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Research Article

Effects of Deposition Periods on the Optical and Structural Properties of Electrochemically Deposited Nickel-Doped Zinc Oxide Thin Films

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Abstract—Thin films of nickel-doped zinc oxides (Ni/ZnO) were fabricated on the fluorine-doped tin oxide (FTO) conductive glass substrates using the method of electrodeposition in this research work. Precursors solutions of zinc acetate dihydrate and nickel chloride hexahydrate were used as sources of Zn and O ions respectively. In the electrodeposition setup, the FTO glass substrate served as the working electrode, silver/silver chloride was used as reference electrode and platinum rod used as the counter electrode. 20 ml of 0.1 M zinc acetate and 4 ml 0.01 M of nickel chloride hexahydrate were used and DC supply of 4.0 volts was maintained while optimizing deposition time to determine their effects on the properties of the films. The optical and structural properties of the films were investigated using X-ray diffraction and UV-VIS spectroscopy technique respectively. The results showed that the deposited thin films of Ni/ZnO have low absorbance but increased up to the range of 1.1 to 1.26 in the visible (VIS) and near-infrared (NIR) regions as deposition time increased to 150 secs. The films also exhibited high values of refractive indices and optical conductivity which were found to be further increased with increase in deposition time and up to the ranges of 6.0 to 7.0 and 9.0×10^{14}-1.2×10^{15} S^{-1} respectively for 150 secs films in the VIS and NIR regions. The bandgap energy decreased in the order 2.60 eV, 2.20 eV, 2.22 eV, 2.02 eV and 1.90 eV for the films formed at 30 secs, 60 secs, 90 secs, 120 secs and 150 secs respectively. The structural analysis revealed that the films have hexagonal crystalline structure with slight perturbations on their structural parameters by deposition time variation. These results suggest that the properties exhibited by the films are strategic for varieties of applications including LEDs, solar cells/photovoltaic cells, photodetector devices etc.

Keywords— Nickel, Electrodeposition, Transparent Conducting Oxides (TCOs), Bandgap, LEDs, Solar Cells.

1. Introduction

Transparent conducting oxide (TCO) materials have gained much attentions for many applications as a result of their interesting physical features and characteristics such as the optical and electrical properties in the recent time. Most TCOs have been known to posses' wide bandgap energies and high transparency within the ultra-violet to infrared spectrum range. The wide application areas of TCO materials such as in, active matrix organic light emitting diodes, solar cell, sensor, photodetectors, photoelectrochemical water splitting, liquid crystal displays (LCDs) and host of other optoelectronic devices, have been highly credited to the good optical and electrical properties of the materials, [1]. The prominent TCO materials that have been studied for these oval applications have been noted to be indium tin oxide (ITO), tin oxide (SnO_2), zinc oxide (ZnO), $ZnSnO_4$, NiO etc. [2]. However, these fields of applications of these TCO materials have limitations as the most popular and prominent one among them in the case of indium tin oxide which has been utilized for many industrial applications has been identified to be highly expensive and toxic in nature, thereby posing a potential threat to human health as compared to others, [3]. In this regard, zinc oxide has been found to possess most of the excellent properties of the TCO materials in addition to be the most relatively available/abundant and non-toxic in origin for many device applications. In reduced form (thin and Nano films), ZnO has been known to exhibits good electrical, mechanical and optical characteristics and

thus command applications in various fields such as photovoltaic, photocatalytic activity, gas sensors, nano ultraviolet lasers, field emission, transparent electrodes, thin-film transistors in solar cells, flat-panel displays and other electronic and optoelectronics devices, [4, 5]. ZnO has also been noted to have high thermal conductivity, transparency, electron mobility and wide bandgap energy in the order 3.37 eV, stable hexagonal wurtzite, zinc blend and rock salt structures at room temperature, [6, 7]. It has equally been found to be an n-type semiconductor material with high exciton binding energy of the order 60 meV at room temperature which are among the characteristics that position them for the versatile fields of device applications such as electronics, solar cells and biological applications, [8, 9]. However, reports have shown that some of the properties exhibited by ZnO have proven counterproductive for further applications of the materials in many other fields, hence there is need for improvement on the properties of ZnO. To achieve this, doping of the ZnO thin films or nano films with foreign materials and depositing the result under certain conditions have been advocated as the handy strategy to adopt. Report has further indicated that ZnO thin films doped with transition elements such as titanium, nickel, aluminum etc., have been found to tailor most of the properties exhibited by the bare ZnO for improved device applications, [10, 11]. In this regard, great efforts have been devoted by many research groups to develop good strategies to improving on both the bare and modified structures/features of the materials for any desired device application.

