology of ZnO films grown on Si at 200 °C process temperature with different film thickness: (a) 69 nm, (b) 38 nm and (c) 9 nm.

4.3.2 ZnO films grown on Si at near room temperature (35 °C)

In case of ZnO films, produced at near room temperature (35 °C), XRR data (see Figure 4.6) concludes growth of high quality pinhole-free ZnO films on Si substrate, with nearly complete surface coverage. The growth rate of ZnO determined with XRR from the deposited films on Si was about 0.7 Å/cycle (at 35 °C), which is in agreement with the previous studies of low-temperature ALD growth of ZnO [167]. The growth rate of ZnO at 35 °C was much lower than that of at 200 °C. The lower growth rate at 35 °C was most probably due to the decreasing reactivity of the precursors and incomplete surface reactions with DEZ and water [82, 167].

Film thicknesses, corresponding growth parameters, surface roughness, and other relevant parameters are summarized in Table 4.2.

From table 4.1 and 4.2, it has been observed that the electron density of near room temperature (35 °C) grown ZnO films was slightly less than that of high temperature (200 °C) grown ZnO films. Additionally, the surface roughness of near room temperature grown ZnO films was a little higher than that of high temperature grown ZnO films.



Figure 4.6: (a) Reflectivity profiles, i.e., specular reflectivity (*R*) normalized with Fresnel reflectivity (R_F), (R/R_F) vs. normal momentum transfer q_z (in Å⁻¹) for different ZnO films grown on Si at 35 °C process temperature, with film thickness: (i) 12 nm, (ii) 41 nm and (iii) 67 nm; R_F is the theoretical reflectivity from an ideal surface. Circles and lines represent the experimental data and theoretical fit respectively. (b) Corresponding extracted electron density (ρ) profile from XRR fits.

Figure 4.7(a) shows representative X-ray diffraction patterns of ZnO films of different thicknesses, grown on Si at 35 °C. Also in case of near room temperature (35 °C) growth, ZnO films exhibited a preferred
orientation along the <0002> direction with the c axis predominantly perpendicular to the substrate surface. The average grain sizes (out-ofplane) were estimated from XRD and summarized in Table 4.2. It has been observed that, the average grain sizes are about 24 nm for thicker ZnO films, but thin ZnO films (at and below 20 nm) show lower grain sizes with decreasing film thickness.



Figure 4.7: (a) X-ray diffraction patterns for ALD grown ZnO films deposited at 35 °C process temperature, on Si substrate; and (b) Reference data: Standard diffraction pattern of hexagonal wurtzite ZnO with a space group of P63mc (JCPDS PDF Card No. 01-079-2205). The observed Si (200) peak at about $2\theta = 33^{\circ}$ is known as kinematically forbidden reflection (or basis-forbidden reflection) for Si (100) substrates, because such reflections can sometimes actually be present due to dynamical scattering events [161-163].

		ZnO films on Si grown at 35 °C							
No. of	ZnO film	SiO ₂	Electron	Surface	RMS of	Mean			
ALD	thickness	thickness	density of	roughness	Surface	grain			
cycles	from	at ZnO/Si	ZnO	from XRR	roughness	size			
	XRR [*]	interface	from	(Å)	from	from			
	(Å)	from	XRR		AFM (Å)	XRD			
		XRR [*] (Å)	(eÅ ⁻³)			(Å)			
200	119	12	1.28	18	10	57			
600	410	11	1.41	23	13	224			
1000	665	13	1.45	29	19	239			

 Table 4.2: ALD grown ZnO films deposited on Si at 35 °C process temperature.

*Estimated experimental resolution for film thickness measurement through XRR technique is π/q_{max} [122], which is ~8 Å for the ZnO/Si systems [q_{max} can be obtained from Figure 4.6(a)].

Photoluminescence (PL) spectra were used to further probe the crystallinity and defect-related information of the near room temperature grown ZnO films on Si. The PL spectra as shown in Figure 4.8, exhibits a strong UV near band edge emission (NBE) around 3.26 eV which corresponds to the crystalline nature of ZnO, along with a weak defect related deep-level green emission (DLE) around 2.3 eV associated with oxygen vacancies (V_0) in the ZnO lattice [136, 137]. The strong NBE and weak DLE indicate the low defect density and good crystalline quality of the ZnO film grown on Si at near room temperature.



Figure 4.8: Photoluminescence (PL) spectra of ZnO films with different thicknesses grown on Si at 35 °C process temperature. NBE corresponds to near band-edge emission and DLE corresponds to defect related deep level emission. The inset displays NBE peaks in log scale.

On further analyses, it is found that the NBE peak of near room temperature ZnO/Si samples could be well fitted by two Gaussian peaks, as shown in Figure 4.9. The peaks are assigned to free exciton (FX) and its phonon replica, FX-2LO, with detectable energy separation of 120 meV, twice the reported value of LO phonon energy of ZnO [164, 165]. The presence of FX-2LO instead of FX-1LO is indicative of high crystalline quality or less disorder [164, 166]. This supports that also at near room temperature (35 °C), high quality crystalline ZnO films were grown on Si with less disorder.



Figure 4.9: Photoluminescence (PL) spectra of ZnO films with different thicknesses grown on Si at 35 °C process temperature. The sums of the three Gaussians are indicated by the thicker solid curves as resultant fits for the experimental data (in circles).

It has been concluded from the structural study that high quality, crystalline, smooth, pinhole free, ZnO thin films with a preferred orientation along the <0002> direction with the c axis predominantly perpendicular to the substrate surface, were grown on Si substrates irrespective of the growth temperatures.

The distinct variations in surface morphology were observed for ZnO thin films as an effect of change in growth temperature (from 200 °C to 35 °C), as shown in Figure 4.10 and Figure 4.11. Wedge-shaped grains (in-

plane size along major and minor axes are ~40 and ~20 nm, respectively) were observed in surface morphology of ZnO thick films (of thickness above 20 nm), grown at higher temperature. In contrast, in case of near room temperature (35 °C) growth, ZnO films showed spherical/circular (~20 nm) in-plane shape in their surface morphology. In both the cases (growth at 200 °C and 35 °C) surface morphology becomes smoother for thinner ZnO films (film thickness is of ~10 nm).



Figure 4.10: Growth temperature dependent surface morphology of ALD grown ZnO films: Top-view SEM images of (a) ~ 70 nm ZnO/Si grown at 200 °C; (b) ~ 70 nm ZnO/Si grown at 35 °C; (c) ~ 10 nm ZnO/Si grown at 200 °C; and (d) ~ 10 nm ZnO/Si grown at 35 °C.

The root-mean-square (RMS) roughness was estimated for characteristic ZnO film thicknesses from AFM images, which were found to decrease in thinner films (at and below 20 nm), as shown in Table 4.1 and 4.2. The results were consistent with the surface roughness obtained from XRR measurements.

The surface roughness of thinner ZnO films (thickness below ~ 20 nm) is found to be less than that of thicker ZnO film (thickness ~ 70 nm) and also observed to decrease with film thickness. This is further corroborated by the smaller grain sizes obtained from XRD data for thinner ZnO films with thickness below ~ 20 nm, as shown in Table 4.1 and 4.2.



Figure 4.11: Growth temperature dependent surface morphology of ALD grown ZnO films: Top-view AFM images of (a) ~ 70 nm ZnO/Si grown at 200 °C; (b) ~ 70 nm ZnO/Si grown at 35 °C; (c) ~ 10 nm ZnO/Si grown at 200 °C; and (d) ~ 10 nm ZnO/Si grown at 35 °C.

4.4 Summary

In summary, the effect of film thickness (in the range of 5 nm to 70 nm) and growth temperatures on the structure and morphology of ALD-grown ZnO thin films have been explored in this chapter. ZnO thin films of different film thicknesses, ranging from ~5 nm to ~70 nm, were grown by ALD on Si substrates at two different growth temperatures, high temperature (200 °C) and near room temperature (35 °C). The structure

and morphology of the ZnO films were studied elaborately. The structural study showed that high quality, crystalline, pinhole free, smooth (with very low surface roughness) ZnO thin films with a preferred orientation along the <0002> direction with the c axis predominantly perpendicular to the substrate surface, was grown on Si substrates irrespective of the growth temperatures. Whereas, the growth temperature dependent distinct variation in the surface morphology of ZnO films were observed. ZnO grown at high temperature exhibited wedge-shaped grains (in-plane size along major and minor axes are ~40 and ~20 nm, respectively) in their surface morphology, and in case of near room temperature growth, a spherical/circular (~20 nm) in-plane shape was predominant.

Surface / Interface effects on the optical properties of ALD grown ZnO thin films

5.1 Outline of work

In this chapter, the surface/interface effects on the optical properties of ALD grown ZnO thin films have been discussed. ALD grown ZnO thin films of different thicknesses (ranging from ~5 nm to ~70 nm) with very low surface roughness and bulklike electron density, on two different selected substrates, silicon (Si) and fused quartz (SiO₂), have been studied to explore the surface/interface effects on optical properties of ZnO. The interface of ZnO/Si (wider-band gap ZnO deposited on narrower-band gap Si, with staggered type band alignment) corresponds to the staggered type-II quantum well, whereas in the case of ZnO deposited on wider band gap SiO₂ corresponds to type-I quantum well.

The real and imaginary parts of the complex dielectric function of ZnO/Si showed monotonically decreasing values with decreasing ZnO film thickness at and below a threshold of about 20 nm. The reduction of the dielectric function with film thickness was explained consistently by the Tanguy–Elliott amplitude prefactor governing the strength of optical interband transitions through the lowering of the electron–hole overlap factor at the ZnO/Si interface. In the case of ZnO/Si, a staggered type-II (spatially indirect) quantum well, holes are scattered into the Si substrate, causing a lowering of the electron–hole overlap factor and thus the reduction of excitonic absorption, consequently a decrease in the real and the imaginary parts of the dielectric function. This hypothesis was

confirmed with ZnO films grown on SiO_2 , where a thin type-I quantum well, consisting of a narrower-bandgap semiconductor grown on a widerbandgap (insulator) substrate, in which both the electron and the hole are confined in the ZnO thin film, leads to an increase in the electron–hole overlap matrix element with decreasing film thickness due to confinement, resulting in enhancement of the excitonic absorption in thinner ZnO films on SiO₂.

Secondly, as an effect of surface and interface in ZnO thin films, a blue shift of the absorption edge with decreasing film thickness at and below ~ 20 nm was also reported. Thickness dependent blue shift, energy vs. $1/d^2$ (where, d represents ZnO film thickness) in two different systems, ZnO/Si and ZnO/SiO₂, showed a difference in their slopes. The observed phenomena were also consistently explained by the corresponding exciton (or carrier/s) deconfinement and confinement effects at the ZnO/Si and ZnO/SiO₂ interface respectively, where Tanguy-Elliott amplitude prefactor plays the key role through the electron-hole overlap factor at the interface.

The study on interface effect on optical properties was carried out with two different sets of ALD grown ZnO samples, grown at two different process temperatures, at high temperature (200 °C) and at near room temperature (35 °C). The consistent trends in the thickness dependent optical properties of the ZnO films as an effect of interface for two different sets of ZnO films (i.e., ZnO samples for two different growth temperature) was observed. Results presented in this chapter are published in peer reviewed journals.^{§,**,††}

[§] Dipayan Pal, Aakash Mathur, Ajaib Singh, Jaya Singhal, Amartya Sengupta, Surjendu Dutta, Stefan Zollner, and Sudeshna Chattopadhyay*, *J. Vac. Sci. Technol. A* **35**, 01B108 (2017).

