Chapter 1

INTRODUCTION
1. Introduction

Zinc oxide (ZnO) is a II-VI compound semiconductor having wide band gap of 3.37 eV. It has large exciton binding energy of 60 meV at room temperature. It shows piezoelectricity. It is nontoxic material which is cheaply available. Variety of nanostructures of ZnO can be grown. Due to these properties, ZnO is a material of huge technological importance. It has applications in optoelectronic devices such as Solar cell [1], Optical wave guide [2], Light emitting diodes (LED) [3] and transparent thin film transistor [4]. It has been applied in surface acoustic wave (SAW) devices [5]. Nanostructures of ZnO has been used as nanogenerators [6] for harvesting energy in nanoscale.

All these interesting properties and applications of ZnO have attracted us for its study in thin film form as well as its nanostructures.

1.1 Crystal structure of Zinc oxide

Zinc oxide naturally crystallizes in Wurtzite structure which belong to the space group P6_{3}mc. The Wurtzite structure is a hexagonal lattice in which each Zn^{2+} ion is tetrahedrally bonded to four O^{2-} ions and vice-versa; this is shown in figure 1. In this structure the Zn terminated face (0001) and O terminated face (000\overline{1}) are the polar faces while the non-polar faces are (11\overline{2}0) and (10\overline{1}0) which contain equal number of Zinc and Oxygen atoms. The plane perpendicular to the c-axis are called basal planes.

Thus there is a polar symmetry along the hexagonal axis. This gives rise to piezoelectricity in ZnO and also plays key role in its crystal growth.

The tetrahedral coordination of ZnO indicates the presence of sp^{3} hybridized covalent bonding, but the strong ionic character of the Zn-O bond, makes ZnO behave like both covalent and ionic compound. The lattice parameters of hexagonal unit cell are a = 3.2495Å and c = 5.2069Å [7].
Fig.1.1 Hexagonal structure of Zinc Oxide (ZnO) showing the polar faces (perpendicular to c-axis) and non-polar faces (parallel to c-axis) [8].
1.2 Defects and Impurities in Zinc oxide

Zinc oxide crystal has native point defect which greatly affects its optical and electrical properties. These defects create electronic states in the band gap which influence its optical emission properties. The as grown ZnO crystal has always found to be n-type. It has been shown theoretically that both Oxygen vacancy $V_O$ and Zinc interstitial $Zn_I$ have high formation energies in n-type ZnO and they are deep level donors[9]. Thus it is considered that neither $V_O$ nor $Zn_I$ exists in measurable quantity. Van de Walle has proposed that hydrogen H is a dominant background donor in ZnO, that were exposed to H during growth [10]. Group III elements Al, Ga and In are donor impurities to ZnO that can substitute Zn upto concentration greater than $10^{20}$ cm$^{-3}$.

The search for high conductivity p-type ZnO still remains an active area of research. It has been predicted theoretically that Li substituted Zn, $Li_{Zn}$ and Na substituted Zn $Na_{Zn}$ creates shallow acceptor levels, but neither produces high-conductivity p-type ZnO[11]. N,P, As and Sb have been used as acceptors to produce n-type ZnO[12], where it is reported that Zn-vacancy in ZnO acts as defect-type acceptor.

1.3 Band structure of Zinc Oxide

The electronic band diagram for wurtzite ZnO is shown in figure 1.2 [13]. The diagram indicates that both the valance band edge maxima and conduction band edge minima occur at $k = 0$ showing ZnO is a direct band gap semiconductor. It has been found experimentally that due to spin–orbit interaction and crystal-field splitting the valance band in ZnO is split up into three subbands A, B and C, as illustrated in in figure 1.2. The A and C subbands of valance band are known to posses $\Gamma_7$ symmetry and the middle subband B possess $\Gamma_9$ symmetry[13]. At 4.2 K the energy band gap of ZnO is 3.43eV.
Fig. 1.2 Band diagram of ZnO showing the splitting of valance band into three subbands A, B, and C due to Crystal field splitting and spin orbit coupling [13].
1.4 Properties of Zinc Oxide