2. Related Work

In the effort to boost on the characteristic feature of ZnO through doping modification and some other processes, the optical properties of titanium doped ZnO thin films fabricated using pulse laser deposition method have been reported to be influenced as a result of Ti doping according, [12]. In their reports, the bandgap energy of ZnO was found to be red-shifted while other optical constants such as refractive index, extinction coefficient and absorption coefficient were discovered to increase as Ti contents increased. The photocatalytic degradation action of nickel doped ZnO on rhodamine B dye (RhB) and other free radicals has been reported by [13] to be enhanced by the introduction of 3 wt% nickel doping into the ZnO matrix. They discovered that thin films of 0.5 M $Zn_{0.97}Ni_{0.03}O$ displayed the best photocatalytic degradation action of about 54 % under UV light and 64 % under solar light as a result of decreased in bandgap energy and high crystalline structure exhibited by the films. The properties of nickel-doped zinc oxide thin films fabricated by co-sputtering reported by [14] have been shown to be significantly influenced by Ni doping levels. In the report, the transmittance and bandgap energy of the thin films were found to decrease slightly by Ni doping and the authors inferred that the films can be alternative material for solar cell applications and precisely photoanode materials in dye sensitized solar cell applications because of their fine nanograin with large surface area composition.

The optical and structural properties of Ni doped ZnO grown using metal organic chemical vapor deposition (MOCVD) have been reported by Manzoor *et al.*, [15] to be influenced by deposition conditions. They discovered based on their analysis that growth temperature and pressure strongly affect the formation of shallow energy states closed to the valence band in the Ni-doped ZnO and as such crystal quality, optical absorption were improved with the band edge reduced from 3.27 to 3.05 eV as growth temperature and pressure decreased from 550 to 450°C and from 100 to 22 Torr respectively. The results of density functional theory calculations performed by [16] to investigate the adsorption of methylene blue and methyl orange on nickel-doped zinc oxide showed that attachment of the dye with the nickel ion is less preferable than that with the zinc ion and doping of nickel ion into the ZnO also strengthens the adsorption of the dyes. They established that the optimum condition for the use of the Ni doped ZnO for photocatalytic actions of adsorption of methylene blue and methyl orange are pH solutions of > 3.8 and > 6 respectively.

The antibacterial and cancer effect of nickel and cobalt doped ZnO nanoparticles grown using solution combustion technique utilizing lemon juice as bio-fuel has been reported by [17]. Their results showed that in cobalt or nickel doped ZnO lattice; antibacterial, anticancer, and oxidative response generation activities were enhanced compared to bare ZnO NPs based on the material activities upon exposure to ultraviolet radiations. They further stated that there was an increase in generation of reactive oxygen species (ROS) by mouse macrophage cells of the deposited nanoparticles of ZnO and Co and Ni doped ZnO and thus are capable of boosting host's immunity by inducing activation of immune cells. Sapkal *et al.*, [18] reported the effects of Ni incorporation on the structural and dielectric properties of Ni-doped ZnO prepared by solvothermal method and discovered through Penn model analysis that dielectric constant of Ni-doped ZnO ceramics decreased with an increasing nickel doping percentage. The authors concluded that at higher nickel doping concentrations, negative dielectric constant values were achieved in the material and stated that materials with such characteristics can be used for developing waveguides and coil-free resonators devices. In this report, the effects of deposition period/time on the structural and optical properties of Ni doped ZnO thin films deposited by electrodeposition method are investigated to determine their suitable areas of device applications.

3. Theory/Calculation

The absorbance of the deposited thin films of Ni/ZnO was measured using UV-VIS Spectrometer while other properties of the films studied based on the measured absorbance include the following:

Transmittance: this property is calculated based on the measured absorbance values of the thin films using Beer-Lambert relation as given by [19].

$$T = 10^{-A} \quad (1)$$

Where A is the absorbance.

Reflectance: this was evaluated using the relation given by [20].

$$R = 1 - (\frac{e}{10})^{A/2} \quad (2)$$

Extinction coefficient: this property determines the degree a material can with stand light intensity before actual extinction from the material. It can be calculated using the equation as given by [21].

$$k = \frac{\alpha\lambda}{4\pi} \quad (3)$$

Where α is the absorption coefficient given by [22]

$$\alpha = \frac{2.303A}{t} \quad (4)$$

t is the film thickness obtained by gravimetric method and λ is the wavelength of UV-VIS light used.

