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Effect of Zn-Doping on the Structural, Optical, and Humidity Sensing Properties of Sol-Gel Synthesized NiO Thin Film

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Abstract*: *This paper presents the fabrication process and characterization process of zinc (Zn) doped nickel oxide (NiO) thin film. The main objective of this research is to investigate the electrical and structural properties of Zn-doped NiO thin film using sol-gel spin-coating method. Zn-doped NiO thin film was prepared by using spin-coating method. The samples were prepared at different doping parameters, which are undoped NiO, 0.5 at.% Zn-doped NiO, 1.0 at.% Zn-doped NiO, 1.5 at.% Zn-doped NiO and 2.0 at.% Zn-doped NiO. The studies of structural properties of the samples were conducted by using an X-ray diffraction. The optical properties of the samples were characterized by using ultraviolet-visible spectroscopy. The spectra of transmittance and absorbance of the samples were studied. The humidity sensing properties of the samples were conducted using humidity chamber and sensor measurement system.

Keywords: Zn-doped NiO; Sol-gel spin-coating; humidity sensing properties.

I. INTRODUCTION

The fabrications of sensor are very essential for advancing technology in the future. The need of smaller component to produce smaller gadget or devices that portable enough to be fit into user pocket as well as components that have lower power consumption for the devices to work longer without charging the battery. However, there are some limitation with what we can achieve with the technological advancement of pursuing the smaller components. The fabrication method such as electron beam lithography system or other fabrication method are too complicated, costly, less flexible, and precision control[1, 2]. Hence, the thin film using sol-gel method is needed to overcome those limitations.

The main objective of this research is to fabricate a zinc (Zn)-doped nickel oxide (NiO) thin film by using sol-gel method. The thin film can be used in sensor device for display's coating, microelectronics, micro-electromechanical system (MEMS) and photovoltaic applications. In order to achieve this main objective, a few sub-objectives can be formulated. First, to fabricate a Zn-doped NiO thin film by using sol-gel method. Second, to understand the electrical properties of the thin film. Finally, to understand the structural properties of the thin film.

Recently, the application of sol-gel process has been escalated in materials science. Sol-gel is a method producing solid materials from small molecules compound[3]. Fibers, monoliths, microspheres fine powders and thin film can be prepared by using sol-gel technology [4] as this technology is easy to use and take a short time to prepare the materials. Sol-gel technology application is not only limited for protective coatings[5], insulating materials and synthesis of nanoparticles [6, 7]. This technology also can be used as a superconductor, lenses, high-strength ceramics, waveguides[8] and last but not least it can be used as catalyst as well as piezoelectric devices[9]. The multi-component oxide systems and low temperature process regimens can be access using sol-gel technology due to its flexibility texture.

Thin film is a material with nanometer or micrometer thickness. It can be produced using deposition technique. The structure of thin film can be divided into amorphous and polycrystalline which depend on its preparation condition and material nature[10]. The preparation of the thin films can be divided into two parts; which are the thin film layer and substrate where the thin film was deposited on the substrate and another part is where the thin film can be deposited of different layers on the substrate such as electrochromic cells and thin film solar cells[10]. There are two deposition technique well known to produce thin film which are physical deposition and chemical deposition. The Zn-doped NiO thin film is prepared using sol-gel spin-coating method which can be classified as the chemical deposition technique due to the used of chemical solution to produce the thin film[11].

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Spin-coating method has been used to prepare the Zn doped NiO thin film. Spin coating is the most effective method given it has a low cost due to its operational environment condition which can be operate in low temperature and does not necessarily need a vacuum environment[1]. It is also can obtains homogenous surfaces and high-quality films within a short period of time.

The nanosized NiO has been known to have admirable properties such as magnetic, electrochromic, optical, electrochemical properties and sensing [12, 13].

The structural and electrical studies need to be done in order to know its unique physical, chemical and mechanical properties before it can be used for other applications. Consequently, this paper used an X-ray diffraction (XRD) method for structural characterization, ultraviolet-visible (UV-vis) spectroscopy for optical characterization and humidity test for humidity sensing properties of the thin film[6].

