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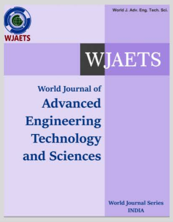

(Research Article)

An understanding of key factors affecting the fabrication of ZnO thin films using CBD Process

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Abstract

The nano structured ZnO thin films are currently attracting considerable attention due to their size dependent properties and further applications in opto-electronic devices, sensors, solar cells, lasers, QLEDs, biomedical field etc. Thin film chemical deposition techniques are of special interest being relatively simple and convenient for large area deposition. Better grain structure with improved orientation of crystallites may be achieved by controlling the rate of reaction. Out of Chemical deposition techniques chemical bath deposition (CBD) is an inexpensive and energy efficient technique, as it does not require any high voltage equipment, works at low temperature and is widely used for deposition of various good quality metal chalcogenide thin films on a variety of substrates. In this article the basic principle underlying this process and film deposition mechanism has been described in detail. The effect of the factors affecting the ZnO film growth and morphology of the crystallites e.g. pH of the bath, nature and concentration of the precursors, effect of counter ion, nature and concentration of the complexing agent, thermal annealing, temperature of the bath, material of substrate and growth time has been analyzed. Various methods of seed layer deposition along with their benefits have been discussed at length.

Keywords: ZnO; CBD; Thin Film; Complexing Agents

1. Introduction

Metal oxides are important functional materials which are playing a very important role in sustainable development[1,2,3,4]. ZnO is one of the most versatile materials of the II-VI group oxide materials that invites consistent attention of the researchers worldwide since forties[5]. It is an odourless, white solid having a density of 5.606 g/cm^3 with 1975°C melting point and is available in abundance in nature[6]. Because of its current and future applications in several novel devices, several reviews[7,8,9,10] and conference proceedings[11,12,13,14] are published exclusively for ZnO nano crystallites to explore the feasibility of commercial application for future devices. It is an n-type semiconductor with a direct wide band gap of 3.37 eV at room temperature, having optical transparency in the visible range[15]. ZnO has higher excitonic binding energy (60 meV) as compared to the room temperature thermal energy (25 meV), making the excitonic recombination process possible even at room temperature, whereas in other wide band gap semiconductors such as gallium nitride, the electron hole plasma transition is the main recombination process[16]. Since the separated electrons and holes are more vulnerable to be trapped by the various defects presented in the crystal, it is desirable to have a material with a large binding energy for optoelectronic applications[17]. One of the major benefits when compared to other large band gap semiconductors in use today (e.g., GaN and ZnSe) is that ZnO is highly resistant to damage from radiation. Moreover it is a direct band gap semiconductor, as opposed to Si which has an indirect band gap. It has an advantage as a transparent electrode material in photovoltaic cells because of its good material properties as compared with Indium tin oxide[18,19]. Due to its *n*-type semiconducting characteristics and excellent thermal stability, ZnO is an active channel for thin film transistors and can be well developed in crystalline form on various substrates[20,21].Zinc

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oxide has emerged as a potential alternate to GaN for optoelectronic applications like light emitting diodes[22,23,24],quantum dot light emitting diodes (QLEDs)[25], piezoelectrics[26] owing to its structure and direct wide band gap[27]. ZnO-NPs may be used in gas sensors[28,29,30,31,32,33,34], biosensors[35,36], fertilizers[37,38,39] and paints[40,41]. They also show anticancer and antimicrobial properties due to their ability to generate reactive oxygen species (ROS), promising to play an important role in biomedical research[42]. ZnO is a versatile functional material that has a diverse group of growth morphologies, such as nanocombs, nanorings, nanohelixes, nanosprings, nanobelts, nanowires and nanocages[43]. The importance of ZnO is further enhanced as its band gap can be tuned to desired value by reducing its particle size to nano scale[44,45,46]. Being non-toxic ZnO-based thin film are becoming an attractive alternative to toxic CdS buffer layers[47] in traditional CIGS thin film solar cell, contributing to the development of more sustainable and efficient thin-film solar cell technologies. and offers a promising pathway to achieve high efficiency, environmental safety, and low-cost manufacturing**.** Thus the cost-effective ZnO optoelectronic devices along with other potential applications, large bond strength and its ability to grow single crystal substrate, low power threshold for optical pumping, radiation hardness, high exciton binding energy, broad chemistry leading to wet chemical etching, biocompatibility, non-toxic and environment friendly nature makes ZnO a strong candidate for future applications in multiple fields of human interest.

