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Characterisation of Zinc Oxynitride Thin Films Prepared Using Zinc(II) Complex of Hexamethylenetetramine as the Precursor

Olumide Oluwole Akinwunmi[1*], Oluwaseun Philip Adelabu[1], Adetokunbo Temitope Famojuro[2], Olakunle A. Akinwumi[1], Priscilla Oluwatumilara Olaopa[1], Kehinde Folorunso Olafisan[1], Ezekiel Oladele Bolarinwa Ajayi[1]

[1]Department of Physics and Engineering Physics, Obafemi Awolowo University, Ile-Ife, Nigeria
[2]Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria
Email: *oakinwunmi@oauife.edu.ng, *ooakinwunmi@gmail.com

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Abstract

A Zinc(II) complex of hexamethylenetetramine was prepared as a single source precursor and used to deposit zinc oxynitride thin films. The thin films were deposited on soda-lime glass substrates using the Metal Organic Chemical Vapour Deposition (MOCVD) technique at the deposition temperature of 370˚C and 390˚C, respectively. The Fourier Transform Infrared Spectroscopy (FTIR) was used to determine the functional groups in the precursor, with stretching frequency for O-H, N-H, and C-H observed. The deposited films were characterized using UV-Visible Spectroscopy, Scanning Electron Microscopy (SEM), Elemental diffraction X-ray (EDX), and X-ray Diffractometer (XRD). A direct bandgap of 3.15 eV and 3.18 eV was obtained from the film deposited at 370˚C and 390˚C, respectively, using the Envelope Method. In comparison, a bandgap of 3.19 eV and 3.21 eV was obtained using the absorption spectrum fitting (ASF) method. The SEM revealed that the film is homogeneous, dense, and compact, composed of cluster grains. The EDX confirmed the presence of Zinc, Nitrogen and Oxygen. The X-ray Diffraction indicated the polycrystalline nature of the film.

Keywords

Zinc Oxynitride, Metal Organic Chemical Vapour Deposition (MOCVD), Precursor, Characterisation, Thin Film

1. Introduction

Transition metal oxynitrides are composite materials that have outstanding prop-

erties which make them useful in the area of micro and optoelectronic devices, sensors, and photoconductors [1]-[6]. A study by Lee *et al.* (2015) [5] revealed that the thin film of zinc oxynitride is becoming a promising transparent semiconductor because of the combination of its unique optical and electrical properties. Properties such as high transparency, durability, efficiency, environmental friendliness, high field-effect mobility, low electron effective mass, and device stability to illumination have made the film promising material for use in solid-state applications [6] [7].

In 2013, Kim *et al.* [8] reported the fabrication of zinc oxynitride based devices of high field-effect mobility, the film shows a very low persistent photoconduction (PPC) which could serve as a replacement for hydrogenated amorphous silicones (a-Si:H) that are characterized with low field-effect mobility and unstable under continuous voltage stress. This limits their use in fabrication of advance and improves display devices such as virtual reality (VR) displays or ultra-high definition (UHD) [9]. Cao *et al.*, in 2015, prepared oxygen doped zinc nitride semiconductor and the electrical characterization shows that the film has a resistivity of 6.2×10^{-4} Ω·cm [10].

Many research groups that have fabricated ZnO:N thin films utilized Zn or ZnO as starting material, employ, nitrogen (N_2) or mixed N_2 - O_2 as a dopant source using high-temperature deposition techniques such as reactive radio-frequency magnetron sputtering [11] [12] and Pulse Laser deposition [1] [13], however, employing metal-organic chemical vapour deposition (MOCVD) technique [14] has not been explored to the best of our knowledge. This could be a result of finding possible metal-organic precursors which would not decompose to elemental units on the substrate. Nevertheless, MOCVD technique provides an avenue for the deposition at low temperature, which could be an advantage for deposition of Zinc oxynitride on flexible substrates. Thus, in this research study, metal-organic chemical vapour deposition (MOCVD) technique was employed to deposit zinc oxynitride films using a single-source precursor of Zinc(II) complex of hexamethylenetetramine with nitrogen as the carrier gas at different temperatures. The films were characterized and their surface morphologies and optical properties were determined.

2. Experimental Details

2.1. Materials

All the chemicals reagents used except distilled water are commercially available and obtained from Sigma-Aldrich. All reagents were used without further purification.

