EFFECTS OF pH ON THE OPTICAL PROPERTIES OF ANTIMONY DOPED ZINC OXIDE THIN FILMS PREPARED BY SOL-GEL DEPOSITION TECHNIQUE.

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ABSTRACT

Antimony doped zinc oxide (Sb:ZnO) thin films were successfully deposited on the pre-treated substrate at 60°C using sol-gel dip coating techniques. The effect of pH value on the structural and optical properties of the films were examined using X-ray diffraction (XRD) and spectrophotometer respectively. The optical results revealed that the films have high absorbance in Ultra Violet (UV) region which decrease towards the Near Infra-red (NIR) region. The films have low transmittance in Ultra Violet (UV) region but high transmittance within Near Infra-red (NIR) region. The deposited films have optical bandgap energy range from 2.25-2.50eV for variation in pH value. X-ray diffraction result revealed hexagon phase of zinc oxide with C-axis orientation. XRD result also showed that increase in pH value led to increase in average crystallite size and improved structure. Dislocation densities and microstrain values decreased with increase in pH value. The films have wide energy bandgap which is used for optoelectronic and thermoelectric device fabrication. Most of our grown thin films have high transmittance values at near infra-red (NIR). These films are good materials to coat the windows of our poultry where infra-red rays will be transmitted in high proportion to heat the young chicks instead of using kerosene stoves and lamps.

Keywords: Antimony, zinc oxide, thin films, optical properties, pH.

INTRODUCTION

Thin film studies have played a pivotal role in advancing various fields of solid-state physics and chemistry, driven by phenomena specific to film thickness, geometry, and structure. The extensive application of thin films in electronics, optics, space science, aerospace, defense, and other industries has fueled their remarkable growth. This research has resulted in numerous innovations, including active and passive devices, piezoelectric components, miniaturized power supplies, rectifiers, amplifiers, sensors, solar energy storage and conversion, magnetic memory, superconducting materials, interference filters, reflecting and antireflection coatings, and more (Kuanr *et al.*, 2008).

Zinc oxide (ZnO) is a natural n-type conductive semiconductor with unique advantage properties such as wide direct bandgap (3.37 eV), huge exciton binding energy (60 meV), and ease of fabrication (Coleman and Jagadish, 2006; Lee *et al*., 2019).

The sol–gel technique has been recognized as one of the promising techniques to achieve the p-type zinc oxide thin film because of its considerable advantages comparing to other methods including simple deposition setting, low-cost system, and low-cost precursor. In sol–gel based methods for thin film deposition, annealing process is a key post-treatment to achieve good quality of the films with enhancement in their optical, physical, and electrical properties.

Hence the academic importance of this work is to survey and vary the pH of the substrates with respect to its effect on the optical properties of the deposited thin films- Antimony doped zinc oxide thin film using sol-gel deposition method as a function of the preparation conditions. Many research works have been carried out on Zinc oxide doping but little or no researches have been carried out focusing on the parameter in this study.

The sol-gel process is a more wet chemical method for the formation of different nanostructures, especially metal oxide nanoparticles. In this method, metal alkoxide is usually used as a precursor and it's dissolved in water or alcohol and converted to gel by heating and stirring via hydrolysis/alcoholysis (Dmitry *et al*., 2021).