With the advent of material science, the field of thin films deposition technology has witnessed considerable attention of researchers. Thin polycrystalline films of ZnO can be prepared by different methods such as spray pyrolysis[48], sputtering[49], pulsed laser deposition[50], sol-gel[51], physical vapor deposition[52], chemical bath deposition (CBD)[53] etc. Among the many different deposition techniques available to grow semiconductor thin films on different substrates, chemical bath deposition (CBD) is considered as the simplest and an inexpensive technique for large area deposition as it does not require any sophisticated equipment, is performed at low temperature. The term CBD is, in general, used for the depositions from aqueous solutions where the desired product is chemically created and gets deposited physically in the same bath. The basic requirements for CBD are precursor solution, a substrate for film deposition and hot air oven. This method has many advantages over other familiar evaporation techniques. The thin film's thickness, size and quality of crystallites, the growth parameters such as deposition rate, can be optimized by adjusting the temperature, pH of the bath, concentration of the precursors, deposition time and nature of the complexing agent[54,55,56,57]. It is a template free technique and does not require expensive substrates such as Si wafer, GaN or Sapphire. In most of the cases no post annealing is required, so it allows possible usage of flexible polymer substrate. Now-a-days metal chalcogenide thin films are widely deposited by CBD. Under controlled precipitation conditions, a good deposition can be produced on suitable substrates during hydrolysis/condensation reactions[58]. CBD occasionally face the problem of lack of reproducibility as compared to other chemical techniques, but considerable reproducibility can be attained by the proper control of growth parameters. Sol-gel, dip coating or spin coating of a sol on a substrate do not fall in the CBD category, as in all of these processes the layer deposition material must be pre-prepared, though the processes proceed through chemical reactions. Successive ion layer adsorption and reaction (SILAR) is a similar method, where a substrate is alternatively dipped in an ionic solution of one precursor, rinsed, then dipped in a solution of the second precursor, kept at certain temperature and finally rinsed with water, resulting in a single monolayer of the desired compound. Hodes[59] explained the basic chemistry of deposition for binary compounds. Besides a simple technique, the deposited crystallites in CBD films are generally quite small. CBD is a wonderful technique to deposit nano-crystalline films as size quantization is exhibited by nano-crystals of few nanometre (nm) sizes, and causes an increase in the optical band gap with decrease in crystal size. While discussing the effect of bath temperature on the crystallite size, it was reported that the higher bath temperature leads to a faster diffusion on the substrate and inter-diffusion between separate crystals leads to larger crystals. The lower bath temperature increases the chance that a sub-critical nucleus will finally grow to a stable size instead of dissolving back.

2. Principle of CBD

The principle of CBD technique is based on the fact that a solid phase is precipitated when the concentration of the reactants super saturates in the bath. At a particular pH and temperature, the precipitation of a solid phase occurs when ionic product of the reactants exceeds the solubility product. However, if the ionic product is smaller than the solubility product, thus produced solid phase will be re-dissolved in the solution[60]. For deposition of material using CBD technique, substrates are immersed in an aqueous solution which contains the metal ion source (M^{n+}), the chalcogenide source, and a complexing agent. A few examples of chalcogenide sources are thiourea ($SC(NH_2)$) for S^{2-} ions and selenourea (CH_4N_2Se) for Se^{2-} ions and water provides oxygen through the formation of OH^- ions. Hydrolysis of the metal ion is controlled using a complexing agent. In this process chalcogenide ions are released at a slow rate under basic conditions in the reaction bath in which free metal ions are buffered at a lower concentration. The concentration of free metal ion [M] is controlled using the complexing agent (A) by the formation of complex species as per the reaction,

$$M\,(A)^{2+} \leftrightarrow M^{2+} + A \qquad \text{... (1)}$$

Here concentration of the free metal ions at a particular temperature is given by the relation

$$K_i = \frac{[M^{2+}]\,[A]}{[M(A)^{2+}]} \qquad \text{... (2)}$$

K_i being the instability constant of the given complex ion. Every complexing agent has its own instability constant. With the increase in instability constant, number of ions released will be increased. Temperature and pH of the reaction bath also affects the stability of the complex. An increase in pH generally makes it more stable while stability is reduced with increase in temperature of the solution. By adjusting the concentration of the complexing agent, the pH and the temperature of the reaction bath, concentration of metal ions can be controlled. Generally, metal chalcogenide are deposited through four important steps[61]. First of all, balance between the complexing agent and water is established followed by formation or dissociation of ionic metal-ligand complexes; afterwards hydrolysis of chalcogenide source takes place leading to the formation of the solid. In principle, the following basic conditions should be satisfied for deposition of a compound by CBD[62]:

- The compound should be created easily through precipitation in the bath.
- The compound should not be soluble in the solution used.
- Uniform depositions may be achieved; if compounds are chemically stable.
- The deposition rate should be preferably slow in order to achieve homogeneous depositions.

