Influence of high nitrogen doping on optical properties of ZnO thin films

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Abstract. ZnO semiconductor is one of the photocatalyst materials that has become a concern in the world of research. This is due to its ability to degrade pollutants effectively, economically and environmentally friendly. Many studies have been developed to enhance the photocatalytic activity of ZnO, one of them by the addition of doping. Increasing the concentration of non-metallic doping on ZnO will affect its energy level so that it can improve the physical properties and optical properties. Nitrogen has been considered as a very good dopant because it has an ionic radius comparable to oxygen and also has small ionization energy. High nitrogen-doped ZnO thin films have been deposited by sol-gel spray coating methods on glass substrate. Using spectrophotometer UV-Vis Materials were characterized to obtain the absorbance spectrum, in order to analyze its optical absorption region. The result shows that all materials have high absorption in the UV region. In general, the graph shows that the absorption spectra in the UV region increase with increasing percentage of dopant and have maximum absorption spectra on the sample with 40% dopant. It indicates that high N-doping enhanced the light absorption capacity of ZnO.

1. Introduction
Semiconductor material currently being developed is a metal oxide semiconductor compound, one of which is ZnO. As a semiconductor material with the ability to degrade pollutants effectively, economically and environmentally friendly [1-4], ZnO has become a concern in the world of research. ZnO also has several favorable properties, including a large band gap (∼3.37 eV), and high exciton binding energy (∼60 meV) [5]. Undoped ZnO is intrinsically n-type semiconductor with high conductivity due to interstitial Zn and O vacancy [6].

It is difficult to obtain a p-type ZnO doping caused by deep acceptor levels, self-compensating effects and low solubility of dopant ion acceptors [7]. Great methods have been made to obtain p-type ZnO by using an acceptor dopant. According to theoretical calculations, nitrogen is the best shallow acceptor candidate for ZnO [8]. Furthermore, nitrogen has been considered as a very good dopant acceptor dopant due to its small ionization energy, similar ionic radius comparable to oxygen, easy to handle, nontoxicity and abundant in nature. Much experiment about the influence of N-doping on the properties of ZnO films has been reported [8]. In addition, N doping in ZnO will improve its optical properties [9].

In this research, ZnO-N thin films with high doping films have been synthesized by sol-gel and spray coating deposition method. The impact of adding high concentration doping was investigated. The results show that the existence form of N-related defect has the significant influence on optical
properties of ZnO:N thin films. Among various defects, ionic substitute nitrogen is a main effective factor narrowing band gap.

2. Materials and Method

2.1. Solution synthesis

ZnO-N solution was made by dissolving Zinc Acetate into 2-propanol with a volume of 26 ml. Then the solution was stirred for 15 minutes using a magnetic stirrer at 60 °C. After 15 minutes, the solution was poured slowly by MEA with 1: 1-mole ratio to Zinc Acetate using injector and re-stirred for 15 minutes so that the solution becomes clear. Urea was used as a source of nitrogen because it is one of the richest source of nitrogen and the price is reasonable. After 15 minutes, the clear solution was added with urea with a predetermined composition of 10%, 20%, 30%, 40%, and 50%, then stirred for 30 minutes in order to make the solution more homogeneous. After 30 minutes, ZnO-N solutions were deposited on glass substrate using spray coating technique.

2.2. Thin films deposition

Before the deposition process began, the glass substrate was first cleaned using methanol, acetone, and distilled water sequentially to clean the substrate surface from impurities on its surface. Then the substrate was placed on a hot plate at a temperature of 450 °C and left for 10 minutes so that the heat on the substrate evenly spread. After it, the solution began to be deposited using a spray gun at a distance of ± 30 cm above the substrate. After the solution was deposition on the substrate, then left it for 60 minutes on the hot plate at a temperature of 450 °C to form crystal structure.

3. Results and Discussion

3.1. Sample synthesis result

ZnO-N thin films as a synthesis result can be seen in Figure 1. The resulting thin films are white, and this indicates that the color of the material is strongly influenced by the doping elements used, namely nitrogen (N). Not too noticeable significant color density differences in each thin films.

![Figure 1. ZnO-N thin films 0%-50%](image)

3.2. Optical properties

The absorbance spectrum of ZnO-N for a wavelength range of 300-800nm can be seen in Figure 2. In general, all samples have a high absorbance value at a wavelength below 400nm, which is known to be the UV wavelength limit. This shows that ZnO-N generally works optimally in the UV light range. Based on Figure 2, it is known that in the wavelength region of less than 400nm, ZnO-N 40% has the highest absorbance spectrum compared to other doping percentages. The ZnO-N 40% particles attached to the glass substrate have the highest density, which is one reason why the ZnO-N 40% sample has the highest absorbance value. Sequentially from the highest absorbance value to the lowest is 40%, 20%, 10%, 50%, and 30%.
Figure 2. UV–visible spectrum of high N doped ZnO samples

The absorbance spectrum in Figure 2 is processed using the tauc plot equation to obtain the band gap value from each sample. To determine the value of the band gap, a plotting relationship between $h\nu$ and $(\alpha h\nu)^2$ is performed. The band gap value can be determined by linear extrapolation of the graph against the x-axis as shown in Figure 3.

Figure 3. The relationship between $h\nu$ and $(\alpha h\nu)^2$ using the tauc plot equation

Figure 4 shows that the band gap value generally decreases with the increasing number of N doping added, this indicates the occurrence of the redshift phenomenon in this experiment. The decrease in energy gap is caused by the emergence of a new energy level between the valence band and
conduction band, as well as the occurrence of the O atom substitution by N atoms [10]. ZnO-N 20% owns the lowest value of the energy band gap. The value of the band gap produced in ZnO-N 0% to ZnO-N 50%, respectively 3.264 eV; 3.253 eV; 3.242 eV; 3.250 eV; 3.246 eV; and 3.246 eV.

![Graph showing the relationship between optical band gap and dopant percentage.](image)

**Figure 4.** The relationship between ZnO-N energy gap value and dopant percentage

### 4. Conclusion
The absorbance spectrum of ZnO-N generally shows optimal light absorption at a wavelength range below 400nm, with the highest absorbance value of 40% ZnO-N and the lowest absorbance value of 30% ZnO-N. Addition of N doping to ZnO generally causes a decrease in bandgap values. The most significant reduction in energy band gap is at 20% ZnO-N with band gap value of 3.242 eV. Significant reduction in energy band gap will increase the effectiveness of thin films photocatalytic making it possible to be utilized in the application of photodegradation of dyes and even bacteria.

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