Refractive index: the refractive index of the grown thin film crystals was calculated using the relation given by, [23].

$$n = \frac{1+R^{0.5}}{1-R^{0.5}} \quad (5)$$

Real dielectric constant: the real dielectric constant of the films was evaluated using the relation as given by [24].

$$\varepsilon_r = n^2 - k^2 \quad (7)$$

Where n and k are the refractive index and extinction of the deposited thin films

Imaginary dielectric constant: the imaginary dielectric of the films was calculated using relation as given by [25].

$$\varepsilon_i = 2nk \quad (8)$$

Optical Conductivity: this property was calculated from the relation as provided by [26, 27].

$$\sigma = \frac{\alpha nC}{4\pi} \quad (9)$$

Where n represents index of refraction of the films, while C represents the light speed in vacuum.

Bandgap energy: this other property is a very important property of thin film material and can be estimated in this work using Tauc formula by plotting $(\alpha h\nu)^2$ as a function of photon energy [28, 29].

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (10)$$

Crystal parameters such as crystallite size and dislocation density and micro-strain: The crystal parameters of the deposited thin films were evaluated using the Wiliamson-Hall (W-H) plots, Scherrer's formula and Wilson relations. In W-H plots, βCosθ (y-axis) is plotted as a function of 4Sinθ (x-axis) and a linear fitting gives intercept (c) on the β_lCosθ axis as kλ/D while the slope represents the micro-strain (ε) of the thin films. The W-H, Scherrer's formula and Williamson and Smallman's relation are stated in equations (11, 12 and 13) as reported in [30-34]

$$\beta Cos\theta = \frac{K\lambda}{D} + 4\varepsilon Sin\theta \quad (11)$$

$$D = \frac{k\lambda}{\beta Cos\theta} \quad (12)$$

$$\delta = \frac{1}{D^2} \quad (13)$$

Where β, θ, λ, D, ε, **δ** are full-weight at half maximum, Bragg's angle, probing X-ray wavelength, micro-strain and dislocation density.

4. Experimental Method and Procedure

The Ni-doped ZnO thin films were deposited using the following materials; zinc acetate dihydrate and nickel chloride hexahydrate – precursors for Zn and O ions sources, FTO conductive glass substrate is the working electrode, silver/silver chloride served as reference electrode, platinum rod:- used as the counter electrode, 100 ml glass beaker:- used as reaction container, distilled water:- used as the reaction medium, Potentiostat (model Zhaoxin: RXN-3010D):- DC supply unit and magnetic stirrer Electrodeposition method with three electrodes configuration scheme was used to deposit the thin films of Ni doped ZnO.

To deposit the thin film on FTO substrate via this method, aqueous electrolytic bath solution of 20 ml 1.0 M of zinc acetate and 4ml 0.01 M nickel chloride hexahydrate was used. The three electrodes were immersed into the bath containing the electrolytic solution and 4.0 volts was maintained from the DC supply setup for 30 seconds. This process was repeated for four more times by varying the time of deposition from 30 secs to 150 secs at interval of 30 secs. Other parameters were maintained constant as displayed in Table 1.

Table 1: Bath parameter for optimization of Ni/ZnO thin films

0.1 M $Zn(C_2H_3CO_2)_2{\cdot}2H_2O$	**0.01 M $NiCl_2{\cdot}6H_2O$**	**Applied potential**	**Time**
Vol. (ml)	Vol. (ml)	Volts	(sec.)
20.00	4.00	4.0	30.0
20.00	4.00	4.0	60.0
20.00	4.00	4.0	90.0
20.00	4.00	4.0	120.0
20.00	4.00	4.0	150.0

The aftermath of the film deposited on the conductive glass substrates were subjected to optical and structural characterisations using UV-Vis spectroscopy and X-ray diffraction method respectively to determine their optical and structural properties.