2.2. Synthesis

The precursor, Zn(II) complex of hexamethylenetetramine was prepared from an aqueous solution of hexamethylenetetramine and zinc acetate. Hexamethylenetetramine (20 g) was dissolved in 100 ml of distilled water. Zinc acetate (16 g)

in 70 ml of distilled water was reacted to the dissolved hexamethylenetetramine and stirred for 24 hours. The solution was oxidized in a stream of air and left for a few days to precipitate. The product (precipitate) was filtered, washed with acetone and distilled water, and then oven-dried at about 30˚C to yield 14.21 g. The prepared precursor was characterized using Agilent Cary 630 FTIR spectrometer at room temperature in the range of 400 to 4000 cm^{-1}.

2.3. Thin Film Deposition

Zinc oxynitride thin films were deposited by pyrolysing Zn(II) complex of hexamethylenetetramine on soda lime glass substrate using metal organic chemical vapour deposition (MOCVD) technique (**Figure 1**) previously reported by Ajayi *et al.* [14]. The precursor (powder) was poured into the unheated receptacle of the MOCVD set up. Nitrogen, at a flow rate of 2.5 dm^3/min was used as a carrier gas at atmospheric pressure and deposited temperatures of 370˚C and 390˚C respectively. The films were deposited for a period of two hours.

2.4. Characterisation of the Films

The Fourier-Transform Infrared spectrum of the precursor was recorded on Perkin Elmer FT-IR spectrometer (Spectrum 100, USA). The surface morphology and elemental composition were examined using ZEISS Ultra plus 55 Field Emission Scanning Electron Microscopy (FE-SEM, Germany): with an accelerating voltage of 2.0 kV equipped with Energy Disperse X-ray (EDX). While the optical properties of the films were analyzed using a dual-beam Shimadzu 1800 UV spectrophotometer. The crystallographic structures of the films were analyzed using a Bruker BV 2D Phase Benchtop (XRD) (PANalytical, Netherland) instrument with 2θ values (5˚ - 90˚) of reflection geometry, a (5.240 s) requisition time per step and operating with a (Cu Kα1) radiation source 50 kV and 30 mA at (λ = 0.15406 nm).

3. Result and Discussion

3.1. Fourier-Transform Infrared Spectrum of the Precursor

The FT-IR spectrum (**Figure 2**) shows the stretching frequency of the Zn(II)

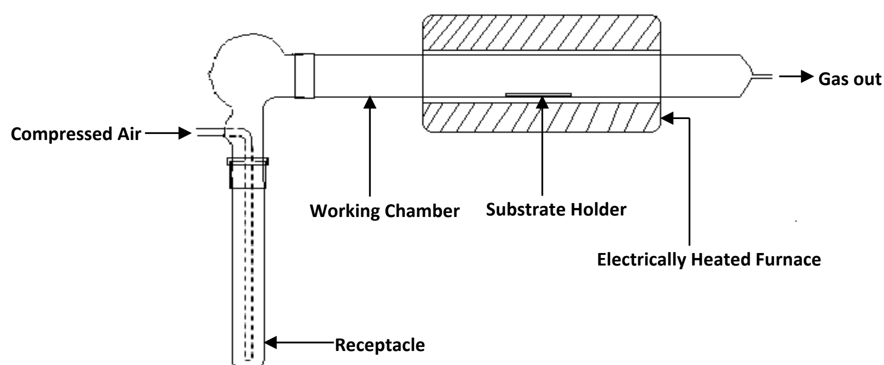


Figure 1. The schematic diagram for the MOCVD chamber.

