Synthesis and Characterization of Ni-doped ZnO Thin Films Grown by Sol-Gel Spin Coating

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Abstract. ZnO thin film doped with nickel has been grown by sol-gel spin coating technique. The thin films were prepared using zinc acetate dehydrate, ISO propanol, and ethanolamine as a precursor, solvent, and stabilizer respectively. For dopant, Nickel (II) acetate tetrahydrate with different concentration of Ni was added to the mixture. The sol-gel was deposited on a corning glass substrate at room temperature with a speed rate of 3000 rpm during 60 seconds. The Ni-doped ZnO thin films were put into a tube furnace for heat treatment at 500°C for 60 minutes. The characterization of the film was studied using X-ray diffraction (X-RD), and the optical transmittance UV-Vis measurements. The X-RD results show that a good crystallite was clearly observed in a hexagonal wurtzite structure with preferential orientation of (101) plane. The optical UV-Vis measurements show that the transmittance value increased with increasing the concentration of a dopant percentage. The optical band gap of Ni-doped ZnO was in the range of 3.20 – 3.23 eV.

Keywords: Sol-gel, spin coating, ZnO thin films

1. Introduction
In recent years, ZnO thin film has received considerable attention due to its optical properties. ZnO material is categorized as a wide band gap that has the band gap energy of 3.3 eV and has a large exciton binding energy of 60 meV [1,2]. The wide range application in optoelectronic and electronic devices of ZnO materials have been applied such as light emitting diodes (LED) [3], piezoelectric transduction [4], and gas sensors [5]. Also, ZnO has high transmittance value in the visible region which is good for solar cell [6]. The band gap energy of the ZnO thin films can be modified by adding with a small concentration of atom into the film. In this case, nickel atom was used as a dopant to change the structural and optical properties of the ZnO thin films.

Varying different techniques have been applied to grow ZnO thin film doped with nickel such as sputtering [7], spray pyrolysis [8], and sol-gel process [9]. Among of these techniques, sol-gel method approach several advantages such as low cost to study the structural and optical characterization, and easy to control the chemical compound.

This study reports the synthesis and characterization of the structural and optical properties of ZnO thin films doped with nickel by various concentration of nickel. The films were fabricated by sol-gel spin coating on corning glass substrates after heat treatment at 500°C during 60 minutes. The samples, then, were characterized using x-ray diffraction (X-RD) to study the grain size and the strain of the
films. UV-Vis spectrophotometer measurement was performed to investigate the transmittance value and the optical band gap of Ni-doped ZnO

2. Experimental Set-Up

ZnO thin films were fabricated using-sol-gel method by dissolving zinc acetate dehydrate as precursor into 20 ml ISO propanol as a solvent. This solution was added with 0.6 mL ethanolamine as stabilizer. Then, Nickel acetate tetrahydrate with different concentration was added to the mixture. This mixture was stirred on the magnetic stirred hotplate at 60°C during 15 minutes with the speed rate of 1000 rpm.

Before the sol-gel was deposited on a corning glass, the glass was cleaned with ethanol, and acetone into each solution during 10 minutes to remove away the unwanted particles; Then, the sol-gel of Ni-doped ZnO thin films were deposited on the corning glass with a speed rate of 3000 rpm during 30 seconds. Next, the samples were heated at 300°C for 10 minutes at rapid thermal processor (RTP) to remove the solvent from the glass. Finally, the Ni-ZnO thin films were inserted into the furnace for annealing in the temperature range of 300°C until 500°C for 60 minutes. Figure 1 shows the flowchart for preparing TiO$_2$ multilayers thin film.

The structural properties of Ni-doped ZnO thin films were characterized using X-ray diffraction measurement with a single scan diffractometer Cu Kα radiation ($\lambda = 1.5406$ Å. The current and the voltage of X-RD were kept a constant at value of 30 mA and 40 kV, with the scan speed of diffractometer was $2^\circ$/min. The grain size and the strain of Ni-doped ZnO thin films were determined using the Debye-Scherrer method and William-Hall (UDM) formulation. The optical transmittance measurements were carried out to characterize the optical properties of the films using a single beam UV-Vis spectrophotometer with a wavelength range of 250 – 800 nm.