3. Film deposition mechanism

The deposition of a solid phase in a chemical bath is composed of following four main steps:

3.1. Nucleation

Nucleation is a process of generation of small solid particles in the solution. It may take place in two ways:

- **Homogeneous Nucleation:** This type of nucleation takes place in the bath solution because of the local variation in the concentration, pH or temperature. When individual ions or molecules collide with each other embryos are formed. They further grow by collecting individual species that strike them. If there are large numbers of embryos, then due to collision with each other they may re-dissolve back in the solution before they grow as stable particles called nuclei.

- **Heterogeneous Nucleation:** Heterogeneous nucleation occurs by the formation of a new phase on the surface of different material. This process results due to the presence of a substrate in the chemical bath solution. Here even the subcritical embryos are survived by adsorption on the substrate because generally less energy is required to form an interface between an embryo and solid substrate as compared to the energy required for homogeneous nucleation. The adsorbed subcritical nuclei may grow further by addition of material from the solution or by surface diffusion. So heterogeneous growth is energetically preferred over homogeneous growth.

3.2. Crystal growth

After the generation of stable nuclei in the bath, the process of crystal growth starts. This may take place in any one of the three ways:

- **Self assembly:** In this process the growth of embryo continues by the adsorption of ionic species on it. Interaction among the building blocks is the main driving force behind self assembly growth.
- **Ostwald ripening:** In this process smaller crystals join together to form larger crystals. Large crystals are more energetically stable due to lower surface to volume ratio. Molecules of smaller particles will tend to diffuse through the reaction solution and deposit to the less stable surface of larger particles in order to lower the energy of the system. Also the smaller particles have a greater solubility due to their bigger curvature, as compared to large particles. To keep the local equilibrium concentration, smaller particles would dissolve into the surrounding solution; solute near the smaller particles will diffuse away, whereas the solute near the large particles will deposit on them. This process will continue till disappearance of smaller particles. The lowering of overall surface energy is the main cause behind the reorganization of surface, Ostwald ripening and the formation of faceted crystals.

- **Aggregation or coalescence:** When the concentration of the particles is high enough, the chances of collision also increase. This may result in either coalescence or a large aggregate until the effect of Vander Waal forces prevails. This process may continue until a large particle is formed.

3.3. Film growth

There are 4 important mechanisms for the compound formation depending upon the bath conditions.

(i) Simple ion by ion mechanism: This is the most simplified mechanism and occurs due to sequential ionic reactions. The common reaction for the mechanism is:

$$M^{n+} + X^{m-} \rightarrow M_mX_n \text{ (Adsorbed on the substrate)} \quad \text{....(3)}$$

Where M^{n+} is a metal ion and X^{m-} is chalcogenide ion. When the ionic product $[M^{n+}][X^{m-}]$ becomes greater than the solubility product (K_{sp}) of M_mX_n, then formation of solid phase M_mX_n takes place. However, if super saturation occurs, a still larger ionic product is required. In other words, if ionic product does not increase beyond, K_{sp}, no solid phase will be formed.

(ii) Simple hydroxide mechanism: Metal hydroxide is formed in the bath solution in the form of colloid or an adsorbed species on the substrate, instead of a precipitate in the solution.

The reaction of X^{m-} ion with the $M(OH)_n$ result in the formation of $M_m X_n$. The reaction follows as:

$$M^{n+} + n\, OH^- \rightarrow M(OH)_n \quad \text{.... (4)}$$

followed by

$$M(OH)_n + X^{m-} \rightarrow M_m X_n + n\, OH^- \quad \text{....(5)}$$

(iii) Complex deposition by ion by ion mechanism: In this mechanism, chelation of free metal cations [M] by the complexing agent takes place which results in a complex ion of the type M-complexing agent. The deposition of ZnO thin film by ion by ion mechanism using HMTA as a complexing agent and zinc acetate as a source of zinc ions, is expected to take place via the following basic steps:

- Zinc ions (Zn^{2+}) interacts with HMTA to form a zinc-HMTA complex in the chemical bath.

$$Zn^{2+} + HMTA \rightarrow [Zn(HMTA)]^{2+} \quad \text{....(6)}$$

- In the presence of hydroxide ions (OH^-), zinc hydroxide $[Zn(OH)_2]$ +HMTA is formed.

$$[Zn(HMTA)]^{2+} + 2OH^- \rightarrow [Zn(OH)_2(HMTA)]^+ + H_2O \quad \text{....(7)}$$

- The zinc hydroxide decomposes to form ZnO after heating and adjusting the pH of the bath.

$$[Zn(OH)_2(HMTA)]^+ \rightarrow ZnO + H_2O + HMTA \quad \text{....(8)}$$

- Ion by Ion Growth takes place on the surface of the substrate:

$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O \quad \text{....(9)}$$

- The overall reaction can be summarized as

$$Zn^{2+} + HMTA + 2OH^- \rightarrow ZnO + HMTA + H_2O \quad \text{....(10)}$$

In this mechanism, HMTA serves as a complexing agent, facilitating the controlled release of zinc ions that participate in the stepwise, ion-by-ion growth of ZnO thin films.