5. Results and Discussion

5.1 Optical Properties of the Deposited Ni-Doped ZnO Thin Films.

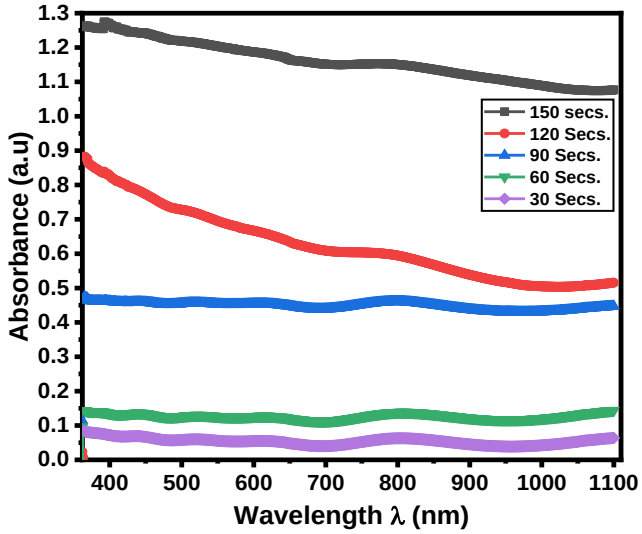

Figure 1: Graph of absorbance against wavelength; Ni/ZnO thin films

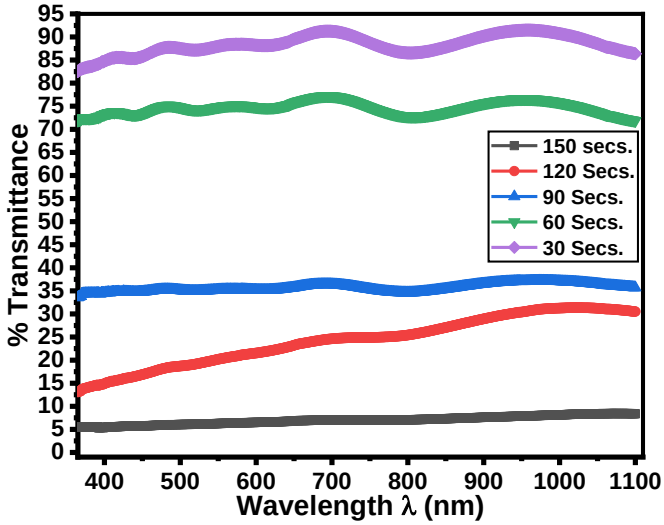

Figure 2: Graph of % Transmittance against wavelength; Ni/ZnO thin films

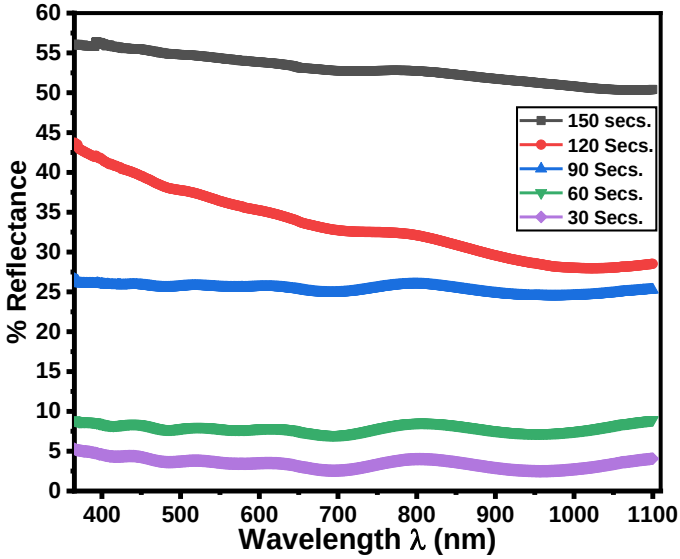

Figure 3: Graph of % Reflectance against wavelength; Ni/ZnO thin films

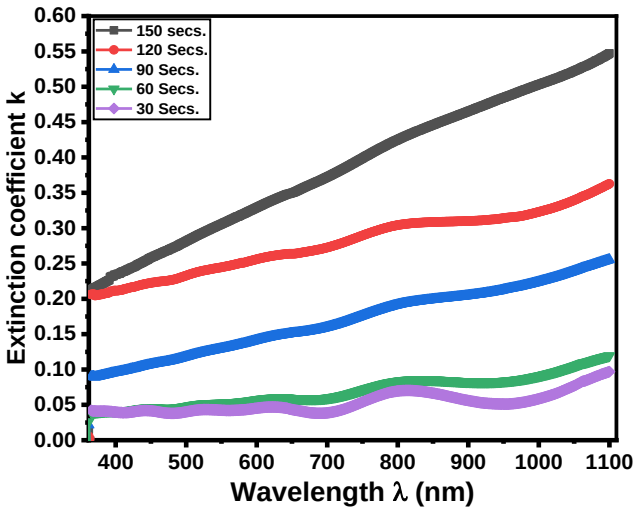

Figure 4: Graph of Extinction coefficient against wavelength; Ni/ZnO thin films

