A. Highly aligned and well oriented ZnO nanorods/ nanotubes synthesized by simple electrochemical deposition method.

6(a) 1.1. Introduction:

In particular, 1D nanostructure has attracted much attention due to the confinement of the other two dimensions, perpendicular to longitudinal direction. Most of the unique optical properties of 1D nanostructure are related to quantum confinement. Due to their high aspect ratios, large specific surface areas and structural confinement on the circumferential dimensions, the 1D nanostructures have demonstrated many novel mechanical, electrical, optical, chemical properties [1-5]. Such properties would directly lead to applications in nanodevices. For those 1D nanostructures of wide band gap semiconductors, such as ZnO (3.37 eV) and GaN (3.44 eV), their lasing property has attracted much attention due to their potential as candidates for ultraviolet (UV) - blue optical devices for a higher optical storage capacity [6-8].

ZnO has gained tremendous attention owing to its astonishing properties and versatility of nanoforms such as nanobelts, nanowires, nanocombs etc [9-12]. With high exciton binding energy of 60 meV, this wide band gap semiconductor (3.37 eV) can be used for various applications such as sensors, solar cells, supercapacitors, piezoelectrical energy generators, etc [13-16]. ZnO crystallizes preferentially in the thermodynamic favorable hexagonal wurtzite structure and due to its large band-gap, pure ZnO is optically transparent. It is very resistive to high-energy radiation, posing it a suitable material for space applications. In pure ZnO the naturally occurring n-type must be caused by oxygen vacancies or zinc interstitials [13]. The formation energy of oxygen vacancies compared to zinc interstitials is much lower. Therefore it can be assumed that oxygen vacancies are more abundant in ZnO and are the main contributor to the n-type conduction.

Furthermore ZnO is easily etched in all acids and alkalis, providing an opportunity for the fabrication of small size devices. Among the various forms of ZnO, vertically-aligned ZnO nanorods/ nanowires / nanotubes arrays with uniform diameter and length distribution are of interest from device application point of view. This chapter deals with the synthesis of highly crystalline and vertically aligned ZnO nanorods (ZNRS) and ZnO nanotubes (ZNTs) on a conducting substrate, by a simple electrodeposition method. Specifically, the ZnO nanotubes (ZNTs) grown on conducting substrates has attracted great attention because of their larger specific surface than that of the nanorods and nanowires, which make them efficient for charge carrier extraction.
Chapter 6a

6(a) 1.2. Introduction to Electrodeposition:

Electrodeposition is a process of coating a thin layer of one metal on top of different metal to modify its surface properties. In electrodeposition, metal ions present in a solution, the electrolyte, are reduced at the surface of an electrode to form a metal layer. This process essentially consists of a conducting substrate, an electrolyte solution containing metal ions, a counter electrode mostly insoluble (Pt) and an electric current or voltage source to control the deposition. The desired potential is applied on the working electrode to and the reaction of interest occurs on its surface. The auxiliary electrode passes all the current needed to balance the current passing through the working electrode. The reference electrode is used only to measure potentials of working electrode. There is no current flow between the working and reference electrodes.

During electrodeposition, first electrolysis of the salt (precursor compound) occurs generating anions and cations, which are directed towards respective electrodes by the electric field (applied potential). These ions get neutralized by electron transfer across the double layer and atoms get incorporated onto the substrate followed by nucleation and growth. Finally formation of monolayer and growth of the electrodeposit takes place. Electrodeposition offers high rate of deposition, high resolution, high shape fidelity, simple scalability, and good compatibility with existing processes. [17]

6(a) 2. Experimental:

6(a) 2.1 Synthesis of ZnO nanorods:

ZnO nanorods were electrodeposited on gold coated silicon substrate (Au/Si) in a electrochemical cell equipped with platinum (Pt) as the counter electrode, and a Saturated Calomel Electrode (SCE) as the reference electrode. Prior to deposition the substrate was rinsed with acetone, ethanol and DI water in sequence for 5 min respectively, and mounted on a copper stub. Electrodeposition was carried out in potentiostatic mode, as it is good in controlling the polarization and content of each element in the compound. The anode-cathode distance was maintained at 2.5 cm and an oil bath was used to keep the reaction temperature at constant value.

An aqueous solution of 1mM of [Zn (NO₃)₂·6H₂O, Aldrich, 99.999%] and 100 mM of KCl was used as an electrolyte. It is well known that the resultant morphology of the deposit can be monitored by controlling the process variables such as nature and concentration of the electrolyte, pH of the electrolyte, temperature, deposition duration, and applied potential. In this regard, effect of applied potential, reaction temperature, deposition duration and pH of the electrolyte on the morphology of the electrodeposited ZnO nanostructures has been investigated A computer controlled electrochemical
analyzer (Model- 1100A series, CH instrument, USA) was used to maintain the cathodic polarization condition with respect to the SCE. After a fixed deposition time, the working electrode was removed and washed in gentle flow of water, and dried in air.

6(a) 2.2 Synthesis of ZnO nanotubes:

For the synthesis of ZnO nanotubes, the as synthesized ZnO nanorods were etched selectively in a chemical bath of 0.125 mM KOH solution at different temperatures for 1 hr duration.

6(a) 2.2.1 Effect of deposition temperature:

In order to study the effect of deposition temperature on phase and overall morphology of the deposited product, the electrodeposition was carried out at two different temperatures, 60 and 70 °C, keeping the other process parameters unchanged (time(90 min), applied potential(-0.9V), pH of the electrolyte (6.2)). The as-synthesized product was characterized using XRD and SEM so as to reveal the effect of deposition temperature on its phase and morphology.

6(a) 2.1.1 X-ray Diffraction analysis:

The typical XRD spectra of the deposit synthesized at bath temperatures of 60 and 70°C are depicted in Fig. 6(a).1. It is interesting to note that the crystalline quality is strongly influenced by the reaction temperature. At lower reaction temperature, it is revealed that the crystalline phase growth is incomplete, whereas at higher temperature (70 °C) the observation of a set of well defined diffraction peaks reveals formation of crystalline phase. The observed diffractions peaks are indexed to the corresponding (h k l) planes of hexagonal wurtzite phase of ZnO (PCPDF No. 79- 0205). The intense diffraction peak observed at 39° corresponds to Au, which is due to presence of thin Au layer on the silicon substrate.

