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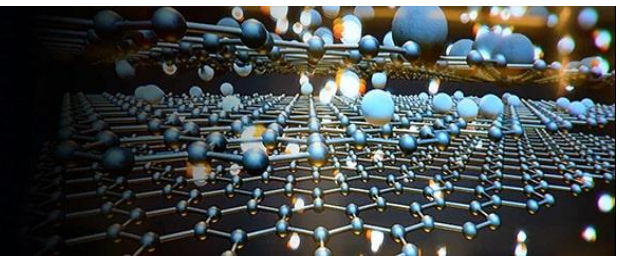

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A study of morphology and structural properties of CBD grown nanoscale ZnO thin films: Effect of deposition time

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Abstract
In the present study, ZnO thin films were deposited by chemical bath deposition technique on a seeded substrate at pH-5.0 with equimolar concentration of HMTA and Zinc Nitrate, for different deposition periods. Structural, morphological and elemental analysis of as deposited thin films was done by using the characterization tools like X-ray diffraction, Scanning electron microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX). Sheet resistance was calculated using four probe method. The study lay a foundation stone for understanding the use of ZnO thin films for further electronic application by correlating the growth period at a selected pH and concentration with the various morphological characteristics of nanocrystalline thin ZnO films.

Keywords: CBD, XRD, SEM, EDX, four probe

Introduction
In recent decades, nano-material-based technologies have revolutionized material science by offering new possibilities for innovation. Nanomaterials possess high surface areas and exhibit unique physical, chemical, and biological properties that distinguish them from their bulk counterparts [1]. They have attracted considerable attention due to their enhanced electrochemical reactivity, thermal conductivity, and nonlinear optical characteristics, enabling a range of specialized applications [2]. Among different metal oxide nanomaterials, zinc oxide based nanomaterials are particularly noteworthy for their tunable optical and chemical properties. By modifying their morphology, ZnO-NPs are highly effective as photocatalytic and photo-oxidizing agents against various chemical and biological species [3, 4]. ZnO-NPs also exhibit biocompatibility and low toxicity in their soluble form, zinc ions (Zn^{2+}) are essential trace elements naturally present in the human body. Additionally, ZnO-based structures demonstrate biodegradability in both bulk and nanoparticle forms [5]. They contribute to intracellular bacterial toxicity by disrupting bacterial cell membranes, further highlighting the antimicrobial potential of ZnO-NPs [6]. ZnO materials have also received broad attention due to their well known performance in electronics, optics and photonics. ZnO is one of the group II-VI binary compound semiconductors, with a direct wide band gap of 3.37 eV at room temperature, having optical transparency in the visible range [7]. So it is a very useful substance to develop transparent opto-electronics devices, sensors etc. Moreover it has large excitonic binding energy of 60 meV which is much larger than the room temperature thermal energy (25 meV), making the excitonic recombination process possible even at room temperature [8]. Since the separated electrons and holes are more vulnerable to be trapped by the various defects present in the crystal, it is desirable to have a material with a large exciton binding energy for optoelectronic applications [9]. The band gaps of semiconductors have significant impact on their optical and electrical properties and importance of ZnO is further enhanced as its band gap can be tuned to desired value by reducing its particle size to nano scale [8, 10, 11]. Due to its *n*-type semiconducting nature and excellent thermal stability (melting point-1975 °C), ZnO is an active channel for thin film transistors and can be well developed in crystalline form on various substrates [12, 13]. Thus the cost-effective ZnO optoelectronic devices along with other potential applications make ZnO a prospective candidate for the next generation of UV and blue light emitters for solid state lighting applications [14]. A variety of methodologies have been reported by several