(iv) Complex decomposition cluster mechanism: Here instead of reacting straight with a free anion, an intermediate complex is formed. For example ZnO deposition in the chemical bath using HMTA is represented as below using this mechanism in the following steps:

- Zinc ions (Zn^{2+}) interacts with HMTA to form a zinc-HMTA complex in the chemical bath:

$$Zn^{2+} + HMTA \rightarrow [Zn\text{-}HMTA] \qquad \text{... (11)}$$

- This complex decomposes on heating:

$$[Zn\text{-}HMTA] \xrightarrow{heat} Zn^{2+} + NH_3 + H_2O + \text{other products} \qquad \text{...(12)}$$

- Formation of Zinc Hydroxide:

$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2 \qquad \text{.....(13)}$$

- Zinc Hydroxide dehydrates to form ZnO Clusters and Nanoparticles

$$Zn(OH)_2 \xrightarrow{heat} ZnO + H_2O \qquad \text{....(14)}$$

As a result of the above reactions, ZnO clusters are formed which further grow as nanostructures. The size and morphology of these nanostructures depend upon factors such as temperature, concentration of HMTA, and growth period.

4. Factors influencing film deposition

A few important factors that influence the deposition process of ZnO thin films as reported in the existing literature surveyed are as follows:

4.1. Nature and concentration of the reactants

The physical growth parameters of the chemical bath and ion concentration play an important role in ascertaining the morphology of the nanostructures deposited during the growth process. The composition and the shape of the particles of the ZnO thin film depend upon the nature and concentration of the precursors and the ligand used. It was observed that the presence of low concentration of citrate ions in the bath resulted in the hexagonal plate like crystals in the ZnO thin film, which grew in helical manner resulting in pillars type structure[63]. Jia *et al*[64] reported that diameter and length of nano rods increased with increasing Zn^{2+} ion concentrations whereas density of nano rods decreased. Mammah *et al*[65] deposited thin films of ZnO using aqueous chemical growth. The concentration of the bath precursors used was found to affect directly the reflectance, absorbance, absorption coefficient, refractive index, direct band gap, real and imaginary dielectric constant, whereas the transmittance of the thin films was observed to vary inversely with the concentration of the precursors. Govender *et al*[66] described the mechanism governing the film deposition and factors that affect the morphology of thin films of ZnO in an aqueous bath on the basis of modeling of speciation and the results revealed that acicular ZnO morphologies could be achieved by reducing the concentration of either of the Zn^{2+} or OH^{-}. The ZnO seed layer could provide nucleation at a lower level of super saturation and also helped to tailor the size of ZnO columns. They further reported that the stage at which the substrate was dipped in the bath was found to be crucial and could affect both the diameter of the rods and optical transmittance of the films.

4.2. Effect of pH

Polycrystalline thin films of ZnO having different morphologies and low resistivity (~ 15 ohm cm) were fabricated using a two-step CBD process on a glass substrate[67]. Effect of pH on the structural morphology of ZnO films was investigated by the addition of different amount of acetic acid. XRD study revealed that the (002) peak became more intense with decrease in pH indicating that addition of acetic acid in reaction solution increased the grain size and improved the crystalline nature of the deposited ZnO films. As the pH value increased above 5.91, well aligned ZnO nano-rods were deposited. The increase in super saturation with an increase in pH may cause large increase in the number of nuclei and as a result ZnO crystals with smaller size are formed. The results indicated that the seed layer, pH value and the counter-ion may affect the crystal size considerably. Electrical resistivity of the films was also observed to be affected by pH of the bath. Saeed and O'Brien[68] reported the deposition of ZnO thin films at different basic pH. They observed that the films deposited at pH 10.5-11 were uniform and adherent, whereas films grown at pH 10 or less were rough and powdery.

4.3. Effect of counter-ion

To investigate the effect of counter-ion, Chu *et al*[67] used zinc nitrate ($Zn(NO_3)_2$), zinc acetate ($Zn(CH_3COOH)_2$) and zinc sulphate ($ZnSO_4$) respectively to deposit ZnO thin film and reported that the SEM images of the ZnO thin films prepared with zinc nitrate showed well aligned nanorods, zinc acetate showed well defined hexagonal ZnO micro-columns while the use of zinc sulphate resulted in nano disc type crystals. They suggested that the change in morphology might be due to the adsorption of counter ions from the solution to the surface of ZnO crystal. Effect of counter ion on the morphologies of crystallites of ZnO films obtained from bath containing ethylenediamine was also reported by Govender *et al*[66] and it was observed that SEM micrographs of thin films of zinc acetate, zinc formate, zinc chloride exhibited twinned star like crystallites with needle like spines, whereas films were found to be less crystalline if deposited from zinc sulphate. The morphology of such films seemed to be a mixture of small flower like particles and larger flat platelet.