ZnO is formed via a precursor such as hydrated zinc hydroxide (Zn(OH)₄²⁻) which dehydrates at enough high temperature (above ~50°C). The transformation rate from precursor to ZnO is extremely sluggish at low temperature, and increases rapidly with increase in the temperature. Therefore, the crystal quality of ZnO electrodeposited at lower temperature is not good because the slow reaction rate.
Figure 6 (a).1: XRD spectra of ZnO nanorods electrodeposited on Au/Si substrate at different reaction temperatures (a) 60° and 70°C.

6(a) 2.1.1.2 SEM analysis:

The SEM images of the as-synthesized products obtained at bath temperatures of 60 and 70°C are depicted in Fig. 6(a).2. Although in both the cases, the overall morphology is characterized by presence of vertically aligned ZnO nanorods, a careful observation of the SEM images reveals change in the areal density of the ZnO nanorods. The areal density estimated from the SEM images is 62 and 48 nanorods/µm², corresponding to deposition temperatures of 60 and 70°C. At higher deposition temperature the areal density is found to be lower, which can be attributed to the kinetics of the various reactions occurring during the electrodeposition process.
Figure 6(a)2: SEM images of the ZnO nanorods synthesized at deposition temperatures (a) 65 °C, and (b) 70 °C.

6(a) 2.1.2. Effect of applied potential:

In order to study the effect of applied potential on the surface morphology, a set of experiments were performed at different values of applied potential viz, -0.6, -0.8, -0.9 volts. The Fig. 6(a)3 depicts the SEM images of the as-synthesized ZnO nanostructures deposited at the aforesaid applied potentials. The SEM images clearly reveal that at lower applied potential (-0.6 V) formation of well faceted ZnO nanorods is not achieved. Also the areal density of these ZnO nanostructures is poor as compared to higher applied potential cases. The observation of well faceted ZnO nanorods with good area density is achieved at an applied potential of -0.8 V, indicating that this is the critical value of the applied potential below which formation of such well defined nanorods is forbidden. Interestingly, further increase in the applied potential leads to narrowing of diameter of the ZnO nanorods. The variation in surface morphology as a function of applied potential can be understood from the kinetics of different reactions occurring during the electrochemical deposition process. The rate of generation of hydroxide ions on the substrate surface at lower value of applied potential (-0.6 V) is slower, and thus the growth of ZnO nanorods is not complete. On increasing the potential more hydroxide ions are generated accompanied with accelerated diffusion of zinc ions in the electrolyte followed by their adsorption on the cathode surface. All this processes promote the growth rate during electrodeposition and thus lead to formation of well faceted ZnO nanorods.
Effect of electrodeposition duration:

In this study, the deposition was carried out for two different deposition durations, 45 and 90 minutes. In both the cases formation of ZnO nanorods is observed (Fig. 6.4). However, the average diameter of the ZnO nanorods is found to be higher for longer deposition duration. It indicates initially the growth of ZnO is faster along rod axis (vertical direction) and as time passes, the growth rate in lateral directions is appreciable resulting into increase in the diameter rather than the rod length.
Figure 6(a).4: SEM images of ZnO nanorods electrodeposited on Au/Si substrate at different deposition times of (a) 45, and (b) 90 min

6(a) 2.1.4. Effect of electrolyte pH:

The morphologies of as-grown ZnO nanostructures electrodeposited in a solution of 0.001 M Zn(NO₃)₂ and 0.1M KCl with different pH values are shown in Fig. 6(a).5. It can be seen that the density of ZnO nanorods and diameter decreases as the pH value of electrolyte increases. On applying a constant potential to the electrode, the bulk pH substantially remains constant while at the interface between electrode and electrolyte, pH increases abruptly as a result of the reduction of nitrate ions

\[
\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO}_2^- + 2\text{OH}^- 
\]

Thus, the generated OH- ions are accumulated and consumed within the double layer to form ZnO deposit on the electrode. But not all the generated OH- ions got consumed which can be inferred from a slight increase in pH value measured after the deposition. The solubility of Zn in solution is related to the pH value of the solution and determines the nucleation density and length of ZnO nanorods. At higher pH value, a large number of nuclei will precipitate on the substrate because of high saturation. The suitable pH value of the solution is determined by the Iso-electric point (IEP), which is defined as the pH at which a particular molecule carries no net electrical charge. If the interface pH is either higher or lower than this IEP (8.7-10.3), the solubility of Zn (II) increases and the degree of saturation of the species decreases. It results in a lower driving force to nucleate and thus less is the ZnO nuclei density. Moreover, because of the lower interfacial energy for ZnO to nucleate on the existing ZnO nuclei than on the substrate surface, further deposition will only accumulate on the existing nuclei.
(a) TEM:

Further morphological and structural characterization of the as-grown ZnO nanorods (synthesized at applied potential of -0.9 V, reaction temperature of 70°C, pH of the electrolyte 6, and deposition duration of 90 minutes) was carried out using TEM. For TEM analysis, a small portion of the specimen was scrapped off from the substrate and dispersed in isopropenol. This solvent was ultrasonicated for 10 minutes. Then a drop of ultrasonicsted solvent (containing the ZnO nanorods in dispersed state) was put onto a carbon coated Cu grid (200 mesh). A typical TEM image (Figure 6(a)).6(a)) reveals the diameter of the ZnO nanorod to be ~ 100 nm. The Fig. 6(a).6(b) depicts a selected area electron diffraction (SAED) pattern of a single ZnO nanorod. The observation of six fold symmetric spot pattern clearly reveals the crystalline nature of the ZnO nanorods synthesized under the prevailing experimental conditions.
Figure 6(a).5: (a) typical TEM image of a single ZnO nanorod, and (b) corresponding SAED pattern.