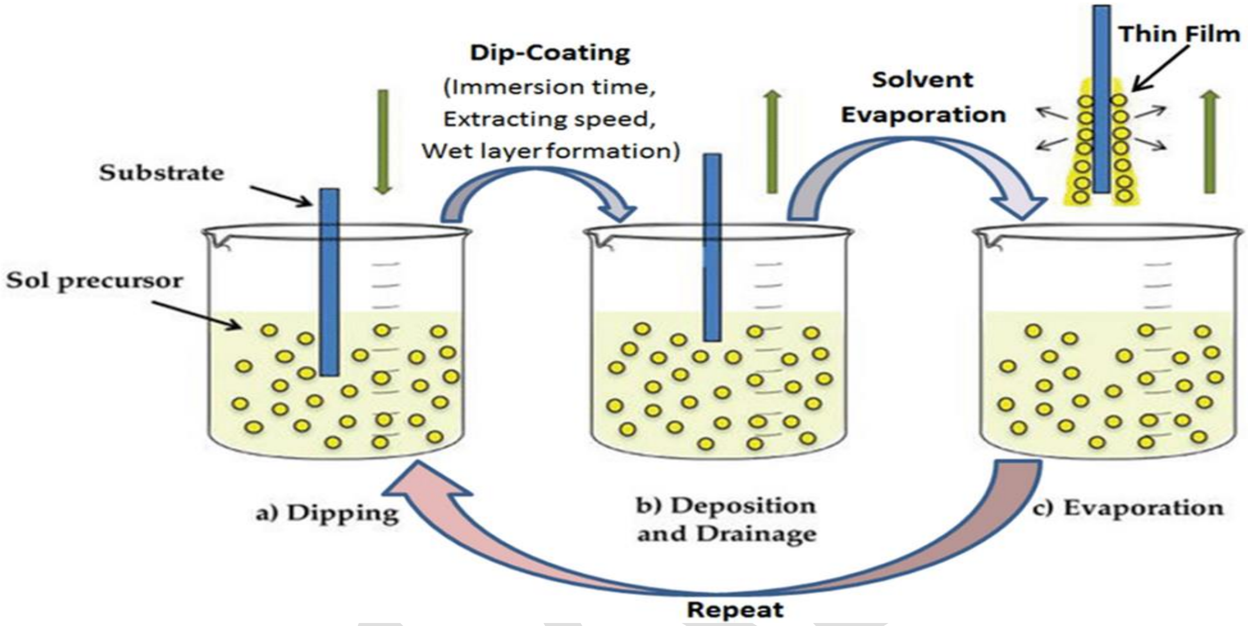

Figure 1: **Schematic diagram of sol-gel deposition process (Mohamed *et al*., 2022)**

Sinornate *et al* (2021) investigated how the annealing atmosphere affects the optical, structural, morphological, and electrical characteristics of Sb-doped ZnO thin films deposited using the Sol-Gel method. X-ray diffraction (XRD) analysis indicated that these films exhibited a pure ZnO hexagonal wurtzite structure without any impurities. The crystallinity of the films deteriorated significantly due to the combined influence of the Sb dopant and the annealing atmosphere, resulting in a reduction in nanoparticle size after annealing in nitrogen and argon atmospheres as well as upon doping. X-ray photoelectron spectroscopy (XPS) results confirmed the successful incorporation of Sb^{3+} into the ZnO lattice, and the shift in XPS spectra for films annealed in a nitrogen atmosphere suggested the formation of nitrogen bonds with zinc.

Çelik et al. (2020) employed the spin coating technique to fabricate uniform thin films of both pure ZnO and Sb-doped ZnO on soda lime glass substrates at room temperature. They investigated the impact of Sb doping on the structural properties of ZnO thin films. The optical properties of the ZnO thin films with Sb concentrations of 0%, 1%, 2%, and 3% exhibited a significant variation in the optical energy band gap, highlighting the influence of Sb dopants. Furthermore, scanning electron microscopy (SEM) images revealed that pure ZnO thin films exhibited a distinctive nanofiber structure, which gradually disappeared with an increase in the doping ratio, resulting in more homogeneous films.

MATERIALS AND METHODS

In this set of experiment, five previously cleaned glass substrates were used. The five substrates were labeled ZB_1, ZB_2, ZB_3, ZB_4 and ZB_5. Five different sol gels sets of antimony doped zinc oxide were prepared by using the sol-gel deposition method. To achieve the variation of pH, five different volumes of 10 mL, 20 mL, 30 mL, 40mL and 50 mL of NaOH were used to synthesize the sol gels. The measured pH values of 9.8, 10.1, 10.4, 10.6 and 10.9 were obtained using a pH meter with sensitivity of ± 0.1. To form an adhesive and uniform thin films on the surface of the microscopic substrate used for the deposition, six (6) successive dips were carried out for each of the synthesized sol gel. The dips were carried out at intervals of 2 minutes. After the dipping process, the synthesized thin films were annealed at 150 ℃ for 30 minutes. Table 1 shows the constituents of the sol gel bath for the deposition.