4.4. Nature and concentration of complexing agent

Most of the ZnO films have been deposited using ammonia as a complexing agent. Ortega–Lopez *et al*[69] suggested that ammonia addition tends to reduce the concentration of the Zn^{2+}ions by generating $Zn(NH_3)_n{}^{2+}$complex ions (where n=1–4, and n=4 is the most stable coordination number) and as a result spontaneous precipitation is avoided. Saeed and O'Brien[68] reported the deposition of ZnO thin films by varying the concentration of ethylenediamine and obtained best films with 0.042 M at pH 10.5. The morphology of the particles was found to change with the concentration of the complexing agent indicating that super-saturation controls the morphology of the zinc oxide crystallites effectively. Chu *et al.*[70] observed rapid growth of crystalline nano-structured ZnO along with a very small quantity of $Zn(OH)_2$ and ZnS phases involving zinc salt, aqueous ammonia and thiourea. They also investigated the effect of ammonia concentration on the morphology of the deposited ZnO film and observed flower like crystals when the concentration of ammonia was 0.75M and columnar ZnO crystals were deposited when the ammonia concentration ranged within 1.4-2.0M. Further increase in the concentration of ammonia to 3.0M, the morphology of the deposited films was observed to be changed having particles without well-defined crystalline phases. The efficiency of dye sensitive solar cell (DSSC) was also found to be affected by the morphology of the crystallites. Cells based on nano flower ZnO film showed improved energy efficiency as compared to ZnO film with columnar nanoparticles. Fabrication of ZnO thin films on a sapphire substrate using a two-step deposition was reported by Hamada[71]. In the first step, ZnO seed layer was deposited using metal oxide chemical vapour deposition (MOCVD) and thereafter ZnO layer was deposited using CBD process using HMTA as a complexing agent. The prepared films exhibited *n*-type conduction with a carrier concentration of $1.9x10^{19}cm^{-3}$ and high carrier mobility of 22.6 $cm^2V^{-1}s^{-1}$. Khallaf *et al*[72] deposited CBD ZnO thin films with different complexing agents: ammonia, ethanolamine (EA), hydrazine, triethanolamine (TEA), methylamine(MA) and dimethylamine (DMA). Ammonia was always added along with any one of the above five complexing agents. All the films were annealed at 400°C. The films obtained using DMA & EA were not of good quality, whereas the films grown with ammonia, hydrazine, TEA and MA exhibited very good transmittance after annealing beyond the absorption edge. The TEA based films when annealed at 400°C were polycrystalline with preferred orientation along the [104] direction. The films were found to be highly resistive. Multi dip deposition could not be performed as etching occurred on dipping the original layer in the fresh bath solution and non-uniform and porous films were deposited. As a result, single deposition of film of thickness 0.2 - 0.7 μm was achieved with single dip. Oxalic acid and urea can also be used as complexing agents to deposit ZnO thin films with band gaps of the order of 3.6 eV and 3.45 eV respectively[73] showing that the particle size was reduced more by oxalic acid as compared to urea. The variation in the concentration of complexing agent affected the morphology of crystallites was proved as hexagonal prisms, plates and rose-like twinned crystals of ZnO were grown using CBD with different concentration of gelatin by Duan *et al*[74]. Sugunan *et al*[75] described that hexamine may be used as a shape modifying molecule. After a growth period of 24 h at 60-95°C, highly non-isotropic nano wires with an aspect ratio more than 150 with diameter ~30nm and length exceeding several microns were observed. Vayssieres[76] deposited thin films HMTA and reported that HMTA is a non-ionic cyclic tertiary amine and with the increase in pH, hydrolysis rate of HMTA decreases. Till date the role of HMTA in the deposition and synthesis of ZnO nanowires is still debatable. Ahuja *et al*[77] reported that HMTA may act as a bi-dentate lewis base that coordinates and joins together two Zn^{2+}ions. Along with the natural fast growth in the direction of the polar surfaces of wurtzite ZnO, HMTA molecules may also attach to the non-polar side facets that results in the anisotropic growth along the [001] direction[78]. HMTA also plays the role of a weak base and act as a pH buffer[66]. HMTA quickly hydrolyzes in water thus producing formaldehyde (HCHO) and ammonia (NH_3) gradually. The process may be expressed as shown in the following reactions.

