IOSR Journal Of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 13, Issue 3 Ser. I (May – June. 2021), PP 74-79
www.Iosrjournals.Org

Structural, Optical and Rectifying Properties of Spray Deposited Ni doped and undoped ZnO Thin Films

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Abstract
Nickel doped and undoped Zinc oxide thin films were prepared on soda-lime glass and indium tin oxide (ITO) coated substrates using a low-cost chemical spray pyrolysis technique. The effect of the Ni doping on the optical, surface morphological and rectifying properties of the thin films were investigated using a Uv-Visible spectrometer, X-ray diffractometer and Keithley multimeter.
The crystallographic studies revealed the polycrystalline nature of the prepared 0%, 2% and 5% Ni-doped ZnO thin film with the prominent peaks corresponding to crystal orientation plane (100), (002), (101),102), (110), (103) and (112) indexed to Zinciate phase that has hexagonal structure (Chinese white) and no traces of secondary phase. Optical analysis of Ni: ZnO thin films revealed that the introduction of Ni in ZnO causes a slight shift of the absorption band to a higher wavelength causing a slight increase in the bandgap ranged from 3.1 *eV to* 3.22 *eV*. *The dark I-V characteristics of samples prepared gave rectifying property which makes it good for optoelectronic applications.*

Keywords: *Optoelectronics, Polycrystalline, rectifying, bandgap*

Date of Submission: 20-05-2021 Date of Acceptance: 05-06-2021

I. INTRODUCTION

Wide bandgap ZnO is gaining more attention among other metal oxide semiconductors owing to its unique optical, structural, electrical and magnetic properties[1,2]. Besides, it is readily available, chemically stable, non-toxic, environmentally friendly and tunable optical properties [3]. ZnO has gained wide attention in various areas of application like solar cell [4, 5,6], light-emitting diode, laser diode [7], gas sensor [8], optoelectronic [9], spintronics, etc. More so incorporation of dopant has been identified as a way to improve the electrical and optoelectronic property of ZnO. More so, doping impurities enhanced the energy states in the band structure in other to narrow the energy bandgap and improve the electrical and optical properties of the host. Doping ZnO with metals like Fe, Ni, Cu, Al, Mn, etc have been reported to improve ZnO properties[3, 5,10, 11,12].

Among the metal dopants, Nickel which belongs to group IV elements in the periodic table stands out as the promising dopant due to its chemical stability and ability to influence the optical, electrical and magnetic properties of ZnO structures [13,14,15]. Ni^{2+} with an atomic radius of 0.69 Å can easily replace Zn^{2+} with an atomic radius in the ZnO lattice without altering the structure of the host ZnO as both have the same valence electron and relatively compatible atomic radius[16,17] . More so, nickel dopant increases the oxygen vacant sites (V_O) in ZnO lattice that give rise to better electronic property in ZnO [17]. Also, Ni in ZnO enhanced the interfacial mobile charge transport mechanism and reduces the rate of charge recombination[3] to have excellent electrical property. Therefore, Thin film Ni-doped ZnO may be a promising alternative when good electrical, thermal, optoelectronic and luminescence properties are required. However, the tendency of structural segregation of phase into NiO and ZnO is a major problem faced when doping ZnO with nickel metal. Hence there is a need to identify a good deposition technique to surmount this challenge. Deposition techniques such as spin coating, sputtering, thermal evaporation, sol-gel[13] and spray pyrolysis[18] have been reported and their results further confirmed that Ni in ZnO alters some properties of ZnO.

Among these thin film preparation techniques spray pyrolysis offers a high advantage over others as it encourages doping to have a stable solid solution, low cost, ability to scale up and it has the tendency to eliminate phase segregation since desired solid is formed under pyrolytic process. Hence, the problem of structural segregation of phase can be easily minimized using the spray pyrolysis technique.

Also, in the most published report, properties like structural, optical and electrical of Ni-doped ZnO thin films are inconsistent with regard to Ni doping concentration. Praveen and Jayakumar, 2019 reported pure

hexagonal phase structure for undoped and 2.5%, 5% and 7.5% Ni-doped ZnO. Also, Singh et al. reported a single-phase structure for 2% Ni doping ZnO and mixed-phase of ZnO and NiO as the concentration increases from 4% upward for Ni-doped nanoparticle prepared by solution combustion technique [18].