The amount of salt used was calculated using equation (1) given below

$$R_{mass} = \frac{\text{Molarity x Molar Mass x Volume}}{1000\text{cm}^3} \qquad 1$$

Table 1: Variation of pH for sol gel dip coated Sb:ZnO thin film

Sample	**Zn(ace) .2H_2O**		**$SbCl_3$**		**NaOH**		**pH**	**No. of Dipping**	**Dip Time (mins)**
	mol/dm^3	Vol. (ml)	mol/dm^3	Vol. (ml)	Mol.	Vol. (ml)			
ZB_1	0.20	50.00	0.04	25.00	0.50	10.00	9.8	6	2.0
ZB_2	0.20	50.00	0.04	25.00	0.50	20.00	10.1	6	2.0
ZB_3	0.20	50.00	0.04	25.00	0.50	30.00	10.4	6	2.0
ZB_4	0.20	50.00	0.04	25.00	0.50	40.00	10.6	6	2.0
ZB_5	0.20	50.00	0.04	25.00	0.50	50.00	10.9	6	2.0

The deposited film thicknesses (t) were evaluated using the gravimetric method given by

$$t = \frac{\Delta m}{\rho A}, \qquad 2$$

where Δm is the mass of the film; A is the surface area of the deposited film and ρ is the bulk density of the material film.

The masses of the deposited films were obtained by finding the difference in mass between the mass of the glass substrate with the film after deposition and the mass of glass substrate before deposition. These differences in mass of the films were measured using analytical weighing balance with sensitivity of 0.001 g.

The optical absorbance values of these sol-gel deposited thin films were obtained using spectrophotometer (model: 756S UV – VIS) at Nano Research Laboratory, Department of Physics and Astronomy, University of Nigeria Nsukka, Enugu State, Nigeria. Other optical properties of the films such as transmittance and energy band gap were calculated as follows.

Transmittance (T) values of the films were evaluated using equation (3) given by (Lokhande *et al*., 2002; Ismail *et al.*, 2014)

$$T = 10^{-A} \qquad 3$$

The energy band gap was estimated using Tauc's model given in equation (3.9) as given by (Tauc *et al.*, 1966, Tezel *et al*., 2017).

$$(\alpha hv)^n = \beta\left(hv - E_g\right). \qquad 4$$

Where β is a constant, $n = 2$ for direct band gap. The energy band gaps of the films were obtained by extrapolating the straight portion of the plot of $(\alpha hv)^2$ against the photon energy (hv)at $(\alpha hv)^2 = 0$.

Crystal structural analyses of the deposited thin films were done using X– ray diffractometer machine. Buker D8 high resolution diffractometer at Material Research Department, iThemba Labs, Johannesburg, South Africa were employed to study the structural properties of these films. From the x – ray diffraction pattern obtained, other structural properties such as d – spacing, full width at half maximum (FWHM) were obtained. The crystallite sizes and microstrains of the films were evaluated using Scherrer's formula. Debye – Scherrer's formula for calculating crystallite sizes of a thin film material is given by (Ravindranah *et al,* 2016; Okoriemoh, *et al.*, 2019) as

$$D = \frac{0.9\,\lambda}{\beta cos\theta}. \qquad 5$$

The dislocation density (δ) of thin films can be estimated using expression as provided by Anbarasi *et al.*, (2016); Hadri *et al.*, (2015) in equation (6).

$$\delta = \frac{1}{D^2}. \qquad 6$$

Micro-strain (ε) of the thin film sample can be estimated using the expression in equation (7) as given by (Awada *et al.*, 2020 and Hadri *et al.*, 2015).