6(a) 2.2.1. SEM of ZnO nanotubes:

ZnO nanotubes were obtained by etching as synthesized nanorods in a controlled way. The conversion of nanotubes from nanorods depends on various parameters such as bath temperature, time, molarity etc. In the present work, effect of temperature and time was investigated keeping other parameters constant. The converted ZnO nanorods at different temperature are shown in Fig. 6(a).6. Fig. 6(a).6(a) shows SEM image of ZnO nanotubes etched at 80°C, etching at the centre of the nanorods takes place but not uniform. When the temperature is too high, etching is uncontrolled and so formed nanotubes are standing apart from the substrate. When the bath temperature was kept at 70°C (shown in Fig. 6(a).6(b)), the tubes so formed were uniform and adhere to the substrate. With further decreasing temperature to 60°C (Fig. 6(a).6(c)), the so formed nanotubes were well aligned to the substrate. Thus the process of formation of nanotubes is just opposite to nanorods. For nanorods, the crystallinity and alignment increases with increasing temperature, however uniform and well aligned nanotubes were obtained at low temperature.
Further time also plays an important role to control the morphology of ZnO nanotubes. The nanorods were kept at 60°C for different time. For more than 90 minutes the morphology was completely distorted and the tubes were no more attached to the substrate. The SEM images of nanotubes etched for 90 min. is shown in Fig.6(a).7. Thus uniform, well aligned nanotubes can be obtained when the bath temperature is 60°C and kept for 60min.

**Figure 6(a).6:** SEM image of nanotubes obtained at a bath temperature of (a) 80°C, (b) 70°C and (c) 60°C.
6(a) 2.2.2. Photoluminescence Spectra (PL):

To characterize the optical properties of ZnO nanotube and nanorod arrays, we have performed photoluminescence (PL) measurements. As an excitation source for the PL experiment, high pressure Xenon (Xe) arc lamp was used. The Xe lamp emitting an intense and relatively stable continuum from 300 to 1100 nm laser (325 nm) was employed. Fig. 6(a).8 shows the room-temperature PL spectrum of ZnO nanotube and nanorod arrays fabricated on the Au coated silicon substrate. Two typical emission peaks at ~382 nm and ~520 nm were observed, which were assigned to UV emission and green-yellow emission, respectively. According to the literature, the UV emission with a peak at ~380 nm has been attributed to the near band edge emission of ZnO. The green-yellow emission is a deep-level transition, originating from the recombination of the holes with the electrons occupying the singly ionized oxygen vacancy. The intensity of the deep-level emission is determined by the concentration of the oxygen vacancies in the ZnO crystal [18-21].

Figure 6(a).7: SEM images of nanotubes kept for 90 minutes.
Figure 6(a).8: PL spectra of (a) ZnO nanorods and (b) ZnO nanotubes
6(a) 3. Growth Mechanism:

6(a) 3.1. ZnO nanorods:

The formation of ZnO nanorods involves following sequences

(a) **Dissociation**: Dissociation of Zinc nitrate to Zinc ions by following reaction

\[
\text{Zn} (\text{NO}_3)_2 \rightarrow \text{Zn}^{2+} + 2\text{NO}_3^- \tag{1}
\]

(b) **Hydrolysis**: Hydrolysis of this nitrate ions results in hydroxide ions.

\[
\text{NO}_3^- + \text{H}_2\text{O} + 2\varepsilon \rightarrow \text{NO}_2^- + 2\text{OH}^- \tag{2}
\]

(c) **Interaction of ions**: The hydrated cations interact with OH\textsuperscript{-} ions and get reduced at the cathode.

\[
\text{Zn}^{2+} + 2\text{OH}^- \leftrightarrow \text{Zn} (\text{OH})_2 \tag{3}
\]

(d) **Dehydration of the hydroxide**: Dehydration of so formed zinc hydroxide at temperature more than 55\textdegree\text{C} results in formation of ZnO.

\[
\text{Zn(OH)}_2 \leftrightarrow \text{ZnO} + \text{H}_2\text{O} \tag{4}
\]

6(a) 3.2. ZnO nanotubes:

It is known that ZnO can be dissolved even with acid generated by the anodic oxidation of water. Thus, we have attempted to combine the synthesis of ZNTs from ZNRs by applying chemical etching process. The experimental results show that the solid ZNRs can then be etched into hollow ZNTs by the chemically generated acid from the oxidation of water. Here, the etching process can be divided into two steps. Firstly, the H\textsubscript{2}O was electrolyzed to O\textsubscript{2} and H\textsuperscript{+}. Then ZnO in the rod form is etched by the H\textsuperscript{+} and forms hollow tubes. This process can be described by the following equations:

\[
\text{H}_2\text{O} \quad \rightarrow \quad \frac{1}{2}\text{O}_2 + 2\text{H}^- + 2\varepsilon^- \tag{1}
\]

\[
\text{ZnO} + 2\text{H}^+ \quad \rightarrow \quad \text{Zn}^{2+} + \text{H}_2\text{O} \tag{2}
\]

In the etching process, the ZNRs were etched according to the overall reaction

\[
\text{ZnO} \quad \rightarrow \quad \text{Zn}^{2+} + \frac{1}{2}\text{O}_2 + 2\varepsilon^- \tag{3}
\]
To form the tubular morphology, the dissolution of ZNRs must be a preferential etches process. As there were no other assistant reagents in the electrolyte, the preferential etch should be related with intrinsic characters of the ZnO nanorods. There may be two possible reasons responsible for the selective etching of ZnO nanorods to nanotubes. First, the metastability of the (001) plane led to the preferential etch in the (001) plane and fastest etching rate in the [001] direction. Second, the unbalanced distribution of defects in the ZnO nanorods led to the preferential etches in the center part of the nanorods [22].

6(a) 4. Field emission:

The field emission properties of the ZnO nanorod and nanotube array with an emitting surface area of 0.2cm$^2$ are shown in Fig. 6(a).9 and 6(a).10. The turn-on field define at emission current density of 1 $\mu$A cm$^{-2}$, was found to be 7.2 V $\mu$m$^{-1}$ for the nanorods as seen from the J –E plot shown in Fig. 6(a).9 (a), and 8.44 for the nanotubes (Fig. 6(a).9(a)).