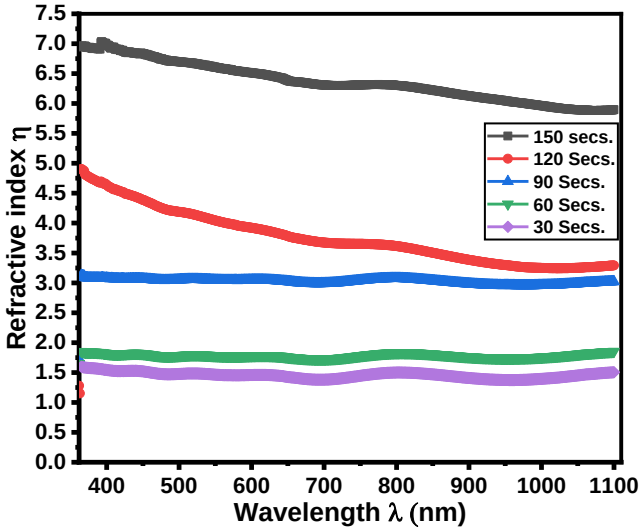

Figure 5: Graph of Refractive index against wavelength; Ni/ZnO thin films

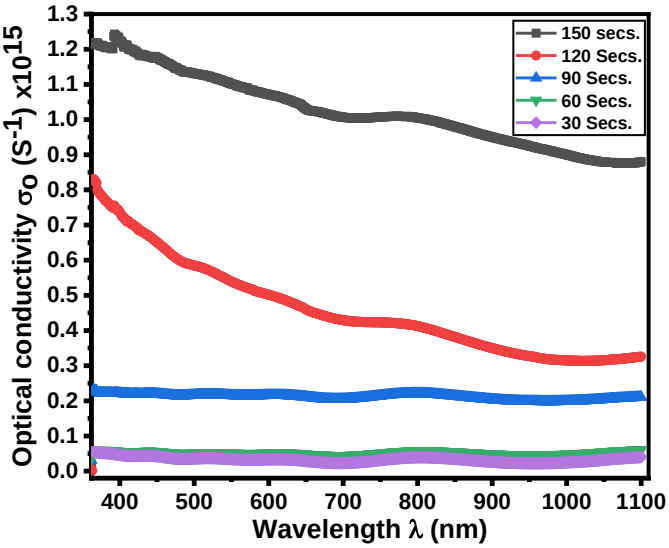

Figure 6: Graph of Optical conductivity against wavelength; Ni/ZnO thin films

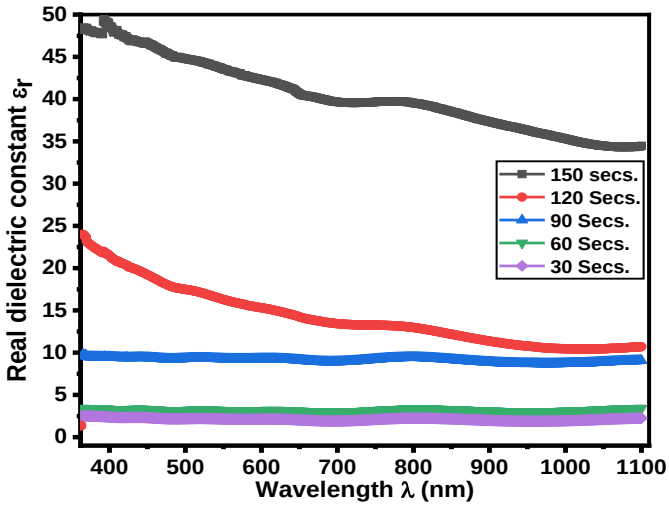

Figure 7: Graph of Real dielectric constant against wavelength; Ni/ZnO thin films

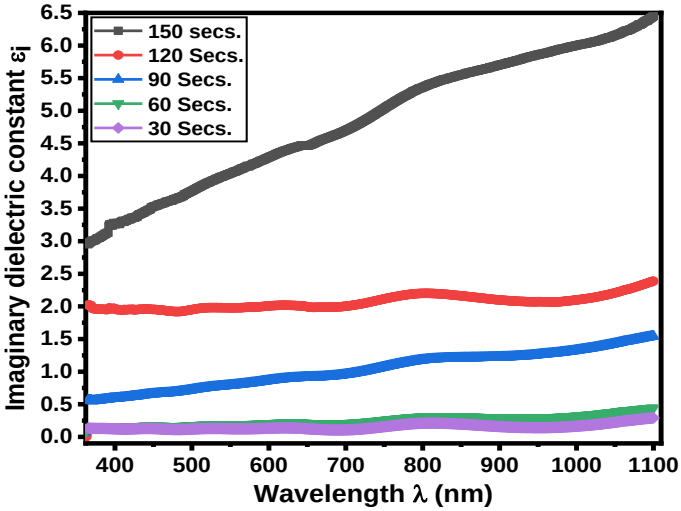

Figure 8: Graph of imaginary dielectric constant against wavelength; Ni/ZnO thin films