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5.2 Experimental

ALD grown ZnO thin films of different thicknesses (ranging from ~ 5 nm to ~ 70 nm) on two different selected substrates, silicon [p-type doped Si (100)] and fused quartz (SiO₂), have been studied to explore the surface/interface effects on optical properties of ZnO.

ALD process parameters are already discussed in Chapter 4, Experimental section.

To study the optical properties of ZnO films, Spectroscopic ellipsometry and UV-Vis spectroscopy techniques have been used.

Spectroscopic ellipsometry (SE) measurements were performed on ZnO thin films deposited on Si substrates in the photon energy range of 0.8–6.5 eV at three incident angles of 60°, 65°, and 70°. Ellipsometry techniques have been extensively used to explore the optical properties of the ZnO films, namely, complex dielectric function, absorption coefficient, and band gap along with the film thickness and roughness, using the WVASE (J.A. Woollam, Co.) software.

UV-Vis absorption spectra of ZnO films, deposited on fused quartz substrates (SiO₂), were measured using a UV-Vis spectrophotometer in transmission mode in the wavelength (λ) range of 190–1100 nm.

5.3 Optical properties of ALD grown ZnO thin films

The optical properties of as-grown ZnO thin films on Si, namely, the complex dielectric function, absorption coefficient, and band gap, were determined using Spectroscopic Ellipsometry in the 0.8–6.5 eV photon energy range. The main advantages of the SE technique are its precision

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and nondestructiveness [95, 96] and, particularly, the ability to measure simultaneously the film thickness, surface roughness and the optical constants of the system [96].

Figures 5.1 shows the ellipsometric angles, ψ and Δ , for 5 nm, 9 nm, 19 nm, 38 nm, 52 nm and 69 nm ZnO films on Si grown at 200 °C. Circles and lines represent experimental data and theoretical fit respectively. It was found that the calculated ψ and Δ are in good agreement with the experimental data. Excellent fits with mean-squared-error below 5 were achieved for all our samples. In this study, for ZnO film thickness of 5, 9, and 19 nm, a three layer model (i.e., air/ZnO layer/Si substrate) and for ZnO film thickness of 38, 52, and 69 nm, a four layer model (i.e., air/surface-roughness layer/ZnO layer/Si substrate) have been used to extract the optical constants of the films, while the optical constants of Si are well known [168]. The Si substrate is about 1mm thick and has been treated as infinite. The surface roughness factor is omitted from the model for the thinner films because the SE is not sensitive enough to detect the surface roughness in very thin films.

ZnO is a direct band gap semiconductor with a fundamental absorption edge at about 3.37 eV, which corresponds to the direct transition [169]. It is known that the excitonic interaction close to the fundamental band edge strongly influences the optical properties of ZnO [169, 170].



Figure 5.1: Ellipsometric angles ψ and Δ as a function of photon energy for ZnO films of (a) 5 nm, (b) 9 nm, (c) 19 nm, (d) 38 nm, (e) 52 nm and (f) 69 nm film thickness, grown on Si substrates, acquired with incidence angles ranging from 60° to 75°; circles and lines represent experimental data and theoretical fit, respectively. These ZnO films were grown at 200 °C.

For the parameterization of the optical properties of ZnO, a Tauc-Lorentz (T-L) model has been employed in this work. The T-L oscillator was developed by Jellison and Modine [171, 172]. The complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) of the ZnO thin films as a function of the photon energy can be written in the following functional form known as the T-L model [96, 171, 172]:

$$\varepsilon_{2}(E) = \frac{AE_{0}C(E-E_{g})^{2}}{(E^{2}-E_{0}^{2})^{2}+C^{2}E^{2}} \cdot \frac{1}{E}(E > E_{g})$$

= 0 (E \le E_{g}) (5.1)

$$\varepsilon_1(E) = \varepsilon_{\infty} + \frac{2P}{\pi} \oint \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi$$
(5.2)

The T-L oscillator model is based on the Tauc joint density of states and the Lorentz oscillator; the fit parameters are A, E_0 , C, E_g and ε_{∞} [96, 171]. The parameter A stands for the transition matrix element, which is proportional to the magnitude of the real and imaginary part of complex dielectric constant [96]. E_0 corresponds to the peak transition energy, which is related to the Penn gap which represents an average separation between the valence band and conduction band [96]. C is the broadening term, related to the degree of disorder in the material [96]. E_g stands for the optical band gap, ε_{∞} is the high frequency dielectric constant, and Pstands for the principal part of the integral [96, 171].

The calculated ε_1 and ε_2 using the best-fit parameters for ZnO thin films on Si with various thicknesses are shown in Figure 5.2. As can be seen in Figure 5.2, the film thickness has a significant effect on the complex dielectric functions of ZnO films on Si. The magnitudes of both the real and imaginary parts of dielectric functions near the band edge significantly drop in thin ZnO films on Si (i.e., at and below 20 nm film thickness). As compared to 69 nm film, the ZnO film on Si with a thickness of 9 nm shows a reduction of ~34% and ~57% in the real and imaginary parts of the complex dielectric function at the photon energy of ~3.3 eV, respectively, while the ZnO film on Si with a thickness of 5 nm shows a drastic reduction of ~46% and ~73%, respectively. The peaks of ε_1 and ε_2



also show a blue shift with the decreasing film thickness (at and below ~ 20 nm).

Figure 5.2: Evolution of (a) real part (ϵ_1) and (b) imaginary part (ϵ_2) of the complex dielectric function with ZnO film thickness. These ZnO films were grown on Si, at high temperature (200 °C).

Using the values of ε_1 and ε_2 , the absorption coefficient, α , for ZnO thin films were calculated, and a plot of α vs. energy for direct band gap ZnO is shown in Figure 5.3. The absorption coefficient at and above the band edge significantly drop in thin ZnO films on Si (i.e., at and below 20 nm film thickness). The results indicate that wider-band gap ZnO deposited on narrower-band gap Si, with staggered type-II alignment [56], absorbs less light with decreasing film thickness, at and below ~20 nm. In this regard, it should be noted that ALD grown ZnO system is known to be

n-type in nature due to the native crystallographic defects such as oxygen vacancies and interstitial zinc which behave as electron donors [5, 51, 173]. The PL results (see Figure 4.3 and 4.8 in Chapter 4) for our ZnO/Si systems are also consistent with the above observation, indicating the presence of similar type of defects in ALD grown ZnO, which suggests the formation n-type ZnO on p-type Si substrate.



Figure 5.3: Absorption coefficients, α of ZnO films of different thicknesses grown on Si at 200 °C. The inset shows wider-band gap ZnO deposited on narrower-band gap Si, with staggered type-II alignment.

Summarizing the observation, ellipsometry results clearly demonstrate that for ZnO/Si system, there is significant drop in the magnitudes of both the real and imaginary parts of complex dielectric functions and in near-band gap absorption in the thinner film thickness window (i.e., at and below \sim 20 nm film thickness).

To explain the significant drop in complex dielectric functions and in near-band gap absorption in the thinner films, we compare the extracted electron density coverage, ρ_{cov} (by fitting the XRR data using Parratt formalism), with the relative (ε_{∞} -1) (which is proportional to valence



electron density, unless the transition matrix element changes [174]) of ZnO, vs. ZnO film thickness in Figure 5.5.

Figure 5.4: (a) Reflectivity profiles, i.e., specular reflectivity (*R*) normalized with Fresnel reflectivity (R_F), (R/R_F) vs. normal momentum transfer q_z (in Å⁻¹) for different ZnO films grown on Si at 200 °C process temperature, with film thickness: (i) 5 nm, (ii) 9 nm, (iii) 19 nm, (iv) 38 nm, (v) 52 nm and (vi) 69 nm; R_F is the theoretical reflectivity from an ideal surface. Circles and lines represent the experimental data and theoretical fit respectively. (b) Corresponding extracted electron density (ρ) profile from XRR fits.

Figure 5.4(a) shows X-ray reflectivity profile for ZnO/Si samples with different ZnO film thickness and Figure 5.4(b) shows the electron density (ρ) profiles (EDPs) of the respective films extracted from XRR fits. This has already been discussed in Chapter 4, section 4.3.1. From Figure 5.4(b), the relative electron density (ρ_{rel}) was estimated using the following equation:

$$\rho_{rel} = \frac{\text{electron density of a given ZnO film}}{\text{bulk ZnO electron density}} \times 100$$
(5.3)

 ε_{∞} was calculated at a photon energy of 0.8 eV. The relative (ε_{∞} -1) was estimated using the following equation given as:

$$(\varepsilon_{\infty} - 1)_{rel} = \frac{(\varepsilon_{\infty} - 1) \text{ of a given Zn0 film}}{(\varepsilon_{\infty} - 1) \text{ of } 69 \text{ nm Zn0 film}} \times 100$$
(5.4)



Figure 5.5: Plot of the extracted relative electron density, ρ_{rel} (by fitting the XRR data using the Parratt formalism), and relative $(\varepsilon_{\infty}-1)$, $(\varepsilon_{\infty}-1)_{rel}$ of ZnO, vs. ZnO film thickness. These ZnO films were grown on Si at 200 °C.

Figure 5.5 shows that for the same thickness range, the valence electron density, proportional to $(\varepsilon_{\infty}$ -1), starts decreasing more sharply at and below 20 nm film thickness, and drops by ~ 45 % in the thinnest film. On

the other hand, XRR results of ZnO films on Si indicate that the electron density of ZnO films remains constant down to 20 nm thickness, and then decreases only a little, by less than 7 %. A slight decrease of the electron density in our thinnest films, obtained from XRR, is not sufficient to explain the following phenomena: (i) the significant drop in (ε_{∞} -1) and (ii) the significant reduction in near-band gap absorption.

The observation can be explained by the Tanguy's proposition on the concept of amplitude pre-factor. According to Tanguy's theory for excitonic absorption, the complex dielectric function, ($\varepsilon = \varepsilon_1 + i\varepsilon_2$), can be written as [58, 175]:

$$\varepsilon(E) = \frac{A\sqrt{R}}{(E+i\Gamma)^2} \left\{ g_a \big(\xi(E+i\Gamma) \big) + g_a \big(\xi(-E-i\Gamma) \big) - 2g_a \big(\xi(0) \big) \right\}$$
(5.5)

Where, amplitude pre-factor, $A = \frac{\hbar^2 q^2}{2\pi\varepsilon_0 m_0^2} \left(\frac{2\mu}{\hbar^2}\right)^{\frac{3}{2}} |e \cdot M_{cv}(0)|^2$ (5.6)

Where, $|\mathbf{e} \cdot \mathbf{M}_{cv}(0)|$ is the dipole matrix element which corresponds to the overlap of electron and hole [58]. *R* is the energy of the fundamental exciton bound state, E_g is the band gap energy, μ is the reduced mass of the exciton and Γ is the broadening of the energy levels [58].

$$g_{a}(\xi) = 2 \ln \xi - 2\pi \cot(\pi \xi) - 2\psi(\xi) - 1/\xi$$
(5.7)

$$\xi(z) = \sqrt{\frac{R}{E_g - z}} \tag{5.8}$$

$$\psi(z) = \frac{d\ln\Gamma(z)}{dz} \tag{5.9}$$

In this study, in thinner ZnO films on Si (at or below 20 nm film thickness), the exciton is deconfined because of the staggered band alignment (schematically shown in Figure 5.6(b)). The electron remains mostly confined in the ZnO conduction band quantum well (at least at low temperatures, where thermal excitation of the electron across the barrier

into the Si substrate can be ignored), while the photo-excited ZnO hole will quickly relax across the interface into the Si substrate. This reduces the overlap of the electron and hole wave functions and thus the amplitude pre-factor, *A*, in the Tanguy dielectric function (Equation 5.5). For thinner films, where the thickness is near or below the excitonic Bohr radius, the delocalization of excitons near the interface plays an important role. These excitons are effectively probed by optical techniques such as ellipsometry, where the excitonic absorption strength modulates the magnitude of the real and imaginary parts of the dielectric function.