Table 1.1 Properties of ZnO compared to In$_2$O$_3$, SnO$_2$ and Si [14]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>ZnO</th>
<th>In$_2$O$_3$</th>
<th>SnO$_2$</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$</td>
<td>eV</td>
<td>3.4 (direct)</td>
<td>3.6(direct)</td>
<td>3.6 (direct)</td>
<td>1.12(indirect)</td>
</tr>
<tr>
<td>Lattice structure</td>
<td></td>
<td>Hexagonal</td>
<td>Cubic</td>
<td>Tetragonal</td>
<td>Cubic</td>
</tr>
<tr>
<td>$a$, $c$</td>
<td>nm</td>
<td>0.325, 0.5207</td>
<td>1.012</td>
<td>0.474,0.319</td>
<td>0.5431</td>
</tr>
<tr>
<td>Density</td>
<td>gcm$^{-3}$</td>
<td>5.67</td>
<td>7.12</td>
<td>6.99</td>
<td>2.33</td>
</tr>
<tr>
<td>Thermal conductivity, $\kappa$</td>
<td>Wm$^{-1}$K$^{-1}$</td>
<td>69\text{</td>
<td></td>
<td>}, 60 \text{\perp}</td>
<td>98\text{</td>
</tr>
<tr>
<td>Thermal expansion coefficient at RT, $\alpha$</td>
<td>$10^6$/K</td>
<td>2.92\text{</td>
<td></td>
<td>}, 4.75 \text{\perp}</td>
<td>6.7</td>
</tr>
<tr>
<td>$e_{33}, e_{31}, e_{15}$</td>
<td>C m$^{-2}$</td>
<td>1.32, -0.57, -0.48</td>
<td>11.7, -5.43, -11.3</td>
<td>0.47, 0.18, 0.2</td>
<td></td>
</tr>
<tr>
<td>$d_{33}, d_{31}, d_{15}$</td>
<td>$10^{12}$C N$^{-1}$</td>
<td>3.75\text{</td>
<td></td>
<td>}, 3.70 \text{\perp}</td>
<td>4.6</td>
</tr>
<tr>
<td>$\varepsilon (0)$</td>
<td></td>
<td>8.75\text{</td>
<td></td>
<td>}, 7.8 \text{\perp}</td>
<td>8.9</td>
</tr>
<tr>
<td>$\varepsilon (\infty)$</td>
<td></td>
<td>3.75\text{</td>
<td></td>
<td>}, 3.70 \text{\perp}</td>
<td>4.6</td>
</tr>
<tr>
<td>$T_m$</td>
<td>°C</td>
<td>1975</td>
<td>1910</td>
<td>1620</td>
<td>1410</td>
</tr>
</tbody>
</table>
Table 1.1 gives the list of important properties of ZnO that has been compared with other Transparent conductors viz. Indium Oxide In\textsubscript{2}O\textsubscript{3}, Tin Oxide SnO\textsubscript{2} and Silicon Si [14]. From the table we observe that oxide semiconductors viz. In\textsubscript{2}O\textsubscript{3}, SnO\textsubscript{2} and ZnO are wide band gap semiconductors with band gap greater than 3.3 eV. This causes transparency for wavelength greater than 360 nm and thus they are used as transparent conductors. Of the semiconductors listed only ZnO exhibits piezoelectricity with piezoelectric stress and strain coefficients $e_i$ s and $d_i$ s respectively. The electromechanical coupling factors are $k_i$ s. ZnO has linear thermal expansion coefficient $\alpha_{\parallel}$ along the a-axis $2.92 \times 10^{-6}$/K, which is lower than In\textsubscript{2}O\textsubscript{3} and SnO\textsubscript{2} and slightly higher than that of silicon. Along the c-axis, linear thermal expansion coefficient, $\alpha_{\perp}$ of ZnO is $4.75 \times 10^{-6}$/K which is higher, than the value along a-axis. All the semiconductors listed have high melting point $T_m$ in the range 1400 °C – 2000 °C.