$$C_6H_{12}N_4 + 6H_2O \leftrightarrow 4NH_3 + 6HCHO \qquad \text{... (15)}$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad \text{... (16)}$$

$$Zn^{2+} + 4NH_3 \leftrightarrow [Zn(NH_3)4]^{2+} \quad \text{... (17)}$$

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2 \quad \text{... (18)}$$

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O \quad \text{...(19)}$$

Fast hydrolysis of HMTA generates a large amount of OH^- in a short interval of time, then due to high pH, Zn^{2+} ions in solution would precipitate rapidly; resulting in the fast consumption of the nutrient and inhibit the growth of oriented ZnO nanostructures[79]. Ammonia produced by the hydrolysis of HMTA is very important as it not only produces a basic environment in the reaction solution that is essential for the production of $Zn(OH)_2$ but also stabilizes Zn^{2+} ions, by coordinating with them. Zinc hydroxide can be dehydrated into ZnO through a number of ways like: by heating in an ordinary oven[21] or in a microwave[80], under ultrasonicator[81] or under sunlight[82]. By controlling the chemical bath parameters such as growth temperature, precursor concentration, and time all the above mentioned reactions (15-19) stay under equilibrium. Generally, the nanowires' density is decided by the precursor concentration whereas morphology and aspect ratio of ZnO nanowires are controlled by the deposition time and temperature of the chemical bath[83]. The above five reactions proceeds extremely slowly at room temperature, but an average growth rate of the ZnO nanowires as high as100nm per minute can be achieved using microwaves as the heating source[84].

4.5. Effect of bath temperature

Drici *et al*[85] deposited ZnO thin film using CBD and reported that minimum temperature at which the deposition occurs was 50^0C. The optimum deposition rate for good quality thin ZnO films was in a temperature range 60-65^0C at pH 11. The sample was annealed for half an hour at 300^0C to get ZnO from Zn $(OH)_2$. Hodes[59] explained the factors controlling crystal size by varying bath conditions. He stated that lower temperature of the bath slows down the re-dissolution of the nuclei; therefore a sub critical nucleus will finally grow to a stable size instead of getting redissolved. This kinetic stabilization of small nuclei increases the number of nuclei in the bath, resulting in a smaller crystallite size. He reported that complex decomposition cluster mechanism results in smaller crystal size in comparison of ion by ion mechanism. Kathrival *et al*[86] reported that with increase in bath temperature, crystallite size also increased. Zinc oxide thin films with a *c*-axis orientation and grain size of the order of 23nm, 26nm and 27nm for bath temperatures at 40^0C, 60^0C and 80^0C respectively were reported. Kathalingam *et al*[87] deposited ZnO thin films on a zinc plate using zinc acetate and ethylenediamine at various temperatures. The bath temperature was found to influence the growth of ZnO crystallite and as the temperature exceeds 50^0C, crystallinity of the film was improved. Also, films grown at higher temperatures resulted in larger grain sizes with decrease in corresponding band gap energy. They observed that best results could be obtained in pH range 9.5-10.5.

4.6. Effect of substrate

Jia *et al*[64] reported the fabrication of ZnO film made up of rods using zinc acetate and methamine as complexing agent on glass substrates which were kept in a $SnCl_2$ /HCl mixed solution for at least 1hour in order to show hydrophilic properties. To study the effect of the substrates on the morphology of ZnO structures, a number of experiments were performed on different substrates, i.e., glass, In_2O_3/Sn (ITO)-coated glass and Au- or Pt-sputtering glass by Xu *et al.*[88]. The growth mechanisms associated with different patterns were observed to depend on the substrate. It was reported that final morphologies of ZnO nanostructures were affected by the natural anisotropy of ZnO and minimization of the surface energy by different substrates. After a growth period of 3h, highly dense, randomly orientated with very small perpendicular growth ZnO crystals showing a long hexagonal rod like shape were deposited on glass substrates. With increase in the precursor concentration and the bath temperature, these microrods started degrading and they became rough. On further increasing the growth period to 18 h, dissolution of ZnO rods was clearly visible as double-tip rods were obtained. At low temperature and precursor concentration, flower like ZnO bunches were observed on Pt-sputtering glass substrate. ZnO crystallites were able to nucleate and grow from special sites on the substrate. The morphology remained the same even after increasing the concentration of the precursors and temperature of the bath. The presence of hexagonal prismatic rods on the substrate indicated that ZnO crystal structure had hexagonal wurtzite nature. Nail like ZnO crystals with single tip ZnO architectures grew perpendicular to the Au-glass substrate with downward tip. When temperature and concentration of precursors were increased, stelliform ZnO crystals were obtained showing that the substrate provided Au crystallites to act as nucleation sites for ZnO growth. On comparing above samples on different substrates with ITO, the morphologies of the crystallites on ITO substrates were found to be quite different. At a low precursor concentration and bath temperature, a vertically oriented ZnO rod array (ZRAs) on large area of ITO substrate was observed. The substrate coverage was found to be dependent on the growth time. ZnO samples prepared with a high concentration of precursor and bath temperature revealed that ZnO crystallites were nucleated directly in the initial stage of nucleation, on the ITO substrate. ZnO rods were grown in the subsequent growth period on these ZnO nuclei. ZRAs were highly directional along their *c*-axes perpendicular to the substrate and covered the entire substrate. Vayssieres *et al*[89] grew ZnO thin layers composed of large 3-dimensional and porous micro rod arrays with high orientation. These films were deposited using equimolar aqueous solution of $Zn(NO_3)$ and HMTA in a laboratory oven heated at 95⁰C for 1-10 hours on polycrystalline $F\text{-}SnO_2$ glass substrate, a bare piece of glass and on a conducting plastic and it was found that the crystal growth and orientation of the ZnO micro rod array were not affected by the type and crystalline nature of the substrates used. Kathalingam *et al*[90] deposited ZnO thin film on a zinc plate using a chemical bath of zinc acetate and ethylenediamine at various temperatures. The use of zinc as a substrate is found to be conducive to smooth adsorption of zinc ions on the surface.