From the J-E curves of both ZnO nanorods and nanotubes, one can say that the emission current density of ZNTs increase rapidly after a threshold value and reaches a maximum of 352.5 $\mu$Acm$^{-2}$ at an applied field of 13.77 V $\mu$m$^{-1}$. However, the maximum emission current density of 51.5 $\mu$A/cm$^2$ was achieved for ZNRs at an applied field of 10 V/µm. Thus the emission current density for the nanotubes is about six times higher than the nanorods of same diameter. This enhancement in emission current density can be attributed to the sharp edges of ZNTs. As field emission is a surface sensitive phenomenon, any change in the surface morphology gets reflected. The as synthesized ZNTs were derived from ZNRs, i.e. having same length but the edges are sharper resulting in an enhanced field emission behavior of ZNTs as compared to ZNRs.

Further the F-N curve corresponding to both ZNRs and ZNTs are shown in Fig. 6(a).9 (b) and 6(a).10(b). Both the F-N curves shows an overall linear behavior, which is in good agreement with the F-N equation. The ZnO nanorods and nanotubes have multiple emitters/spikes with variation in diameter and distance between the consecutive sheets resulting in an average effect of linearity in F-N plot.
Figure 6(a).9 (a) Field emission current density versus applied electric field (J-E) plot and (b) corresponding F-N plot of ZnO nanorods.

Figure 6(a).10: (a) Field emission current density versus applied electric field (J-E) plot and (b) corresponding F-N plot of ZnO nanotubes.

Emission current stability is one of the decisive parameter for field emission. To check the stability of both ZNRs and ZNTs, the emission current was recorded over a period of 3hrs at a preset value of 1µA and shown in Fig. 6(a).11. Interestingly, ZnO nanotubes exhibits excellent stability while stability of nanorods exhibits some fluctuations in the form of spikes. These spikes can be attributed to the absorption-desorption and migration of residual gas molecules on the surface of emitter. The
average emission current seems to be stable over the entire duration of the measurement. A nearly constant average current of ZnO nanotubes is remarkable and important for the application purpose. This significant stability suggests a good contact between Au/Si substrate and the ZnO nanorods and nanotubes.

Figure 6(a).12: Emission current stability curves at a preset value of 1 μA of (a) ZnO nanorods and (b) ZnO nanotubes
Typical field emission images of ZnO nanorods and nanotubes corresponding to different applied potential are shown in Fig. 6(a).13. The temporal changes in the spots intensity are observed to proportionate with the observed emission current fluctuations (Fig. 6(a).12).

6(a) 5. Conclusion:

- Well oriented, highly crystalline ZnO nanorods were synthesized on conducting substrate (Au/Si) by a simple electrodeposition method. The processing parameters such as potential, time, pH of the electrolyte and temperature were varied one by one keeping other constant to obtain the desired morphology.
- The as synthesized nanorods were further etched by a simple process to obtain ZnO nanotubes of same length. The etching process was found to be opposite to synthesis of nanorods. Further, ZNTs exhibits enhanced field emission behaviour over ZNRs, which can be attributes to the sharp protrusions of ZNTs resulted after etching.
- Comparative field emission analysis of ZnO nanorods and nanotubes suggest nanotubes morphology superior over nanorods of same length, which can be attributes to the sharp edges of the nanotubes.
- Further remarkable current stability of both ZnO nanorods and nanotubes suggest a good electrical contact with the substrate which is of considerable interest from the application point of view.
References:


(B) Synthesis of 2-D ZnO nanosheets on ITO substrate and their field emission investigations.

In this section synthesis and characterization of 2D form of ZnO is discussed. The 2D-ZnO structures (nanosheets) were synthesized on ITO coated glass substrates employing electrodeposition route. Furthermore, its field emission properties were investigated. The FE results and analysis was complemented by density functional theory calculations to present a plausible explanation for enhancement in the field emission properties of the ZnO nanosheets.

6(b) 1. Introduction:

The preceding chapters deals with synthesis, characterization and field emission investigations 2D structures like GNRs and TMDs. Due to nanometer scale thickness, high surface-to-volume ratio and superior properties suitable for applications in electronics, optoelectronics, energy storage and conversion devices, variety of 2D nanostructures such as nanosheets, nanowalls, nanoplates of metal oxides, chalcogenides, nitrides and carbides have been investigated [1-5]. As stated in the introduction chapter, amongst numerous semiconducting metal oxides, ZnO is a fascinating nontoxic wide band gap material with excellent physical and biocompatibility properties. It is also realized that this is the only material possessing richest family of 0D, 1D and 2D nanostructures. In comparison to the 1D nanostructures of ZnO, fewer studies have been reported on the growth and applications of its 2D nanostructures such as nanosheets, nanoflakes and nanowalls [6-10]. However, 2D ZnO nanostructures do exhibit potential or variety of applications. Due to its buckling behavior, coupled with semiconducting and piezoelectric properties, the ZnO nanosheets are suitable candidate for an efficient DC power generator with enhanced and more stable power-generating performance [6]. Fig. 6(b).1 shows a comparative publication statistics of 2D ZnO in past decade. The results were taken from web of science. The results shows that with increasing research on layered structures, the research interest in 2D ZnO nanostructures has also increased.

This chapter gives synthesis and field emission investigation of ZnO nanosheets arrays grown by electrodeposition on ITO coated glass substrates.
Figure 6(b). 1: Publication statistics of 2D ZnO nanosheets. The data is compiled using web of science

6(b) 2. Experimental:

ZnO nanosheet arrays were grown on ITO coated glass substrate employing electrodeposition route, comprised of a three electrode set up monitored by a computer controlled electrochemical analyzer. Prior to electrodeposition, the ITO substrate (1×1 cm²) was cleaned by acetone, ethanol and deionized water and dried at room temperature. An aqueous electrolyte of 0.01M zinc nitrate was prepared by dissolving 0.2974 g of zinc nitrate hydrate was dissolved into 100 ml of distilled water. After complete dissolution of zinc nitrate, 0.01M (0.074gm) potassium chloride was added in the electrolyte. The potassium chloride acts as supporting electrolyte. Electrodeposition was carried out with an electrochemical analytical instrument (PG262A, Technoscience Ltd.) in a standard three electrodes system with a Pt wire as counter electrode, Ag/AgCl as reference electrode. ITO coated glass substrate acted as working electrode. Electrodeposition was carried out at -1.1V potential with continuous stirring of the solution at 70°C for 2 h. The as-prepared ZnO on ITO substrate was calcined at 60°C for 25 minutes followed by annealing at 200°C for 8 hours in air.
6(b) 3. Characterization:

6(b) 3.1 X-ray diffraction analysis:

Figure 6(b).2 shows the XRD patterns of the ZnO nanosheets deposited on ITO coated substrate and the pristine ITO coated glass substrate. The observation of a set of well defined diffraction peaks indicates crystalline nature of the as-grown sample. All the major diffraction peaks are matched to the Wurtzite ZnO structure (JCPDS-036-1451). No characteristic diffraction peaks of other phases was observed. The (100) peak appears to be more sharp, indicating their preferred growth along (100) direction. This suggests that the use of a low deposition temperature and a large negative potential in the present work suppresses the formation of the chlorinated zinc hydroxyl salt and promotes the reduction of Zn$^{2+}$ to metallic zinc. Typically ZnO owing to its wurtzite structure prefers to grow in (002) direction due to its faster growth rate along c-axis. In our case, the preferred growth direction of ZnO nanosheets along (100) direction is possibly due to the faster growth process at low temperature [11, 12].

![XRD pattern](image)

**Figure 6(b).2**: XRD patterns of the electrodeposited ZnO on ITO coated glass substrate black colored) and pristine ITO coated glass substrate (red colored).

6(b) 3.2 SEM analysis
The morphology of the electrodeposited ZnO on ITO coated glass substrate was studied using SEM and fig. 6(b).3 shows the corresponding SEM images. Interestingly, formation of vertically aligned and randomly oriented ZnO nanosheets covering the entire substrate surface is observed under the prevailing experimental conditions. The intercrossed sheet structures have the very small thickness. Fig. 6(b).3(b) and (c) represent the SEM images of the ZnO nanosheets recorded at higher magnifications, which clearly show their ultra fine thickness in the range of 10 to 50 nm and of micron size (~2 to 5 µm). The elemental composition obtained from EDAX spectrum reveals presence of Zn and O in the deposit complementing the XRD analysis indicating ZnO phase.

**Figure 6(b).3:** SEM images of the electrodeposited ZnO on ITO coated glass substrate recorded at different magnifications.
6(b) 3.3 Raman Spectroscopy analysis:

The samples were also characterized by a Micro Raman spectrometer with a laser excitation wavelength of 488 nm. Fig. 6(b).3 depicts a typical Raman spectrum of the ZnO nanosheets. The peaks observed at 326, 432, and 570 cm\(^{-1}\) are assigned to \(E_{2\text{H}}-E_{2\text{L}}\), \(E_{2\text{H}}\), and \(E_{1\text{L}}\) vibrational modes of ZnO lattice, respectively. The \(E_{2\text{H}}\) mode involves only oxygen atoms and the \(E_{1\text{L}}\) mode is associated with oxygen deficiency, indicating that oxygen vacancies exist in the nanosheets [13]. In addition the broad features in the Raman spectra indicate the presence of defects and oxygen vacancies due to the higher sensitivity of Raman scattering to crystal imperfections [14-16].

![Raman Spectrum of ZnO Nanosheets](image)

**Figure 6(b).3:** Raman spectrum of the ZnO nanosheets electrodeposited on ITO coated glass substrate.

6(b) 3.4 Photoluminescence Spectroscopy analysis:

Photoluminescence spectroscopy has gained significant important as a powerful characterization tool not only probing the optical properties of semiconducting nanostructures, but offering potential to characterize various 'defects' and their associated energies in the given nanostructure. The PL emissions in different regions can be generally attributed to the shape and size of the nanostructures, as well as the
nature of defects present in the material. The photoluminescence (PL) analysis was performed by using a pulsed laser (λ = ) as an excitation source and a typical PL spectrum recorded at room temperature is shown in figure 6(b).4. The PL spectrum shows an intense band edge emission around ~ 395 along with a weak emission at ~ 465 nm. The weak deep level emissions around 465 nm is due to the oxygen vacancies in ZnO which can occur in different charge states: the $V_\phi$ state which is neutral relative to the lattice, the singly ionized $V_o^-$ state and the $V_o^{--}$ state, which does not trap any electrons and is doubly positively charged with respect to the lattice [12,16]. The ratio of intensities of the band edge emission to the defect level is found to be quite high, indicating presence of fewer defects in the sample. Thus the PL analysis confirms good purity of the ZnO nanosheets electrodeposited at relatively lower temperature on ITO coated glass substrate.

Figure 6(b).4: Photoluminescence spectrum of the ZnO nanosheets electrodeposited on ITO coated glass substrate.

6(b) 4 DFT calculations:
The work function of the synthesized 2D nanosheets arrays were estimated using density functional theory (DFT). The work function (U) was estimated to get better understanding of the field emission behavior of ZnO nanosheets. Theoretical calculations were performed using density functional theory as implemented in the CASTEP code [11]. The work function of the synthesized 2D nanosheets arrays were estimated using density functional theory (DFT). The work function (U) was estimated to get better understanding of the field emission behavior of ZnO nanosheets. Theoretical calculations were performed using density functional theory as implemented in the CASTEP code [11]. Ultrasoft pseudopotentials were used to describe the core electrons [12]. The Perdew, Burke and Ernzerhof (PBE) generalized gradient approximation (GGA) was employed for describing the exchange-correlation potentials [13].

![Figure 6(b).5](image.png)

**Figure 6(b).5:** (a) Side and view of O\textsubscript{vac} ZnO (001) surface consider as the system for calculation, four big balls indicated with arrow represent here the neighbour Zn atoms of vacant O atom, (b) demonstrate the electrostatic potential as function of fractional coordinates of O\textsubscript{vac} ZnO (001) surface, (c) Schematic to show the shifting of Fermi level toward vacuum due to O vacancy. Vacuum potential is indicate by E\textsubscript{v}, work function is denoted as \( \phi \) and Fermi level is denoted as E\textsubscript{f}. 