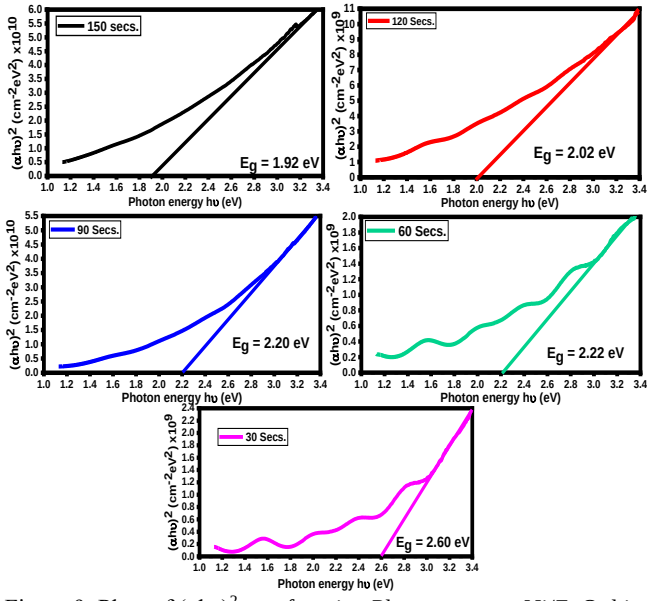

Figure 9: Plots of $(\alpha h\nu)^2$ as a function Photon energy; Ni/ZnO thin films

5.2 Structural Properties of the Ni-Doped ZnO Thin Films

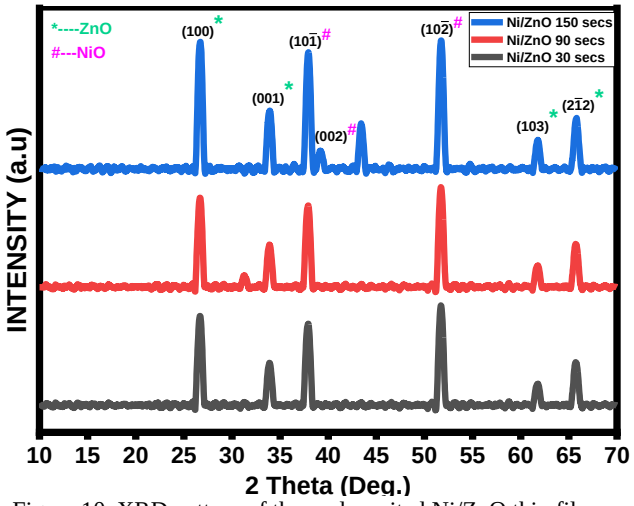

Figure 10. XRD pattern of the as deposited Ni/ZnO thin films

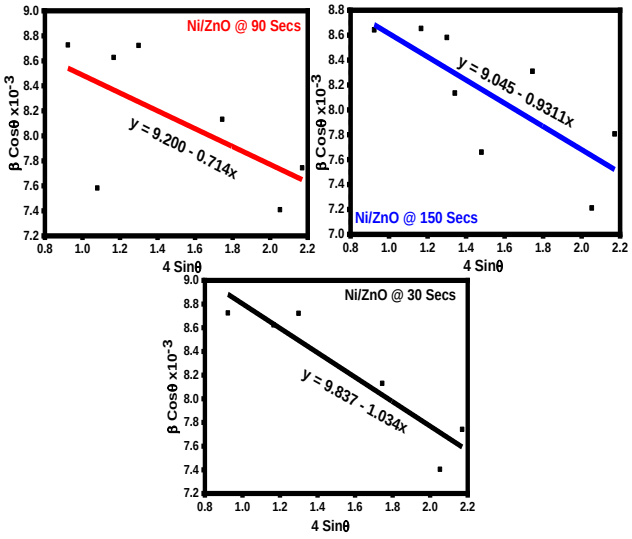

Figure 11. The Williamson-Hall (W-H) analysis of deposited Ni/ZnO thin films

Table 2: Crystal Parameter Estimations of the Deposited Ni/ZnO Thin Films

Samples	Williamson-Hall (W-H) Analysis			Scherrer, Williamson and Smallman's relations calculations (average values)		
	Crystallite size (nm)	Micro-strain x10^{-3}	Dislocation density x10^{-3} (nm^{-2})	Crystallite size (nm)	Micro-strain x10^{-3}	Dislocation density x10^{-3} (nm^{-2})
Ni/ZnO@ 30 Secs	14.095	1.034	5.033	16.925	5.901	3.532
Ni/ZnO@ 90 Secs	15.069	0.714	4.403	17.11453	6.063	3.457
Ni/ZnO@ 150 Secs	15.329	0.931	4.256	17.12951	5.811	3.446