4.7. Effect of deposition time

To study the effect of thickness on optical and electrical properties of ZnO thin films prepared by CBD, Selma *et al*[91] deposited thin films on glass slides using zinc sulphate and ammonia solution in a beaker and the solution were stirred with a magnetic stirrer. The thickness of the film is found to increase linearly at a fast rate with time initially but saturates after some time at some terminated thickness, afterwards the rate decreased resulting in a terminal thickness. The saturation behaviour of the film thickness may be due to eventual reduction in the ionic product of ZnO. By varying the deposition time, morphology of the crystallites was also observed to change. Hexagonal tubes are obtained during CBD process of ZnO deposition if left in the solution for a longer time due to preferential dissolution of the Zn basal plane[59].

4.8. Effect of Thermal Annealing

The increase in crystal size due to the post-deposition annealing depends not only on material and the annealing atmosphere but also on temperature and time of annealing[59]. Ortega-Lopez *et al*[69] deposited ZnO thin films by adding H_2O_2 in the chemical bath containing $ZnCl_2$, NH_4OH and NH_4Cl as precursors. The film deposited corresponds to a ZnO_2 phase with [122] preferential orientation, but after thermal annealing at 350⁰C for two hours, a ZnO polycrystalline phase with good optical transmittance and reduced order was produced. Ali[92] prepared ZnO thin films on micro-corning glass slides using zinc acetate, triethanolamine and sodium hydroxide in deionized water for 2hr 15 min. in a water bath maintained at 80⁰C. Slides were annealed at different temperatures (300⁰C, 350⁰C and 400⁰C) for 12 minutes. Effect of thermal annealing showed that the films deposited at 350⁰C exhibited minimum dislocation density and micro strain with the maximum grain size and minimum band gap.

4.9. Effect of Media

Offiah *et al*[93] studied the effect of medium by using three solvents polyvinyl alcohol (PVA), polyvinyl pyrrolidon (PVP) and distilled water with zinc sulphate and ammonia to deposit ZnO thin films. The band gap of the as-deposited ZnO thin film using the PVA medium was 1.60eV which was increased to 2.95eV after annealing the sample at 400ᵒC. The samples deposited using PVP and water medium showed lower band gaps values. Higher annealing temperatures improved the band gaps of the films grown in all the media. The transmittance of the as-deposited zinc oxide thin films using the PVP medium is considerably higher than those of the PVA and water deposition media.