The characterization study of the thin film was done by comparing the NiO thin film with different doping concentration of Zn. There are five parameter used for characterization which are undoped NiO, 0.5 at.% Zn-doped NiO, 1.0 at.% Zn-doped NiO, 1.5 at.% Zn-doped NiO and 2.0 at.% Zn-doped NiO in this paper. Each sample was deposited for 5 layers using the same process.

II. METHODOLOGY

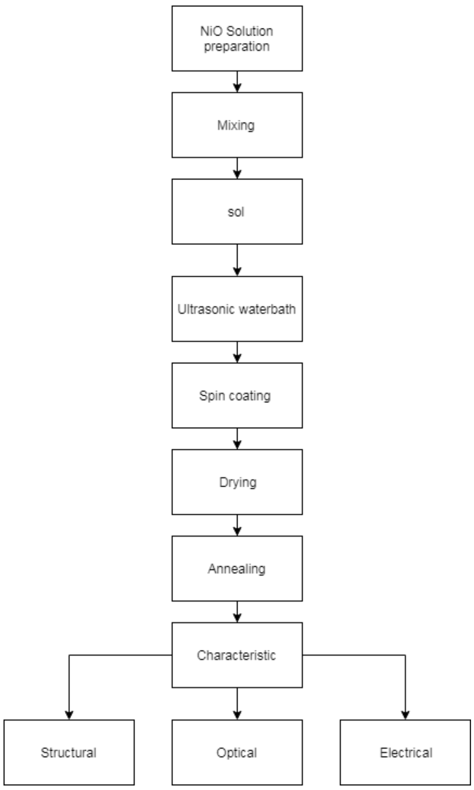

Fig. 1. Flow of the preparation and characterization of Zn-doped NiO at different concentration

Fig. 1 shows the preparation flow of NiO thin film deposited on the glass substrate by using sol-gel spin coating method. The preparation flow consists a few steps which started with a preparation of precursor solution. Next is the sonication process, where the precursor solution in the beaker was soaked in the deionized (DI) water in the ultrasonic water bath. Then, the spin coater device was used to deposited the thin film on the glass substrate. The films were then dried in an electrical oven and then been spin-coated again up to five layers. Next, the film samples were annealed at 400 °C for 2 hours. Finally, the characterization of the thin film was done at the end of the process. There were three types of characterization processes conducted, namely structural, optical and electrical properties.

A. Preparation of precursor solution

There are a few steps used to prepare the NiO thin film using sol-gel spin-coating. First, the NiO precursor solution was prepared by liquefy nickel acetate ($Ni(CH_3 CO_2).4H2O$) powder in a solvent consist of diethanolamine ($C_4H_{11}NO_2$) and ethylene glycol monoethyl ether ($C_4H_{10}O_2$). The solvent was then placed in the ultrasonic water bath containing DI water to undergo sonication process in 50°C for 30 minutes. The solution was then stirred for 1 hour on a magnetic stirrer with 500 rpm to complete the solution precursor. The process was repeated with addition of zinc acetate dihydrate ($(C_4H_6O_4Zn).2H_2O$) in the solution to produce 0.5 at.% Zn-doped NiO, 1.0 at.% Zn-doped NiO, 1.5 at.% Zn-doped NiO and 2.0 at.% Zn-doped NiO films. Fig. 2 shows the precursor solution of Zn-doped NiO.

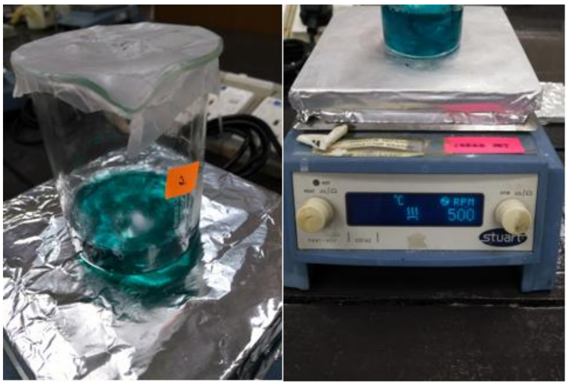

Fig. 2. Zn-doped NiO precursor solution on the magnetic stirrer

B. Preparation of Zn-doped NiO thin film

The Zn-doped NiO thin films was prepared using spin-coating technique where the speed of the spin-coater was set up at 4000 rpm for 60 seconds. The glass substrate was placed on the chuck in the spin-coat machine. The vacuum on the chuck then was turned on to ensure the glass substrate would not fall when the chuck is spinning. The Zn-doped NiO solution was dropped on the glass substrate after 5 seconds of the start-up time to ensure the chuck spin constantly at 400rpm to avoid the solution from forming spots or dots on the glass substrate. The thin film was deposited evenly without any spot on the glass substrate as can seen in Fig. 3.

