On the Structural Study and Morphological Changes of Thermally Oxidised Metallic Zinc Thin Films with Low Oxidation Temperature

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ABSTRACT: In this work metallic zinc thin films were grown on synthesised glass at 150^{o}C substrates temperature under vacuum pressure using thermal evaporator and oxidised in an open air with different low oxidation temperatures of 200^{o}C, 300^{o}C and 400^{o}C respectively.The effect of oxidation temperature on the structure and morphological properties of the films was investigated. Phase identification, orientation and morphology of the films were studied by XRD and FESEM.The structural investigation reveals that thermally oxidised metallic Zn films has a preferred (011) orientation instead of the usual (002) orientation indicating that the growth of ZnO crystallites have preferential (011) plane at low oxidation temperature.Similar peaks were observed at different Bragg angles revealing the presence of unreacted metallic Zn films which is attributed to poor flux diffusion of oxygen into the Zn films during the oxidation process is as a result of low oxidation temperatures. In addition, the films morphological studies shows that the films undergo a phase transformation as the oxidation temperature increased from 200^{o}C to 300^{o}C then to 400^{o}C.

Keywords: Thermal oxidation, ZnO thin films, structural properties, morphology, diffusion, XRD, FESEM.

1. INTRODUCTION

The use of metal oxide semiconductor thin films including zinc oxide (ZnO) has incredibly attracted the attention of materials scientists and engineers in the recent years due to their low cost, availability and good performance in high temperature environment with inherent properties like large band gap, higher electron mobility as well as high breakdown field strength which are highly required in most optoelectronic devices [1], [2], [3].ZnO is one of the most promising and multifunctional semiconductor materials with some fascinating physical, chemical and optoelectronic properties that suits several applications such as ultra violet (UV) electronics, spintronic devices, solar cell technology, sensors and most especially as transparent conducting oxide film [4], [5]. Several methods have been used to grow ZnO thin films including sol-gel, solvothermal, sputtering, spray pyrolysis and thermal oxidation [2]. Thermal oxidation has been reported to be simple, efficient and cost effective[6]. Synthesis of ZnO using thermal oxidation usually involve high oxidation temperature mostly above the melting point of the metallic zinc as source material [3], [6], [7]. However, the reports on the synthesis of ZnO using thermal oxidation at low oxidation temperature are scarce in the literature [3].A study on the morphological properties of ZnO thin films synthesised by thermal oxidation at low oxidation temperature (below melting point of Zn) of evaporated metallic Zn films is presented in this work.

2. EXPERIMENTAL

2.1 Preparation and Deposition of Metallic Zinc (Zinc)Thin Films

Metallic zinc (Zn) thin film was deposited under vacuum pressure of1.15×10^{-5} torrusing EDWARD Auto306 thermal evaporator with FL400 deposition chamberon glass substrates. Figure 1 gives the illustration of the experimental set-up for the deposition. The metallic Zn thin film was evaporatedfrom the source material (Zn pellets) situated on a molybdenum (evaporation) boat to the substrate (Corning 7059 glass) kept at 8cm distanceand elevated substrate temperature of 150^{o}C which is supported by heat-controllable substrate holder, a constant deposition rate of 2nm/secwas maintained to obtain Zn films of 150nm thickness.