5. Growth of seed layer on the substrates

Homogeneous nucleation is a fast process and produces larger particles as precipitates within the solution as compared to slow heterogeneous nucleation process which occurs at the substrate surface as the particles grow slowly to form a film. These two processes compete with each other in the bath solution and homogeneous reaction tries to disrupt the heterogeneous growth of the film on the substrate. In order to overcome this problem, nanoparticles in the form of ZnO seeds can be used to grow ZnO thin films on arbitrary substrates while using wet chemical methods. Seed layer is beneficial in the heterogeneous growth at lower levels of supersaturation[66] because activation energy barrier is lower for heterogeneous nucleation as compared to homogeneous nucleation. The interfacial energy between crystals and substrates is normally lower than that between crystals and reaction solution[80]. Seed layer can be coated on the substrate prior to wet chemical growth in a number of ways. Greene *et al*[94] were able to grow ZnO nanowires on 4-inch silicon wafer and 2-inch plastic substrates demonstrating the ease of commercial scale up by spin coating the nanocrystallites as seeds. By making use of seed layer, wafer-scale synthesis can be easily attained[95]. Green *et al*[96] reported that well-aligned ZnO nanowires can be attained using ZnO nano crystal as seeds. These seeds are obtained by thermally decomposing zinc acetate on the substrate. The alignment of ZnO nanowires was strongly dependent on the humidity level during the seed deposition process[80]. Fang *et al*[97] presented a procedure to deposit ultrathin ZnO nano fibres with high density using a substrate of zinc metal in a mixture of ammonia, alcohol and water showing that the nanowires' density may be controlled by controlling the seed layer thickness. Liu *et al*[98] deposited seed layer on thermoplastic polyurethanes (TPU) substrates using sputtering and observed that density of the ZnO arrays depend on the thickness of the seed layer up to a limit; but when the seed layer thickness exceeded this limit, the nanowire density was observed to be less sensitive. Xu S *et al*[99] reported that density of ZnO nanowires was found to be dependent not only on the density of ZnO seeds but also on the spin speed. In order to get good quality films, the seed layer should stick to the substrate firmly. Improved adhesion to the substrate can be achieved by depositing an intermediate metal layer, on inorganic substrates or by introducing an interfacial bonding layer such as tetra-ethoxysilane molecules on a polymer substrate[100]. The quality of seed layer was also found to be dependent on the choice of the counter ion[101]**.** The seed layers of ZnO prepared by spin coating using zinc nitrate exhibited dendrites and those using zinc acetate were homogeneous. The film prepared using zinc nitrate showed a fast and poorly ordered crystallites as compared to that using zinc acetate. Hamada *et al*[71] deposited a highly *c*-axis oriented ZnO seed layer using zinc acetyl-acetonate as a source material by plasma enhanced MOCVD. Ultrasonic spray pyrolysis was used to grow ZnO seed layer on cleaned glass substrates by K. Mosalagae *et al*[102] using zinc acetate dihydrate ($Zn\ (CH_3COO)_2).2H_2O$) and mixture of ethanol and di-ionized water. For further CBD growth process of ZnO nanorods on the seeded substrate, equal molar concentrations of zinc nitrate hexahydrate ($Zn\ (NO_3)_2.6H_2O$) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) were mixed in the bath. The effect of CBD growth parameters — specifically growth time, temperature, and precursor concentration — on the morphology, structural, optical, and vibrational properties of nanorods was studied. The results showed that the length and diameter of the nanorods increased with higher growth precursor concentration, temperature and time. Structural analysis revealed that the nanorods exhibited a wurtzite ZnO structure with a dominant (002) peak.

6. ZnO Composite Films

Kokotov and Gary Hodes[103] deposited composite films of CdS/ZnO from a solution containing Zn and Cd salts with thiourea as a complexing agent. It was observed that CdS/ZnO films grow, either ZnO nucleation is created on the substrate (in-situ or ex-situ) or when the concentration of NH_3 is less than 0.5 M. XRD and UV-VIS spectra confirm the presence of both CdS and ZnO. ZnS/CdS film is grown if the concentration of NH_3 is more than 0.5 M or substrate is not activated. Wang *et al*[104] deposited ZnO+Ag composite thin film on glass substrate (with prior dip in $SnCl_2$/HCI solution to develop hydrophilic properties). Zinc acetate and hexamethylenetetramine were used to prepare pure ZnO film. The ZnO film was further dipped in a solution of silver nitrate and hexamethylenetetramine. It was observed that silver particles were deposited on the glass substrate, rather than on ZnO rods. Composite film showed decreased transmittance in comparison to the pure ZnO. Due to the surface silver nanoparticles plasmon resonance the intensity of the NBE emission peak increases while that of the blue emission peak decreases.

7. Conclusion

Based on the above literature survey, it is obvious that chemical bath deposition process is an economical technique that can be effectively used for deposition of uniform ZnO thin films. CBD is performed at lower temperatures compared to other deposition techniques like Physical Vapor Deposition (PVD) or Chemical Vapor Deposition (CVD). This makes it suitable for depositing films on heat-sensitive substrates, such as flexible materials or polymers. By adjusting parameters such as bath temperature, concentration of precursors, and deposition time, it is possible to control the composition and properties of the deposited film. This allows for customizing the film’s characteristics to meet specific needs in various applications. Band gap can also be tailored due to smaller size of CBD nanocrystals as they show size quantization. The morphology of nanoparticles in thin films can be changed by changing physical conditions of the bath. Thick films with a smaller crystal size can be formed by depositing on an existing thin film from a new bath solution. This process can be repeated number of times to get the desired thickness. So besides cost effectiveness it is a good technique for large area deposition. Overall, Chemical Bath Deposition offers a low-cost, scalable, and versatile method for ZnO thin-film deposition with a wide range of applications like optoelectronic devices, sensors, thin film solar cells etc.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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