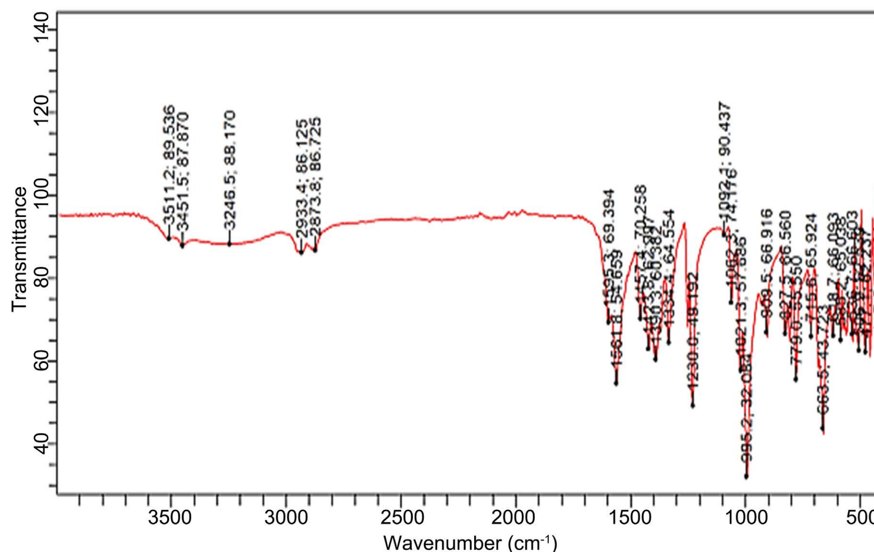


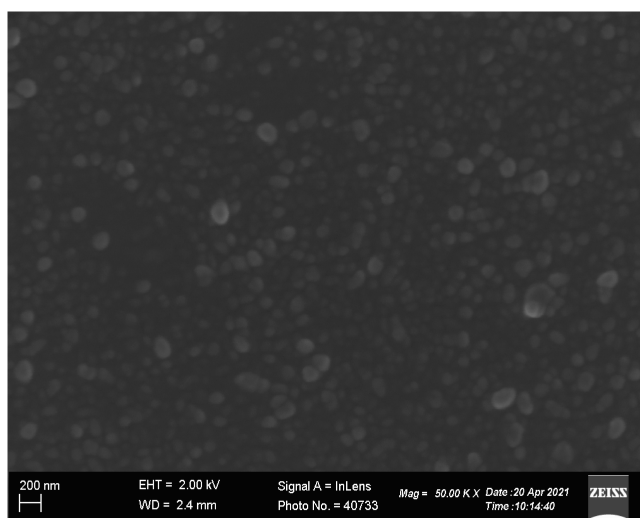
Figure 2. FT-IR spectrum of precursor material: Zinc(II) complex of hexamethylenetetramine.

hexamethylenetetramine precursor. The spectrum shows that the precursor exhibits basic absorption bands. The major peaks are at 3511.2 cm^{-1}, corresponding to O-H stretching vibration of coordinated water molecules, and broad band's between 3451.5 and 3246.5 cm^{-1} correspond to a coordinated tertiary amine. The bands at 2933.4 cm^{-1} and 2873.8 cm^{-1} are due to the stretching vibrations of symmetric C-H and between 700 cm^{-1} and 600 cm^{-1} is the zinc to nitrogen (Zn-N) bond.

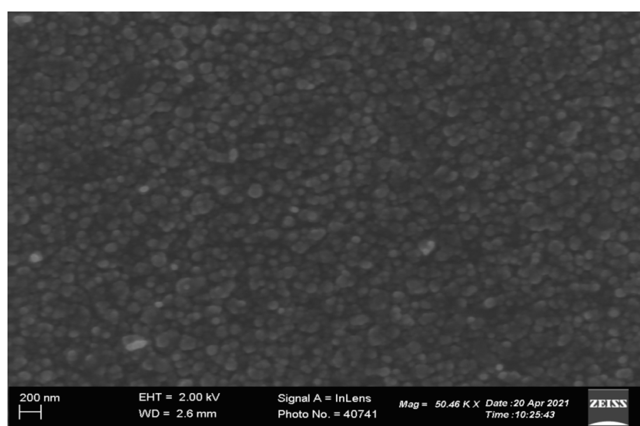
3.2. Scanning Electron Micrograph Morphology (SEM) and Energy Dispersive X-Ray (EDX) of the Films

Figure 3(a) & **Figure 3(b)** show the micrographs of the surface morphology of zinc oxynitride films deposited on soda lime glass at the temperature of 370˚C and 390˚C, respectively. The estimated average grain size of the film deposited at 370˚C is less than 105 nm obtained by ImageJ software. It was observed from the two monographs that the films of discrete grains are homogeneously dispersed. As expected, the grain size reduced at the higher temperature of 390˚C, and the film became more compact with an average grain size of 100 nm. This was consistent with the result obtained by Ayouchi *et al.* (2014) [1]. It was observed that grain size varies with temperature through the MOCVD technique, similar to what was reported for the Pulse Layer Deposition method [13]. The as-prepared films are without any form of cracks and the grains were distributed uniformly across the substrate. This shows that the deposited films adhere to the substrate very well. Also, the films are polycrystalline and the grains are nearly hexagonal in shape.