Furthermore, Rajeh et. al., (2016) reported that Ni doping does not affect the crystal growth plane of ZnO for thin film of Ni-doped ZnO prepared by spray pyrolysis [19].

Moreso, Harpreetpal et al. reported a decrease in optical bandgap from 3.80 to 3.54 eV with the introduction of 2% Ni^{2+} and further decreased to 3.08 eV as Ni^{2+} dopant concentration increases from 2 to 4%. However, as the concentration of Ni^{2+} dopant is further increased to 6%, the bandgap increases from 3.80 to 3.96 eV [20]

Furthermore, Yildiz et al, 2011 reported a decrease in electrical conductivity as the concentration of Ni dopant in ZnO increases. They observed that increasing the Ni dopant causes the surface trap density to increase which causes decrease in the electrical conductivity, rather Ni^{2+} which is a good metal is expected to improve the electrical conductivity and decrease the electrical resistivity of ZnO as Ni^{2+} substituting Zn^{2+} site and there is no possibility lattice distortion since they both have relatively ionic radius [21]

More so, little or no result was published on the effect of Ni dopant on the dark current-voltage characteristics of ZnO thin film owning to the fact that it is important properties that is use to determine diode parameters (saturation currents, series resistance, shunt resistance, and diode factor) that dictate the performance of any electronic devices, hence; in this study, we have reported the optical, crystallographic structural and dark I-V characteristics of Ni-doped and undoped ZnO thin film prepared by low-cost spray pyrolysis.

II. MATERIAL AND METHODS

Prior to the sample preparation, the substrates (soda lime glass and ITO coated glass) were cleaned by washing with detergent, rinsed with distilled water, ultrasonically decreased in methanol, ethanol and isopropanol and dried in the vacuum oven. Analytical graded Nickel acetate ($Ni(CH_3COO)_2.3H_2O$) and zinc acetate ($Zn(CH_3COO)_2.2H_2O$) were used to prepared in equal molarity of nickel acetate and zinc acetate precursors. To have the desired films the precursor solution was mixed such that the dopant nickel acetate was 0%, 2% and 5% by volume of the host zinc acetate. The solutions were stirred for 30 minutes before spraying onto clean substrates placed on hot plate with temperature (350 ± 10) °C. Also, deposition parameters such as carrier gas flow rate, nozzle – substrate distance and pressure were optimized to have good quality thin films. The chemical equation of prepared Ni: ZnO thin film is represented in equation (1):

$$Ni(CH_3COO)_2.3H_2O + Zn(CH_3COO)_2.2H_2O \xrightarrow{\Delta H} Ni{:}ZnO + 2NH_4 + + 6CO_2 + 3CH_4 + 2H_2 + H_2O \quad (1)$$

Prepared samples were characterized by GBC Emma X-ray diffractometer and the SHIMADZU UV-3600UV-VIS spectrophotometer for crystallographic structural and optical analysis respectively. Also, the I-V characteristics of the film prepared on ITO coated glass were measured in dark at room temperature using the two-point probe attached with Keithley source meter (2400 series). The silver paste was used as the contact electrode on ITO and deposited Ni-doped ZnO layers.

III. RESULTS

The x-ray diffractograms of the prepared 0%, 2% and 5% Ni-doped ZnO thin films are depicted in figure 1.