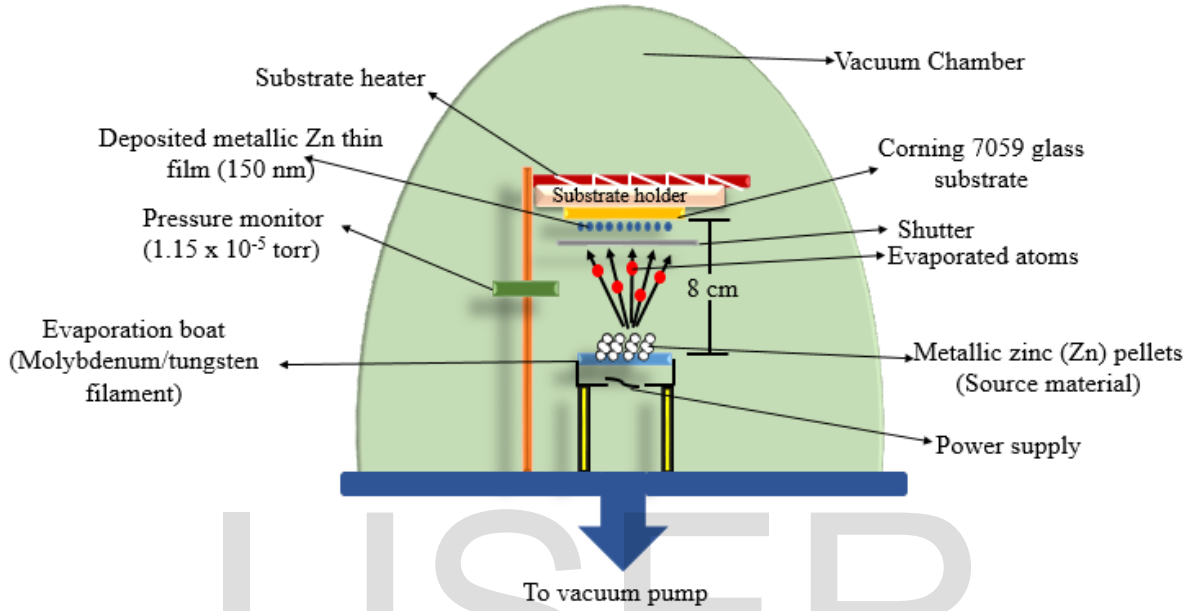

Fig. 1.Experimental set-up of thermal evaporation system for the deposition of the metallic Zn thin films.

2.2Thermal Oxidation of Evaporated Metallic Zinc (Zn) Films

After deposition, the oxidation of the films was carried out in open air using a horizontal Carbolite201 tubular furnace as demonstrated in Figure 2.

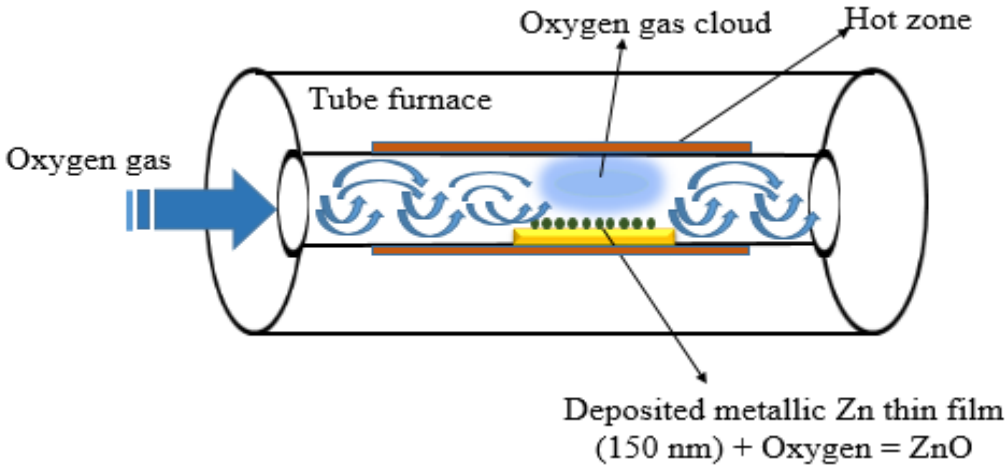

Fig. 2. Thermal oxidation of the metallic Zinc (Zn) thin films.

The as-grown metallic Zn films were oxidised,with ramping rate of 10°C/min from room temperatureat 200^{o}C, 300^{o}C and 400^{o}C under ambient atmosphere fortwo hours as dwelling time,

followed by a cooling down to room temperature with the same rate. The samples were designated as $Z_{150/200}$, $Z_{150/300}$ and $Z_{150/400}$.

2.3 Characterisations

The surface morphology and elemental compositions were investigated by Field Emission Scanning Electron Microscope (FESEM) (JEOL JSM - 7600F) equipped with an Aztec and INCA microanalysis system with 50mm^2 silicon drift detector, as well as INCA wavelength dispersive spectrometer (WDS) system as energy dispersive X-ray (EDX) spectrometer for elemental composition measurement.The films structural determination was achieved using an XRD system (D8 Advance Diffractometer, X'Pert' Powder PANALYTICAL Bruker,42kV, 40mA) with a monochromatic Cu-K_α ($\lambda = 1.54060$Å)radiation. The system was operated in a scan mode of 0.040^o with a constant counting times of 3.17 s/step for 2θ values between 25° and 60°. The electrical characteristics of the films were carried out with a four point probe set-up (QUADPRO-301-6).