However, for thicker ZnO films on Si, with film thickness above ~ 20 nm (schematically shown in Figure 5.6(a)), delocalization phenomenon will still occur at the ZnO/Si interface, but the contribution of probed interface is much less, resulting in negligible effect in dielectric function.



Figure 5.6: Models/Schematic: (a) and (b) wider-band gap ZnO deposited on narrower-band gap Si, with staggered type-II alignment for thicker films (film thickness above ~20 nm) and thinner films (film thickness less than ~20 nm) respectively.

To understand this phenomenon clearly, ZnO thin films have been deposited on fused quartz (SiO₂) substrate, where, ZnO deposited on wider band gap SiO₂ corresponding to type-I quantum well [57]. The surface/interface effects on the optical properties have been explored. Figure 5.7 shows comparison of energy band diagrams of ZnO/Si and ZnO/SiO₂ systems.



Figure 5.7: Comparison of energy band diagrams of ZnO/Si and ZnO/SiO₂ systems: (a) wider-band gap ZnO deposited on narrower-band gap Si, with staggered type-II alignment [56]; (b) ZnO deposited on wider band gap SiO2 corresponding to type-I quantum well [57].

Before studying the optical properties, the structural study of ZnO thin films were conducted to confirm that whether there is any structural difference in ZnO thin films grown on these two substrates, Si and SiO₂.

X-ray reflectivity studies have also been done on ZnO films deposited on fused quartz (SiO₂) at 200 °C. Figure 5.8(a) shows specular reflectivity (*R*) normalized with Fresnel reflectivity (*R_F*), for ZnO/SiO₂ samples with different ZnO film thickness grown at 200 °C. It should be noted that ZnO films grown on fused quartz (SiO₂) substrates (ZnO/SiO₂ samples) show similar film thickness, electron density profile, and surface roughness, as observed for ZnO/Si systems. The growth rate of ZnO determined with XRR from the deposited films on SiO₂ was same as observed in ZnO/Si samples, i.e. 1.6 Å/cycle (at 200 °C).



Figure 5.8: (a) Reflectivity profiles, i.e., specular reflectivity (*R*) normalized with Fresnel reflectivity (R_F), (R/R_F) vs. normal momentum transfer q_z (in Å⁻¹) for different ZnO films grown on SiO₂ at 200 °C process temperature, with film thickness: (i) 9 nm, (ii) 19 nm, (iii) 38 nm, (iv) 52 nm and (v) 69 nm; R_F is the theoretical reflectivity from an ideal surface. Circles and lines represent the experimental data and theoretical fit respectively. (b) Corresponding extracted electron density (ρ) profile from XRR fits.

Film thicknesses, corresponding growth parameters, surface roughness, and other relevant parameters, for both the systems (ZnO/Si and ZnO/SiO₂) grown at 200 $^{\circ}$ C are summarized in Table 5.1.

Figure 5.9 shows representative X-ray diffraction patterns for ALD grown ZnO films of different thicknesses deposited at 200 °C process temperature, on Si and SiO₂ substrates. The results indicate the formation of hexagonal wurtzite ZnO with a space group of P63mc, which matches with the standard diffraction pattern of hexagonal wurtzite ZnO (JCPDS PDF card number: 01-079-2205). XRD pattern of ZnO film shows much stronger ZnO (002) peak with respect to ZnO (101), whereas standard powder XRD pattern of hexagonal wurtzite bulk ZnO shows maximum intensity at ZnO (101) peak (JCPDS PDF card number: 01-079-2205). This clearly indicates that ZnO film exhibits preferred orientation along <0002> direction with c axis perpendicular to the substrate surface. Average grain sizes (out-of-plane) calculated from XRD for both the systems (ZnO/Si and ZnO/SiO₂) grown at 200 °C are shown in Table 5.1. The average grain sizes are about 20 nm for thicker ZnO films, but thin ZnO films (at and below 20 nm) show lower grain sizes with decreasing film thickness (see Table 5.1). Results showed that crystal structures of ALD grown ZnO on Si and SiO₂ substrates are similar.



Figure 5.9: X-ray diffraction patterns for ALD grown ZnO films deposited at 200 °C process temperature, on (a) Si and (b) SiO₂ substrates; (c) Reference data: Standard diffraction pattern of hexagonal wurtzite ZnO with a space group of P63mc (JCPDS PDF Card No. 01-079-2205). The observed Si (200) peak at about $2\theta = 33^{\circ}$ is known as kinematically forbidden reflection (or basis-forbidden reflection) for Si (100) substrates, because such reflections can sometimes actually be present due to dynamical scattering events [161-163].

	ZnO/Si						ZnO/SiO ₂				
No. of	ZnO film	SiO ₂	Electron	Surface	RMS of	Mean	ZnO film	Electron	Surface	RMS of	Mean
ALD	thickness	thickness	density	roughness	Surface	grain	thickness	density	roughness	Surface	grain
cycles	from	at ZnO/Si	of ZnO	from XRR	roughness	size	from	of ZnO	from XRR	roughness	size
	XRR [*]	interface	from	(Å)	from AFM	from	XRR [*]	from	(Å)	from AFM	from
	(Å)	from	XRR		(Å)	XRD	(Å)	XRR		(Å)	XRD
		XRR [*] (Å)	(eÅ ⁻³)			(Å)		(eÅ ⁻³)			(Å)
30	53	0	1.39	7		< 50					
60	94	0	1.51	7	11	56	90	1.42	14	11	~30
120	194	9	1.48	15	15	123	194	1.42	16	14	133
230	389	10	1.51	18		208	373	1.48	24		218
300	515	12	1.5	19		194	523	1.5	24		212
410	684	9	1.5	19	18	212	685	1.49	21	19	214

Table 5.1: ALD grown ZnO films deposited at 200 °C process temperature, on Si and SiO₂ substrates.

*Estimated experimental resolution for film thickness measurement through XRR technique is π/q_{max} [122], which is ~8 Å for the ZnO/Si and ZnO/SiO₂ systems [q_{max} can be obtained from Figure 4.1(a) and 5.8(a)].

Figure 5.10 showed that surface morphologies of ALD grown ZnO on Si and SiO₂ substrates are similar.

The root-mean-square (RMS) roughness was estimated for characteristic ZnO film thicknesses from AFM images, which were found to decrease in thinner films (at and below 20 nm), as shown in Table 5.1. The results were consistent with the surface roughness obtained from XRR measurements.

It should be noted that structure and morphology of ALD grown ZnO films on Si and SiO₂ substrates deposited at 200 °C process temperature are similar.



Figure 5.10: Top-view AFM images of ~70 nm ZnO films deposited on Si and SiO₂ substrates (at 200 °C process temperature).

Now, the surface/interface effects on the optical properties of ZnO thin films have been explored. The absorption coefficients of ZnO/Si systems, shown in Figure 5.11(a), were compared with that of the ZnO/SiO₂ shown in Figure 5.11(b). Figure 5.11(a), shows that wider-band gap ZnO deposited on narrower-band gap Si, with staggered type alignment, absorbs less light with decreasing film thickness, at and below ~20 nm. Whereas, in case of ZnO deposited on wider band gap SiO₂ corresponding to type-I quantum well, the thinner ZnO films show higher absorption coefficient at band edge, shown in Figure 5.11(b).

As already discussed, in case of ZnO deposited on Si, which is a staggered type-II quantum well, shown in inset of Figure 5.11(a), the photo generated holes at ZnO are deconfined to the Si substrate at the interface, whereas electrons are confined in ZnO thin film, causing a

lowering of electron-hole overlap factor and thus exhibits low excitonic absorption in thinner films, consequently bringing about a decrease in real and imaginary parts of the dielectric function.



Figure 5.11: (a) Absorption coefficients, α (determined from Ellipsometry) of ZnO films of different thickness grown on Si at 200 °C. The inset of (a) shows wider-band gap ZnO deposited on narrower-band gap Si, with staggered type-II alignment; and (b): Absorption coefficients, α (determined from UV-VIS) of ZnO films of equivalent thickness grown on fused Quartz (SiO₂) at 200 °C. The inset of (b) shows ZnO deposited on wider band gap SiO₂ corresponding to type-I quantum well.

Inset of Figure 5.11(b) illustrates the ZnO $/SiO_2$ system, which is a thin type-I quantum well, consisting of a narrower-bandgap semiconductor grown on a wider-bandgap substrate. In this case, both the electron and the hole are confined in the ZnO film, which leads to an increase in the electron-hole overlap matrix element in thin ZnO films, resulting in higher absorption coefficient at the band edge.

In this study, the absorption coefficients for ZnO/Si samples were calculated from ellipsometry data, while, the absorption coefficients for ZnO/SiO₂ samples were estimated from UV-VIS absorption spectra, measured in transmission mode. Absorption coefficients of thicker ZnO films (~ 69 nm) for both the systems, ZnO/Si and ZnO/SiO₂, show similar values (~1.5 x 10^5 cm⁻¹) indicating negligible effect of the interface (ZnO/substrate). With decreasing film thickness, the absorption coefficient of thinner ZnO films (at and below ~20 nm) was found to decrease for ZnO/Si samples whereas that increases for ZnO/SiO₂ samples.

These observations show that the thickness dependent variations of the optical properties of ZnO thin films are also influenced by the choice of the interface (ZnO/substrate). The observations show the significant effect of surface and interface in determining the optical properties of ZnO films.

To calculate the band gap, a plot of $(\alpha h\nu)^2$ vs energy for ZnO films of different thickness grown on Si at 200 °C is shown in Figure 5.12, where α is the absorption coefficient of ZnO films in ZnO/Si system. A clear blue shift of the absorption edge has been observed with decreasing film thickness, from 38 nm to 5 nm, see Figure 5.12. The electronic transitions between the valence band (V.B.) and conduction band (C.B.) in the crystal start at the absorption edge, which corresponds to the band gap energy, E_g [132].

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Figure 5.12: A plot of $(\alpha h v)^2$ versus energy (hv), where absorption coefficients, α (determined from Ellipsometry) of ZnO films of different thickness grown on Si at 200 °C.

On the other hand, Figure 5.13 shows plot of $(\alpha hv)^2$ vs energy for ZnO films of different thickness grown on SiO₂ at 200 °C, where α is the absorption coefficient of ZnO films in ZnO/SiO₂ system. It can be seen that the absorption edge shifted to higher energy as the film thickness decreases.

Chapter 5



Figure 5.13: A plot of $(\alpha h\nu)^2$ versus energy (hv), where absorption coefficients, α (determined from UV-Vis absorption spectroscopy) of ZnO films of different thickness grown on SiO₂ at 200 °C.

The optical band gap of the ZnO films has been determined using the Tauc model [132, 133] and the Davis and Mott model [134] in the high absorbance region:

$$\alpha(\nu)h\nu = B(h\nu - E_g)^n \tag{5.10}$$

Where, E_g is the optical band gap, *B* is a constant, hv is the incident photon energy and $\alpha(v)$ is the absorption coefficient. For direct transition, n = 1/2 was found to be more appropriate for ZnO films because it gives the best linear curve in the band-edge region [135, 176]. The band gap energy, E_g , can be obtained by extrapolating the linear portion to $(\alpha hv)^2 =$ 0 in that figure.

