Effects of Dimethylamine (DMA) And Ethylenediaminetetraacetic Acid (EDTA) on Optical, Structural And Morphological Properties of Zinc Oxide Thin Films Prepared By Chemical Bath Deposition Technique

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Abstract- The ZnO films were prepared by Chemical Bath Deposition (CBD) technique without employing any stirring technique using weak and strong complexing agents such as Dimethylamine (DMA) and Ethylenediaminetetraacetic acid (EDTA). The optical, structural, and morphological properties of ZnO films have been investigated. When the complexing agent were DMA and EDTA, the X-ray diffraction (XRD) patterns from the values of interplanar spacing of a=3.351Å and c=5.226Å were hexagonal structure. The film grown using EDTA was well defined grains with a thickness in the range 0.5 – 0.7µm while the SEM micrograph of DMA film has no well defined crystallites and this was due to restriction on precipitation. The films prepared in absence of complexing agent shows reflections along (002), (200) and (203) planes corresponding to formation of hexagonal wurtzite structure of zinc oxide and formed a network of flakes and magnified cauliflowers of diameter 0.8-1µm. The optical band gap for DMA and EDTA associated thin films were 3.3 and 3.35Ev respectively. Therefore, the effect of complexing agent on the crystal phase of ZnO films was generally found. The thin films obtained in this research could be used in high density data storage systems, solid-state lighting (where white light is obtained from phosphors excited by blue or UV light-emitting diodes), secure communications and bio-detection.

Index Terms- Band gap, Chemical Bath Deposition (CBD). Dimethylamine (DMA), Ethylenediaminetetraacetic acid (EDTA), Morphology, X-ray Diffraction (XRD), ZnO thin films.

I. INTRODUCTION

Thin films are basically any kind of material layer with a thickness on the order of few atoms to few micrometers. The films are not a new technology; they can be seen as far back as 1500BC where decorative gold leaf artwork was found from ancient Luxor, the artwork had gold with a thickness of about 0.3µm [12]. Even though these films are not new technology. They have found their way into scientific and commercial applications. In the recent years, indium thin oxide (ITO) has been playing an increasingly important role in the manufacture of display device electrodes, touch panels and solar cell for use in liquid crystal display (LCD) and plasma televisions as the market for these products continues to expand [1]. ITO is now an essential part of these electronic products. Rapidly growing demand for the rare indium metal that makes up ITO has resulted in dwindling reserves and roller coaster prices that have left the supply situation less than stable.

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In the face of what looks like an ever rising tide of demand for indium, researchers are racing the clock to find alternatives before the supply runs out. One promising candidate is ZnO thin films. While the ITO has expanded with the development of products like flat panel display (FPD) televisions, their penetration rate has not even reached 10% of the global market [1]. So far there has been enough ITO to go round. The problem is that the indium contained in ITO, today's primary transparent conductive film material, is rare metal facing the risk of depletion and typically found in limited geographical areas like China. There is a concern that indium will soon be of the strategic resource lists of every country in the world, disrupting the chance for any steady flow of indium in the near future. As the popularity of FPD televisions, touch screen monitors, and solar cells gains greater momentum, ITO alone will not be able to cover the demand. Today the list of indium free transparent conductive films materials include the tin oxide (SnO2), based titanium oxide (TiO2), magnesium hydroxide ($Mg(OH)_2$), as well as zinc oxide (ZnO) based materials such as AZO and gallium-doped zinc oxide (GZO). Zinc oxide is a promising transparent conductive film material [1]If you looked at Zinc oxide in terms of availability (resource abundance), there is about 10,000 times more tin oxide and 100,000 times more zinc oxide than there is ITO. While we would run through the entire indium supply inside a year, there is enough zinc oxide to last for 100,000 years. Zinc oxide also costs less than one percent of the total indium price tag. The advantages of zinc oxide in solar cell applications make up for its shortcomings in films that are 100nm or less thick [1] Furthermore, the control over the properties of zinc oxide through chemical route has attracted increasing interest. Many methods of deposition of ZnO thin films were reported. Of all these methods, CBD is the most successful and best method to obtain low cost CdS thin films that have optimal features for photovoltaic device applications because of it is an efficient, cost effective, and large scale method [2] Earlier work on the chemical bath deposition of zinc oxide used ammonia as the complexing agent and in this case, the stirring was always employed, and sometimes, electric and magnetic field were applied. Obviously this external means deserve additional setups for the CBD [8]. The effect of complexing agent on nucleation and growth mechanism has been sparsely studied [10]. The aim of this work is to investigate the morphology, crystal structure, and optical properties of ZnO thin films using weak and strong complexing agents i.e. Dimethylamine (DMA) and Ethylenediaminetetraacetic acid (EDTA) respectively without employing any stirring technique by chemical bath deposition method in order to show the potential that Zinc oxide transparent conductive films holds for the future.