![Figure 1](attachment:image.png)

**Figure 1.** The flowchart for of the ZnO:Ni with various concentration of nickel.
3. Results and Discussion

3.1. Structural characterization

Figure 2 displays the X-ray diffraction patterns of Ni-ZnO thin films with various concentrations of nickel 0%, 1%, and 3%, respectively. It was clearly observed from Figure 2 that the X-RD spectra without nickel appear at diffraction angles of 31.84°, 34.49°, 36.24°, 47.47°, 56.72°, 62.89°, and 67.73°, respectively. These angles are related to the plane of (100), (002), (101), (102), (110), (103), and (112) respectively (JCPDS: 04-03-6608). Also, it is shown in Figure 2, the intensity of (002) plane was higher than that other plane. The grain size of this plane is larger than that (002) plane at nickel concentration of 1% and 3% indicating that the preferential plane orientation of ZnO thin film without nickel was taken place in (002) plane. However, this intensity reduced significantly when the concentration of nickel was increased to 3%. In contrast to (002) plane, the intensity of (101) plane is higher in the sample where nickel has concentration of 3%. This indicated that ZnO thin films with nickel concentration of 3% have plane orientation in (101) plane. The change of preferential plane orientation is probably due to the incorporation of nickel atom in the ZnO films. This can be looked in Table 1 where the grain size of the (101) plane with 3% nickel concentration is larger than that 1% nickel. Moreover, there was a shift of diffraction angle to 31.76°, 34.33°, 36.16°, 47.50°, 56.58°, 62.93°, and 68.26° respectively in ZnO: Ni the thin film (Ni=3%) with the same plane of the samples without nickel.
Table 1. The structure parameters of Ni-doped ZnO thin films after annealing at 500°C for 60 minutes with various concentrations of nickel 1% and 3%, respectively.

| Ni Concentration (%) | 2θ (hkl) | Scherrer Method [8] | William Hall Plot-Method [9] Uniform Deformation Method (UDM) |
|----------------------|----------|---------------------|-------------------------------------------------|
|                      |          | Size (nm) | Average Size (nm) | Strain | Size (nm) | Strain (x10^-3) |
| 1                    |          | 31.78 (100) | 14.39 | 0.0092 | 21.91 | 4.24 |
|                      |          | 34.44 (002) | 13.38 | 0.0092 |          |          |
|                      |          | 36.24 (101) | 11.21 | 0.0104 |          |          |
|                      | 47.80 (102) | 14.33 | 12.74 | 0.0049 |          |          |
|                      | 56.69 (110) | 13.88 | 0.0055 |          |          |          |
|                      | 63.03 (103) | 10.05 | 0.0069 |          |          |          |
|                      | 67.91 (112) | 8.14 | 0.0080 |          |          |          |
| 3                    | 31.76 (100) | 13.93 | 0.0095 |          |          |          |
|                      | 34.33 (002) | 13.17 | 0.0093 |          |          |          |
|                      | 36.16 (101) | 12.67 | 0.0092 |          |          |          |
|                      | 47.50 (102) | 10.01 | 0.0011 | 18.5 | 13.55 |
|                      | 56.58 (110) | 8.12 | 0.0086 |          |          |          |
|                      | 62.93 (103) | 5.28 | 0.0012 |          |          |          |
|                      | 68.26 (112) | 8.12 | 0.0086 |          |          |          |

Results from X-ray diffraction (X-RD) measurements were used to calculate the grain size (D) of the Ni-doped ZnO thin films with various different concentration of nickel using the Debye-Scherrer formulation [10],

$$ D = \frac{k \lambda}{\beta \cos \theta} $$  \hspace{1cm} (1)

where $k$ is a constant number, $\lambda$ is the wavelength of x-ray diffraction (Cu Ka, $\lambda = 1.5406$ Å), $\beta$ is the full width at half-maximum (FWHM) of the peak, and $\theta$ is the Bragg angle, respectively. Based on Figure 1, the structures parameters of Ni-doped ZnO are tabulated in Table 1. As can be shown in Table 1, the average grain size of Ni-doped ZnO was calculated using the Debye-Scherrer formulation. Based on this formulation, the average grain size of Ni-doped ZnO with 1% of nickel concentration is 12.74 nm. This size reduced slightly to 10.01 nm when the concentration of nickel increased to 3%. Also, we used the William-Hall Method (UDM) to determine the grain size and the strain of the thin films using the equation (2) [11], to confirm the grain size results of Ni-doped ZnO thin film that was calculated from the Debye-Scherrer formulation.