The increase in the band gap energy or band gap expansion induced by the quantum confinement is a well-known phenomenon [27, 177, 178]. Based on the effective mass approximation (EMA) theory [179], band gap energy, E_g in a confined nanostructure can be written as [27]:

$$E_g(eV) = E_{g,bulk} + \frac{F}{d^2}$$
(5.11)

Where, $E_{g,bulk}$ is the band gap energy of the bulk, *F* is the quantum confinement constant and *d* is the confined dimension, i.e. the film thickness.



Figure 5.14: Band gap of ZnO films having different film thickness deposited on Si and SiO₂ at 200 °C vs. $1/d^2$, *d* is the film thickness. Dotted lines show the corresponding best linear fits.

The band gap, E_g , calculated for ZnO/Si and ZnO/SiO₂ systems for different film thickness, *d* are shown in Figure 5.14. Best linear fits show different slopes, 1.8 eV-nm² and 6 eV-nm², for ZnO/Si and ZnO/SiO₂ systems respectively, which attributes to the substrate dependent variation in thickness induced exciton confinement effect. It should be noted that the observed slope for ZnO/SiO₂ system, is consistent with the results obtained for ZnO/sapphire system [27], which also corresponds to a type-I quantum well. Results indicate that thickness induced effective exciton confinement effect is weaker in case of ZnO/Si system. The fitted bulk band gap energy for ZnO/Si and ZnO/SiO₂ systems are 3.27 eV and 3.2 eV respectively, which are in close agreement with the band gap value of bulk ZnO (free exciton emission peak observed at 3.20 eV, corresponding to the band gap) [28].

The proposed model can explain the observed weaker thickness dependency in blue-shift in band gap energy with decreasing film thickness for ZnO/Si system, with respect to ZnO/SiO₂ system, which corresponds to the effect of weaker exciton confinement or effectively supports the exciton deconfinement effect in ZnO/Si system.



Figure 5.15: (a) Absorption coefficients, α (determined from Ellipsometry) of ZnO films of different thicknesses grown on Si at 35 °C. The inset of (a) shows wider-band gap ZnO deposited on narrower-band gap Si, with staggered type-II alignment and (b) absorption coefficients, α (determined from UV-Vis absorption spectroscopy) of ZnO films of equivalent thickness grown on fused quartz (SiO₂) at 35 °C. The inset of

(b) shows ZnO deposited on wider band gap SiO_2 corresponding to type-I quantum well.

Likewise, in case of near room temperature growth, we observed the similar interface dependent trends in thickness dependent optical properties of ZnO (Figure 5.15).

5.4 Summary

In summary, spectroscopic ellipsometry results clearly demonstrate that thin wider-band gap ZnO on a narrower-band gap substrate, Si, experience exciton deconfinement (lower absorption, refractive index) at interface, which is pronounced at thinner film thickness window, i.e., at and below ~20 nm film thickness. Whereas the similar ZnO films deposited on SiO₂ substrates, show thickness induced excitonic confinement effect in thinner film thickness window. Furthermore, ZnO thin films in ZnO/Si system show weaker thickness dependency in blue shift in band gap energy with respect to ZnO/SiO₂ system, which corresponds to weaker exciton localization effect in ZnO/Si system. The observations were clearly explained in terms of Tanguy-Elliott amplitude pre-factor.

These observations show that the thickness dependent variations of the optical properties of ZnO thin films are also influenced by the choice of the interface (ZnO/substrate). The observations show the significant effect of surface and interface in determining the optical properties of ZnO films. The knowledge developed through this study will be useful in choosing the appropriate interface and optimum film thickness of ZnO films for its various applications in opto- and nano- electronics to achieve the best performance of that particular device.

ALD grown ZnO thin films: Application as efficient binder-free cathode for highperformance rechargeable aluminium-ion batteries

6.1 Outline of work

Application of ALD grown ZnO in a specific utility as an efficient electrode in rechargeable battery was discussed in this chapter. Zinc oxide (ZnO) has been regarded as a promising electrode material in Li-ion batteries due to its high theoretical capacity (987.8 mAh g⁻¹), high lithiumion diffusion coefficient, in addition to its non-toxicity, environmental friendliness and very low cost. It is worth mentioning that for triply charged Al³⁺ ion insertion, the theoretical capacity of ZnO could reach as high as ~2960 mAh g⁻¹. Hence it remains absolutely essential and worthwhile to conduct in-depth study on ZnO as a potential cathode material for rechargeable Al-ion battery application. Due to the low cost, higher safety, low-flammability, lower reactivity, environmental friendliness and natural abundance of Al, the Al-ion battery, as new efficient electrical energy storage device, has displayed excellent prospects.

The continuous, uniform and pinhole-free, conformal nature of ALD grown ZnO thin film of active electrode material can eliminate any possibilities of interference/contribution of the current collector to the performance of the electrode in the battery. Moreover, ALD grown highly c-axis oriented ZnO thin films show enhanced conductivity than those with randomly oriented grains, which facilitates the required electrical

contact and enhanced pathways for electron/ion transfer/transport kinetics in the potential electrode. Thus, ALD grown ZnO thin film on current collector was studied to explore its potential as efficient electrode in fabrication of light-weight binder-free battery. In this part of the work, we report for the first-time binder-free ZnO synthesized by ALD as a novel cathode material for the rechargeable Al-ion batteries.

Nanoscale ZnO, directly grown on current collector through ALD, shows high electrochemical performance as a binder-free cathode for rechargeable Al-ion batteries (AIBs). Al coin cell fabricated using binderfree ALD grown ZnO cathode (ZnO ALD-E) manifests an initial discharge capacity of 2563 mAh g⁻¹, and remains at 245 mAh g⁻¹ at a current rate of 400 mA g⁻¹ after 50 cycles with almost 95% Coulombic efficiency. Distinct and consistent plateaus in discharge/charge curves reveal the Al-ion insertion/extraction process and electrochemical stability of the battery. The delivered discharge capacity of the battery with ZnO_ALD-E cathode is significantly higher (about 10 times higher) than that of batteries fabricated using a conventional ZnO cathode composed of ZnO powder (nanoparticles or bulk) and binder with conductive carbon. Ex-situ XRD and Photoluminescence spectroscopy in different discharge/charge states of Al/ZnO_ALD-E battery reveal the structural information of ZnO_ALD-E, upon Al-ion intercalation/deintercalation. Such remarkable electrochemical performance is attributed to the binderfree, well-defined textured nanostructures of ALD grown ZnO cathode with c-axis orientation along the surface normal, facilitating good electrical contact and enhanced pathways for electron/ion transfer/transport kinetics. As a result, ZnO_ALD-E turns out to be a potential candidate for being used as the electrode in fabricating high efficiency rechargeable Al-ion battery. The present study shows a multifaceted approach for identifying and predicting promising Al-ion insertion properties for advanced Al-ion-based energy storage material. The approach reported here is potentially applicable for other relevant
electrode materials (with a large volume change and low electric conductivity) and may suggest a new path to produce high efficiency next generation green rechargeable batteries. Results presented in this chapter are published in peer reviewed journal.^{‡‡}

6.2 Experimental

6.2.1 Synthesis of ZnO

ZnO thin films were deposited on stainless steel at reactor temperature, 35 °C using a BENEQ TFS-200 ALD reactor. The precursors for zinc and oxygen were diethyl zinc (DEZ, Zn (C_2H_5)₂, Sigma-Aldrich) and deionized (DI) water, respectively. Nitrogen (N_2 , 99.999 % purity) was used both as a carrier and the purging gas. The precursors were alternately introduced into the reactor using their intrinsic vapor pressures from external containers kept at 18 °C. The reactor pressure during the growth was kept at 2.5 mbar. One ALD reaction cycle consisted of a 1 s exposure to DEZn, followed by a 2 min N_2 purge, a 1 s exposure to H₂O, and then another 2 min N_2 purge. The relatively long purging time was used due to the extremely low deposition temperatures in order to make sure that there was only one precursor at a time in the ALD reaction chamber. The thicknesses of the ZnO films were tuned by altering the number of ALD cycles: 120 and 220, and the samples were named as ZnO_ALD-E1 and ZnO_ALD-E2 respectively.

A Sartorius CPA225D microbalance with a resolution of 0.01 mg was used to measure the weight of ZnO films.

6.2.2 Electrochemical Analysis

^{‡‡} Dipayan Pal, Aakash Mathur, Ajaib Singh, Srimanta Pakhira, Rinki Singh, and Sudeshna Chattopadhyay*, *ChemistrySelect* **3**, 12512 (2018).

The electrolyte was prepared by mixing AlCl₃ (Sigma-Aldrich, 99.99%) purity) with 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl, Sigma-Aldrich) together with 1.3 : 1 molar ratio to form the ionic liquid. The assynthesized ZnO thin films via ALD were used as the cathode in tests with CR2032 coin-type cells. These cells were assembled in an argon-filled glove box with high purity Al foil as the counter and reference electrode and a Whatman glass microfiber as the separator. The electrochemical performance of ALD grown ZnO cathodes has been compared with that of the ZnO-bulk cathodes and ZnO-nano cathodes. For that purpose, ZnO bulk particles (particle size, $\sim 0.5 \mu m$) and ZnO nanoparticles (particle size, ~ 30-50 nm) were mixed with the conductive additive and polymer binder to form the pasted electrode on stainless-steel current collector. The electrodes (abbreviated as ZnO bulk-E and ZnO nano-E) were composed of 60% ZnO particles (bulk particles and nanoparticles, Sigma-Aldrich), 10% acetylene black (conductive carbon, Sigma-Aldrich), and 30% polyvinylidenefluoride (PVDF, Sigma-Aldrich) as the binder, dissolved in N-methyl-2-pyrrolidone (NMP) solvent. The resultant slurry was then coated uniformly on the stainless steel current collector and dried. The asfabricated ZnO-bulk and ZnO-nano cathodes were also tested with 2032 coin-type cells. Galvanostatic charge/discharge, cyclic voltammetry and galvanostatic intermittent titration technique (GITT) were performed using battery testing system (CH Instruments, CHI423B). In GITT, the batteries were discharged and charged at 400 mA g⁻¹ for 10 min and rested for 1 hour. The current pulse was repeated until the potential reached the cutoff limit. The diffusion coefficient of Al³⁺ was calculated according to the following equation:

$$D_{Al^{3+}} = \frac{4}{\pi} \left(\frac{iV_m}{zFA}\right)^2 \left[\frac{\left(\frac{dE_S(x)}{dx}\right)}{\left(\frac{dE(\tau)}{d\sqrt{\tau}}\right)}\right]^2 \approx \frac{4}{9\pi\tau} \left(\frac{mV_m}{MA}\right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2$$
(6.1)

Where, D_{Al3+} is the ionic diffusion coefficient, *i* is the applied current (A), V_m is the molar volume (cm³ mol⁻¹) of the electrode material, *z* is the

charge number of the ionic species (z = 3 for D_{Al3+}), F is the Faraday constant (C mol⁻¹), A is the contact area (cm²) between the electrode and the electrolyte, x is the moles of Aluminium per mole electrode (e.g., x in the term Al_xZnO). The approximation in Equation 6.1 is valid when experimentally measured dE_{τ} shows a linear relationship with $d\tau^{1/2}$. ΔE_s is the change in the equilibrium electrode potential (V) after each current pulse of duration τ (sec) and ΔE_{τ} is the change in the electrode potential (V) measured during each current pulse of duration τ (sec). m and M are the mass (g) and the molecular weight (g mol⁻¹) of the active material, respectively.