groups for deposition of ZnO nano-structures on different substrates [15, 16]. Few common techniques are: wet chemical techniques [17], metal organic chemical vapor deposition (MOCVD) [18], physical vapor deposition [19], molecular beam epitaxy (MBE) [20], pulsed laser deposition [21], electrospinning [22], sputtering [23], etc. Most of these techniques are performed at high temperature and require expensive instrumentation where as wet chemical techniques are comparatively simple, and less expensive. Out of all the wet chemical techniques, chemical bath deposition (CBD) method has been found to be a simple and cost effective method as it is a low temperature technique and is widely used for the deposition of different metal chalcogenide thin films [24, 25]. CBD refers to depositions from solution (usually aqueous) where the required deposit is both chemically generated and physically deposited in the same bath [26]. It is a very useful technique for large area deposition. It produces good deposits on suitable substrates by the controlled precipitation via hydrolysis and/or condensation reactions of metal ions and/or complexes from aqueous solution [27]. It is an inexpensive technique as it does not require any high voltage equipment and works at low temperature. In a typical experimental set up, the substrates are immersed in a solution containing the chalcogenide source, metal ions and complexing agent [28]. The aim of present study is to deposit nano scale thin films using CBD and study their structural and electrical properties. Attempts were made to deposit highly transparent and homogeneous ZnO thin films using CBD by selectively adjusting the pH as well as the concentration of chemical bath at 90°C using ZnO seed layer [29] at glass substrate. The obtained ZnO thin films were characterized for their morphological, structural and elemental analysis through SEM, XRD and EDX. In order to understand the electrical behavior, sheet resistance of all the samples were also measured using four probe method.

Materials and Methods

The deposition was carried out using a two step process: coating of ZnO seeds on the glass substrate and further growth of thin films on the seeded substrate. AR grade chemical were procured from sigma Aldrich for the synthesis of ZnO thin films and used as purchased without any further purification. The substrates used were microscopic glass slides procured from Blue Cross India and cut into size of 2 x 2 cm^2. Individually prepared aqueous solutions of "zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$)" and "Hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$)" were mixed together in equal volume in three different beakers. The concentrations of both precursors were fixed at100 mM in each bath and were adjusted to pH-5 as optimized in the previous study [29] using concentrated nitric acid. Three pre-seeded glass substrates were immersed into these aqueous solutions in a slanting position. To optimize the growth time, the beakers were kept in an oven at 90 °C for 60 min, 90 min and 120 min respectively. After the incubation period, the glass slides were rinsed with distilled water and then air dried. Fig.1 gives the schematic of the deposition of ZnO thin films for various growth periods. Table (1) gives the growth parameters of the deposition of ZnO thin films for various growth periods.

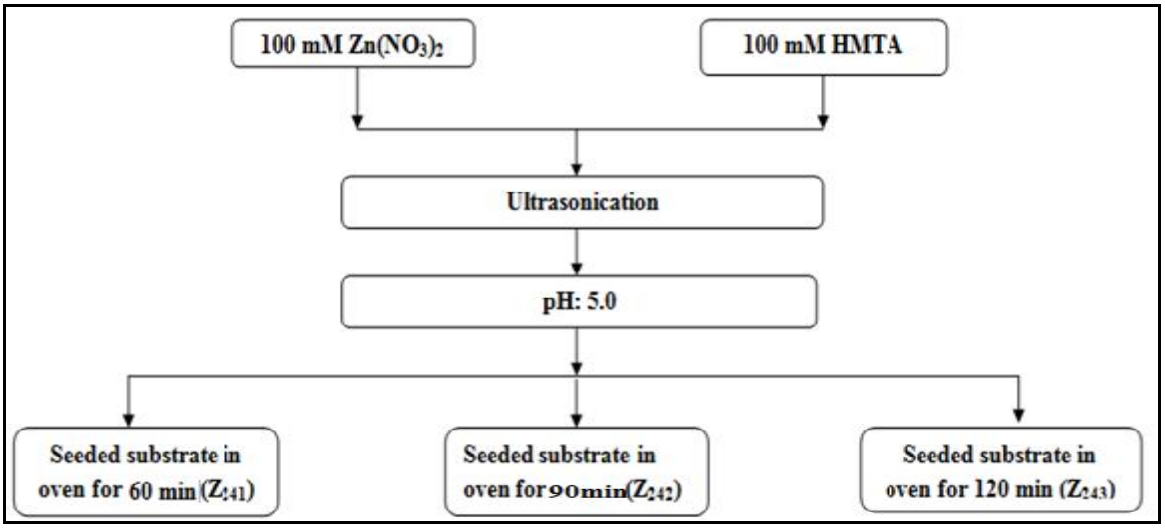

Fig 1: Schematic for the deposition of ZnO Thin Films for different Growth Periods