The EDX attached with the SEM confirmed the presence of Zinc, Oxygen, Nitrogen. Silicon and Calcium could be traced to the soda-lime substrate used. The EDX monogram is shown in **Figure 4**.



(a)



(b)

Figure 3. (a) SEM analysis of zinc oxynitride thin film deposited at 370˚C. (b): SEM analysis of zinc oxynitride thin film deposited at 390˚C.

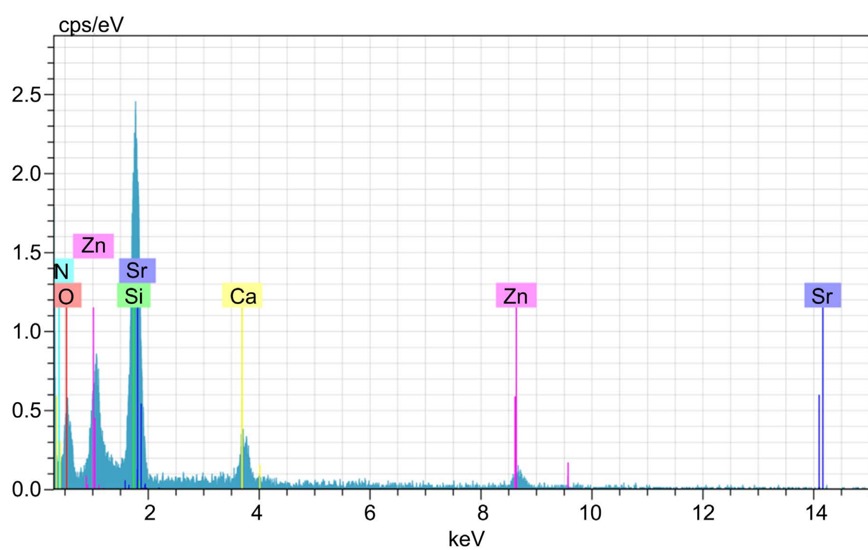


Figure 4. EDX analysis of zinc oxynitride thin film deposited.

3.3. Optical Characterisation

Figure 5 shows the optical spectral of the zinc oxynitride films deposited at the deposition temperature of 370˚C and 390˚C, studied in the range of wavelength 350 - 800 nm at room temperature. The two films deposited at different temperatures show a sharp fundamental absorption edge at about 420 nm, which indicates that the deposited materials have a wide energy bandgap. The films are highly transparent with a transmittance value of 80% - 90% in the visible region. The shoulder seen at the absorption edge at 420 nm (which is usually observed in zinc oxynitride films [13] [15] may be attributed to the few traces of Zn-O stretch present on the surface of the films [2] [15]. In addition, the corresponding adjacent maxima and minima interference in the transmittance spectra indicates that the films are uniform [16]. The thickness of the thin films was estimated from the two corresponding transmittance maxima and minima, that is, λ_2 and λ_1 [16].

Thickness,

$$t = \frac{1}{2n\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)} \tag{1}$$

where n is the refractive index of the material, λ_2 and λ_1 are the two corresponding maxima and minima, respectively. The refractive index was assumed to be 2 (the refractive index of zinc nitride ranges from 1.8 - 2.4 [3]). The estimated film thickness is 358 nm at 370˚C and 404 nm at 390˚C.

The absorption coefficient, α, was obtained by Lambert's formula

$$\alpha = \frac{1}{t}\ln\left[\frac{1}{T}\right] \tag{2}$$

where t is the thickness of the film, T is the optical transmittance values. The energy bandgap of zinc oxynitride films was obtained by examining the dependence of the absorption coefficient on photon energy. The dependence obeyed the direct transition equation (n = 1/2) of the general form.