Discussions

The plot of absorbance of the deposited thin films of Ni/ZnO at different deposition time as a function of wavelength is displayed in figure 1 to determine the effect of time variation on the absorbance of the films. The figure showed that the absorbance of the deposited thin films of Ni/ZnO was changed from low values of the order 0.1 for the film deposited at 30 secs within the visible (VIS) and near infrared

(NIR) regions of electromagnetic spectrum to higher absorbance values as deposition time increased. The absorbance of the films increased to very high values in the range of 1.1 to 1.26 throughout the VIS and NIR regions for the film deposited at highest time of 150 secs. The increments in the absorbance of the films as a result of varying the deposition time is crucial for application of the material in many devices fabrications. Figure 2 represents the plot of percentage transmittance of the deposited thin films of Ni/ZnO against wavelength to study the transmittance characteristics of the films for device applications. The figure revealed that the low absorbance exhibited by the films deposited at lower deposition time is compensated by high transmittance ~ 82% to 92% for the films deposited at 30 secs within the VIS and NIR regions of electromagnetic spectrum. This high transmittance however, decreased with an increase in deposition time with the film deposited at highest time of 150 secs having the lowest percentage transmittance of the order 5% within the VIS and NIR regions. The plot of percentage reflectance of the films as a function of wavelength is presented in figure 3 to investigate the percentage reflection of the deposited Ni/ZnO thin films at different electromagnetic spectrum for device applications. The figure showed that the deposited thin films have quite low reflectance but increased as deposition time increased throughout the VIS and NIR regions of electromagnetic spectrum. The film deposited at highest deposition time of 150 secs has the reflectance in the range of 50 – 56% while the film deposited at lowest time has the lowest percentage value of the order 5% throughout the VIS and NIR regions. This result showed that deposition time variation has significant effect on the reflectance property of the deposited Ni/ZnO thin films and thr obtained result is suitable for optical coating applications. The plot of extinction coefficient of the deposited thin films of Ni/ZnO as a function of wavelength is presented in figure 4. From the figure, it can be observed that the films generally have low values of extinction coefficient but increased with an increase in the deposition time and wavelength. This suggest that films have higher values of extinction coefficient in the NIR region and generally influenced by deposition time. The film deposited at highest time of 150 secs has the highest value in the range 0.225 – 0.55 while the film deposited at lowest time of 30 secs has the lowest value in the range of 0.04 – 0.10 within the VIS and NIR regions. This result showed by the fabricated thin films of Ni/ZnO positioned the films for photodetector application as the rate at which light energy fade off the material is record low. The graph of refractive index of the films against wavelength is displayed in figure 5 to study the effect of deposition time on the refractive index of the films within the VIS and NIR regions of electromagnetic spectrum for suitable areas of applications. The graph showed that the deposited thin films exhibit high values of refractive index and increased with an increase in the deposition time throughout the VIS and NIR regions. The film formed at deposition time of 150 secs has the highest refractive index values in the range of 6.0 to 7.0 while the films deposited at lowest time of 30 secs has the lowest refractive index of the order 1.5 throughout the VIS and NIR regions. The high values of refractive index exhibited by the deposited thin films make them good materials for optical fibre, waveguide and photovoltaic cells applications. Figure 6 represent the graph of optical conductivity against wavelength for the Ni/ZnO thin films at different deposition time. The figure showed that the optical conductivity of the films is influenced by deposition time variation by increasing its values as deposition time increased. The film deposited at time of 150 secs has the highest optical conductivity value in the range 9.0×10^{14} – 1.2×10^{15} S^{-1} while the film 30 secs deposited at lowest time has value ~$\times10^{13}$ S^{-1} within the VIS and NIR regions of electromagnetic spectrum. The graph of real dielectric constant of the films as a function of wavelength is displayed in figure 7. The real dielectric constant of the films is observed to increase from the low value ~ 2.5 for the film deposited at lower time of 30 secs to the highest values in the range 35 – 48 for the film formed at highest deposition time of 150 secs within the VIS and NIR regions. The films deposited at higher deposition time tend to decrease as wavelength increased. The imaginary dielectric constant of the films (figure 8) was also found to increase deposition period but the values exhibited by the films are generally low compared to the real dielectric constant values and increase with an increase in wavelength. The films deposited at times of 30 and 60 secs have the lowest values ~ 2.5 while the film deposited at highest deposition time of 150 secs has the highest value in the range 3.0-6.5 within the VIS and NIR regions. The plots of $(\alpha h\nu)^2$ as a function photon energy to determine the bandgap energy of the deposited thin films of Ni/ZnO are displayed in figure 9. The bandgap energy of the films estimated through extrapolations on the photon energy axes of the plots in the figure showed that the direct bandgap energy of the films decreased as deposition time increased. The estimated bandgap values for the deposited thin films as displayed in the plots are 2.60 eV, 2.20 eV, 2.22 eV, 2.02 eV and 1.90 eV for the films deposited at 30 secs, 60 secs, 90 secs, 120 secs and 150 secs respectively. These results showed that deposition time has great effects on the bandgap energy of Ni/ZnO thin films deposited under this condition and the obtained values are strategic for varieties of electronic and optoelectronic device applications including LEDs, solar cells/photovoltaic cells etc.