II. REVIEW OF RELATED THEORIES

There are many methods to fabricate thin films, some of them are: Electrodeposition [10], Chemical bath deposition [2], Sol-gel spin coating technique [9], SILAR method [16], Pulsed Laser Deposition [18], Metal Organic Chemical Vapour Deposition[13], Close Spaced Sublimation and so on. Among them, the chemical bath deposition (CBD) has been proven to be the most suitable method to produce thin Cds thin films for photovoltaic applications because of it is an efficient, cost effective, and large scale method [8]. [7] investigated chemical deposition of ZnO thin films using six different complexing agents namely: ammonia, hydrazine, ethanolamine, triethanolamine, methylamine and dimethylamine. It was found that; as -grown film consists mainly of cubic ZnO2 that was transformed into hexagonal ZnO after annealing. [13] investigated both EDA and NH4OH as complexing agents for CBD of ZnO and concluded that the growth of ZnO was unstable for the perturbation of EDA concentration. They reported that films grown with EDA showed quite poor adhesion and poor uniformity, while films grown with ammonia showed good adhesion and uniformity. [4] reported growing nanostructure ZnO thin films using zinc nitrate/zinc acetate as Zn precursor and urea/hexamethylenetramine as complexing agents. They have shown that microwave activated CBD-ZnO films were crystalline and no additional heat treatment/annealing is necessary. The effect of complexing agent on CdS thin films by chemical deposition method was investigated by [8]. They observed that when ammonia was used as complexing agent, the cluster-by cluster deposition was dominant, which leads to formation of films with rough morphology; while, when using EDTA as complexing agent, the ions-by-ions deposition favours the formation of thin films with smooth morphology. As for the optical properties of chemical bath deposited CdS films, the derived film using EDTA as complexing agent has more significant transmission in the visible region than that using ammonia as complexing agent, which was ascribed to different crystal structures, morphologies, and thicknesses of two CdS films [7].

III. RESEARCH METHODOLOGY

The technique for deposition was chemical bath deposition (CBD) on microscopic slides (25.4mm x 76.2mm x 1.0mm). Twocomplexing agents namely: Ethylenediaminetetraacetic acid (EDTA) and Dimethylamine (DMA) were chosen to investigate and compare their effect on the morphology, crystal structure, and optical properties of ZnO thin films. Firstly, the slides were cleaned using acetone and alcohol, and then put into de-ionized water under ultrasonic stirring for 30 minutes. The chemical bath was an aqueous solution of 50mM of zinc acetate and 0.1M KCl was introduced to increase the conductivity of the electrolyte. The temperature of the chemical bath was 60^0C and the pH was adjusted to 10.5 using ammonia. A deposition time of 30 min were chosen for all experiments. After deposition, the slides were removed from the chemical bath, and cleaned for several times with de-ionized water, then dried in N2. Finally, it was then subjected to annealing for 1hr at 400^0C. The morphology of the films was determined by scanning electron microscopy (SEM). The optical properties of the films were examined by spectrophotometer ranging from 400 to 1000nm. The crystal phase of the films was determined by X-ray diffraction (XRD). The optical transmission and reflectance of the films was examined by spectrophotometer ranging from 400 to 1000nm. The transmittance T and reflectance R data was used to calculate absorption coefficients of the films at different wavelengths. The absorption coefficient, α is given by the relation:

$$T = (1 - R)\exp(\alpha d) \quad (1)$$

Where d is the film thickness. The absorption coefficient data were used to determine energy band gap, Eg , using the relation:

$$\alpha hv = (hv - E_g)^{1/2} \quad (2)$$

Where hv is the photon energy. The crystal phase of the films was determined by X-ray diffraction (XRD).