$$\alpha = A\left(h\nu - E_g\right)^n \tag{3}$$

where h is Planck's constant, ν is the frequency, E_g is the energy bandgap, and A is the energy-independent constant. The exponent, n, depends on the type of transition, n =1/2, 3/2, 2, or 3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden optical transition, respectively. Figure 6 shows the plot of $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) for zinc oxynitride thin films by extrapolating the straight region in the graph to $(\alpha h\nu)^2 = 0$ The optical bandgap estimated was 3.15 and 3.18 eV for the film deposited at 370˚C and 390˚C, respectively. The shift in the energy band bag is due to the increase in thickness as the temperature increases. The value of the energy bandgap obtained in this research study is similar to the reported values of the bandgap of zinc oxynitride [5] [13]. ASF method was also used to estimate the band gaps of the deposited

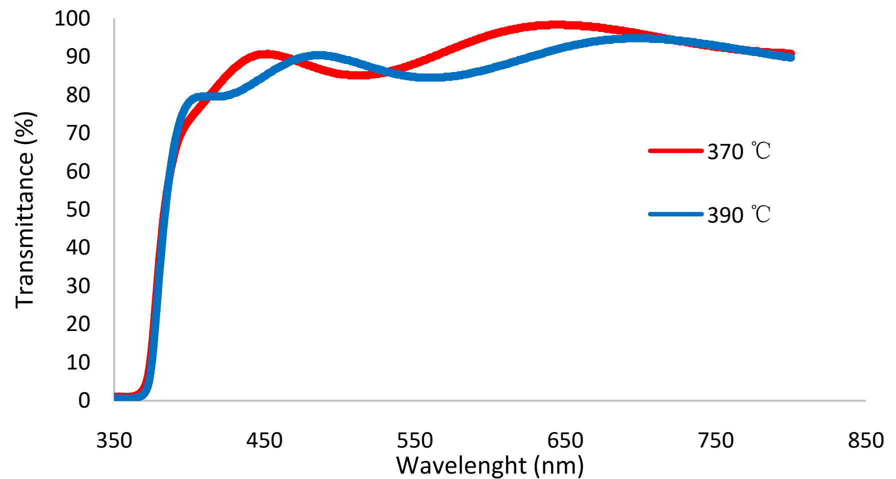


Figure 5. Transmittance against wavelength.

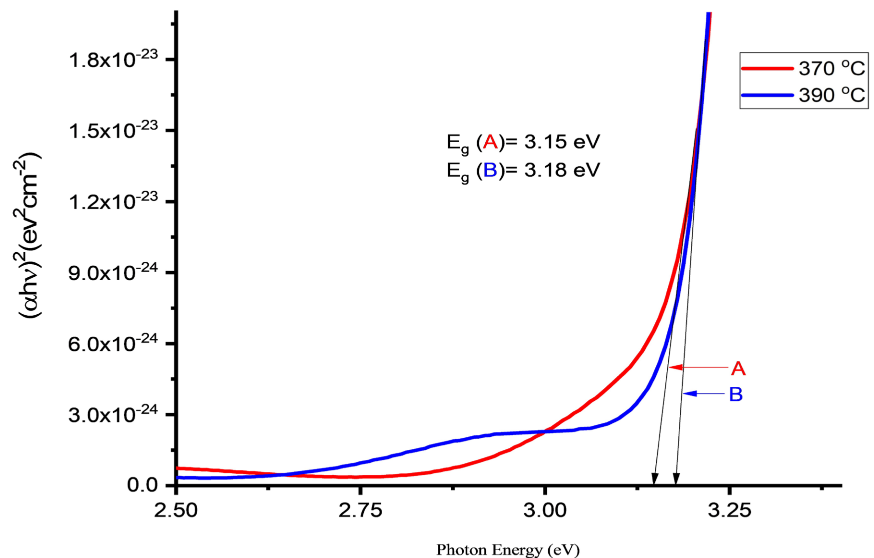


Figure 6. $(\alpha h\nu)^2$ against photon energy.

films by plotting the graph of $(abs/\lambda)^2$ against $(1/\lambda)$ and extrapolating the straight path to $(1/\lambda) = 0$. The values of the estimated band gaps were found to be 3.19 eV and 3.21 eV for films deposited at 370˚C and 390˚C, respectively, as shown in **Figure 7**.