Brillouin zone sampling was made with the Monkhorst Pack scheme and a K-Point grid of 7x7x1. It was found that cut-off energy of 400 eV is sufficient to give well-converged results. The structures were optimized until the total energy converged to less than $10^{-5}$ eV/atom and the maximum force converged to lower than 0.01 eV/Å. The approach $E_{xc}+U$ has been introduced and $U$ value of 8 eV has been used to account for the on-site Coulomb repulsion of Zn 3d electrons [14].

The (2x2) supercell of ZnO (001) has been taken here for the calculations. Figure 6(b).5(a) show the side view of ZnO (001) surface with oxygen vacancy in the third layer. According to our results, we considered the ZnO (001) surface with O vacancy; the O atom has been removed from the arbitrary lattice site. The four big balls (shown in Fig. 6(b).5(a)) indicate the Zn atoms bound to three oxygen atom (red balls) around O vacancy and the comparatively small balls are the Zn atoms bounded with four oxygen atom. The Mulliken charge analysis shows that the four Zn atoms (neighbor of O$_{vac}$ atom) have less positive, which revealed increase of unshared d electron around vacancy. So by deoxygenating this surface, the O vacancy enhanced the Zn$^+$—Zn$^+$ interactions; stretching of distance between Zn atoms with other O atoms, i.e. increasing of bond length. Consequently, the unsaturated Zn atoms are trying to make bond (interaction increases) among themselves to form metal cluster, subsequently increase of electron density around the vacancy. The unshared d electrons form a donor state claimed as an impurity energy state, this cause shifting of Fermi level toward vacuum, shown in our schematic band structure (Fig. 6(b).6(b)). This will take part in the modification of work function. Fig. 6(b).5(b) demonstrates the electrostatic potential as a function of fractional coordinate for O$_{vac}$ ZnO. The estimated work function is about 4.94 eV for O vacant ZnO (001) surface, which is about 0.21 eV lesser than pure ZnO (001) surface ($\phi = 5.15$ eV), demonstrate in the fig.6 (b).5(c). This indicates that the barrier height for the tunneling electron is less in case of O$_{vac}$, which will additionally increases the field emission current (apart from the geometrical enhancement factor, explain in the next section). The estimated electronic structures suggest that the O$_{vac}$ enhance the electron donating ability of the surfaces to a good extent.

6(b) Field Emission:

For FE studies the ZnO nanosheets/ITO sample was attached on a copper stub with a vacuum compatible silver paste. The cathode (sample) was held parallel to anode, a semitransparent phosphor screen. The distance between the cathode and anode was manipulated by using a linear mechanical drive. The FE measurements were performed at a base pressure value of $1\times10^{-8}$ mbar. Prior to the FE measurements, pre-conditioning of the emitter was carried out by constant potential of -1 KV potential with respect to anode for 20 minutes. The residual ion bombardment on the emitter is expected to remove
the adsorbed species, along with some loosely bound asperities, offering a chance of cleaning the emitter surface.

The emission current density was measured with increasing applied electric field and the typical curve \((J-E)\) plot is shown in fig.6(b).6(a). From the \(J-E\) plot the turn on field, defined as the field required to draw emission current density of \(0.1\mu A/cm^2\) is found to be \(2.4V/\mu m\) and the threshold field (which is defined as the applied field required to draw emission current density of \(50\mu A/cm^2\)) is \(6.4\) \(V/\mu m\). The current density increases rapidly after the threshold field value. The observed values of the turn on and threshold fields are comparable with the other nanoforms of ZnO and attributed to the ultra low thickness (offering high aspect ratio) of the ZnO nanosheets.

![Figure 6(b).6: (a) emission current density versus applied field (J-E) curve, and (b) F-N plot of the ZnO nanosheets electrodeposited on ITO substrate](image)

Figure 6(b).6(b) shows the corresponding Fowler-Nordheim (F-N) plot derived from the observed \(J-E\) characteristic. The F-N plot exhibits overall linear behavior with a decrease in the slope (saturation tendency) in the high applied field range.

Furthermore the FE behavior of other ZnO nanoforms was compared with the ZnO nanosheets. The comparative FE behavior of other ZnO nanostructures is shown in Table 6(b).1. The low turn-on field and high field enhancement of ZnO nanosheets as compared to the existing ZnO nanoforms makes it a promising material for field emission application.
Table 6(b).1: Comparison of the values of turn-on field reported for different nanoforms of ZnO.

Emission current stability of ZnO nanosheets are also investigated at a preset value of 1µA over a period of 3 h. The corresponding current stability curve (i-t plot) is shown in figure 6(b).7, which indicates no obvious degradation of the emission current density. The emission current exhibits variations initially and stabilizes later on. Such initial variations in the emission current followed by stabilization indicates that the emitter surface is un-cleaned or there is noticeable amount of adsorbed species on the emitter surface, which eventually desorb due to continuous ion bombardment. Once the emitter surface becomes cleaner, stabilization of current is anticipated. The striking feature of ZnO nanosheets is that the average current remains nearly constant with no sign of degradation. The remarkable stability of the field emission current is likely due to the good contact between ITO substrate and the ZnO nanosheets. This is very important from application point of view.

<table>
<thead>
<tr>
<th>ZnO nanoforms</th>
<th>Turn-on field at 0.1 µA/cm² (V/µm)</th>
<th>Refer.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoneedle</td>
<td>2.4</td>
<td>17</td>
</tr>
<tr>
<td>Nanocavity</td>
<td>4.1</td>
<td>18</td>
</tr>
<tr>
<td>Bottlelike</td>
<td>4.6</td>
<td>18</td>
</tr>
<tr>
<td>Nanotubes</td>
<td>7</td>
<td>19</td>
</tr>
<tr>
<td>Nanowires</td>
<td>8</td>
<td>20</td>
</tr>
<tr>
<td>Nanosheets</td>
<td>2.4</td>
<td>Present work</td>
</tr>
</tbody>
</table>
Figure 6(b).7: Emission current versus time (I-t) plot of the ZnO nanosheets electrodeposited on ITO substrate studied at pre-set value of 1µA over 3 hrs duration.