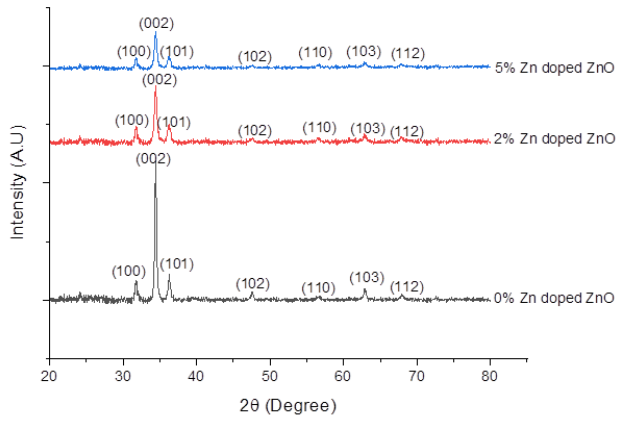

Figure 1: x-ray diffractograms of the prepared Ni-doped and undoped ZnO thin film

Figure 2 (a) shows the spectra of the optical transmittance for the prepared 0%, 2% and 5% Ni-doped ZnO films. Figure 2(b) present the Plots of $(\alpha h\upsilon)^2$ against $(h\upsilon)$ to evaluate direct energy bandgap of the prepared films by extrapolation of the straight part to the $(h\upsilon)$axis

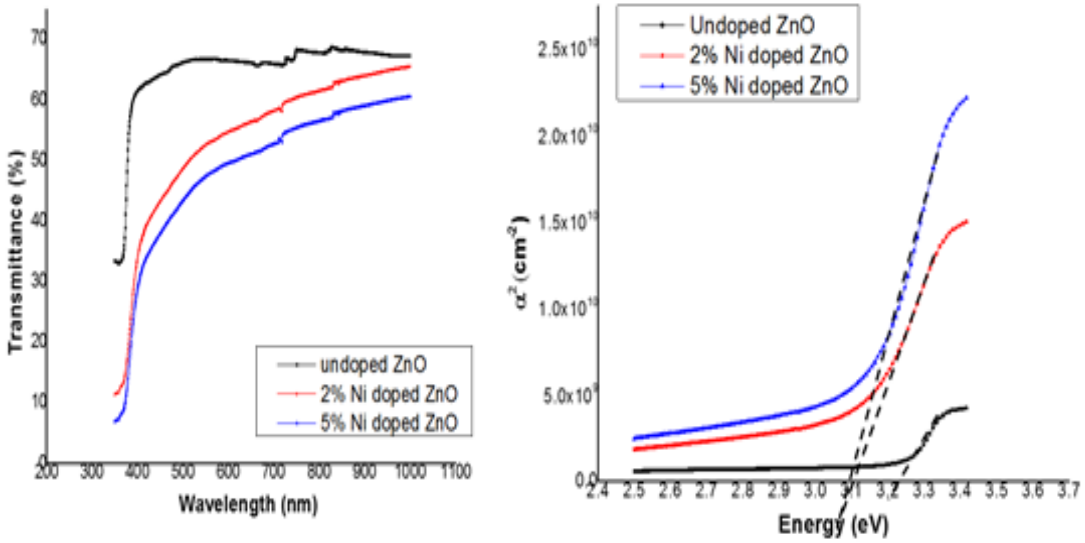

Figure 2 (a) Optical Transmittance and (b) Energy Bandgap plots of the prepared Thin films

To investigate the rectifying property of the prepared 0%, 2% and 5% Ni-doped ZnO/ITO thin, Ag metal contact was selectively made on ITO and ZnO layers of thin films. The current-voltage characteristics of ITO/ZnO/Ag structures with different Ni doping concentrations are studied under (dark condition) reverse bias conditions. Figure 3 shows the current-voltage characteristics of 0%, 2% and 5% Ni-doped ZnO/ITO thin films in dark and measured at room temperature (300 K).