1.5 Zinc Oxide thin films

Thin films of Zinc Oxide can be prepared by various techniques. These are Sputtering [15], Chemical Vapour Deposition (CVD) [16], Laser ablation [17], Sol-gel process [18, 19], Spray pyrolysis [20].

We have used the Sol-gel process of ZnO film synthesis for our study.

Sol-gel process of film preparation has following advantages:

(i) Controllability of composition

(ii) Simplicity in processing

(iii) Cost effectiveness.

1.5.1 Method of preparation of ZnO thin film by sol-gel process

In this process we have used Zinc acetate dihydrate Zn(CH\textsubscript{3}COO)\textsubscript{2}.2H\textsubscript{2}O (ZAD) as the precursor material for ZnO film preparation. For the sol preparation, 10% solution of Zinc acetate dihydrate was prepared in boiling isopropanol at 84 °C which is stirred over a magnetic stirrer. The colour of the solution turns milky after 15 minutes of stirring and heating. Then 6-10 drops of Diethanolamine is added to the solution by a 5 ml dropper and is kept for heating and stirring. Diethanolamine acts as sol stabilizer. The solution now turns transparent, while its heating and stirring was continued for further
30 minutes. Then the solution under stirring was allowed to cool to room temperature. This prepared sol is used for spin coating the substrate.

We have used spin coating technique of film preparation in our study. In this method of coating the cleaned substrate is fixed to the rotating stage using double sided tape. We then take the sol in a 5 ml dropper and put six drops at the centre of the substrate and allow it to rotate at 3000 rpm for 20 seconds. The rpm and rotation duration can be varied depending on the experiment. The wet coated film on the substrate is called Xerogel. This film is then allowed to dry in a griller oven at 100 °C and then annealed at 450°C for 1 hour in air in furnace. Drying at 100°C is required before annealing at high temperature, to avoid the cracking of the solid film. The annealing temperature of the film can be varied depending on the experiment. In this way multiple coating of the substrate is done to get the workable thickness of the film. Figure 1.3 shows the summary of ZnO film preparation by sol-gel process using the flow chart.
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Fig. 1.3 Flowchart of ZnO film preparation by sol-gel process
1.5.2 Physics and Chemistry of Sol-gel method of ZnO film preparation

A detail review on sol-gel processes of ZnO film preparation has been reported by Lamia Znaidi [21]. In the sol-gel process a molecular precursor in a homogeneous solution undergoes following successive transformations:

(i) hydrolysis of the molecular precursor;
(ii) polymerization via successive bimolecular additions of ions, forming oxo-, hydroxyl, or aquabridges;
(iii) condensation by dehydration;
(iv) nucleation;
(v) growth [22,23].

Depending on the nature of the molecular precursors, two sol-gel routes are currently used: metal alkoxides in organic solvents or metal salts in aqueous solutions [24]. The main methods of ZnO preparation is intermediate between the two sol-gel methods since they use metal salts in alcoholic solutions. ZnO films are obtained starting from inorganic salts such as nitrates, chlorides, perchlorates - or organic salts like acetates and acetylacetonates, dissolved in alcoholic media. In such media the process involves two steps. The first one consists of in situ formation of alkoxide or alkoxy-complexes. In the second step, these complexes undergo transformation through hydrolysis and polymerization to lead to the oxide.