3.4. Structural Properties from X-Ray Diffraction (XRD) Analysis

The X-ray diffraction patterns of zinc oxynitride films deposited at the deposition temperature of 370˚C and 390˚C are shown in **Figure 8**. The index of the diffracted peaks was carried out to determine the structure of the deposited films by comparing the data with standard JCPDS No. 350762 and JCPDS No. 361451, which corresponds to cubic zinc nitride and hexagonal zinc oxide respectively. It was seen in the diffractograms that the deposited films are polycrystalline in structure due to the intense peaks that occur at diffraction angle, $2\theta = 31.21˚$,

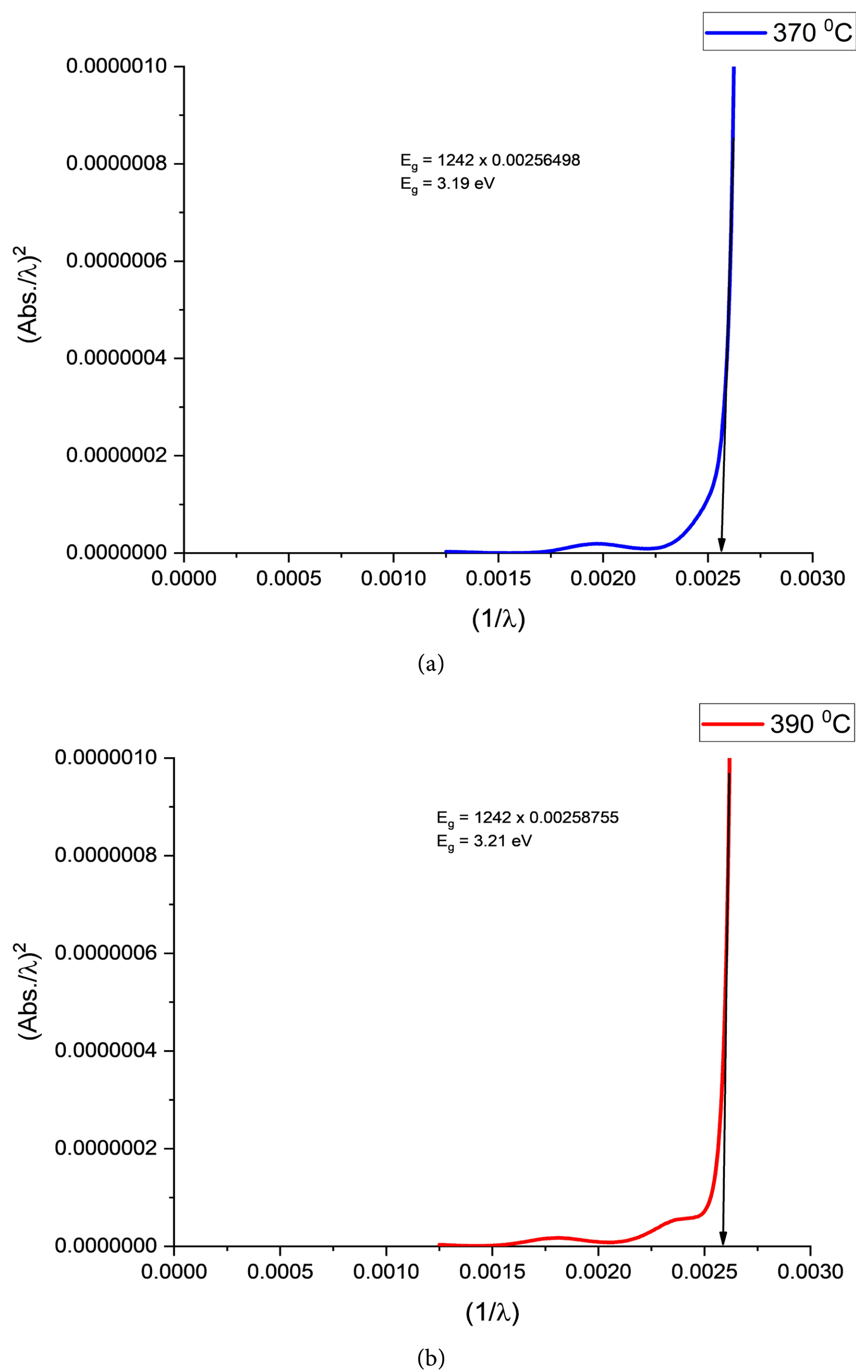


Figure 7. (a) $(A/\lambda)^2$ against $(1/\lambda)$ at 370˚C; (b) $(A/\lambda)^2$ against $(1/\lambda)$ at 390˚C.

