Optical properties of double layer thin films zinc oxide doping aluminum (ZnO/Al) were deposited on glass substrates by sol gel method spray coating technique

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Abstract. Thin films of double layer of ZnO/Al has succeeded in deposition on a glass substrate using sol-gel method and spray coating techniques. Variations of doping Al as much as 2%, 4%, 6% and 8%. ZnO precursor synthesized using zinc acetate dehydrate (Zn(COOCH₃)₂·2H₂O), isopropanol ((CH₃)₂CHOH) and monoethanolamine (MEA) were stirred using a magnetic stirrer for 45 minutes. ZnO precursor get homogeneous and then added of aluminum nitrate nonahydrate predetermined doping concentration and stirred again for 15 minutes. Deposition solution is done by the spray on a glass substrate and then heated at a temperature of 450°C. A layer of ZnO/Al deposited over the ZnO to produce a thin layer of a double layer. Optical properties layer of ZnO/Al characterized using UV-Vis spectrophotometer. Based on data from UV-Vis absorbance was determined the value of the energy band gap. Pure and dopped layers has different energy due the Al dopping. For pure ZnO layer has energy band gap of 3.347 eV and decreased to 3.09 eV for ZnO layer with Al dopant.

1. Introduction

Semiconductor materials as good photocatalysts can be used to degrade pollutants or toxic compounds namely Zinc Oxide (ZnO), Titania (TiO₂), Tungsten Oxide (WO₃) and Zinc stannate (Zn₂SnO₄) [1]. One of the semiconductor material that is readily available and nontoxic nature is ZnO. Some forms of ZnO are in the form of nanoparticles, powder, and a thin film. Several active research on thin layers, one of which is a thin layer of ZnO, largely because of its unique properties and advantages for its application [2]. The form of a thin layer is preferred to avoid the separation of the catalyst after the detoxification process.

Material Zinc Oxide (ZnO) has the energy band gap of 3.37 eV which is able to absorb active in UV light. However, for a more efficient photocatalyst, the material must be able to absorb visible light in the spectrum of sunlight. Thus, for ZnO material to be able to absorb UV light and visible light, the energy band gap of ZnO should be minimized. The energy band gap is getting smaller will increase the transfer of electrons from the valence band to the conduction band so that the hole is very important for the formation of hydroxyl radicals that are used for the degradation of pollutants formed in photocatalytic applications [3]. Methods used to expand the range of absorption of the light spectrum and minimize the energy band gap is by doping the semiconductor oxide.

The optical properties and structure of ZnO are affected by deposition parameters as well as the provision of doping. One of them is causing doping Aluminium seed morphology to increase the
surface area coating and efficiency of photocatalytic activity [4]. The number of doping Al provided can affect the characteristics of the thin layers desirable [9,10]. Characteristics of thin layers is expected better with some of the controls provided in addition to the doping concentration, also add layers that form the double layer deposited [6]. A thin film using a double layer of ZnO:Al has a higher absorbance values up toward the infrared waves [5]. ZnO doped Al thin film of double layer structure is expected to have better properties than single layer so that the photocatalyst can be more efficient. This thin film can be prepared by a method commonly referred as deposition of growing a thin layer.

Many techniques of deposition on thin film are by pulsed laser deposition, RF magnetron sputtering, chemical vapor deposition, spray pyrolysis and sol gel method. Among some of these techniques, sol-gel method is considered better, because the deposition of a thin film of either small or wide area and a complicated shape on a variety of substrates at room temperature so that it does not require air vacuum device [2]. Deposition on a substrate is also be done with the casting method, such as dipcoating, spin coating, slot-die coating and spray coating. One method that is more suitable for the manufacture of thin films is spray coating, because it can be done using equipment that is reasonably under room temperature conditions [8].

2. Experimental

2.1. Preparations of ZnO and ZnO:Al precursor

The process of making a thin film and double layer of ZnO ZnO/ZnO:Al done by sol-gel method of spray coating techniques. Molarity solution of 0.5 M with Al doping variation in molarity percentage by 2, 4, 6 and 8%. The preparation process and the manufacture of precursors to be done with a thin film of several stages which will be explained in the next section.