1.5.2.1 Precursors

Metal salts are generally used as precursors due to low cost, facility of use and commercial availability. The metal salts can be both inorganic and organic. Inorganic salts like nitrates are often used, as precursors for sol-gel ZnO-based materials, even though their main drawback is the inclusion or difficult removal of anionic species in the final product [25, 26]. Using zinc acetate as a precursor, the acetate groups, as contaminants of the gel, decompose under annealing producing volatile by-products [26]. Bahnemann et. al. [27] synthesized transparent colloidal suspensions of zinc oxide in water, 2-propanol, acetonitrile, and using different zinc salts. They have reported that the anion, in zinc salt, is critical for the preparation of transparent and stable ZnO colloids.
The use of zinc perchlorate instead of zinc acetate yields a turbid suspension; i.e., coagulation of the particles takes place, the acetate acts as stabilizer of the colloidal sol. Also, the experiments with \( \text{ZnCl}_2 \) or \( \text{Zn(NO}_3\text{)}_2 \) reveal a faster coagulation than in the case of \( \text{Zn(ClO}_4\text{)}_2 \) following the initial formation of a clear colloidal suspension.

### 1.5.2.2 Solvents

The solvent in the sol-gel method of ZnO film preparation must have a relatively high dielectric constant so that it can dissolve the inorganic salts [22, 28, 29]. Most alcohols are dipolar, amphiprotic solvents with a dielectric constant that depends on the chain length [30]. Alcohols with low carbon number, up to 4, are mostly used as solvents such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-methoxyethanol. Among all the monoalcohols, the most used are the ethanol and 2-propanol. Hosono et al. [28], studied the chemical reactions of zinc acetate dihydrate to ZnO preparation using different types of solvents, i.e. methanol, ethanol, and 2-methoxyethanol. Zinc acetate dihydrate (ZAD) was more soluble in methanol than in ethanol or 2-methoxyethanol according to dielectric constants of these alcohols. The reflux time necessary for the formation of ZnO increases with the solutions in order, MeOH (12 h) \( << \) EtOH (48 h) \( << \) 2-ME (72 h). Also, the XRD analysis of particles, obtained from the three alcoholic solutions of ZAD revealed, after refluxing, the formation of intermediate product as \( \text{Zn}_5(\text{OH})_8(\text{Ac})_2 \cdot 2\text{H}_2\text{O} \) called layered hydroxide zinc acetate (LHZA). This complex (LHZA) was also observed by Meulenkamp [31] using ethanol as a solvent and by Fujihara et al. [32] and Wang et al. [33] using methanol. Finally these complexes undergo hydrolysis and inorganic polymerization leading to the formation of sols consisting of zinc oxide nanoparticles.

### 1.5.2.3 Additives

Additives are chemical species having at least one functional group. They act as basic or acid and/or chelating agent. Alkali metal hydroxides, carboxylic acids, alkanolamines, alkylamines, acetylacetone and polyalcohols are used for this purpose. They facilitate the zinc salt dissolution in alcoholic media. ZAD has a limited solubility in alcohols like ethanol and 2-propanol in the absence of other agents or heating. The agents, like (mono- to tri-) ethanolamines or lactic acid help in complete dissolution and formation of a stable sol [34]. Furthermore, the additives play the role of chelating and stabilizing ligands, which avoid the rapid precipitation of zinc hydroxide and allow
stable dispersions to be formed. The amino groups and/or the hydroxyl groups of alkanolamines coordinate the metal atoms of alkoxides, thus improving the solubility and stability against hydrolysis of the alkoxides [35]. The addition of alkanolamine in zinc acetate provides a clear solution. MEA a bidentate ligand, coordinate with zinc atoms; one way by acting as a chelating ligand and the other way so as to bridge two zinc atoms [35]. Inorganic bases, lithium or sodium hydroxide is used to form stable dispersions of colloids.