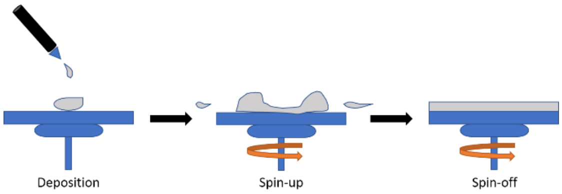

Fig. 3. Process of spin-coating technique

After the spin-coating process, the samples then were heated at 250 °C for 5 minutes in a furnace. Then, the same processes of spin-coating and heating were repeated up to 5 times to improve the thickness of the films. Finally, the samples were annealed at 400 °C for 2 hours in the furnace.

C. Characterization of the Zn-doped NiO thin film

i. Structural properties

The crystalline structures of Zn-doped NiO film was observed via XRD patterns. The result of each different thin film parameter sample was compared and studied. The result graph of intensity over the diffraction angle, 2θ was studied and observed.

ii. Humidity sensing properties

To study the humidity sensing properties of the samples, the samples were exposed to humidity in the humidity control chamber and the current-voltage-time, (IVt) have been measured [11]. Copper electrode has been used to supply the voltage to the samples. The samples have been supplied with 5V supply and the current, I over time, t(s) was measured. The relative humidity, RH of the chamber was controlled in the range 40-90%. The graphs of response curve, stability, and sensitivity with respect to current, I over time, t(s) were measured and studied.

iii. Optical properties

The optical studies of Zn-doped NiO film conducted using UV-Vis spectroscopy. The transmittance over the spectral range 300-1500 nm was measured in the process. The graph of transmittance over the spectral range was studied and observed.

III. RESULT AND DISCUSSION

A. Structural properties

Fig. 4 shows the XRD patterns of undoped and doped NiO thin film at different Zn concentration of 0.5 at.%, 1.0 at.%, 1.5 at.% and 2.0 at.%. The patterns show that all samples are amorphous structure where the XRD pattern shows a single broad diffused peak instead of sharp peak to indicate the crystallinity structure on the thin film. This phenomenon occurs due to surface tension and surface to-volume to ratio (Ostwald ripening law)[14] on the thin film where the samples have a hard structures but not in well-defined shape. Therefore, the X-ray beam in XRD machine cannot detect the NiO or Zn structure due to its not well-defined shape and the results shows amorphous structure. The amorphous structure can be influenced by the number of layers of the thin film and the annealing temperature, whereby by increasing the annealing temperature and increasing the layer of the thin film, the higher the crystallites of NiO that can be seen in XRD graph [15].