$$ \beta_{hkl \cos \theta} = \frac{ka}{D} + (4 \epsilon \sin \theta) $$  \hspace{1cm} (2)

The grain size and the strain of Ni-doped ZnO thin film were calculated using the UDM methods by assuming that the strain is uniform in all crystallographic direction. From equation (2), the term of $\beta_{hkl \cos \theta}$ in the left hand side of equation (2) is potted to $(4\epsilon \sin \theta)$ of the second term in the right hand side. The results would give the slope and y-intercept of the fitted line where the slope indicates the strain and the y-intercept represents of the crystalline size of Ni-doped ZnO thin film, respectively. Figure 3 displays the UDM figure of the fitted line in the equation (2) for Ni-doped ZnO thin film after annealing at 500°C for 60 minutes with various concentration of nickel. As shown in Figure 3, the slope of the fitted line in Figure 3a (concentration of nickel is 1%) is smaller than that Figure 3b (concentration of nickel is 3%) indicating that the strain of Ni-doped ZnO with nickel 1% is lower than nickel 3%. Meanwhile, the grain size of the film was 21.91 nm for nickel 1%, and 18.5 nm for nickel 3%.
Figure 3. The William-Hall (UDM) analysis of Ni-doped ZnO thin film with various concentrations of nickel 1%, and 3%, respectively annealed at 500°C for 60 minutes. The fitting-data results shows that y-intercept represents the grain size and the slope represents the strain of the films.

3.2. Optical characterization

Figure 4 depicts the optical transmittance UV-Vis of ZnO thin films doped after annealing at 500°C for 60 minutes with various nickel concentration of 0%, 1%, and 3%, respectively. With nickel concentration of 0%, the transmittance value was around 15% at wavelength of 400 nm. This value increased at was around 25% when the nickel concentration of 1%. When the concentration of nickel was further increased to 3%, the transmittance value reduced again to about 15%. This number is lower than that previous study where the transmittance value was around 80% [12,13]. In this study, they used aluminum atom as a dopant. From the transmittance spectra, the band gap energy of Ni-doped ZnO thin films can be obtained with use the equation [14]:

$$(\alpha h\nu)^2 = A (h\nu - E_g)$$  \hspace{1cm} (3)

where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, $E_g$ is the optical band gap and $A$ is a constant.

Figure 4. The optical transmittance of Ni-doped ZnO thin films with various concentrations of nickel 0%, 1% and 3%, respectively.
Figure 5. Plot of \((\alpha h \nu)^2\) in respect to \(h \nu\) Ni-doped ZnO thin films with different concentration of nickel after annealing at 500°C for 60 minutes.

Figure 5 displays the linear extrapolation of \((\alpha h \nu)^2\) in regard to energy \((h \nu)\). The intercept of linear line toward the x-abscissa would give the optical band gap energy of Ni-doped ZnO thin films. As shown in Figure 5, the band gap energy was 3.195 eV without nickel atom in the samples. This value is well confirmed with the previous study where the optical band gap energy in this study was 3.2 eV. The band gap energy reduced to 3.189 eV when the concentration of nickel was 1%. Again, this optical band gap was further reduced to 3.028 eV at the concentration of nickel was 3%. The reduction of the band gap energy in Ni-doped ZnO is probably due to the improvement of crystalline of the film after the nickel concentration was increased.

4. Conclusion
We have studied the structural and optical characterization of Ni-doped ZnO thin films with varying the nickel concentration after annealing at 500°C for 60 minutes. The X-RD results show that a good crystallite was observed in a hexagonal wurtzite structure with preferential orientation of (002) plane without nickel. The plane orientation was change to the plane of (101) when the nickel concentration increased to 3%. The optical UV-Vis measurements show that the transmittance value increased with increasing the concentration of a dopant percentage. The optical band gap of Ni-doped ZnO thin films was in the range of 3.20 – 3.03 eV.

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