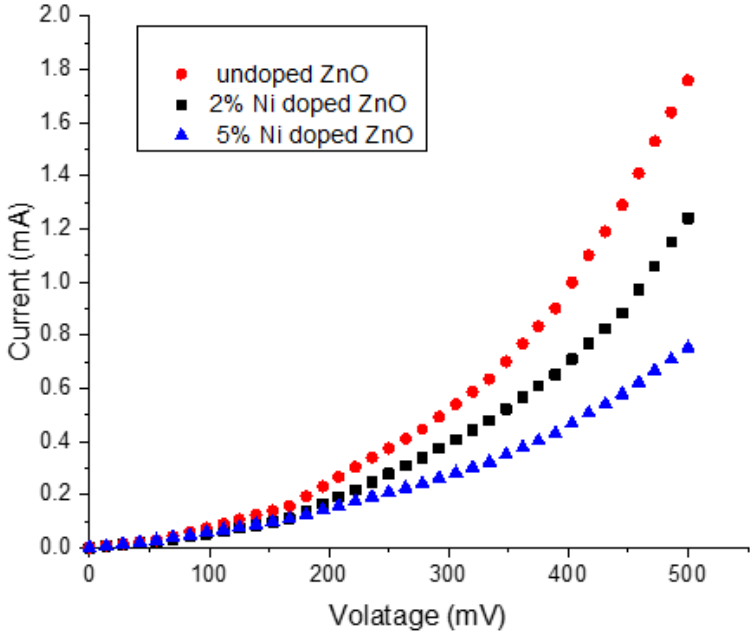

Figure 3. I-V characteristics of the prepared Thin Films

IV. DISCUSSION

The presence of significant peaks in the XRD of the prepared thin films indicates the polycrystalline nature of the prepared film. The introduction of Ni dopant in ZnO shows no significant phase shift. However, the most prominent peaks decrease and slightly broadened as Ni^{2+} increases in ZnO while peaks slightly increase with the increase in Ni in ZnO. The prominent peaks at diffraction angle 31.770^0, 34.422^0, 36.253^0, 47.537^0 56.603^0, 62.864^0 and 67.963^0 corresponds to crystal orientation plane (100), (002), (101),102), (110),

(103) and (112) which is indexed to Zinciate phase that has hexagonal structure (Chinese white) having lattice parameter $a = 3.2417$ Å and $c = 5.1876$ Å according to JCPDS with card number 00-036-1451.[22]
Also, no other secondary phases were observed. This suggests that Ni^{2+} perfectly substitutes the Zn^{2+} lattice site in the ZnO sites in forming a solid solution of Ni:ZnO. A similar effect had been reported by several authors[2, 5, 6,23]. The pure phase obtained further confirmed that the spray pyrolysis technique and the deposition parameters are suitable for preparing doped ZnO thin film.
The crystal size of the deposited thin films was determined using Debye-Scherrer's equation [24,25]

$$D = \frac{K\lambda}{\beta cos\theta} \qquad (3)$$

Where, D is the crystal size, λ is the wavelength (1.5406 Å for CuKα), β is the full width at half maximum (FWHM) and $K = 0.94$.
The crystal decreases with an increase in Ni^{2+} in the ZnO host from 37nm- 32 nm. The Ni dopant affect the microstructure of the crystals during crystal growth which causes the deceases and broadened of the (101) orientation plane leading to decrease in crystal size. Moreover, the reduction in crystalline size is expected since Ni^{2+} with smaller ionic radii of (0.69 Å) perfectly substituted Zn^{2+} with larger ionic radii of 0.74 Å site in ZnO crystal site causing residual strain on the crystal [19, 20]
The spectra of the optical transmittance for the prepared Ni- doped ZnO and undoped films reveal that the prepared films have higher transmission within the ultraviolet-visible region of the electromagnetic spectrum. The optical transmission of decreases continuously in the visible region with increasing Zn dopant from 2% to 5%. More so, a slight shift of the absorption edge towards a longer wavelength (red shift) was observed as Ni dopant increases from 2% to 5% in ZnO thin film figure 2(a). The gradual decrease with increasing Ni dopant agrees with the results reported Ghosh et al., 2008[23]. The optical bandgap of the films was obtained using the Tauc's formula. [26, 27]

$$\alpha(h\upsilon) = A\left(h\upsilon - E_g\right)^n$$

Where, E_g is the bandgap, A is a photon energy independent parameter, $h\upsilon$ is the photon energy, n is a factor which determines the type transition, ZnO is a direct bandgap semiconductor, therefore, band structure for Ni-doped ZnO is determined by considering n = 2 and $\frac{1}{2}$ for direct allowed and indirect allowed transition respectively. α is the absorption coefficient, given by equation [28]