ZnO precursor namely Zinc acetate dihydrate (Zn(COOCH\textsubscript{3})\textsubscript{2}H\textsubscript{2}O) as much as 2,853 grams were dissolved into 26 ml of Isopropanol, then stirred for 15 minutes. After stirring for 15 minutes, the solution was then added 0.778 ml Monoethanolamine (MEA), and then stirred back on the magnetic stirrer at room temperature (25°C) for 15 minutes until the solution (precursor) homogeneous. If it is homogeneous, the precursor solution is ready for the deposition process.

Furthermore, the formation of precursors ZnO:Al namely Zinc acetate dehydrate (Zn(COOH\textsubscript{3}).2H\textsubscript{2}O) as much as 2,853 grams dissolved in 26 ml Isopropanol was stirred for 15 minutes on magnetic stirrer. Then the solution was added MEA as much as 0.778 ml and stirred again for 15 minutes at room temperature (25°C) until a homogeneous solution. Furthermore, homogeneous solution is added aluminum nitrate nonahydrate (Al(NO\textsubscript{3}).9H\textsubscript{2}O) in accordance with the concentration ratio of the molarity percentage that is consecutive, 2, 4, 6 and 8% (0.099; 0.203; 0.311; and 0.424 gram) and stirred for 15 minutes on magnetic stirrer. ZnO precursor solution and the double layer of ZnO/ZnO:Al that has been created is stored in the bottle and ready for the deposition process.

2.2. Preparations of ZnO:Al thin films

ZnO deposition process and double layer ZnO/ZnO:Al on a glass substrate using spray coating techniques. The glass substrate which has been cleaned is placed on a hot plate at a temperature of 450°C for 10 minutes. Precursor solution put into the spray gun and a precursor sprayed evenly onto a glass substrate. Spraying is done in sequence according to the concentration ratio of doping. Especially for double layer ZnO/ZnO:Al, deposition is done by spraying a solution of ZnO first and then followed by spraying a solution of ZnO:Al with each concentration doping.

After the deposition process is completed, a thin film annealing for 1 hour at a temperature of 450°C. Annealing process is done so that the growth and nucleation in the precursor formed evenly on the surface of the glass substrate. A thin film formed then is cooled to room temperature (25°C) and characterized.

3. Result and Discussion
The energy gap of a thin film is calculated based on the value of absorbance and transmittance of visible uv spectrometer with a wavelength range of 300-800 nm. Absorption peak of ZnO:Al 8% at 364 nm is shown in Figure 1. This indicates that a given doping can shift the absorption wavelength toward larger wavelength of visible light. The highest absorption peak lies at a wavelength of 368 nm ZnO:Al samples with doping 6%. The percentage transmittance of pure ZnO by 79.4% experienced an increase after the increase in doping and the highest in doping Al 4% that is equal to 91.8% and then decreased again on doping Al 8%, ie 81.8% as at show in Figure 2. Improved spectral transmittance of a sample occurs in the visible region as much as to 79-91%.

![Figure 1. UV Visible absorbance spectra of undoped ZnO and ZnO:Al.](image1)

![Figure 2. UV Visible transmittance spectra of undoped ZnO and ZnO:Al.](image2)
The addition of Al doping also affects the energy gap of thin film where it is influential to the electron transition. The value of energy band gaps of ZnO thin film with variation of dopped Al are listed in Table 1. The energy gap decreased greatly at 3.098 eV on sample with Al doping of 8% as shown in Figure 2.

![Tauc plot bandgap of ZnO:Al 8%](image)

**Figure 3.** Tauc plot bandgap of ZnO:Al 8%

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| Thin films | Band gap (eV) |
|------------|--------------|
| ZnO:Al 0%  | 3.347        |
| ZnO:Al 2%  | 3.099        |
| ZnO:Al 4%  | 3.123        |
| ZnO:Al 6%  | 3.109        |
| ZnO:Al 8%  | 3.098        |

**Table 1.** Optical bandgap values of ZnO with variation of dopped Al

4. Conclusions
A thin film of a double layer of ZnO:Al successfully formed and the energy gap was calculated based on the data shown in figure 1, 2 and table 1. After the doping, the value of the energy gap decreased from 3.347 eV into 3.098 eV. The most significant drop occurred in the sample with 8%. Smaller energy gap is needed to accelerate the process of electron transitions that is good for photocatalyst applications. The highest peak of the absorption spectrum lies at a wavelength of 368 nm is the sample with 6% Al doping. It shows the concentration of the sample absorption in the UV region. Transmittance value for samples with doping is 79-91% in range.

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