Table 1: Growth parameters for thin films of ZnO deposited for different growth periods

Sample code	$Zn(NO_3)$ Conc.	HMTA Conc.	pH	Deposition Time(min)	Deposition Temp (°C)
Z_{241}	100 mM	100 mM	5.0	60	90
Z_{242}	100 mM	100 mM	5.0	90	90
Z_{243}	100 mM	100 mM	5.0	120	90

Results and Discussion

The synthesis of ZnO nanocrystalline thin films using Chemical Bath Deposition with zinc nitrate and hexamethylenetetramine, involves the controlled nucleation and growth of ZnO nanoparticles in the solution. The pH of the solution plays a pivotal role in this process by facilitating the formation of ZnO through the hydrolysis and decomposition of HMTA, which serves as a slow-release source of hydroxide ions (OH^-). HMTA functions as both a complexing agent and a buffer. At a pH of approximately 5, HMTA gradually hydrolyzes, producing ammonia and formaldehyde. The generated ammonia reacts with water to form ammonium and hydroxide ions. Hence, ammonia could stabilize Zn^{2+}ions through reversible reaction of creating and decomposing of zinc-ammonia complex. The hydroxide ions, released from HMTA decomposition, then react with Zn^{2+} ions to form zinc hydroxide. Since zinc hydroxide is relatively unstable, it dehydrates to produce

zinc oxide (ZnO) [30]. The ZnO nuclei subsequently form and grow, resulting in thin films.

$[(CH_2)_6N_4] + H^+ \rightarrow [(CH_2)_6N_4H]^+$

$[(CH_2)_6N_4H]^+ + 3H^+ + 4NO_3^- + 6H_2O \rightarrow 4NH_4^+ + 4NO_3^- + 6CH_2$

$Zn^{2+} + 4NH_3\ H_2O \rightarrow [Zn(NH_3)_4]^{2+} + 4H_2O$

$[Zn(NH_3)_4]^{2+} + 4H_2O \rightarrow Zn(OH)_2 + 4\ [NH_4]^{2+} + 2OH^-$

$Zn(OH)_2 \rightarrow ZnO + H_2O$

Thickness of ZnO Thin Films

Thickness of ZnO thin films deposited for different growth time were calculated using the equation [31], $t = \frac{m}{A\rho}$, where t is the thickness of the film, m is the weight gain, A is the area of the deposited film, ρ is the density of the thin film material which was taken as 5.606g/cm^3. The calculated values of thicknesses of samples Z_{241}, Z_{242} and Z_{243} were found to be 535 nm, 668 nm and 802 nm respectively.

Structural and Morphological Properties

For the structural information X-ray diffraction (XRD) was recorded by XPERT-PRO diffractometer (45 kV, 40 mA) equipped with a Gionometer PW3050/60 working with Cu K ALPHA radiation of wavelength 1.5406A˚ in the 2θ range from 5 to 80 for all the three films (Fig.2) and it was observed that all the three samples were amorphous.