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction

The crystalline phases of thermal oxidation grown ZnO films at elevated substrate temperature of 150^{o}C with different low oxidation temperatures of 200^{o}C, 300^{o}C and 400^{o}C are identified in XRD patternsas illustrated in Figure 3.

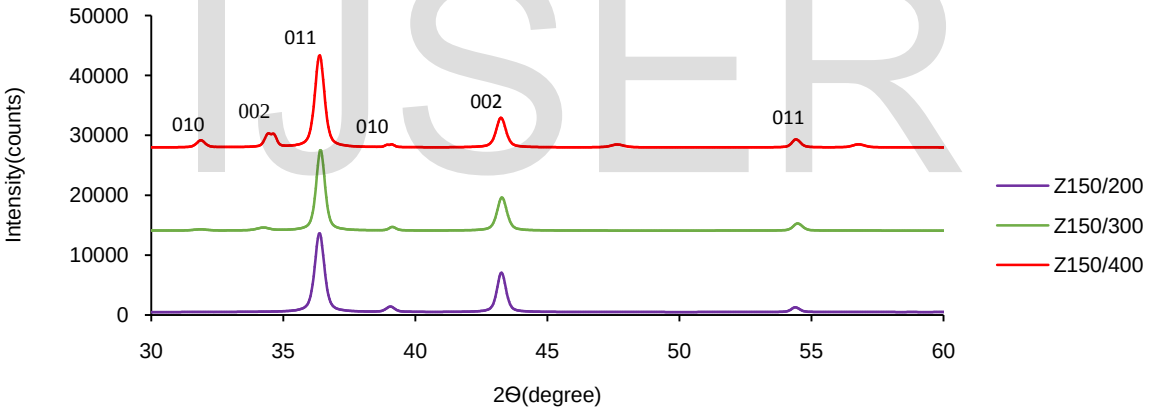

Fig. 3. XRD patterns of thermal oxidation grown ZnO films at elevated substrate temperature of 150^{o}C with different low oxidation temperatures of 200^{o}C, 300^{o}C and 400^{o}C.

The filmsshow clear diffraction peaks at 2θ = 32.03^o, 34.39^o, 36.32^o, 39.07^o, 43.35^o and 54.63^{o}corresponding to (010), (002), (011), (010), (002) and (011) planes respectively. The peak at 2θ = 36.47° with (011) orientation has a pronounced textured structure of hexagonal ZnO structureas well as the peaks at 32.23°and 34.55° are indexed to ZnO hexagonal (wurtzite) structure as previously observed by [3]. The sharp peaks (010), (002) and (011) observed at 39.07^o, 43.35^o and 54.63^o are associated with un-oxidised Zn hexagonal system of space group P63/mmc (ICSD:247158; 52259),this might be attributed to poor flux diffusion of oxygen into the Zn films during the oxidation process as a result of low oxidation temperatures which is lower than 420^{o}Cmelting point of the Zn films leading.The ZnO films are observed to have preferentially grown along (011) orientation instead of the usual (002) orientation, indicating growth of ZnO crystallites have preferential (011) plane at low oxidation. It is further observed that as the oxidation temperatures increased so also (010) and

(002) ZnO peaks become more pronounced.The lattice parameters 'a' and 'c' values of the prominent peak (011) observed at 2θ = 43.35°are calculated using the relations in(1) and (2)[8].

$$a = \sqrt{\frac{1}{3}}\frac{\lambda}{\sin\theta} \quad (1) \qquad c = \frac{\lambda}{\sin\theta} \quad (2)$$

Where, λ is the wavelength of the CuK_{α} X-rays used (1.54060 Å) and θ is the diffraction angle at which the maximum intensity was observed.Using the Miller indicesof this plane (011), the interplanar spacing (d) is evaluated using the relation in (3) [9]. Also, the average crystallite size (D) of the oxidised metallic Zn thin films were deduced using Debye Scherrer's formula in (4) [4].

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2} \quad (3)$$

$$D = \frac{0.9\lambda}{\beta Cos\theta} \quad (4)$$

Where, β is the Full Width at Half Maximum (FWHM).The average strain of the ZnO thin films was calculated using the Stokes–Wilson (5) [10].

$$\varepsilon_{str} = \frac{\beta}{4Tan\theta} \quad (5)$$

The microstructural parameters that characterise the oxidised ZnO at different low oxidation temperatureare presented in Table 1.

Table 1. Structural characteristics for prominent (011) orientation at different low oxidation temperatures of the ZnO thin films.