MEA acts as a complexing agent, which retards the Zn$^{2+}$ condensation; however, its presence also increases the pH, which promote the formation of ZnO. The acetate group plays a very relevant role, by complexing Zn$^{2+}$ in competition with the MEA. The complex chemical relationships of the main species are indicated in figure1.4. The three nucleophilic species (MEA, HO$^-$ and CH$_3$COO$^-$) compete for the Zn$^{2+}$ Lewis acid center: attack of an HO$^-$ group leads to the formation of small zinc-oxo-acetate oligomers, which are expected to be formed in the initial stage, from gradual forced hydrolysis of Zn-MEA or Zn-OCOCH$_3$ soluble complexes during aging. The progressive condensation of the hydrolyzed moieties gives rise to colloids or precipitates. This gives rise to stable acetate-capped colloidal nanometric particles in dilute solutions.
Fig. 1.4 Chemical equilibria taking place in the initial solutions followed by Hydrolysis and condensation on heating which results in Soluble or colloidal condensed moieties that can be deposited as film precursors; [36].
1.5.2.4 Growth mechanisms
Spanhel and Anderson [37] have reported that there are two possible ways of describing the growth of ZnO crystals; by Ostwald ripening and by aggregation. In this growth process, as soon as the smallest stable molecular clusters are formed, they rapidly combine to give the next most stable aggregate. The primary aggregates then further rapidly combine to give the next most stable secondary aggregate and so on.
Meulenkamp [38] suggested that the particle growth in colloidal systems can take place in two ways. The first one corresponds to Ostwald ripening: large particles grow at the expense of smaller particles, which have a higher solubility according to the so-called Ostwald–Freundlich equation. The second way describes growth by the addition of reactive precursors available in solution to already existing particles. The rate of particle growth is governed by the concentration of precursors or dissolved species and their reactivity, which depends on the number of particle surface atoms, and the solution composition. Tokumoto et. al. [39] reported that the formation of ZnO colloidal particles in an alcoholic solvent consists of two stages. During the early stage of phase transformation, small oligomers are continuously formed. At advanced stages, the aggregation of the oligomers leads to crystalline wurtzite, the primary colloidal particles. The primary particles then aggregate and form the secondary colloidal particles. The growth of the colloidal particles is a stepped, discontinuous, process which indicates that the predominant mechanism of aggregation is heterogeneous coagulation. This mechanism of growth leads to a hierarchical structure.

1.5.2.5 Nucleation and growth
It has been reported by Spanhel [40] that at least four different “primary particles or clusters” serving as initiators of the ZnO colloid growth, from ZAD as precursor, could be identified. The nature of these “primary particles or clusters” depends strongly on the synthesis conditions chosen viz. initial salt concentration, the temperature and time of the thermal treatment, the nature of alcohol solvent as well as the humidity, storage and analysis conditions. Among these primary particles, are Zn₅(OH)₈(Ac)₂·2H₂O and Zn₄O(Ac)₆. In other respects, Meulenkamp [38], prepared ZnO nanoparticles by addition of LiOH to an ethanolic zinc acetate solution. He showed that control of the particle size
was improved by the influence of temperature, water, and reaction products during the aging of ZnO sols. Water and acetate accelerates the particle growth. Hu et. al. [41] have synthesized ZnO nanoparticles by precipitation from zinc acetate in a series of n-alkanols from ethanol to 1-hexanol as a function of temperature. The kinetics of nucleation and growth are expected to be strongly dependent on the properties of the solvent. For the shorter chain length alcohols, ethanol and 1-propanol, nucleation and growth are retarded compared to longer chain length alcohols, from 1-butanol to 1-hexanol, where nucleation and growth are fast. The particles size increases with increasing temperature for all solvents and increases with alkanol chain length. In fact, during the growth of colloidal ZnO nanoparticles, the alcohols not only provide the medium for the reactions, but also act as ligands to help to control the morphology and particle size of ZnO.

1.5.2.6 Film formation

In sol-gel method, ZnO films are prepared by dip- or spin-coating of substrate from sols freshly prepared or aged at room temperature or around 60 °C. The heat treatment of the deposited films is carried out in two steps. For the first step, a pre-heat treatment (40–500°C) is applied during a short time for solvent evaporation and organic compounds removal [42-46]. The second step, a post-heat treatment is employed in order to obtain a well-crystallized films and the final decomposition of organic by-products varying from 250 to 900 °C, according to the substrate nature.