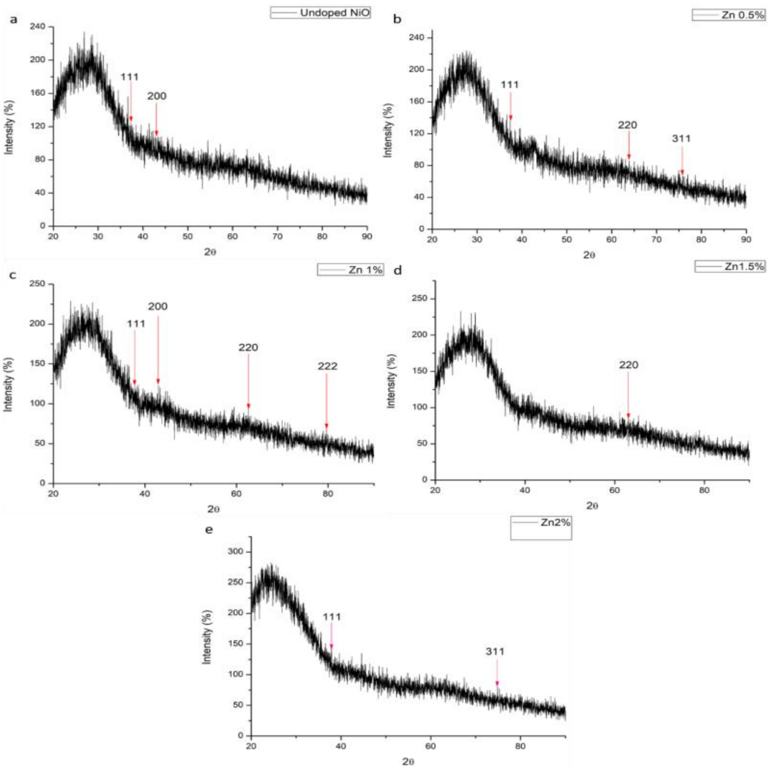

Fig.4. XRD patterns of a) undoped NiO, b) 0.5 at% Zn-doped NiO, c) 1 at% Zn-doped NiO, d) 1.5 at% Zn-doped NiO, and e) 2 at% Zn-doped NiO

B. Optical properties

The optical transmission spectra of the undoped NiO, 0.5 at.% Zn- doped NiO, 1.0 at.% Zn-doped NiO, 1.5 at.% Zn-doped NiO and 2.0 at.% Zn-doped NiO samples with the wavelength range of 300-800nm can be seen in Fig. 5. The spectrum shows transmittance over wavelength at different Zn dopant concentration. As shown in the figure, the transmittance increases as the Zn-dopant concentration increases. The average transmittance was calculated for all the samples and it is increased as the dopant concentration increases, in which the average transmittance is 87.515, 91.457, 94.337, 95.001 and 96.716 % for undoped NiO, 0.5 at.% Zn- doped NiO, 1.0 at.% Zn-doped NiO, 1.5 at.% Zn-doped NiO and 2.0 at.% Zn-doped NiO samples respectively. Thus, transmittance characteristics of optical thin film are significantly influenced and affected by the dopant concentration. This behavior may be connected to microstructural appearance of prepared films, as the photon scattering increases by crystal defects [16].

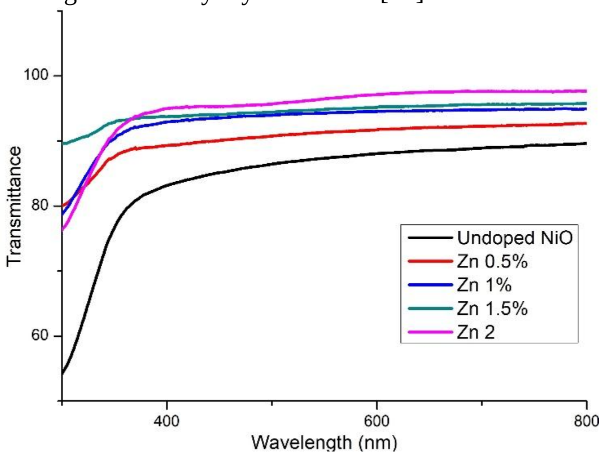

Fig. 5. The transmittance for NiO and various Zn doped NiO thin films.

Fig. 6 shows the dependence of absorbance on the wavelength in range 300-800 nm. It can be observed that the absorption decreases with the increasing of Zn dopant into NiO solution and the optical band gap decreases due to absorption edges shift to longer wavelength. Higher absorption can be seen on the shorter wavelength (UV region) while lower absorption occurs at longer wavelength (Vis region). This action can be explained where at high wavelength the incident photon have insufficient energy to combine with atoms, therefore the photon will be dispatch. It is vice versa photon condition in longer wavelength where the photon have sufficient energy to energize electron from valence band to conduction band, thus the photons finally absorbed within the material [17].