6.2.3 Materials Characterizations

The film thickness of the ALD grown ZnO films was estimated using Spectroscopic ellipsometry (SE) technique. The crystalline structures of the as-grown ZnO films were investigated by X-ray diffraction (XRD). The photoluminescence (PL) emission from the ZnO films was measured at room temperature. The morphologies of the electrodes were observed with Field Emission Scanning Electron Microscopy. Furthermore, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy studied were also performed.

6.3 Structure Characterizations and Electrochemical properties

In this study, ZnO cathodes, ZnO_ALD-E, were prepared by growing ZnO film on stainless steel (SS) current collector (15.5 mm diameter disk) employing atomic layer deposition (ALD) technique under the operation temperature of 35 °C. ZnO films of two different thicknesses were formed on the current collectors by controlling the ALD cycles, namely 120 and

220 cycles, corresponding to the following electrodes ZnO_ALD-E1 and ZnO_ALD-E2 with ZnO film thicknesses 22 nm and 39 nm respectively. The thickness of the ZnO film was accurately estimated using nondestructive spectroscopic ellipsometry (SE) technique, shown in Figure 6.1 and Table 6.1, and correspondingly the mass of the ZnO films in ZnO_ALD-E1 and ZnO_ALD-E2 were estimated as 0.02 mg and 0.04 mg and which were found to be consistent with the measured weight of the active materials by using the microbalance.



Figure 6.1: Ellipsometric angles ψ and Δ plot as a function of photon energy for (a) ZnO_ALD-E1 and (b) ZnO_ALD-E2; grown on stainlesssteel substrates, acquired with incidence angles ranging from 60° to 70°; circles and lines represent experimental data and theoretical fit, respectively. (c) Ellipsometric angles ψ and Δ plot as a function of photon energy for bare stainless-steel substrate, acquired with incidence angles ranging from 60° to 70°; circles and lines represent experimental data and theoretical fit, respectively. (d) The model [180, 181] used to fit the ellipsometric data for ZnO_ALD-E, consisting of a stainless-steel (SS)

substrate, stainless-steel surface roughness layer (i.e., interface roughness), ZnO layer, and a surface roughness layer.

Figure 6.1(a) and (b) show experimentally measured and fitted spectra of the ellipsometric angles, ψ and Δ , for as-deposited ZnO ALD-E (ALD grown ZnO on stainless-steel disk). In this work, the parameterized semiconductor oscillator function (PSEMI) model [180, 181] has been used to fit the experimental ellipsometry data. For this study, a five layer model (i.e. air/surface-roughness layer/ZnO layer/stainless-steel substrate roughness layer/stainless-steel substrate) has been used to extract the film thickness, where the stainless-steel substrate is about 1 mm thick and has been treated as infinite. Surface and interface roughnesses are modeled by a Bruggeman type effective medium approximation [182, 183] with 50% of voids and 50% of material (i.e., surface layer would contain 50% of ZnO, and ZnO/steel interface layer would contain 50% of steel), as shown in Figure 6.1(d). The model assumes pinhole-free, continuous, ZnO layer, conformally grown on rough stainless-steel disk (or current collector), since in general, the films grown using ALD are typically continuous, pinhole-free and extremely conformal to the underlying substrate [44, 75, 77]. It has been found that the calculated ψ and Δ are in good agreement with the experimental data. Good fits with MSE (mean-squared-error) value less than 10 were achieved [184] for the sample. Ellipsometry data of bare stainless-steel (SS) substrate was also analyzed for the reference purpose, as shown in Figure 6.1(c). The estimated surface roughness of bare stainless-steel disk is about 9 nm from ellipsometry data analysis, which is consistent with the results obtained for ZnO_ALD-E samples, as shown in Table 6.1. Summary of the extracted values of the film thickness, surface and interface roughnesses and corresponding mass of the ZnO films from the ellipsometry data analysis is shown in Table 6.1.

Table 6.1: The summary of the extracted values of the ZnO layer thickness (on stainless-steel substrate), surface and interface roughnesses and corresponding mass of the ZnO films from the ellipsometry data analysis.

Sample	Steel Surface	ZnO layer	ZnO Surface	Calculated	
	Roughness	Thickness	Roughness	ZnO mass	
	(nm)	(nm)	(nm)	(mg)	
ZnO ALD-E1	8.0 ± 1.2	15.2 ± 0.6	6.0 ± 0.7	0.023	
ZnO_ALD-E2	8.5 ± 0.5	29.2 ± 1.2	11.7 ± 1.6	0.040	
Stainless-steel	9.5±0.8				
disk					

From Table 6.1 and Figure 6.1(d), considering the conformal ZnO layer coating on rough steel substrate thorough ALD technique, the estimated effective ZnO film thickness including the contribution of corresponding roughnesses in ZnO_ALD-E1 and ZnO_ALD-E2 are about 22 nm and 39 nm respectively. The typical growth rate for the ZnO on steel was found to be about 1.8 Å per cycle through ellipsometry measurements, shown in Figure 6.1 and Table 6.1, which is in agreement with the previous studies of ZnO growth by ALD [159, 185, 186].

The structural and morphological information of as grown ZnO_ALD-E were obtained by XRD, Photoluminescence (PL) spectroscopy and Field-emission scanning electron microscopy (FESEM).



Figure 6.2: Characterization of pristine ZnO_ALD-E: (a) X-ray diffraction pattern; (b) Room temperature photoluminescence (PL) spectra, indicating sharp near band edge (NBE) and broad deep level (DLE) emissions; (c) and (d) FESEM image of ZnO_ALD-E in two different magnifications.

Typical XRD data for room temperature (35 °C) ALD grown ZnO film on stainless-steel current collector (SS 304) is shown in Figure 6.2(a). It is worth noting that the continuous three diffraction peaks at 31.71°, 34.2° and 35.98° match well with the (100), (002), and (101) planes of hexagonal wurtzite ZnO (JCPDS PDF card number: 01-079-2205). Results indicate the formation of hexagonal wurtzite ZnO with a space group of P63mc, whereas the presence of strong ZnO (002) (in comparison to ZnO (101)) peak, clearly indicates that the ZnO film exhibits preferred orientation along <0002> direction with c axis perpendicular to the substrate surface (or oriented along surface normal), indicating the growth of textured ZnO film on SS, the current collector.

The crystalline domain size of ZnO was calculated using the Scherrer's equation [160] and is approximately 18 nm, which is in good agreement with the SEM image shown in Figure 6.2(d).

Room temperature photoluminescence (PL) spectra was used to further probe the crystallinity and defect-related information of the as grown ZnO_ALD-E. The typical PL spectra of ZnO_ALD-E as shown in Figure 6.2(b), exhibits a strong UV near-band-edge emission (NBE) around 3.4 eV which corresponds to the crystalline nature of ZnO, along with a broad defect related deep-level green emission (DLE) around 2.3 eV associated with oxygen vacancies (and interstitial Zn ions) in the ZnO lattice [136, 187].

FESEM was performed to obtain the morphology information of ZnO_ALD-E. Figure 6.2(c) and (d) are the representative SEM images of pristine ZnO film (on SS) with two different magnifications. The surface morphology from the SEM images indicates the formation of smooth ZnO film, consisting of wedge-shaped grains (in-plane sizes along major and minor axes are about 20 and 10 nm, respectively). Such shape is consistent with earlier reported findings on ALD-grown ZnO films [159].

To investigate the electrochemical performance of the ALD grown cathode, ZnO_ALD-E of Al-ion batteries (AIBs), the galvanostatic discharge/charge measurements were executed in a voltage range of 0.8 - 0.05 V and at a high current density of 400 mA g⁻¹ (for even higher current density, 800 mA g⁻¹, the cell performs in similar manner till 10th cycle, and after that pronounced capacity fading was observed).



Figure 6.3: Electrochemical characterizations of Al/ZnO_ALD-E batteries. (a) Initial discharge/charge curves of ZnO_ALD-E1 at a current density of 400 mA g^{-1} . (b) Galvanostatic discharge-charge profiles of ZnO_ALD-E1 at a current density of 400 mA g^{-1} for the 4th, 5th and 8th cycle. (c) Cyclic voltammogram (CV) of ZnO_ALD-E1 for the 4th, 5th and 8th cycle at the scan rate of 0.1 mV s⁻¹. (d) Cycle performance and Coulombic Efficiency plot of ZnO_ALD-E1 from the second cycle onwards at a current density of 400 mA g^{-1} . All capacity calculations are based on the mass of ZnO. (e) Representation of ALD grown binder-free ZnO cathode, ZnO_ALD-E1. Optical image of the steel current collector (SS) before and after the growth of thin ZnO film by ALD technique and the open circuit potential of the Al/ZnO_ALD-E battery; corresponding

assembled coin cell by the series connection of three Al/ZnO_ALD-E1 batteries, which lights up an LED indicator (f).

Figure 6.3(a) shows the initial cycle of discharge/charge curves for Al/ZnO_ALD-E1. The initial discharge/charge capacity is 2563 and 1639 mAh g^{-1} , respectively, with Coulombic efficiency of 64%. Figure 6.3(b) shows the discharge/charge curves of the same battery for the 4th, 5th and the 8th cycles. Two pairs of completely overlapped discharge and charge plateaus exist at 0.45 V, 0.2 V and 0.6 V, 0.35 V respectively, which correspond to the insertion (intercalation) and extraction (deintercalation) of Al in the framework of ZnO and indicate that the reaction proceeds in two steps [63, 156, 188, 189]. Such two steps reaction can be attributed to the manifestation of the insertion and extraction of Al-ions in two oxidation states, into and from the ZnO ALD-E cathode [188], or can be assigned to Al-ions insertion and extraction into two kinds of crystallographic sites of ZnO [63, 189]. Furthermore, the cyclic voltammogram (CV) in the voltage window (0.8 - 0.02 V) at a scan rate of 0.1 mV s⁻¹, as shown in Figure 6.3(c), presents two reduction peaks (E'_{R} and E''_{R}) at 0.35 V and 0.2 V, and their corresponding oxidation peaks $(E'_{O} \text{ and } E''_{O})$ at 0.6 V and 0.4 V, which are in good agreement with the galvanostatic discharge and charge plateaus. The peak position and peak current values were nearly identical even after 8 cycles, and the results demonstrate the electrochemical stability of the battery.

The cycling performance at the current density of 400 mA g^{-1} (the specific discharge and charge capacity and corresponding coulombic efficiency for different cycles) is shown in Figure 6.3(d), which manifests the second cycle discharge capacity of 1418 mAh g^{-1} and remains at 245 mAh g^{-1} after 50 cycles with about 95 % Coulombic efficiency. The results clearly indicate that the performance of the ZnO_ALD-E electrode

is quite promising in Al-ion battery application, with respect to the available literature [62, 190, 191]. To the best of our knowledge, this Alion battery system reported in this work delivers the highest capacity in the initial discharge/charge cycles, in the history of AIBs and hold a reasonable high capacity even after 50 cycle discharge/charge. Such high initial discharge/charge capacity was also observed by Songtao Lu *et al.*, for ZnO on carbon black as nanostructured anode materials in Li-ion battery application [192]. The cycling performance of ZnO_ALD-E was tested for larger number of cycles also; see Figure 6.4, which demonstrates a reasonable discharge capacity of ~135 mAh g⁻¹ after 100 cycles with about more than 90 % coulombic efficiency.