$$\varepsilon = \frac{\beta}{4tan\theta} \qquad 7$$

RESULTS AND DISCUSSIONS

(a) Film Thickness versus pH

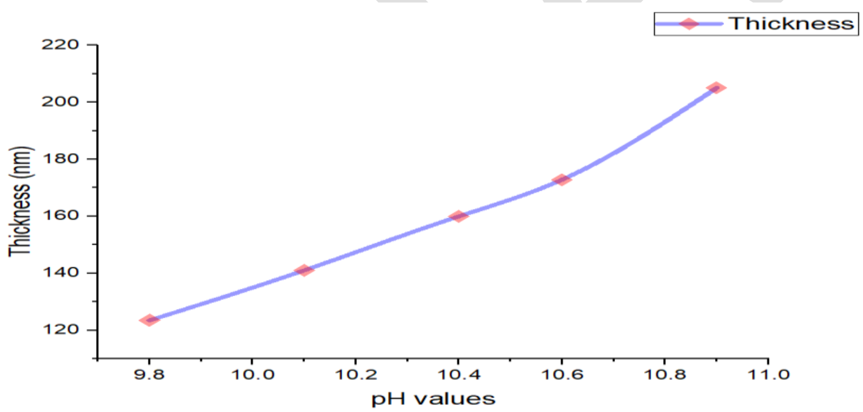

Fig 2: Graph of film thickness versus pH values.

Fig 2 shows the variation of the thin film thickness with pH values. It was recorded that the film thickness increases as the pH value increases. This could be attributed to the deposition of more antimony atoms with increasing pH values as confirmed by the EDXS analysis.

(a) **Absorbance**

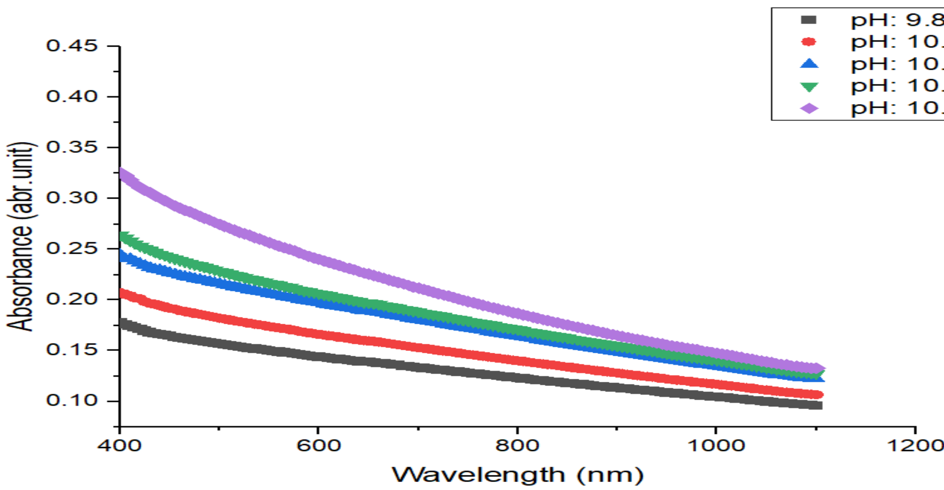

Fig 3: Graph of absorbance against wavelength for Sb:ZnO thin film with variation in pH values.

Fig 3 shows the graph of absorbance against wavelength for Sb:ZnO thin film with different pH values. In general, it was observed that the absorbance decreased with increase in wavelength and increased with increase in pH value.