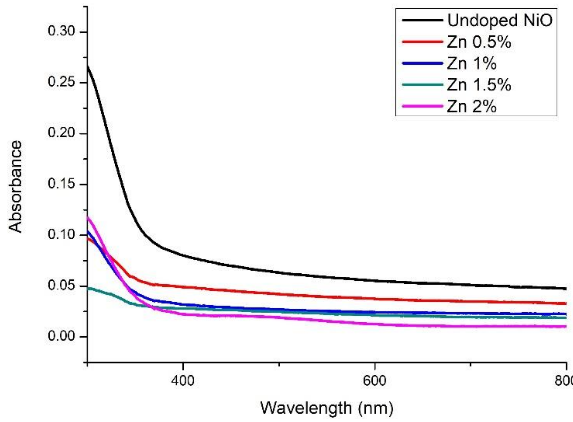

Fig. 6. The absorbance for NiO and various Zn doped NiO thin films.

C. Humidity sensing properties

The measurement of humidity sensor in room temperature signified that the current linearly increased with the increasing of relative humidity percentage (RH%) value due to more water vapour absorbed by Zn-doped NiO. Fig. 7 shows the response curve of the samples after conducting the humidity test. The graph shows the current, I over time, t(s). The samples have been supplied with 5V bias and the current, I over time, t(s) was measured. The relative humidity, RH of the chamber is controlled in the range 40-90% and the samples were measured for 1 cycle at room temperature.

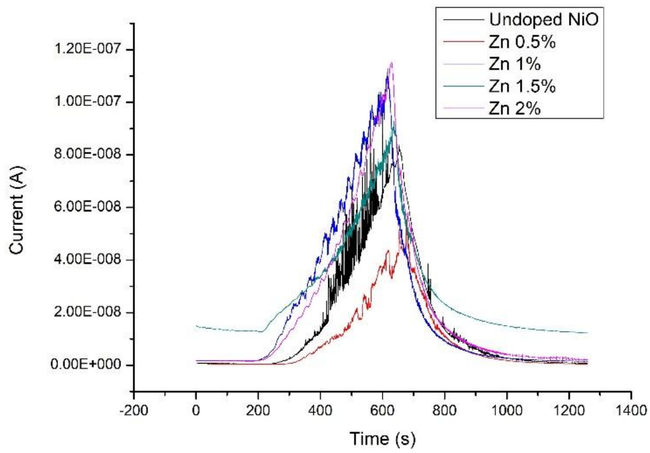

Fig. 7. Response curve of various Zn-doped NiO concentration using humidity sensing.

Based on Fig. 7, the sensitivity of undoped NiO is 191.816, 0.5 at.% Zn- doped NiO is 160.789, 1.0 at.% Zn-doped NiO is 63.192, 1.5 at.% Zn-doped NiO is 7.3677 and 2.0 at.% Zn-doped NiO is 64.42.The sensor response decreases with the increasing of Zn-doped NiO percentage. However, the response fluctuates where the sensitivity of humidity increased again from 7.3677 to 64.42 when the Zn-doped NiO was increased up to 2.0 at.% Zn-doped NiO. From the graph in Fig. 7, it can be seen the sensitivity of the current for every sample increases with the increasing of RH%. This happened due to more water vapor has been absorbed by Zn-doped NiO thin film [14]. As the RH% increased, the water molecule became free [18].

Therefore, the surface of Zn-doped thin film gradually became liquid like and the proton easily hopped between the water molecule on the surface of thin film which led to electrical charge transport.

IV. CONCLUSION

As for conclusion, the objectives of this project were successfully achieved. The samples of Zn doped NiO thin film was successfully fabricated using so-gel spin-coating method. The samples consist of five parameter that are undoped NiO, 0.5 at.% Zn doped NiO, 1.0 at.% Zn doped NiO, 1.5 at.% Zn doped NiO and 2.0 at.% Zn doped NiO. The studies of structural properties of the samples have been conducted by using XRD. XRD results shows that the films are in the amorphous structure because of the annealing temperature at 400 ºC. The studies of optical properties of the samples have been conducted by using UV-Vis. The transmittance and absorbance graph obtained shows that the transmittance and absorbance value of the samples are strongly dependent on the Zn dopant concentration. The higher the Zn dopant, the higher the transmittance value of the samples and the lower the absorbance value of the samples. The studies on humidity sensing properties were conducted using humidity chamber and IVt curve. The sensitivity of the humidity sensor based on Zn-doped NiO film decreased with the increasing Zn-doped NiO. However, the sensitivity increased again when the value of Zn-doped NiO increased up to 2 at.%.

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