6(b) Conclusions:

- ZnO nanosheets were synthesized on ITO coated glass substrates by a simple electrodeposition route for the first time under optimized experimental conditions and their field emission properties were investigated.
- The as synthesized nanosheets are 10-50 nm thick and ~2-5 µm long. The nanosheets are uniformly distributed over the entire substrate with a strongly adhesion with the substrate.
- Field emission studies suggest 2D ZnO nanosheets as a possible cold cathode material with a low turn-on field value and good emission current stability.
- To understand the observed field emission behavior of ZnO nanosheets arrays, DFT calculations were carried out. The estimated electronic structures suggest that the oxygen vacancies ($O_{vac}$) enhance the electron donating ability of the surfaces to a good extent.
References


(C). Synthesis of ZnCo$_2$O$_4$ microflowers and their field emission characteristics.

This part of the chapter deals with the synthesis and field emission investigation of Zinc nanocomposite with cobalt. Present work is an attempt to explore field emission behavior of spinel structure of ZnCo$_2$O$_4$.

6(c) 1. Introduction:

Flower like structures, due to their large proportions of numerous thin open edges, are considered as a favorable material for field emission applications. In general a flower like structure is self-assembled form of 1D or 2D nanostructures [1-4]. The lateral emission from the top surface or due to the electric field enhancement on the edges of the nano-slices, these structures has shown enhanced field emission behavior. In this chapter we report the growth of ZnCo$_2$O$_4$ (ZCO) flowers consisting of 2D nanosheets prepared by a simple low temperature chemical approach and their field emission properties were investigated for the first time. The ZCO compound so obtained is a normal cubic spinel having four tetrahedral primitive cells [5-7].

6(c) 2. Experimental:

ZnCo$_2$O$_4$ microflowers were synthesized using Zinc Nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O, 99.5%) and Cobalt Nitrate hexahydrate (Co(NO$_3$)$_2$.6H$_2$O, 97%) as precursors via hydrothermal technique. In a typical experiment, 3 mmol of Zn(NO$_3$)$_2$.6H$_2$O and 6 mmol of Co(NO$_3$)$_2$.6H$_2$O were first dissolved in 20 ml of DI water and then 60 mmol of urea (CH$_4$N$_2$O) was added to it under constant stirring condition. The net volume of 60 ml solution was made by adding DI water to it. After stirring the solution for about an hour it was transferred to a 100 ml borosilicate glass bottle and was kept at 90 °C in an oven for 12 h, followed by cooling to room temperature. The resultant was first collected by centrifugation and then washed repeatedly with DI water and ethanol to remove any impurity as well as unreacted ions. The as collected precipitate was further heated at 200 °C for 8 hrs.
6(c) 3 Characterisations:

6(c) 3.1 FESEM:

The morphology of the as synthesized ZnCo$_2$O$_4$ microflowers is analysed using FESEM and the images are shown in Fig. 6(c).1. The diameter of the microspherical structure as shown in Fig.6(c).1(b) is within the range of 6-10 µm. The ZCO nanoplates (Fig. 6(c).1(c)), having thickness of the order of ~20-30 nm, stacked together to form the flower structure.

Figure 6(c).1: FESEM images of spinel ZnCo$_2$O$_4$ flowers: (a) uniform formation of ZnCo$_2$O$_4$ flower-like microspheres and (b) an enlarged portion shows the 2D nanosheets which wrap up to form the spherical structure. (c) Further magnification reveals the thickness of the nanosheets which lies within the range ~20-30 nm. (d) EDS pattern of the ZCO sample.
The EDS pattern shown in Fig.6(c).1(d) contains peaks from all the three composing elements contained in the as prepared ZCO sample. Both Co and O show characteristic X-ray emission from their respective K-shells whereas in case of Zn, the X-ray emission occurs due to the electron returning to the L-shell. The atomic percentage and weight percentage of the constituting elements is given in Table-6(c).1, with the corresponding shells shown inside the parentheses.

Table 6(c).1:

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn (L)</td>
<td>8.52</td>
<td>2.07</td>
</tr>
<tr>
<td>Co (K)</td>
<td>16.30</td>
<td>4.40</td>
</tr>
<tr>
<td>O (K)</td>
<td>18.43</td>
<td>18.33</td>
</tr>
</tbody>
</table>

6(c) 3.2 XRD:

Fig. 6(c).2 shows the XRD spectrum of as synthesized ZnCo$_2$O$_4$. The intense peak in the diffraction pattern of ZCO sample indicates prominent growth along (311) direction. The diffraction peaks are attributed to the cubical spinel structured ZCO (JCPDS file: 23-1390).

![Figure 6(c).2: XRD spectra of ZnCo$_2$O$_4$ microflowers](image)
6(c) 3.3 Raman analysis:

Raman spectroscopy was performed by a micro Raman spectrometer (Renishaw inVia Raman microscope) with a laser excitation wavelength of 532 nm and laser power of 1 mW/cm². A typical spinel structure consists of 56 atoms in total, while the simplest primitive cell structure consists of only 14 atoms. Thus only 42 vibrational modes can be realized, out of which 3 are acoustic and 39 are optical mode vibrations [8, 9]. Fig. 6(c).3 shows the Raman spectra of ZCO spinel structure.

![Raman Spectra of ZnCo₂O₄ Microflowers](image)

**Figure 6(c).3:** Raman spectra of ZnCo₂O₄ microflowers

The band at 472 cm⁻¹ can be assigned to the Raman active mode \( E_g \) and corresponds to the strong vibration due to the stretching of the bonds between Co-O and Zn-O. The sharp band at 512 cm⁻¹ arises due to the stretching of the Co-O bond corresponds to \( F^{(2)}_{2g} \) mode. The peak at 610 cm⁻¹ corresponds to \( F^{(1)}_{2g} \) symmetry. The band at 682 cm⁻¹ reveals the \( A_{1g} \) mode with a Raman shoulder peak at 658 cm⁻¹ to which again the vibrational mode \( A_{1g} \) is assigned. Peaks from 610 cm⁻¹ to 682 cm⁻¹
corresponds to the Co-O bond stretching. All the peaks defined here are attributed to cubic spinel structured ZCO and other normal spinels which are structurally more or less similar to ZCO (such as ZnCr$_2$O$_4$) as illustrated in earlier reports [8, 16-21].