The rapid capacity decay in the first few cycles could be attributed to the formation of an SEI layer and the decomposition of the liquid electrolyte or possible incomplete reactions [191]. On the other hand the observed irreversible capacity loss in the initial cycles can also be ascribed to the possibility that Al ions are trapped in the framework of ZnO and cannot be extracted to contribute to charge capacities [193]. The similar phenomenon is also observed in other metallic oxide systems [193, 194].

The reason for the origin of two discharge/charge plateaus in galvanostatic measurement, have been discussed further in this chapter along with detailed XPS measurements and data analysis.

The magnitude of the calculated discharge capacity was also tested through lighting up the LED lamp in the following manner. The open circuit potential of the assembled Al/ZnO_ALD-E battery is about 0.83 V. The series connection of three Al/ZnO_ALD-E cells and a red LED lamp is illustrated in Figure 6.3(f). Obviously the three cells can create a voltage (i.e., more than 1.9 V) that lights the LED lamp up. It is noteworthy that with these three Al-ion cells (Al/ZnO_ALD-E), for only (0.02 mg \times 3) 0.06 mg of cathode materials, ZnO (without any binder or other related chemical components), the LED can glow for ~ 5 minutes [circuit shown

in Figure 6.3(f)] at a stretch for the first cycle, which is very much consistent with the observed first galvanostatic discharge capacity, 2563 mAh g^{-1} , of the Al/ZnO_ALD-E battery, as shown in Figure 6.3(a).



Figure 6.4: Cycle performance and Coulombic Efficiency plot of ZnO_ALD-E1 from second cycle onwards at a current density of 400 mA g^{-1} in the voltage range of 0.8-0.04 V.

The Table 6.2 summarizes the electrochemical performance of different cathode materials observed in the reported literatures of Al-ion battery, which indicate that the observed performance of ZnO_ALD-E is impressive in the realm of Al-ion battery research.

Table 6.2: Electrochemical performance of different cathode materials vis a vis the Al-ion battery research area (summary of some recent literatures) and comparison with this study.

Reference	Cathode material	Reported maximum cycle no.	Discharge/Charge capacity (mAh g ⁻¹)			Coulombic efficiency at final cycle (%)
			1 st discharge capacity	1 st charge capacity	Final cycle discharge capacity	
ACS Appl. Mater. Interfaces 2015 , 7, 80 [194]	Binder-Free V_2O_5 Current density: 44.2 mA g ⁻¹	5 cycle	239 mAh g ⁻¹	Not shown	185 mAh g ⁻¹ (at 5 th cycle)	
J. Electrochem. Soc. 2016 , 163, A1070 [63]	Mo ₆ S ₈ Current density: 12.8 mA g ⁻¹	16 cycle	170 mAh g ⁻¹	90 mAh g ⁻¹	105 mAh g ⁻¹ (at 16 th cycle)	95 % (at around 16 cycle)
ACS Nano 2017, 11, 11135 [195]	Vanadium Carbide (MXene)					
	(i) Multilayered (ML) Vanadium Carbide: Current density: 10 -100 mA g ⁻¹	45 cycle	335 mAh g ⁻¹	178 mAh g ⁻	\sim 100 mAh g ⁻¹ (at 45 th cycle)	92-100 % (at around 45 cycle, depending on the rate current)
	 (ii) Few layered (FL) Vanadium Carbide: Current density: 100 mA g⁻¹ (discharge), 1000 mA g⁻¹ (charge) 	100 cycle	160 mAh g ⁻¹	125 mAh g	75 mAh g ⁻¹ (at 100 th cycle)	~98 % (at around 100 cycle)
ACS Appl. Mater. Interfaces 2017 , 9, 21251 [156]	TiS ₂ Current density: 5 mA g ⁻¹	50 cycle	50 mAh g ⁻¹ (at room temp)	20 mAh g ⁻¹ (at room temp)	35 mAh g ⁻¹ (at 50 th cycle) (at room temp)	97 % (at around 50 cycle) (at room temp)
			70 mAh g ⁻¹ (at 50°C)	40 mAh g ⁻¹ (at 50°C)	70 mAh g ⁻¹ (at 50°C)	100% (at 50°C)
ACS Appl. Mater. Interfaces 2017 , 9, 28486 [193]	Li ₃ VO ₄ @C Current density: 20 mA g ⁻¹	100 cycle	137 mAh g ⁻¹	85 mAh g ⁻¹	48 mAh g ⁻¹ (at 100 th cycle)	100 % (at around 100 cycle)
J. Electrochem. Soc. 2017 , 164, A2304 [196]	MoO ₂ Current density: 100 mA g ⁻¹	100 cycle	90 mAh g ⁻¹	253 mAh g ⁻¹	25 mAh g ⁻¹ (at 100 th cycle)	65 % (after 100 cycle)
Results from this work	ZnO_ALD-E1 Current density: 400 mA g ⁻¹	100 cycle	2563 mAh g ⁻¹	1639 mAh g ⁻¹	250 mAh g ⁻¹ (at 50 th cycle) 135 mAh g ⁻¹ (at 100 th cycle)	~ 95 % (at around 50 cycle) 90 % (at around 100
					cycic)	cycle)

The cycling performance curves for ZnO films of different thicknesses, ZnO_ALD-E1 and ZnO_ALD-E2, show almost identical discharge/charge capacity per unit area vs cycle profile, see Figure 6.5. The results indicate that the thickness of the active layer of the ZnO film in ZnO_ALD-E is equal or less than the film thickness of the ZnO_ALD-E1, which is about 20 nm. In this report, the discharge/charge capacity per unit mass has been calculated by considering the mass of the possible maximum active ZnO layer, i.e., about 20 nm thick ZnO layer on circular stainless steel current collector of 15.5 mm diameter. It can be concluded that the reported high discharge/charge capacity of ZnO_ALD-E in AIBs is the minimum estimated value for the ALD grown ZnO electrode.



Figure 6.5: Cycle performance (discharge/charge capacity per unit area vs. cycle number) of ZnO_ALD-E1 and ZnO_ALD-E2.

For comparison, we also tested with coin cells that were fabricated by using commercially available ZnO nanoparticles and ZnO bulk particles cathodes, prepared by mixing with conductive additive and polymer binder (weight ratio, ZnO: conductive additive: binder = 60:10:30, the thickness of the electrode is about 20 µm), in which stainless-steel was

also used as the current collector, referred as ZnO_nano-E and ZnO_bulk-E respectively. Galvanostatic electrochemical charge-discharge cycling of the test cells was performed, under a potential window of 0.8 - 0.05 V, and at the charge-discharge current density of 100 mA g^{-1} . Figure 6.6(a) shows the voltage profiles for the initial discharge/charge cycle for the cells fabricated using ZnO nanoparticles (ZnO nano-E) and ZnO bulk powder (ZnO_bulk-E) as the cathodes. The cycling performance at the current density of 100 mA g^{-1} (the specific discharge and charge capacity for different cycles) are shown in Figure 6.6(b), which reveals the significantly low discharge/charge capacity (about 10 times lower) of the Al-ion batteries, fabricated using ZnO_nano-E and ZnO_bulk-E, with respect to ZnO_ALD-E as cathodes [shown in Figure 6.3(d)]. The discharge/charge capacity for a given cycle (e.g., the sixth cycle) of the cells using ZnO_ALD-E, ZnO_nano-E and ZnO_bulk-E as the cathode are shown in Figure 6.6(c), for the comparison purpose. ZnO nano-E and ZnO_bulk-E delivered an initial discharge capacity 226 mAh g⁻¹ and 59 mAh g⁻¹ respectively as cathodes in Al-ion batteries, much lesser (order of magnitude less) than that of cell fabricated using ZnO ALD-E as the cathode. The discharge voltage plateau at about 0.45 V in the galvanostatic discharge curves of the ZnO_ALD-E cathode is much higher than that of the ZnO_nano-E and ZnO_bulk-E cathodes.



Figure 6.6: (a) Initial discharge/charge curve of ZnO_nano-E and ZnO_bulk-E at a current density of 100 mA g^{-1} . (b) Cycle performance of ZnO_nano-E and ZnO_bulk-E at a current density of 100 mA g^{-1} . (c) Galvanostatic discharge-charge profiles of ZnO_ALD-E, ZnO_ nano-E and ZnO_bulk-E for the 6th cycle.

This improvement is attributed to the properties of the binder-free cathode, as well as the effect of oriented growth of ZnO through ALD technique,

which not only enhanced the charge exchange between the ZnO active material and the stainless steel collector, but may have also improved the migration of the ions within the large-scale textured ZnO cathode (ZnO_ALD-E), as shown schematically in Figure 6.7.



Figure 6.7: Schematic illustration of the Al/AlCl₃-[EMIm]Cl/ZnO_ALD-E battery during the discharge process.

The comparison study provides the possible explanation of exhibition of high electrochemical storage capacity of ALD grown ZnO electrode (ZnO_ALD-E), as theoretically expected, which is difficult to achieve/observe in conventional ZnO electrode, synthesized with a conductive additive and polymer binder.

The influence of stainless-steel current collector on electrochemical performance of Al/AlCl₃[EMIm]Cl/ZnO_ALD-E battery system was excluded by performing the galvanostatic measurement with the battery, assembled with stainless steel as current collector, and with no active material, and shown in Figure 6.8 which shows that the specific capacity of stainless steel in acidic AlCl₃-[EMIm]Cl (AlCl₃ : [EMIm]Cl = 1.3 : 1)

is almost negligible, which is fairly consistent with the previous observation on electrochemical performance of stainless-steel current collector by Jiali Jiang *et al.*[193]



Figure 6.8: Galvanostatic discharge-charge profiles of stainless steel for the 1^{st} , 2^{nd} , 5^{th} and 10^{th} cycle under the potential window of 0.8 - 0.05V.

In this context, it should be noted that the interface between the electrode (ZnO layer) and current collector (steel) is typically under the "impermeable boundary condition" where the atom/metal-ions cannot penetrate the back of the electrode (based on well known, mathematically established theory) [108, 197]. So, the reported electrochemical storage capacity or specific charge capacity of ZnO_ALD-E is due to the ZnO layer only, where ZnO thin film is only act as active cathode material (consequently, the weight of ZnO layer has been considered to calculate the specific charge storage capacity, as discussed earlier in details).

The discharge/charge reaction process of the Al/AlCl₃-[EMIm]Cl/ZnO ALD-E battery system can be formulated as the following equations [191, 193]

In the discharge process:

Cathode: $ZnO + xAl^{3+} + 3xe^{-} \rightarrow Al_x ZnO$ (6.2)

Anode: $Al + 7AlCl_4^- - 3e^- \rightarrow 4Al_2Cl_7^-$ (6.3)

In the charge process:

Cathode:
$$Al_x ZnO - 3xe^- \rightarrow ZnO + xAl^{3+}$$
 (6.4)

Anode: $4Al_2Cl_7^- + 3e^- \rightarrow Al + 7AlCl_4^-$ (6.5)

Hence, the schematic representation of the as-prepared aluminium-ion battery during the discharge process is presented in Figure 6.7. On the cathode side, predominantly Al-ions intercalate and deintercalate in/from the framework of ZnO during the discharge and charge process, respectively. On the anode side, $Al_2Cl_7^-$ is produced by the reaction of metallic Al with $AlCl_4^-$ during discharging, and the reverse reaction occurs during charging [193]. It can be deduced that $Al_2Cl_7^-$ is the electrochemically active ion in the electrolyte, which is present when the molar ratio of AlCl₃ to [EMIm]Cl is greater than 1.1:1 [193] (in our case it is 1.3:1).