Sample	2θ (°)	β (°)	a (Å)	c (Å)	d-spacing (Å)	D(nm)	Micro-strain (x 10^{-3})
$Z_{150/200}$	36.87	0.3936	2.81	4.87	2.81	21.27	5.15
$Z_{150/300}$	36.47	0.354	2.84	4.92	2.84	23.62	4.69
$Z_{150/400}$	36.43	0.3936	2.84	4.93	2.84	21.24	5.22

3.2Morphological Properties of Zinc Oxide (ZnO) Thin Films

The chemical composition demonstrates high purity of ZnO thin films grown at elevated substrate temperature of 150°C and low oxidation temperature of 200°C, 300°C and 400°C using thermal oxidation method. The morphological evolution of the thermally oxidised metallic Zn films grown at elevated substrate temperature of 150°C and oxidised with different low oxidation temperatures of 200°C, 300°C and 400°C are revealed by FESEM micrographs as illustrated in Figure 4.

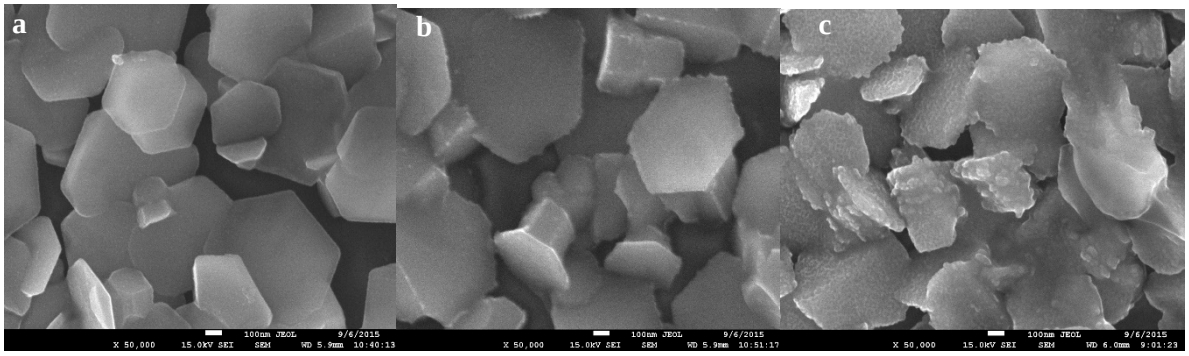

Fig.4.FESEM micrographs of thermally oxidised Zn films with oxidation temperature of(a) 200^{o}C (b) 300^{o}C and (c) 400^{o}C all grown at elevated substrate temperature of 150^{o}C.

$Z_{150/200}$ with a lowest oxidation temperature of 200^{o}Cexhibits a hexagonal nanoplatelet-like shape (Figure 4a), when the oxidation temperature increased to 300^{o}C ($Z_{150/300}$), the film undergo a phase transformation with a mixed structures of nanorod/nanoarc-like shapes as observed in Figure 4b. As the oxidation temperature further increased to 400^{o}C ($Z_{150/400}$), another mixed structures revealingnanoflake/nanoarc-like shapes were observed (Figure 4c). The study as well revealed that $Z_{150/200}$, $Z_{150/300}$ and $Z_{150/400}$ exhibit average grain size 60.62nm, 64.46nm and 68.98nm respectively. It was observed that the increase in oxidation temperature give rise to larger average grain size with improved crystalline quality. The phase transformation confirm the dependence of the crystallinity and the size of the crystallites of the oxidized Zn filmson the process temperature as previously noted in the literature [4], [11].

4. CONCLUSIONS

Metallic Zn films were deposited on glass substrate at an elevated substrate temperature of 150^{o}C using thermal evaporator, the oxidation of the films was carried out in open air with different low oxidation temperatures of 200^{o}C, 300^{o}C and 400^{o}C. The structural investigation reveals that the thermally oxidised metallic Zn films preferentially grow along (011) orientation instead of the usual (002) orientation indicating that the growth of ZnO crystallites have preferential (011) plane at low oxidation temperature, similar peaks were observed at different Bragg angle revealing the presence of unreacted metallic Zn films which is attributed to poor flux diffusion of oxygen into the Zn films during the oxidation process as a result of low oxidation temperatures. In addition, the films morphological studies show that the films undergo a phase transformation as the oxidation temperature increased from 200^{o}C to 300^{o}C and then to 400^{o}C.

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