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ORIGINAL ARTICLE

# ALD grown nanostructured ZnO thin films: Effect of substrate temperature on thickness and energy band gap

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**Abstract** Nanostructured ZnO thin films with high transparency have been grown on glass substrate by atomic layer deposition at various temperatures ranging from 100 °C to 300 °C. Efforts have been made to observe the effect of substrate temperature on the thickness of the deposited thin films and its consequences on the energy band gap. A remarkably high growth rate of 0.56 nm per cycle at a substrate temperature of 200 °C for ZnO thin films have been achieved. This is the maximum growth rate for ALD deposited ZnO thin films ever reported so far to the best of our knowledge. The studies of field emission scanning electron microscopy and X-ray diffractometry patterns confirm the deposition of uniform and high quality nanosturtured ZnO thin films which have a polycrystalline nature with preferential orientation along (100) plane. The thickness of the films deposited at different substrate temperatures was measured by ellipsometry and surface profiling system while the UV–visible and photoluminescence spectroscopy studies have been used to evaluate the optical properties of the respective thin films. It has been observed that the thickness of the thin film depends on the substrate temperatures which ultimately affect the optical and structural parameters of the thin films.


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## 1. Introduction

Zinc oxide (ZnO) is known to be as n-type semiconductor and a transparent conductive oxide with excellent optoelectronic properties like wide band gap (3.37 eV), high dielectric constant, high exciton binding energy (60 meV), and high thermal stability (Özgür et al., 2005). Hence, it is used in a wide range

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of applications such as solar cells, gas sensors, optoelectronic devices, biosensors and transducers (Klingshrin, 2007; Look et al., 1999; Pearton et al., 2003; Reynolds et al., 1996; Wraback et al., 1999). ZnO thin films have been prepared by many methods such as RF-magnetron sputtering (Krupanidhi and Sayer, 1984), ion beam-assisted reactive deposition (IBAD) (Zhang and Brodie, 1994), chemical vapor deposition (CVD) (Minegishi et al., 1997), pulsed laser deposition (PLD) (Ryu et al., 2000), molecular beam epitaxy (MBE) (Kang et al., 1998; Segawa et al., 1997) and atomic layer deposition (ALD) (Guziewicz et al., 2008; Keun Kim et al., 2005; Lim et al., 2004). ALD method is a special modification of chemical vapor deposition for self-limiting film growth. It can be considered as one of the best techniques to synthesize nanostructured thin films of the order of few angstroms (Keun Kim et al., 2005; Lim and Lee, 2007; Lim et al., 2004). ALD reactions use two chemicals, typically called precursors which react with the surface of a material one at a time in a sequential, self-limiting manner. When the precursors are exposed to the substrate surface repeatedly, a fine quality ultra-thin film is deposited. Slow deposition growth rates of ALD facilitate several processes as an advantage to ensure uniform high quality and pinhole defect free films over large areas. ALD grown ZnO thin films have gained substantial interest in the field of semiconductor research because of their high purity, ultra thinness and crystallinity which influence the optical and electrical properties of the film and make it a suitable candidate for optoelectronics applications. The optoelectronic devices require optical coating of high quality (good surface uniformity, high packing density, good adhesion with underlying substrate, low defect density) and precise thickness control which depends on the deposition method being used (Martinu et al., 2014).

The structural and optical properties are greatly influenced by the substrate temperature of the thin film, however, there have been few research articles on the substrate temperature dependent thickness and the associated changes in the structural, optical and electrical properties of the ZnO thin films (Ahmad et al., 2015). These physical properties of ZnO thin films are affected by the mechanism and growth conditions such as substrate temperature, pressure, precursors and thickness (Enigochitra et al., 2015). For optoelectronic devices based on ZnO thin films, influence of a parameter such as substrate temperature on the structural and optical properties is of great importance (Rahal et al., 2014). This work aims to achieve maximum growth rate of ZnO thin films deposited by ALD at different substrate temperatures and the associated changes on the thickness and energy band gap.

### *1.1. Experimental setup*

In our present study we have used Syskey Atomic Layer Deposition system for the deposition of ultra-thin ZnO layers. Diethyl zinc, $Zn(C_2H_5)_2$ precursor and water as an oxidant have been used in this experiment. Before the deposition of thin films, the substrate (glass slides) was cleaned in an ultrasonic bath with solvents (trichloroethylene, acetone and isopropanol) and finally with deionized water. ALD reaction mechanism for ZnO thin films cycle may be summarized in a single equation:

$$Zn(CH_2CH_3)_2 + H_2O \rightarrow ZnO + 2C_2H_6 \tag{1}$$

Cyclic repetition of the above process results into layer by layer growth of ZnO thin films at atomic scale. In all experiments both precursors were kept at room temperature 22–24 °C in the lab, while a substrate temperature was increased from 100 °C to 300 °C with an interval of 50 °C. During all experiments the water ($H_2O$) pulsing time was kept constant at 15 ms, DEZ pulsing time 60 ms and purging flow time 10,000 ms. We achieved the maximum growth of ZnO thin films at a substrate temperature of 200 °C i.e., 0.56 nm per cycle which is evident to be the best deposition rate using ALD ever reported in the literature (Chaaya et al., 2013; Lim et al., 2004; Singh et al., 2014).

### *1.2. Thin film characterization*

Different physical properties of the deposited ZnO thin films have been characterized by several techniques. The surface characterization have been performed by field emission scanning electron microscopy (FESEM-JSM7600F JEOL – Japan), while the XRD (Ultima-IV; Rigaku, Japan) patterns gave the crystalline structure and phases of grown ZnO thin films. Ellipsometry (Horiba UVISEL, France) and surface profiler (Dektak, Bruker-Germany) have been used for thickness measurements of the thin films. Finally the UV–visible spectrometer (Perkin Elmer Lambda 750) and photoluminescence (PL) spectrometer (RF-5301PC-Shimadzu, Japan) devices have been used to investigate the optical properties of the thin films.

## 2. Results and discussion

### *2.1. Surface characterization*

Surface morphology studies of thin films have been conducted using FESEM. Fig. 1 shows the FESEM images of ZnO thin films at a high resolution. It has been observed that the particle size of ZnO thin films increases with the increase in temperature up to 200 °C and decreases when the temperature was increased further from 200 °C to 300 °C. These changes in the particle size at different substrate temperatures show the effect of temperature on growth mechanism of the thin film. The decrease in the energy band gap ($E_g$) with the increase in the films thickness is due to the increase in localized density of states near the band edges which results in the decrease in $E_g$ with thickness. The decrease in direct $E_g$ with the increase in film thickness can also be associated with an increase in particle size (Seval et al., 2010). This shows the dependence of $E_g$ on the thin film thickness. These results are also in good agreement with the literature (Alnajjar, 2012).

### *2.2. Thickness measurement*

The thickness of the films has been measured by ellipsometry (Horiba UVSEL, France). We observed 14.1 nm, 27.6 nm, 33.4 nm, 30.7 nm and 23.07 nm thicknesses for 100 °C, 150 °C, 200 °C, 250 °C and 300 °C substrate temperatures respectively. These results were also confirmed with the surface profiling system (Dektak Bruker, Germany).

### *2.3. Structural characterization*

For the structural analysis of ZnO nanostructured thin films, we have used X-ray diffraction (XRD) measurements. The