1.6 Zinc Oxide one dimensional nanostructures

One-dimensional (1-D) ZnO nanowires/rods have been widely studied for its technological applications. C.Y. Lu et. al.[47] have developed ZnO nanowire UV sensor. Z.L.Wang et. al.[48] have developed nano power generators using ZnO nanowires.
The methods for synthesizing ZnO nanorods are Chemical Vapour Deposition (CVD) [49], metal organic CVD [50], thermal evaporation [51], the template method [52], and electrochemical deposition [53]. However, these methods involve strictly controlled synthesis environment, complicated procedures and expensive instruments. In our work we have used two simple, cost effective and rapid synthesis methods for fabricating ZnO nanorods:
(i) The hydrothermal method [54]
(ii) Thermal decomposition of Zinc acetate dihydrate in air [55].

1.6.1 Hydrothermal process
The first publication on hydrothermal synthesis of ceramics dated from the middle of the 19th century [56]. At the beginning, the geologists tried to simulate in the laboratory natural hydrothermal phenomena occurring in the Earth’s crust. The development of pressure engineering vessel in the 19th century determined the enhancing of researches in the field of hydrothermal synthesis in Germany, France, Italy and Switzerland. In the 20th century the main centres for studying and development of the hydrothermal techniques were in USA, Russia and Japan. In the 20th century hydrothermal synthesis was clearly identified as an important technology for material synthesis mainly for single crystal growth [56]. Due to the severe conditions required for the single crystal growth in the hydrothermal conditions (supercritical conditions), the commercialization was very difficult. In the recent years the interest in commercialization of the hydrothermal methods enhanced in part due to the possibilities to obtain a large family of materials under mild conditions (temperature <350°C, pressure < 100 MPa) [56]. Riman [56] defined hydrothermal synthesis as a process that utilizes single or heterogeneous phase reactions at temperatures > 25°C and elevated pressures > 100 kPa to crystallize ceramic materials directly from solutions. The pressure is the vapor pressure above the solution at the hydrothermal parameters namely temperature, composition and concentration of the precursor solutions. Some additives are used: mineralizing agent (organic / inorganic) to control pH and to promote solubility and other agents (organic / inorganic) to control the morphology or to promote the particle dispersion. A significant number of powders and films can be obtained in hydrothermal
conditions at temperatures in the range 25-200°C and pressures <1.5 MPa. This hydrothermal synthesis breakthrough made it more interesting for the industry.

Some advantages of the hydrothermal synthesis are presented below:

(i) Hydrothermal synthesis is an environmentally friendly procedure due to the fact that it takes place at lower temperatures and pressures closely to the living conditions on Earth. Other processes require higher temperatures and higher/lower pressures and therefore they are considered environmentally stressed as shown in figure 1.5 [57]. Low reactions temperatures avoid problems related to the volatilization of components and stress induced defects;

(ii) The rate and uniformity of nucleation, growth and aging can be controlled;

(iii) Powders, fibers, single crystals, monolithic bodies, coatings on metals, polymers, and ceramics can be prepared;

(iv) The costs for energy, instrumentation and precursors are lower. According to [57] a large quantity of energy is necessary to create melt, vapor, gas, plasma comparing to the formation of an aqueous solution at the same temperature. The time and energy consuming is lower for the hydrothermal processes due to the fact that mixing and milling steps are not necessary.