6(c) 3.3. TEM:

Fig. 6(c).4 shows TEM and HRTEM images of as synthesized microflowers. The d-spacing calculated with HRTEM are in good agreement with XRD results.

![TEM and HRTEM image of ZnCo$_2$O$_4$ microflowers](image)

**Figure 6(c).4:** TEM and HRTEM image of ZnCo$_2$O$_4$ microflowers

6(c) 4. Growth mechanism:

The hydrothermal method comprises of various growth and nucleation stages in order to produce the final flower like structures.

The growth mechanism of ZCO flower structure is described by a graphical illustration as shown in Fig.6(c).5. In the presence of a dielectric solvent like water and at a temperature of 90°C, the
Zn and Co precursors produce Zn$^{2+}$ and Co$^{3+}$ ions respectively due to the process of hydrolysis. Thereafter, a nucleation process takes place in which Zn$^{2+}$ and Co$^{3+}$ ions coordinate among themselves to form nanosheet like structures which is facilitated by the presence of sufficient amount of urea acting as an active surfactant in the reaction mixture [10]. To minimize the surface energy inside the mixture solution, the nanosheets start aggregating to form dandelion like structures. Their further growth results in the final flower like microstructures [11].

Figure 6(c).5: Growth mechanism of ZnCo$_2$O$_4$ microflowers.

6(c) 5. Theoretical calculations:

Theoretical calculations were performed using density functional theory (DFT) as implemented in the CASTEP code [11]. Ultrasoft pseudopotentials were used to describe the core electrons [13]. The Perdew, Burke and Ernzerhof (PBE) generalized gradient approximation (GGA) was employed for describing the exchange-correlation potentials. Brillouin zone sampling was made with the Monkhorst Pack scheme and a K-Point grid of 7x7x1. It was found that the cutoff energy of 400 eV is
sufficient to give well-converged results. The structures were optimized until the total energy converged to less than $10^{-5}$ eV/atom and the maximum force converged to lower than 0.01 eV/Å. ZCO (111) was built by cleaving the geometrically optimized ZCO (space group Fd-3m) structure followed by further relaxation. Thus obtained ZCO (111) cell had lattice parameter of $a = b = 8.101$ Å, which is in good agreement with previously reported values [14, 15]. A vacuum slab of length 20 Å was used in perpendicular direction to the ZCO (111) plane to ward off the spurious interactions with its own periodic image. The theoretical calculations results are summarized in Fig.6c.6. The top and side view of optimised structure of (2x2) supercell of ZCO (111) surface are shown in Fig. 6(c).6(a) and 6(c).6(b) respectively. Fig. 6(c).6(c) shows the electrostatic potential as a function of fractional coordinate for ZCO (111) surface. Considering the ZCO as stoichiometry, the work function has been estimated to be about 5.22 eV.

**Figure 6(c).6:** Optimized structure of ZnCo$_2$O$_4$(111) surface (a) top view and (b) side view, the zinc, cobalt and oxygen atom are denoted with grey, blue and red balls respectively. The lattice parameter direction is indicated by the arrow shown in the inset of (b), the electrostatic potential along c-axis considering vacuum as reference energy is shown in (c). $E_f$ and $E_v$ correspond to the Fermi and vacuum energy.
6(c) 6. Field emission studies:

For field emission measurements the ZnCo$_2$O$_4$ powder was sprinkled over carbon tape coated on a copper stub and loaded in a manner as to parallel phosphor coated conducting glass anode screen. The distance between the cathode and anode was manipulated by using a linear mechanical drive. Prior to readings the emitters were kept at about 10KV for few minutes. The FE measurements were carried out inside a vacuum chamber at low pressure of about 2.8 x 10$^{-8}$ Torr. The typical curve of the emission current density as a function of the applied field ($J$-$E$) plot is shown in Fig. 6(c).7 (a). The $J$-$E$ curve shows that, as the applied voltage is increased, the emission current increases very rapidly. The turn on field, defined as the field required to draw emission current density of 1µA/cm$^2$ is found to be 8.6V/µm and the threshold field (which is defined as the applied field required drawing emission current density of 0.1mA/cm$^2$) is 12.2 V/µm. The lower turn-on field value is attributed to the thin and sharp edges of the microflowers which are vertically align. The values of the turn-on and threshold field are found to be reproducible.

Fig. 6(c).7(b) shows the corresponding ln ($J/E^2$) versus (1/E) curve depicted as F-N plot derived from the observed J-E characteristics. The F-N plot shows deviation from linear behavior with two slopes, indicating the semiconducting nature of the emitter. The observed nonlinearity in semiconductors can be explained through band structure. At lower applied electric field, it is believe that electrons emits from the conduction band states only, with increasing applied field, the valence band electrons also tunnel out and contribute to the emission current.
Figure 6(c). 7 (a) Field emission current density versus applied field (J–E) curve of ZnCo$_2$O$_4$ and (b) corresponding Fowler Nordheim (F-N) plot.
The field emission current stability of ZnCo$_2$O$_4$ microflowers has been investigated at a preset value of 1µA. The current versus time (I-t) plot recorded over duration of 3 h is shown in fig. 6(c).8 and it shows no obvious degradation of emission current. Inset of fig.6(c).8 shows the field emission image of the emitters operated at an electric field of 13.2 Vµm$^{-1}$. The emission spots on the fluorescent screen are uniform and denser and also consistent with the emitter morphology.

Figure 6(c).8: Field emission current stability (I–t) plot of the ZnCo$_2$O$_4$ with an inset FE image captured at emission current density.

6(c) 7. Conclusions:

- Spinel structure ZnCo$_2$O$_4$ microflowers were synthesized by a simple hydrothermal method.
- The microflowers are composed of ZnCo$_2$O$_4$ sheets, with thickness of ~20-30 nm stack together to form flower morphology. Moreover the diameter of the microspherical structure is within the range of 6-10 µm.
ZnCo$_2$O$_4$ microflowers with lower turn on field and high emission current density propose it as a promising material for application purpose. Further the microflowers exhibits fair current stability.
References