33.67˚, 35.71˚ and 56.04˚. The peaks at 2θ = 31.21˚correspond to (222) plane, 33.67˚to (321) plane, 35.71˚ to (400), and 56.04˚ to (600) plane. A closer look at the observed d values of films (2.8635, 2.6597, 2.5123, and 1.6397 Å) shows they are closer to the d values of zinc nitride (2.824, 2.614, 2.445, and 1.6297 Å) more than the d values of zinc oxide (2.8143, 2.6033, 2.4759 Å and no d values ascribed to ZnO diffraction at 2θ = 56.04˚) [17]. It was observed that the deposition temperature influenced the structural properties of the films. When the

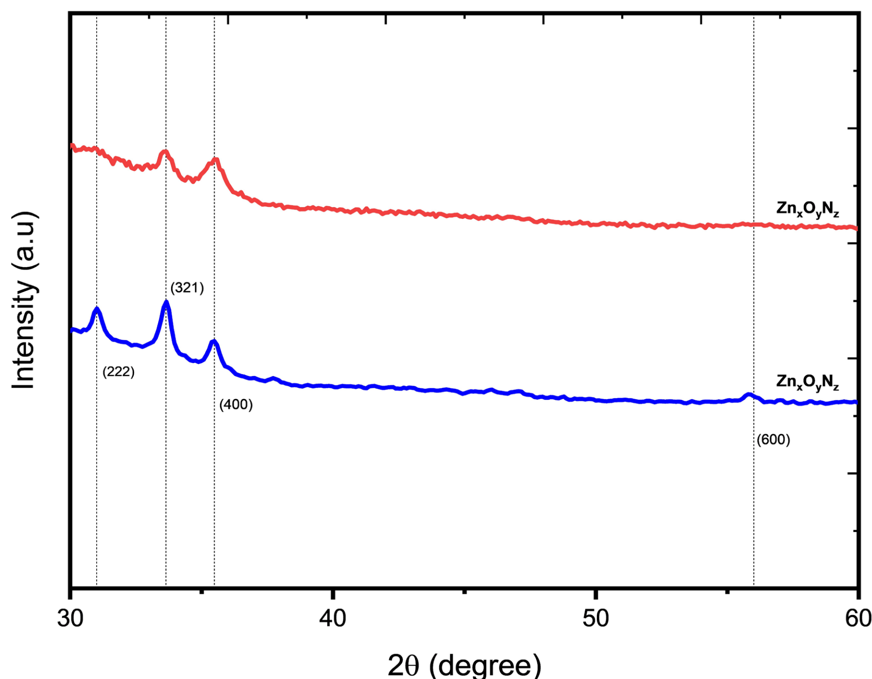


Figure 8. XRD patterns of the Zinc Oxynitride films deposited at the deposition temperature of 370˚C and 390˚C.

substrate temperature was increased to 390˚C, some of the peaks found in the films deposited at 370˚C disappears, which is due to the decrease in crystallinity as the temperature increases, which may be attributed to the out-diffusion process of nitrogen [18].

4. Conclusion

The thin films of zinc oxynitride were prepared using the MOCVD technique at deposition temperatures of 370˚C and 390˚C on a soda lime glass substrate at the flow rate of 2.5 dm^3/min using Zinc(II) complex of hexamethylenetetramine as the precursor. The precursor was characterized by FTIR, while the deposited thin films were characterized by XRD, Uv-Vis, SEM and EDX, respectively, for their structural, optical surface morphology and elemental composition. The XRD results showed that the thin films are polycrystalline in nature with hexagonal structure. The temperature was also found to influence the crystallinity of the deposited thin films. The optical bandgap of the deposited thin films was found to be 3.15 eV and 3.18 eV for films deposited at 370˚C and 390˚C, respectively. Also, the ASF method was used to estimate the energy band gaps of the films and the values of the bandgaps were found to be 3.27 eV and 3.19 eV for films deposited at 370˚C and 390˚C, respectively. It was also observed that temperature influenced the optical band gaps of the deposited thin films. The results from SEM show that the thin films adhere well to the substrate, and the films are homogeneously dispersed on the substrate. The EDX confirms the presence of zinc, nitrogen and oxygen in the thin films. All these properties show that the

deposited films are viable for optoelectronics and photonics applications.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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