(b) **Transmittance**

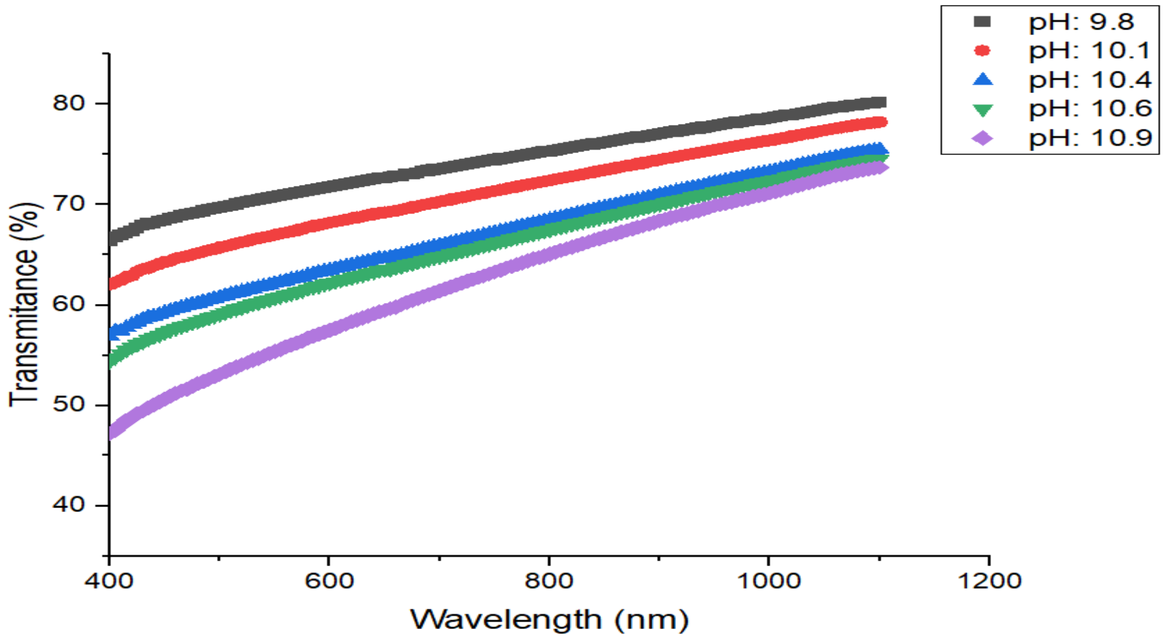

Fig 4: Graph of transmittance against wavelength for Sb:ZnO thin film with variation in pH values.

Fig 4 shows the graph of transmittance wavelength for Sb:ZnO thin film with different pH values. From the above graph, it was seen that transmittance increased as the wavelength increases but decreased with increase in pH value i.e the higher the wavelength the higher the transmittance and the higher the pH value the lower the transmittance.

(c) **Structural analysis of Antimony doped Zinc oxide thin films with different pH values**