(v) Hydrothermal processes can be combined with electrochemical, mechanical, microwave techniques. Hydrothermal synthesis is a soft solution processing (SSP) [57] which allows in situ fabrication of shaped, sized, oriented ceramic materials without firing, sintering or melting steps. The increasing interest in hydrothermal synthesis is illustrated by the growing of number of scientific papers.
Fig. 1.5 Pressure dependence on temperature for different processing routes [57].
In the last years hydrothermal methods were intensively studied and were applied to obtain nanomaterials: powders, thin/thick films, nanorods, fibers, nanotubes. Some of the recent examples are presented below: nanotubes arrays of barium titanate (BT) and barium strontium titanate (BST) were synthesized under hydrothermal conditions taking oxidized titania nanotubes as templates [58]; submicron, spherical $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$ powders were prepared by microwave-hydrothermal route using potassium titanyl oxalate, barium and strontium titanates as precursors; the mineralizing agent was potassium hydroxide [59]; barium titanate powders were obtained by hydrothermal route starting from barium hydroxide and anatase [60]; thin films based on BST were grown on titanium electrodes in aqueous solutions by hydrothermal-electrochemical method starting from barium and strontium hydroxides deposited on anodized titanium [61]; thin or thick ferroelectric films (PZT for example) were obtained by electrophoretic deposition using a trifunctional additive [62]; PZT thin films were obtained by a hydrothermal method [63, 64]; $\text{Fe}_2\text{O}_3$ nanoparticles were synthesized in hydrothermal conditions in aqueous organic microemulsion under mild conditions [65]; alkali-metal titanates [66] and single crystalline spinal cobalt ferrite nanorods [67] were also synthesized in hydrothermal conditions; indium hydroxide nanocubes (around 70nm length) have been prepared by a hydrothermal synthesis [68]. In this thesis also ZnO nanorods has been synthesized by this hydrothermal technique.

1.6.2 Chemistry of hydrothermal synthesis of ZnO nanorods

The growth of ZnO nanorods by hydrothermal process follows certain chemical reactions that have been established [69]. Zinc nitrate hexahydrate salt provides Zn$^{2+}$ ions required for building up ZnO nanowires. Water molecules in the solution provide O$^{2-}$ ions. The hexamethylenetetramine (HMTA) during the ZnO nanowire growth, act as a weak base, which would slowly hydrolyze in the water solution and gradually produce OH$^-$. This is important in the synthesis process because, if the hexamethylenetetramine hydrolyzes very fast and produces a lot of OH$^-$ in a short period of time, the Zn$^{2+}$ ions in solution would precipitate out very quickly due to the high pH, which would have little contribution to the ZnO nanowire oriented growth,
and eventually results in fast consumption of the nutrient and prohibits further growth of ZnO nanowires.

\[
\begin{align*}
(CH_2)_6N_4 + 6H_2O & \leftrightarrow 4NH_3 + 6HCHO \\
NH_3 + H_2O & \leftrightarrow NH_3 \cdot H_2O \\
NH_3 \cdot H_2O & \leftrightarrow NH_4^+ + OH^- \\
Zn^{2+} + 2OH^- & \leftrightarrow Zn(OH)_2 \\
Zn(OH)_2 & \leftrightarrow ZnO + H_2O
\end{align*}
\]

The growth process of ZnO nanowires can be controlled through the above listed chemical reactions. All the five reactions are in equilibrium and can be controlled by adjusting the reaction parameters, such as precursor concentration, growth temperature and growth time, in order to push the reaction equilibrium forward or backward. In general, precursor concentration determines the nanowire density. The growth time and temperature control the ZnO nanowire morphology and aspect ratio.

1.6.3 Works on ZnO nanorods by hydrothermal process

Hydrothermal solution synthesis [70-71] and electrochemical deposition in porous membranes were investigated to produce oriented ZnO nanorods and tubes respectively. Although oriented nanowires and nanorods have attracted wide attention, the direct fabrication of large arrays of complex nanostructures with controlled crystalline morphology; orientation and surface architectures remains a significant challenge.

Zhengrong et. al.[72] reported a low-temperature, environmentally benign, solution based approach for the preparation of complex and oriented ZnO nanostructures and the systematic modification of their crystal morphology. Using controlled seeded growth and citrate anions that selectivity adsorb on ZnO basal planes as the structures directing agents, they prepared large arrays of oriented ZnO nanorods with controlled aspect ratios, complex film morphologies made of oriented nanocolumns and nanoplates and complex bilayers showing in situ column-to-rod morphological transitions.