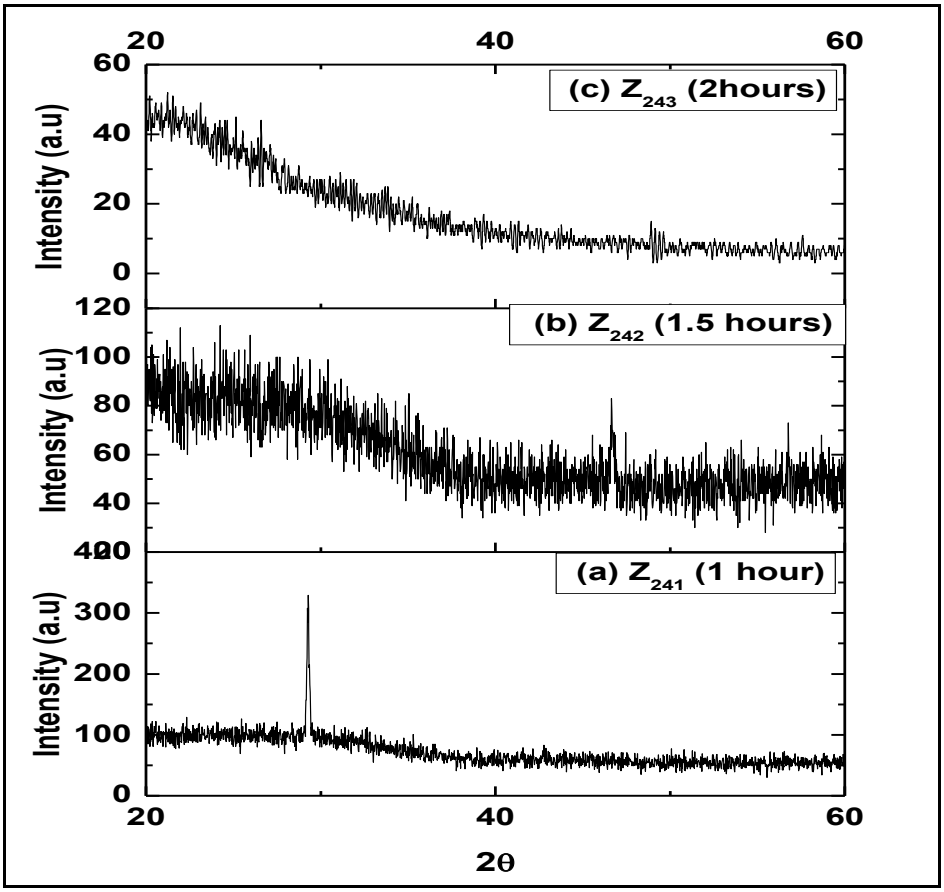

Fig 2: XRD patterns of ZnO thin films deposited for different growth time

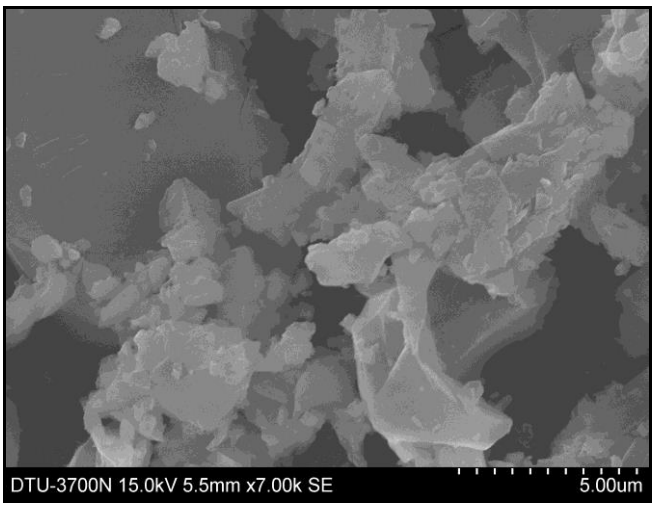

Fig 3(a): SEM Image of Sample Z_{241}

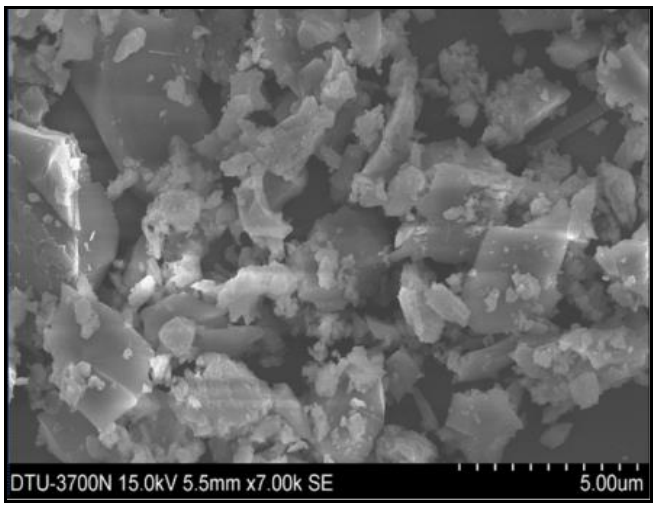

Fig 3(b): SEM Image of Sample Z_{242}

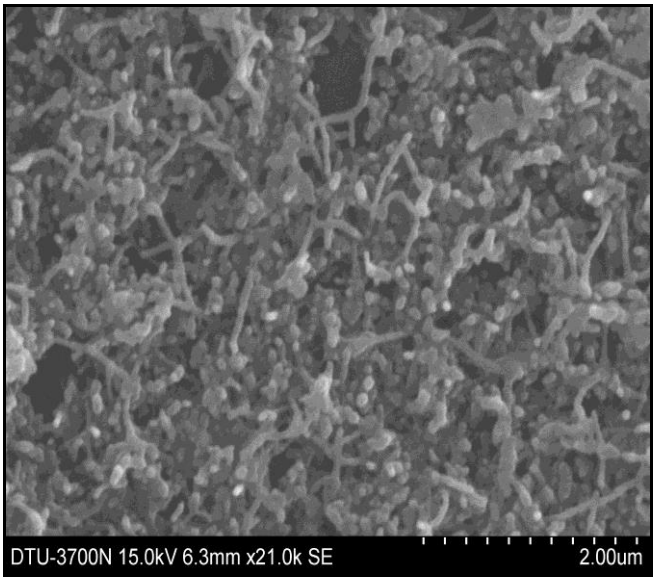

Fig 3(c): SEM Image of Sample Z_{243}

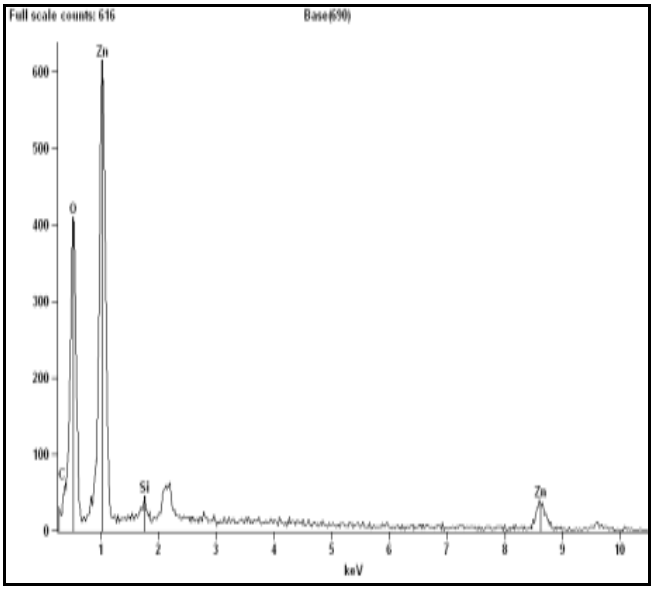

Fig 4(a): EDX Image of Sample Z_{241}

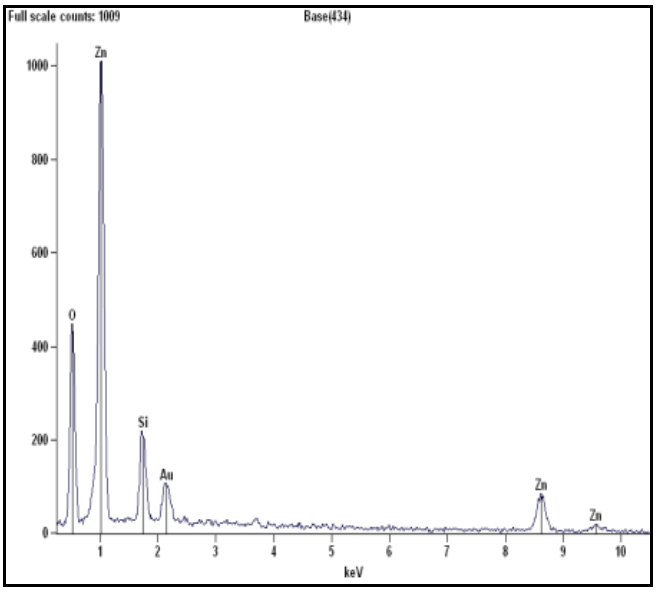

Fig 4(b): EDX Image of Sample Z_{242}

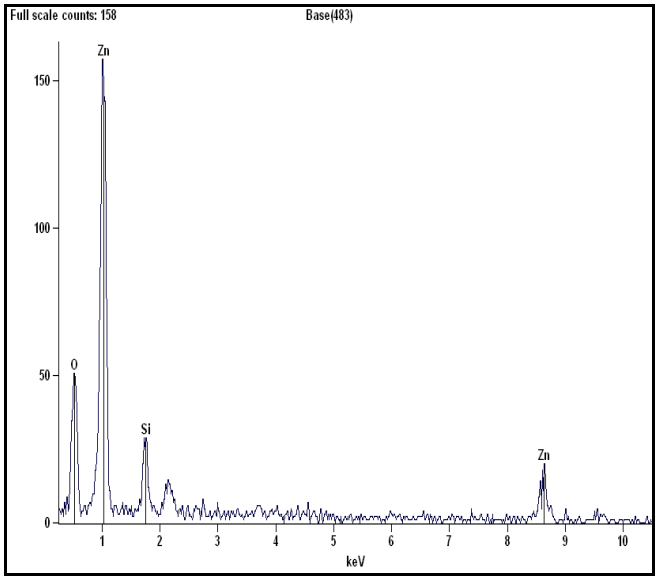

Fig 4(c): EDX Image of Sample Z_{243}

Extensive SEM studies were conducted to interpret the role of growth time on the morphology of "ZnO thin films". SEM micrographs revealed change in morphology and stoichiometry with growth period. Fig.3 (a) shows ZnO growth in the form of a rough sheet on the substrate for Z_{241}. However increase in growth time results in agglomeration of ZnO crystallites without any orientation for sample Z_{242} (Fig.3 (b)). On the contrary Z_{243} showed poorly oriented branched and twinned