Figure 6.9: Potential profiles from GITT measurement during the electrochemical insertion/extraction of Al ions into/from the framework of ZnO in 1st discharge process.

Galvanostatic intermittent titration technique (GITT) measurement was carried out to investigate the Al ion diffusion coefficients of ZnO_ALD-E in discharge states; as demonstrated in Figure 6.9. The Al³⁺ diffusion coefficient is in the range of 10^{-15} to 10^{-19} cm² s⁻¹ in the first discharge cycle. The similar value of Al-ion diffusion coefficient has also been observed in the available literature of Al-ion battery [63, 156].

To get further insight into the structural information of ZnO_ALD-E upon Al intercalation/deintercalation, the ex-situ XRD measurements of electrodes after 50 cycles (at charged state) was executed, and compared with that of pristine ZnO_ALD-E in Figure 6.10.



Figure 6.10: (a) XRD data of ZnO_ALD-E (i) pristine, (ii) after 1st discharge, (iii) after 50th charge; and (b) Reference data. Standard Diffraction pattern of hexagonal wurtzite ZnO with a space group of P63mc (JCPDS PDF Card No. 01-079-2205). The two dashed vertical lines show shifted ZnO (100) and ZnO (002) peaks in 1st discharge and 50th charged samples.

As mentioned earlier, for pristine ZnO_ALD-E three diffraction peaks at 31.71°, 34.2° and 35.98° match well with the (100), (002), and (101) planes of hexagonal wurtzite ZnO (JCPDS PDF card number: 01-079-2205). However, the diffraction peaks of the wurtzite structure surprisingly shifted towards higher angles after first discharge, suggesting decreasing d spacing. It is easy to observe from Figure 6.10 that the

displacement distance towards the right is approximately 0.9° for (002) planes, after first discharge, suggesting decreasing c lattice constants corresponding to the decreasing of d space (about 0.06 Å calculated by Bragg equation) along with the insertion of Al^{3+} into ZnO ALD-E. The incorporation of Al into the ZnO matrix may have reduced the lattice constant because of its smaller ionic radius (Al³⁺ 0.53 Å vs. Zn²⁺ 0.74 Å), as reported by other groups [156, 198, 199]. The decreased lattice parameter could be caused by the very small, highly charged Al-ions in the interstitial position of ZnO frame work reducing the repulsion between two consecutive planes [156]. Another possible explanation could be that the intercalated Al occupied Zn sites during the discharge process [156, 198, 199]. The excess Al impurities occupy interstitial sites instead of substitutional sites [199]. Figure 6.10 clearly indicates that the crystallinity of ZnO_ALD-E decreases and that the displacement distance still remains about 0.9° after 50 cycles. On the basis of the results, it can be concluded that the structure of ZnO ALD-E will slightly distort irreversibly to accommodate the insertion of Al-ion (in the initial cycles and remain stable in the subsequent cycles). However, such a decrease in crystallinity of electrode materials is an accumulation process upon repeated Al intercalation and deintercalation during the discharge/charge cycling. Therefore, the gradual deterioration of crystallinity upon cycling may account for the capacity loss of ZnO_ALD-E electrode in the subsequent cycles. A similar phenomenon was also observed in AIBs with Li₃VO₄@C microsphere composite as cathode material [193]. ZnO ALD-E shows an extra XRD peak after cycling, at around 30.9°, which may be assigned as ZnAl₂O₄ gabnite phase [198, 200] (JCPDS PDF card number: 00-005-0669).

Since the intensity and spectral content of PL peaks are the direct measure of impurities, structure, chemical composition, kinetic process and energy transfer [201], the room temperature PL of ZnO_ALD-E cathode was studied in the discharge state, Al intercalated ZnO_ALD-E,

for first and fifty cycles, as shown in Figure 6.11(b) and (c) respectively, whereas PL of ZnO_ALD-E at pristine condition and in the 50th cycle in charged state, Al deintercalated ZnO_ALD-E, are shown in Figure 6.11(a) and (d) respectively. As mentioned earlier the pristine ZnO ALD-E exhibits the peak at 3.44 eV corresponding to the near band edge (NBE) peak that is responsible for the recombination of the free excitons of ZnO [202, 203].



Figure 6.11: Gaussian fits for the room temperature photoluminescence (PL) spectra of ZnO_ALD-E1 at different states: Left panel: (a) pristine, (b) after 1st discharge, (c) after 50th discharge, and (d) after 50th charge. The sum of the Gaussian components is indicated by the thicker solid line as resultant fit for the experimental data (in circles). Right panel represents the corresponding data in log scale to clearly indicate the band edge shifts, shown in black dashed lines.

The ZnO_ALD-E in the discharge states shows the broad (FWHM ~ 0.2 eV to 0.5 eV) NBE peak at the lower energy region (3.44 eV to 3.11 eV) as compared to the pristine ZnO film (ZnO_ALD-E)) indicating the reduction of the band gap, attributed to the band edge bending due to the doped Al-ion induced donor level below the conduction band [198, 204, 205], which suggests the Al intercalation into the ZnO framework/film (Al: ZnO_ALD-E discharge), during the discharge process. Furthermore, consistent results were observed at charged state, where the electrode shows the retention of the NBE peak position (3.35 eV) and the peak width (~ 0.2 eV) towards the pristine ZnO_ALD-E, attributed to the deintercalation of Al-ion from ZnO film during the charging (Al: ZnO_ALD-E charge).

The other PL deep level peaks in the visible region (blue and green emissions) for Al: ZnO_ALD-E_discharge samples, are predicted to originate from the interstitial Zn and/or Al (~ 2.88 eV), vacancy in Zn ($V_{Zn} \sim 2.76 \text{ eV}$), interstitial Zn and/or Al ions (~ 2.6 eV) and oxygen vacancy (~ 2.3 eV) [136, 137, 192]. Possible assignment and details for the peaks for all the samples were displayed in Table 6.3. It should be noted that the blue emission (with green co-emission) enable Al: ZnO_ALD-E discharge for optoelectronic device applications such as LEDs as well. Additionally, the enhancement of blue emissions would be beneficial for the light emitting and biological fluorescence labeling applications [136] of these Al intercalated ZnO films.

Sample	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6
	(FWHM)	(FWHM)	(FWHM)	(FWHM)	(FWHM)	(FWHM)
Pristine	3.44 eV	3.3 eV	—	2.78 eV	2.5 eV	2.23 eV
ZnO_ALD-	(0.25 eV)	(0.3 eV)		(0.22 eV)	(0.33	(0.42
E1					eV)	eV)
ZnO_ALD-	3.11 eV		2.89 eV	2.76 eV	2.58 eV	2.3 eV
E1 after 1 st	(0.5 eV)		(0.17 eV)	(0.16 eV)	(0.35 eV)	(0.38 eV)
discharge						
ZnO_ALD-	3.12 eV		2.88 eV	2.76 eV	2.62 eV	2.31 eV
E1 after	(0.49 eV)		(0.16 eV)	(0.14 eV)	(0.39 eV)	(0.4 eV)
50 th						
discharge						
ZnO_ALD-	3.35 eV	—	3.01 eV	—	2.67 eV	2.48 eV
E1 after	(0.21 eV)		(0.34 eV)		(0.25 eV)	(0.26 eV)
50 th charge						(0.2007)

Table 6.3: Peak positions (eV) and FWHM (eV) for all the peaks

 deconvoluted from photoluminescence data fitting.

To better understand the Al-ion intercalation/deintercalation mechanism, X-ray photoelectron spectroscopy (XPS) was carried out for ZnO_ALD-E electrodes in pristine state (i.e. before discharge-charge cycles), and in different discharge/charge states. Figure 6.12(a) shows XPS spectra of pristine ZnO_ALD-E1. In the pristine ZnO_ALD-E1, Zn 2p and O 1s peaks are present and obviously there is no signal of Al 2p. Figure 6.12(b) shows the XPS spectra of ZnO_ALD-E1 after first

discharge, which clearly indicates the presence of Al 2p peak, corresponding to the intercalation of Al-ion into the ZnO_ALD-E cathode. It was also observed that the intensity of Zn 2p peak becomes very weak after first discharge. The observation is consistent with the XRD results, which refers to the possible interpretation of the intercalated Al occupied Zn sites during the discharge process [156, 198, 199]. The strong Al 2p signal, of ZnO_ALD-E1 at discharged state, becomes negligibly small after complete charge process, as shown in Figure 6.12(c). The result clearly indicates the deintercalation of Al ion from ZnO_ALD-E cathode during the charging process.



Figure 6.12: XPS survey spectra of ZnO-ALD-E1: (a) pristine, (b) after 1st discharge and (c) after 50th charge.

To get the information on charge states of Al-ions, taking part in the intercalation and deintercalation process, the high resolution XPS spectra of Al 2p for Al/ZnO_ALD-E1 (at different discharge and charge states) were analyzed, and shown in Figure 6.13. The XPS spectra of Al 2p for pristine ZnO ALD-E1 (or before cycling), after 1st discharge plateau for first cycle, after 2nd discharge plateau for first cycle and after charge plateau of first cycle are illustrated in Figure 6.13(c), (d), (e) and (f) respectively. The obtained Al 2p peak intensities were normalized with respect to the corresponding O 1s intensity, as shown in Figure 6.13 (d), (e) and (f). As expected, there is no Al 2p signal in pristine ZnO ALD-E1 (Figure 6.13(c)). The peak positions of Al 2p in XPS spectra, corresponding to 1st and 2nd discharge plateaus for first discharge cycle, are at 74.4 eV and 74.6 eV respectively (Figure 6.13(d) and (e)). The observed peak shift can be ascribed to the two different oxidation states of Al-ions (e.g., Al^{1+} , Al^{2+} , or Al^{2+} , Al^{3+}). It should be noted that the XPS peak of Al 2p shifts from \sim 73 eV to \sim 75 eV for metallic Al (i.e., Al⁰) to Al^{3+} ion states [206, 207]. The results indicate that the observed two discharge plateaus at different potentials (~0.45 eV and ~0.2 eV) in the galvanostatic measurement, can be attributed to the manifestation of the insertion and extraction of Al-ions in two oxidation states, into and from the ZnO_ALD-E cathode [188]. Consistent Al 2p peak shifting, towards lower binding energy side (~74.2 eV), was observed for XPS spectrum of Al/ZnO ALD-E1 after first cycle charge plateau, as shown in Figure 6.13(f). Corresponding Galvanostatic discharge/charge curves and cyclic voltammetry results are illustrated in Figure 6.13(a) and (b) respectively for the convenience.



Figure 6.13: (a) 1st cycle discharge/charge curves of ZnO_ALD-E1 at a current density of 400 mA g⁻¹; (b) Cyclic voltammogram (CV) of ZnO_ALD-E1 at the scan rate of 0.1 mV s⁻¹; Left panel of (c), (d), (e) and (f) show profiles of open circuit potential, 1st discharge plateau (1st cycle), 2nd discharge plateau (1st cycle) and charge plateau (1st cycle) respectively of ZnO_ALD-E1; Right panel of (c), (d), (e) and (f) show corresponding XPS spectra of Al 2p for ZnO_ALD-E1 in different discharge/charge states [(I) before cycling, (A) after 1st discharge plateau (1st cycle), (B) after 2nd discharge plateau (1st cycle) and (A') after charge plateau (1st cycle)]. The obtained Al 2p peak intensities were normalized with respect to the corresponding O 1s intensity [in Right panel of (d), (e) and (f)].