IV. RESULTS AND DISCUSSION

The effects of complexing agents on the phases of ZnO films were investigated by means of X-ray diffraction (XRD). The observed‘ d values of the films were compared with [11] and are in good agreement with the standard ‘d’ values. Both the samples show reflections along (103), (104. The reflections of hexagonal wurtzite structure of lattice constant a=3.351Å and c=5.226Å were observed. In addition to reflections along (103), (104, the reflections along (002), (200) and (203) were also observed for the films deposited using EDTA. The films prepared in the absence of complexing agent shows reflections along (002), (200) and (203) planes corresponding to formation of hexagonal wurtzite structure of zinc oxide. In addition to these peaks, there were also reflections along (101) and (112) which correspond to metallic zinc formation. The films deposited without complexing agent were grayish black with luster.
The absorption coefficient α of the film was estimated from equation 1. This equation was also used in estimating the band gap of 3.3 and 3.35Ev for DMA and EDTA respectively. This was done by extrapolating the linear portion of the curve to zero. These observed band gap is in

agreement with [10].There was a sharp absorption edge at around 350-850nm and a transmittance that exceeds 60% was observed in the visible region. When DMA was used as complexing agent, there was no clear absorption edge and there was low transmittance. The unclear absorption edge and low transmittance observed was responsible for the poor quality. Figure 2a shows the SEM of the Zinc oxide thin films obtained in the absence of complexing agent. The thin films obtained formed a network of flakes and magnified cauliflowers of diameter 0.8-1µm. Figure 2b show the SEM of Zinc oxide thin films obtained in the presence of EDTA and DMA respectively. The film grown using EDTA was well defined grains with a thickness in the range 0.5 – 0.7µm after annealing at 4000C in air for 1hour, the film grown using EDTA maintained the same quality after annealing. SEM micrograph of DMA has no well defined crystallites and this was due to restriction on precipitation. This leads to consideration that the influence of complexing agent molecules is more on the crystal growth and nucleation of ZnO. Similar results were reported by [10].

We can learn the complexing agent effects on the morphology of as-deposited films. Fig. 2b reveals that when DMA was the complexing agent for CBD, the films were rough and has quite a lot of colloidal particles. Fig. 2c shows that the complexing agent of EDTA leads to very smooth film. During the CBD of ZnO films, it is believed that there are two possible pathways, i.e., clusters-by-clusters deposition via ZnO colloidal particles formed in the solution, and ions-by-ions deposition via metastable complex comprising Zn^{2+} and O^{2-} agents [5] These two deposition pathways are competitive, which depends on the effective concentrations of Zn^{2+} and O^{2-} ions and ZnO particles. When the effective concentrations of Zn^{2+} and O^{2-} are high and that of ZnO particles is low, ions-by-ions deposition is dominant in CBD process; on the contrary, the clusters-by-clusters deposition dictates the CBD process [10]. [17] have proved that clusters-by-clusters deposition is highly undesirable and it yields powdery and non-adherent films; on the contrary, the ions-by-ions deposition is expectable and it leads to uniform films. The effective concentration of Zn^{2+} ions in the solution using EDTA as the complexing agent was extremely high and the formation of ZnO colloidal particles in the solution was greatly suppressed, therefore, the ions-by-ions deposition dictated the film deposition, thus, resulting in smooth morphology. In contrast, the effective concentration of Zn^{2+} ions in the solution using DMA as the complexing agent was quite low and the formation of ZnO colloidal particles was appreciable, thus, the clusters-by-clusters deposition led to poor morphology.