The pattern x-ray diffraction analysis carried out on the fabricated Ni/ZnO films is shown in figure 10. The X-ray diffraction pattern showed sharp diffraction peaks at the two theta peak positions are as shown in the figure. These sharp diffraction peaks signified that the deposited thin films have crystalline structures. These two theta diffraction peaks almost matched well with the standard JCPDS card no: 00-101-1259 for Zinc oxide (ZnO) with space group P63mc and hexagonal crystal structure. The diffraction peaks also matched well with standard JCPDS card no: 00-901-6308 for theophrastite (NiO_2) with space group P-3m1 and crystal system-trigonal (hexagonal axes). The Williamson-Hall (W-H) analysis plots of the diffraction peak positions for the samples of the films fabricated at 30 secs, 60 secs and 150 secs are presented in figure 11. The plots were done to determine the crystal parameters of the films such as crystallite size and micro-strain. The obtained values of these parameters using the Williamson-Hall (W-H) analysis in

addition to the values calculated using Scherrer and Williamson-Smallman's relations are presented in Table 2. The obtained results from the two methods as displayed in the Table 2 indicated that deposition time variation has minimal effects on the structural parameters of the deposited thin films of Ni/ZnO.

6. Conclusion and Future Scope

In conclusion, the investigations of the effects of deposition time variation on the structural and optical properties of nickel doped zinc oxide thin films showed that most of the optical properties were influenced by deposition time variations. The absorbance of the films was discovered to increase to values in the range of 1.1 to 1.26 throughout the VIS and NIR regions for the film formed at highest time of 150 secs. The transmittance of this film decreased to the order of 5% within the VIS and NIR region and this alteration in the physical feature of ZnO is crucial for considerable application of the material in many devices. The extinction coefficient of the films is quite low with film deposited at highest time of 150 secs having the highest value in the range 0.225 – 0.55 in the VIS and NIR regions. These low values of extinction coefficient positioned the films for photodetector device application. The index of refraction as well as the optical conductivity of the films were also found to be high and increased with an increase in the deposition time throughout the VIS and NIR regions and the results are paramount for optical fibre, waveguide and photovoltaic cells device applications. The energy gap of the films is red-shifted as deposition time increased with the estimated values of 2.60 eV, 2.20 eV, 2.22 eV, 2.02 eV and 1.90 eV for the films deposited at 30 secs, 60 secs, 90 secs, 120 secs and 150 secs respectively and the obtained values are strategic for varieties of applications including LEDs, solar cells/photovoltaic cells etc. The structural probing of the films structures via x-ray diffraction technique revealed that Ni/ZnO films exhibit crystalline structures with preferential crystal planes of (100), (101) and (102). The values of crystal parameters like crystallite size, micro-strain and density of dislocation obtained using Williamson-Hall (W-H) analysis and Scherrer formula were found to be minimally affected by varying the deposition time of Ni/ZnO thin films.

For future scopes of the work, we recommend that other material properties like morphologies, magnetic and I-V characteristics of the deposited thin films of this nature be carried out to further determine the suitability of the material for any other applications.

Data Availability
The data to this work is available on demand.

Conflict of Interest
Authors declared that they do not have any conflict of interest during the period of the work.

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Authors' Contributions
The first, second, fifth carried the experimental preceding of the work. The second and third Authors supervised the project to completion. The fifth author draft the literature and data analysis of the work. Seventh and eighth authors contributed in the experimental settings in the laboratory for the work. The second and the remaining authors contributed in attracting the research fund used in carrying out the work. All the authors reviewed and edited the manuscript and gave their approvals.

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