Figure 6.14: Raman spectra of ZnO_ALD-E1 for pristine, after 1st discharge and after 1st charge states.

Another important confirmatory study for Al intercalation in ZnO lattice, for Al/ZnO_ALD-E system, was carried out through Raman scattering measurement.

Raman scattering is sensitive to the crystal lattice structure of ZnO via its vibrational properties. Raman spectroscopy is a non-destructive characterization technique, based on inelastic light scattering that provides information about the phonon vibrational and rotational mode properties of the material. Wurtzite-type ZnO belongs to the space group $C_{6\nu}^{4}$ with two formula units in the primitive cell [146, 147]. The zone-center optical phonons can be classified according to the following irreducible representations [146]:

$$\Gamma_{opt} = A_1 + E_1 + 2E_2 + 2B_1 \tag{6.6}$$

The B_1 modes are silent modes. Both A_1 and E_1 are polarized phonons having each longitudinal optical (LO) and transverse optical (TO) components. E_2 is nonpolarized phonon having two frequencies E_2^{high} and E_2^{low} [146, 147, 208]. The Raman spectra of the pristine ZnO_ALD-E1 and after discharge-charge states are displayed in Figure 6.14. The peak at 221 cm⁻¹ in the pristine ZnO could be attributed to the $2E_2^{low}$ mode [146]. and this peak is getting shifted in the cycled electrodes. In the pristine ZnO, the A₁ symmetry peak 290 cm⁻¹ that can be assigned to $B_1^{high} - B_1^{low}$ mode [146, 209] is also found to be shifted to lower wavenumber after discharge-charge states. This peak shift to lower wavenumber can be related to intrinsic host lattice defects in ZnO where the defects have become activated vibrating complexes due to the incorporation of Al dopants [209]. This shift may be caused due to the introduction of Al ion in the ZnO lattice [209]. Also, this peak is getting enhanced in the discharge-charge samples, which confirms substitution of Al in ZnO [210]. E_1 (TO) mode at 403 cm⁻¹ [211] for the pristine sample disappeared after discharge-charge, and this peak is shifted to lower wavenumber after discharge-charge, which could be attributed to the A_1 (TO) mode [211]. The mode at 506 cm^{-1} in the pristine sample is the surface phonon modes (SPMs) [210, 211]. These SPMs are getting enhanced in the dischargecharge sample, which can be correlated with the addition of Al into the ZnO matrix [210]. The mode at 662 cm⁻¹ in the pristine sample is attributed to the multiple phonon (contribution from TA+LO) modes [146, 211], and this peak is also present in the discharge-charge samples.

6.4 Summary

In summary, ALD grown ZnO thin films were for the first time used as an active novel cathode material for the rechargeable aluminium-ion batteries, which manifests the initial discharge capacity of 2563 mAh g^{-1} and remains at 245 mAh g^{-1} after 50 cycles. This cathode is synthesized by

directly depositing ZnO on stainless-steel current collector. Distinct and consistent plateaus in discharge/charge curves reveal the Al-ion insertion/extraction process and electrochemical stability of the battery. The delivered discharge capacity of the battery with ZnO_ALD-E cathode is significantly higher (about 10 times higher) than that of batteries fabricated using a conventional ZnO cathode composed of ZnO powder (nanoparticles or bulk) and binder with conductive carbon. Ex-situ XRD and Photoluminescence spectroscopy in different discharge/charge states of Al/ZnO_ALD-E battery reveal the structural information of ZnO_ALD-E, upon Al-ion intercalation/deintercalation. Ex-situ X-ray photoelectron spectroscopy (XPS) of ZnO_ALD-E electrodes was carried out in different discharge/charge states to evaluate the detailed intercalation/deintercalation mechanism of Al into/from the framework of ZnO. Besides, Raman spectroscopy in different discharge/charge states of Al/ZnO ALD-E battery revealed the structural stability of ZnO, upon Alion intercalation/deintercalation.

Such remarkable electrochemical performance of ZnO_ALD-E is attributed to the binder-free, well-defined textured nanostructures of ALD grown ZnO cathode with c-axis orientation along the surface normal, facilitating good electrical contact and enhanced pathways for electron/ion transfer/transport kinetics. The results presented in this work may pave the way for the production of low-cost and green aluminium-ion batteries in the future for advanced energy storage.

Conclusions and Scope for Future Work

This chapter summarizes all the conclusions drawn based on research work reported in this thesis. This chapter also discusses possible future scope of work that can be carried out for further development in this field.

7.1 Conclusions

In this work, in first part, ALD technique was employed to grow ZnO thin films of different thicknesses (ranging from ~5 nm to ~70 nm) with very low surface roughness and bulklike electron density, on two different selected substrates, silicon (Si) and fused quartz (SiO₂), to study the surface/interface effects on optical properties of ZnO. The interface of ZnO/Si (wider-band gap ZnO deposited on narrower-band gap Si, with staggered type band alignment) corresponds to the staggered type-II quantum well, whereas in the case of ZnO deposited on wider band gap SiO₂ corresponds to type-I quantum well. The real and imaginary parts of the complex dielectric function of ZnO/Si showed monotonically decreasing values with decreasing ZnO film thickness at and below a threshold of about 20 nm. The reduction of the dielectric function with film thickness was explained consistently by the Tanguy–Elliott amplitude prefactor governing the strength of optical interband transitions through the lowering of the electron-hole overlap factor at the ZnO/Si interface. In the case of ZnO/Si, a staggered type-II (spatially indirect) quantum well, holes are scattered into the Si substrate, causing a lowering of the electron-hole overlap factor and thus the reduction of excitonic

absorption, consequently a decrease in the real and the imaginary parts of the dielectric function. This hypothesis was confirmed with ZnO films grown on SiO₂, where a thin type-I quantum well, consisting of a narrower-bandgap semiconductor grown on a wider-bandgap (insulator) substrate, in which both the electron and the hole are confined in the ZnO thin film, leads to an increase in the electron–hole overlap matrix element with decreasing film thickness due to confinement, resulting in enhancement of the excitonic absorption in thinner ZnO films on SiO₂.

As an effect of surface and interface in ZnO thin films, a blue shift of the absorption edge with decreasing film thickness at and below ~20 nm was also reported. Thickness dependent blue shift, energy vs. $1/d^2$ (where, d represents ZnO film thickness) in two different systems, ZnO/Si and ZnO/SiO₂, showed a difference in their slopes. The observed phenomena were also consistently explained by the corresponding exciton (or carrier/s) deconfinement and confinement effects at the ZnO/Si and ZnO/SiO₂ interface respectively, where Tanguy-Elliott amplitude prefactor plays the key role through the electron-hole overlap factor at the interface.

The optical study was conducted on two different sets of ALD grown ZnO samples, grown at two different growth temperatures, at high temperature (200 °C) and at near room temperature (35 °C), where we observed the consistent results with similar interface dependent trends in thickness dependent optical properties of ZnO.

The structure and morphology of the ZnO films were studied elaborate. The structural study showed that high quality, crystalline, smooth ZnO thin films with a preferred orientation along the <0002> direction with the c axis predominantly perpendicular to the substrate surface, was grown on both the substrates irrespective of the growth temperatures. Whereas, the growth temperature dependent variation in surface morphology of ZnO films were observed. ZnO grown at high temperature exhibited wedge-shaped grains (in-plane size along major and minor axes are ~40 and ~20

nm, respectively) in their surface morphology, and in case of near room temperature growth, a spherical/circular (~20 nm) in-plane shape was predominant.

Application of ALD grown ZnO in a specific utility as an efficient electrode in rechargeable battery was explored in second part of our study. Zinc oxide (ZnO) has been regarded as a promising electrode material in Li-ion batteries due to its high theoretical capacity (987.8 mAh g⁻¹), high lithium-ion diffusion coefficient, in addition to its non-toxicity, environmental friendliness and very low cost. It is worth mentioning that for triply charged Al^{3+} ion insertion, the theoretical capacity of ZnO could reach as high as ~2960 mAh g⁻¹. Hence it remains absolutely essential and worthwhile to conduct in-depth study on ZnO as a potential cathode material for rechargeable Al-ion battery application. Due to the low cost, higher safety, low-flammability, lower reactivity, environmental friendliness and natural abundance of Al, the Al-ion battery, as new efficient electrical energy storage device, has displayed excellent prospects.

The continuous, uniform and pinhole-free, conformal nature of ALD grown ZnO thin film of active electrode material can eliminate any possibilities of interference/contribution of the current collector to the performance of the electrode in the battery. Moreover, ALD grown highly c-axis oriented ZnO thin films show enhanced conductivity than those with randomly oriented grains which facilitates the required electrical contact and enhanced pathways for electron/ion transfer/transport kinetics in the potential electrode. Thus, ALD grown ZnO thin film on current collector was studied to explore its potential as efficient electrode in fabrication of light-weight binder-free battery. In this part of the work, we report for the first-time binder-free ZnO synthesized by ALD as a novel cathode material for the rechargeable Al-ion batteries.

Nanoscale ZnO, directly grown on current collector through ALD, shows high electrochemical performance as a binder-free cathode for

rechargeable Al-ion batteries (AIBs). Al coin cell fabricated using binderfree ALD grown ZnO cathode (ZnO ALD-E) manifests an initial discharge capacity of 2563 mAh g⁻¹, and remains at 245 mAh g⁻¹ at a current rate of 400 mA g⁻¹ after 50 cycles with almost 95% Coulombic efficiency. Distinct and consistent plateaus in discharge/charge curves reveal the Al-ion insertion/extraction process and electrochemical stability of the battery. The delivered discharge capacity of the battery with ZnO_ALD-E cathode is significantly higher (about 10 times higher) than that of batteries fabricated using a conventional ZnO cathode composed of ZnO powder (nanoparticles or bulk) and binder with conductive carbon. Ex-situ XRD and Photoluminescence spectroscopy in different discharge/charge states of Al/ZnO_ALD-E battery reveal the structural information of ZnO ALD-E, upon Al-ion intercalation/deintercalation. Such remarkable electrochemical performance is attributed to the binderfree, well-defined textured nanostructures of ALD grown ZnO cathode with c-axis orientation along the surface normal, facilitating good electrical pathways for electron/ion contact and enhanced transfer/transport kinetics. As a result, ZnO ALD-E turns out to be a potential candidate for being used as the electrode in fabricating high efficiency rechargeable Al-ion battery. The present study shows a multifaceted approach for identifying and predicting promising Al-ion insertion properties for advanced Al-ion-based energy storage material. The approach reported here is potentially applicable for other relevant electrode materials (with a large volume change and low electric conductivity) and may suggest a new path to produce high efficiency next generation green rechargeable batteries.
7.2 Future Prospects

Integrating the benefits from different aspects of the present study, there is much scope to extend this work further in future. Some possible studies are described below:

- It would be of great interest to apply the current films in devices such as TCOs in thin film solar cells in order to measure their efficiency.
- Based on the acquired knowledge on interface effect on optical properties of ZnO thin films, the suitable materials can be chosen to design the desired heterojunction to tune the optical properties of the material to enhance the efficiency for its particular device application. The proposition can be further extended to tune other relevant properties as well.
- In addition, due to their low growth temperature, the films could be also grown on polymer substrates for applications in flexible thin films photovoltaics.
- Following the similar approach other relevant electrode materials (with a large volume change and low electric conductivity) can be fabricated to overcome the present day issues, to achieve higher efficiency in rechargeable batteries.
- Atomic layer deposition of ZnO could be used to modify/coat the surface of novel electrode material for improvement the performance of batteries.

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