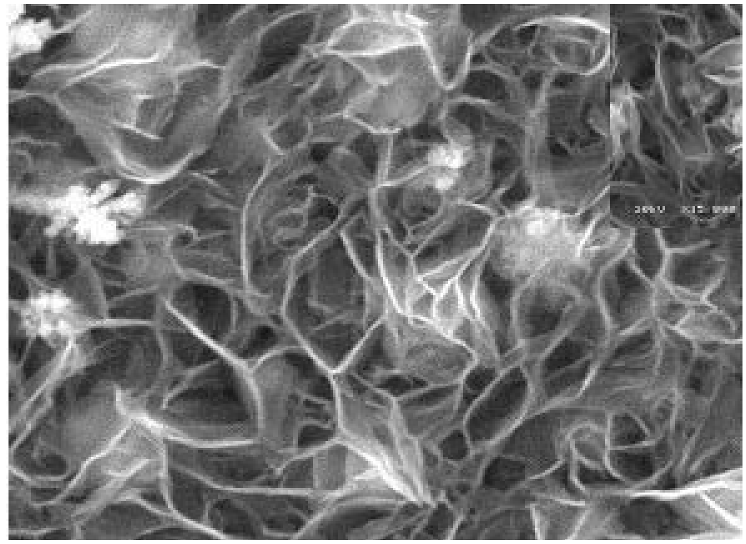

Fig 2a: SEM micrographs of Zinc oxide thin films without complexing agents

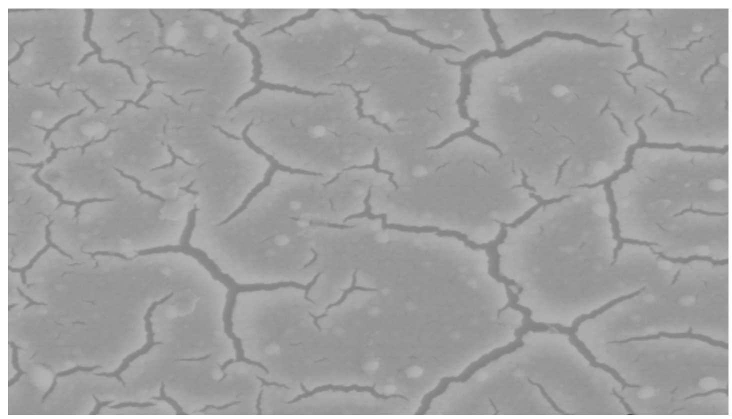

Fig 2b: SEM micrographs of Zinc oxide thin films using DMA as complexing agents

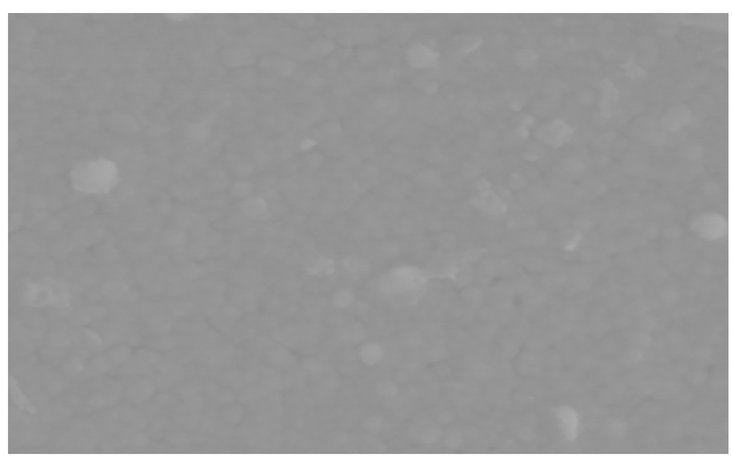

Fig 2c: SEM micrographs of Zinc oxide thin films using EDTA as complexing agent

V. CONCLUSION

The effect of complexing agents on structural, morphology optical and nucleation and growth mechanism were studied successfully. Different structural and morphological changes were observed for the films deposited in the absence and presence of complexing agents. From the XRD study it is concluded that for the phase pure ZnO film formation addition of complexing agents are needed in view to get desired pH. Flakes like structure and cauliflowers are obtained for the samples deposited without complexing agents. After use of complexing agents the morphology changes to granular and compact structure for EDTA and DMA respectively. When DMA was used as the complexing agent, the clusters-by -clusters deposition is dominant, which leads to the formation of films with rough morphology; while, when using EDTA as the complexing agent, the ions-by-ions deposition favours the formation of films with smooth morphology. Moreover, the effect of complexing agent on the crystal phase of ZnO films was found, that is, the films were of hexagonal when using DMA and EDTA as complexing agents. As for the optical properties of chemical bath deposited ZnO films, the derived film using EDTA as complexing agent has more significant transmission in the visible region than that using DMA as complexing agent, which is ascribed to different crystal structures, morphologies, and thicknesses of two ZnO films. The thin films obtained in this research has important applications in high density data storage systems, solid-state lighting (where white light is obtained from phosphors excited by blue or UV light-emitting diodes), secure communications and bio-detection.

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