Ming Wang et. al. [73] investigated the photoluminescence of ZnO nanorod arrays on Si substrate. They found strong UV emission and a broad weak green emission. They further investigated the origin of green emission by varying the post treated conditions.
Sea-Fue Wang et al. [74] studied the effect of preparation conditions on the growth rate, morphology and crystallinity of ZnO nanorod arrays on seeded substrates. In particular they found that largest growth rate for \([\text{Zn(NO}_3\text{)}_2]/[\text{C}_6\text{H}_{12}\text{N}_4]\) ratio =1. Doubling of growth rate and enhancement in crystallinity of ZnO nanorods with mechanical stirring of the solution. They also found the linear increase of radial and axial dimensions of ZnO nanorods with increase in reaction time up to 4 hours.

G. Kenanakis et al. [75] prepared c-axis oriented ZnO nanorod arrays on seeded glass and si substrates. They found preparation of thin ZnO seed layer is crucial for c-axis orientation. They also found that aqueous solution growth on bare substrates leads to the formation of flower like nanostructures, consisting of randomly oriented nanorods. The grown nanorods were highly transparant in the visible region while the complex nanostructures do not show high transmittance. N. Shakti et al. [76] have prepared ZnO nanorods by hydrothermal process and found ultra violet emission at room temperature, the electrical property of nanorods showed rectifying behaviour.

### 1.6.4 Chemistry and growth mechanism of ZnO nanorods prepared by thermal decomposition of Zinc acetate dihydrate

The thermal decomposition of zinc acetate dihydrate have been studied by Thermo Gravimetric–Differential Scanning Calorimetry to understand its thermal stability and decomposition temperature [55]. In the start of the process zinc acetate dehydrate undergoes thermal dehydration and becomes anhydrous zinc acetate. Further decomposition of anhydrous zinc acetate in the temperature region of 150–280°C, causes the formation of \(\text{Zn}_4\text{O(CH}_3\text{CO}_2\text{)}_6\), which finally decomposes into ZnO. The gaseous products generated during the thermal process, are water (H\(_2\)O), carbon dioxide (CO\(_2\)), acetone ((CH\(_3\)_2CO) and acetic acid (CH\(_3\)COOH), respectively. These products reached their highest concentration at about 270°C, as the reaction equation indicates (1.6)–(1.9). As the temperature increased, the ZnO nanowires were formed by the following chemical reactions:

\[
\text{Zn(CH}_3\text{COO)}_2\cdot 2\text{H}_2\text{O} \xrightarrow{\text{heat}} \text{Zn(CH}_3\text{COO)}_2 + 2\text{H}_2\text{O} \uparrow \tag{1.6}
\]
\[
4\text{Zn(CH}_3\text{COO)}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{heat}} \text{Zn}_4\text{O(CH}_3\text{COO)}_6 + 2\text{CH}_3\text{COOH} \uparrow \tag{1.7}
\]
Thus zinc acetate dihydrate thermal process can be considered a process of dehydration, vaporization/decomposition, and ZnO formation. Therefore, in the ZnO nanowire synthesis experiment, the temperature was set and maintained at 300 °C and for about 3 hours for a complete decomposition of zinc acetate dihydrate.

The growth of ZnO nanorods via thermal decomposition of zinc acetate dehydrate is considered to follow Vapour-solid (VS) growth mechanism.

In the VS growth process, oxide vapor generated from the solid oxide material in a high-temperature region is transported and directly deposited onto a substrate in a lower temperature region. Surface defects or dislocations of the substrate provide favorable nucleation sites for the oxide vapor. The vapor condenses on these sites, forming seeds for a continuous deposition of oxide vapor.

In our work, we have synthesized ZnO film by sol-gel spin coating process [77] and investigated quantum confinement effect in them. Li and Al doping of ZnO films were performed and their structural, optical and electrical properties were studied. We have also synthesized ZnO nanorods both by hydrothermal process and thermal decomposition of Zinc acetate dehydrate. We have applied ZnO nanorods array prepared by hydrothermal process as vibration sensor, utilizing its piezoelectric property.
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[63] Patent EP 1020937
[64] Patent EP 1039559