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right)$$

Where, t is the film thickness and *T is* the optical transmittance. The bandgap slightly decreased from 3.22 eV to 3.11 eV as Ni dopant increases in ZnO. The decrease in the bandgap of the prepared Zn doped ZnO films may be due to structural defects experienced by ZnO host lattice as Ni ion substitute Zn site resulting in a decrease in crystal size that caused to small red shift observed and a slight decrease in energy bandgap. The decrease in the bandgap of the film with the addition of Ni dopant may have occurred due to the sp-d exchange interactions between the band electrons and the localized d electrons of the Nickel transition metal ion. [29, 30,31]
Figure 4 represents the schematic energy band diagram of ZnO and Ni-doped ZnO. The valence and conduction bandgap due to interaction in Ni-doped ZnO associated energy bandgap narrowing. However, valence band edge is dominated by O 2p orbitals and conduction band edge is dominated by Zn 4s and Ni 3d while, in Ni^{2+} doped compounds, valence band edge is dominated by Zn 4s and Ni 3d in contrast to ZnO. The sp-d exchange originates in Ni doped compounds due to the contribution of Ni^{2+} 3d electrons to the conduction band. The Ni-doped ZnO extends the possibility of ZnO bandgap tailoring for applications in the Ultraviolet to Visible region.

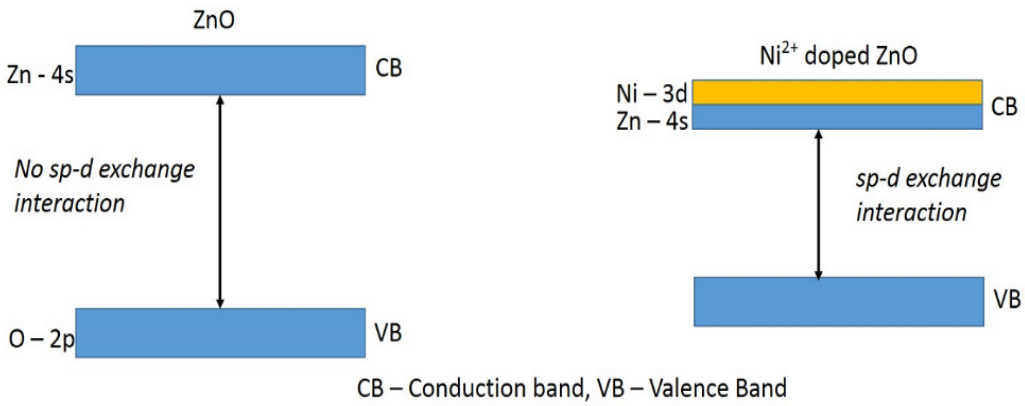

Figure 4: Schematic Energy Band Diagram of ZnO and Ni-doped ZnO Thin films

The rectifying nature of current-voltage characteristics of the fabricated structures indicates the existence of a barrier between the interface of ITO and ZnO thin film

The rectifying properties of samples can be expressed by the Shockley diode equation [24, 32].

$$I = \mathrm{I}_0 \left[\exp\left(\frac{\mathrm{eV}}{\mathrm{n}\kappa\mathrm{T}}\right) - 1\right] \quad (5)$$

Where, I_0 is the reverse saturation current, e is the electronic charge, n is the ideality factor, k is Boltzmann's constant and T is the absolute temperature.

The rectifying nature of the prepared ZnO samples slightly improves with the presence of Ni dopant in the ZnO host. The presence of Ni^{2+} impurities of the material gave agood response to the rectifying characteristics needed for possible optoelectronics device application.

V. CONCLUSION

Low cost spray pyrolysis was used to prepared 0%, 2% and 5% Ni-doped thin films, the compositional, morphological and optical analysis of the prepared films reveal that the crystal size of the film decreases with an increase in Zn dopant in the ZnO which enhanced the optical behaviors and exhibit energy bandgap ranging between 3.22 - 3.11 eV. Hence; Ni^{2+} impurities in ZnO thin film gave good rectifying characteristics for possible optoelectronic device applications.

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ACKNOWLEDGEMENT

The authors acknowledged the Management and staff of NASENI Center of Excellence in Nanotechnology and Advanced Materials, Akure, Nigeria for providing some of the research facilities.