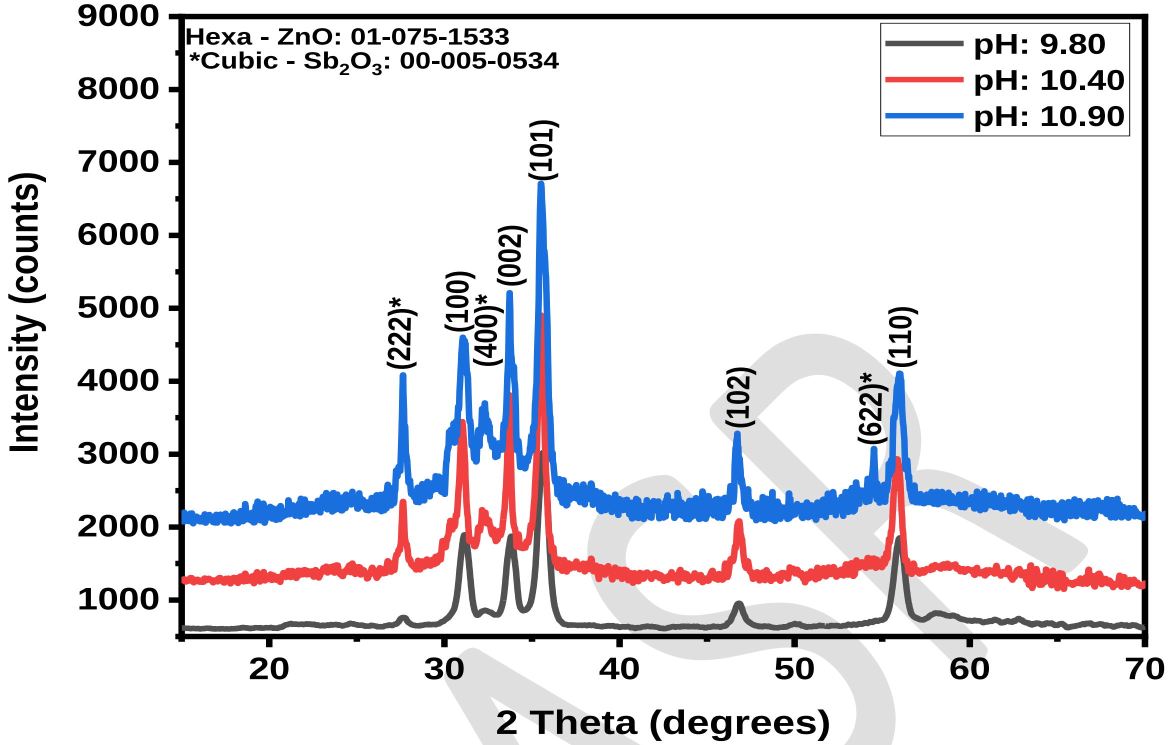

Fig 5: X– ray diffraction pattern of antimony doped zinc oxide (Sb:ZnO) thin films formed at different pH values of 9.80, 10.40 and 10.90.

Figure 5 shows the x – ray diffraction pattern of antimony doped zinc oxide (Sb:ZnO) thin films formed at different pH values of 9.80, 10.40 and 10.90. The pattern shows that the deposited Sb:ZnO thin films contained mixed structural phases of hexagonal ZnO and cubic Sb_2O_3 corresponding to JCPDS file number (01-075-1533) and (00-005-0534). Sb:ZnO thin film deposited under pH of 9.80 has diffraction peaks at 31.151°, 33.810 °, 35.637 °, 46.809 ° and 55.987 ° which correspond to miller indices of (100), (002), (101), (102) and (110). Similar peaks positions were observed for Sb:ZnO thin films deposited under pH values of 10.40 and 10.90. Sb:ZnO thin film deposited under pH value of 10.40 has diffractions peaks at 27.635 °, 31.016 °, 32.660 °, 33.690 °, 35.520 °, 46.807 ° and 55.849 ° while Sb:ZnO thin film deposited under pH value of 10.90 has diffractions peaks at 27.649°, 31.029°, 32.429°, 33.784°, 35.588°,46.744°54.504° and 55.945° which correspond to miller indices of (222), (100), (400), (002), (101), (102) (622) and (110). One additional peak corresponding to Sb_2O_3 was observed for film deposited under pH value of 10.40 while two additional peak were observed for film deposited under the pH value of 10.90. Minor changes in peak position were observed as pH values increase from 9.80 to 10.90. The intensities of the x – ray diffraction spectra increased as pH values increased from 9.80 to 10.90. The average crystallite sizes of 16.522 nm, 19.583 nm, and 23.506 nm were obtained for Sb:ZnO thin films deposited under pH values 9.80, 10.40 and 10.90 respectively. Dislocation densities were recorded as 16.522×10^{15} lines/m^2, 19.563×10^{15} lines/m^2 and 1.904×10^{15} lines/m^2 respectively. Microstrain values were 6.616×10^{-3}, 6.017×10^{-3} and 4.873×10^{-3} respectively. The results show that crystallite sizes of the films increase as pH values increase. Also, dislocation densities and microstrain values decrease with increase in pH values.

CONCLUSION

Sb:ZnO thin films were successfully deposited on the glass substrate by solgel deposition technique. The optical results revealed that the films have high absorbance in Ultra Violet (UV) region which decrease towards the Near Infra-red (NIR) region. The films have low transmittance in Ultra Violet (UV) region but high transmittance within Near Infra-red (NIR) region. The result also suggests that the films have low or moderate Reflectance, Refractive index, Real dielectric constant and Optical conductivity in the UV region which tends to minimum in the NIR region. These parameters decreased as the wavelength increased but increased with increase in pH value. XRD result also showed that increase in pH value led to increase in average crystallite size and improved structure. Dislocation densities and microstrain values decreased with increase in pH value.

Based on the study's findings sol-gel deposition method has been proven to be an effective method to improve the optical properties of Antimony doped Zinc oxide thin films. It has been shown that doping Zinc oxide thin film with Antimony thin film improves its optical propertis.

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