structures parallel to the substrate (Fig. 3 (c)). It has been reported that the axial growth of polar surfaces have a relatively different growth rate from that of lateral growth of non-polar surfaces [32]. As a result, the morphologies of the three samples were observed to be strongly dependent on the growth period.

Energy Dispersive X-Ray Spectroscopy (EDX)

EDX spectra ((Fig. (4(a), 4(b) and 4(c)) indicate that all the ZnO thin films grown for different time period were pure as manifested by the absence of impurity peaks. However, the presence of a small peak of silica may be attributed to the substrate material.

Sheet Resistance

Four-point collinear probe method is one of the most common ways of measuring the resistivity of thin, flat materials, such as semiconductors or conductive coatings on different substrates. The four-point probe technique[33] involves bringing four equally spaced probes in contact with a material of unknown resistance. A DC current is supplied between the outer two probes, and a voltmeter measures the voltage difference between the two inner probes. The resistivity is calculated from geometric factors, the source current, and the voltage. In the present study, a single instrument: A Keithleysource meter (model-2450) (SMU) was used to measure sheet resistance. The sheet resistances for Z_{241}, Z_{242} and Z_{243} were observed to be $8.1x10^{8}\Omega$/square, $7.75x10^{8}\Omega$/square and $6.8x10^{8}\,\Omega$/square respectively.

Conclusion

On the basis of the above experimental results obtained during the present investigation, it was observed that the all the samples deposited with an equimolar concentration (100mM) of zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and

Hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$) mixed in equal ratio at a pH 5.0 for different time period were pure and amorphous in nature. It was observed that growth period had a strong effect on morphology of the crystallites. The sample Z_{241} **(**deposition time period of 1 hour) showed the highest sheet resistance out of all the prepared samples.

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