Analysis of the optical properties of ZnO thin films deposited on a glass substrate by the So-gel method

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Abstracts
Zinc oxide (ZnO) has attracted the attention of researchers as a photocatalyst material, because ZnO has a wide direct band gap (3.37 eV) and is a semiconductor material with a large excitation binding energy (60 meV). ZnO is a photocatalyst that has many advantages, namely cheap, non-toxic, and theoretically very active under UV irradiation. The most interesting thing about ZnO semiconductor compared to other semiconductors is that ZnO can absorb most of the solar spectrum. However, there is a weakness of the ZnO semiconductor, namely the very fast recombination of charge carriers and the ZnO semiconductor has a low efficiency in the visible region which causes the ZnO semiconductor to have a wide band gap, that is the weakness of ZnO. It is necessary to choose the right method to overcome this deficiency of ZnO. One way that can be done is to increase the photocatalytic ability of zinc oxide, it is necessary to develop it in the manufacture of thin films. The method used in the manufacture of Thin Film is using the sol-gel spray coating method. The first stage is through the manufacture of ZnO precursors by dissolving zinc acetate dehydrate with isopropanol solvent through stirring, then the second stage by adding Monoethanolamine. This stirring lasted for 30 minutes at a temperature of 70°C, the precursor concentration was prepared with three different concentrations which included concentrations of 0.1, 0.3, and 0.5 M. ZnO precursor deposited on the substrate glass is blown at 400 °C. Optical properties are carried out by recording the transmittance and absorbance which are affected by increasing concentrations. The optical transmission spectra show that the transmission increases with decreasing concentration and the maximum transmission in the visible region is about 90% for ZnO thin films prepared with 0.1 M. The optical band gap value produced by the thin film of 0.1 M precursor concentration resulted in an energy band gap of 3.11 eV; thin films of 0.3 M precursor concentration produced an energy band gap of 3.07 eV; and thin film of 0.5M precursor concentration produced an energy band gap of 3.06 eV.

Keywords: ZnO precursor; photocatalyst; optical band gap; so-gel method; thin films

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1. Introduction

In today's technological developments, semiconductors is a material that is still being developed. Semiconductor is a material whose conductivity is between conductors and insulators. This material can act as an insulator under normal conditions and can turn into a conductor if given certain treatment, for example irradiated with light. Study regarding this semiconductor is still being developed, especially on the structure of the basic material forming it in order to obtain optimal properties.

Nano science and technology has revolutionized various industrial sectors. The development of nanoparticle materials today is very important. The advantages possessed by nanoparticles are in the comparison value between surface area and volume which is larger when compared to similar particles in large size. Applications that are often used are related to nanoparticles such as ZnO (zinc Oxide) materials which are determined by their fundamental properties. ZnO is widely used in various applications, as a catalyst and as a catalyst support, and as a semiconductor. ZnO has a number of unique properties in that its chemical compounds can combine with semiconductor compounds. Zinc Oxide belongs to the category of n-type semiconductor materials. ZnO has several structures, namely wurtzite (B4), zincblende (B3), and roxalt (B1).

There are many kinds of metal oxides, zinc oxide (ZnO) has attracted the attention of researchers as a photocatalyst material, because the energy band gap of ZnO is 3.37 eV. ZnO also has a large excitation binding energy of 60 meV [1]. ZnO has many applications such as light emitting diodes [2], field-effect transistors [3], gas sensors [4], photodiode ([5], solar cell [6], Photocatalys [7]. the wide energy band gap of Zinc oxide (ZnO) and high transparency in the visible range [8].

The photocatalyst process of the ZnO semiconductor occurs when the energy from the rays is given according to the band gap energy of the semiconductor material, so that there will be chemical transformation [9]. The electron-hole pair produced from this ZnO semiconductor useful in the degradation of organic pollutants.

ZnO in the form of thin film is one way to improve efficiency, crystallinity, morphology, optical properties and electricity for the better. There are several techniques that can be used to fabricate a thin layer of ZnO such as chemical vapor deposition (CVD) [10], thermal evaporation [11], sputtering [12], sol-gel [13], and others. The sol-gel method is more advantageous due to precise compositional control, ease of preparation, capable of providing homogeneous layers at the molecular level [14]. The composition can be modified, stoichiometric control, it is possible to produce layers over a large area.

ZnO is a photocatalyst that has many advantages, namely cheap, non-toxic, and theoretically very active under UV irradiation. [15]. things that become interesting when compared to Another semiconductor, ZnO has the ability to absorb for most of the solar spectrum. However, the disadvantage is that there is a very fast recombination of charge carriers and another disadvantage is that it has a fairly low efficiency in the visible region. Because the wide band gap is the main limitation of ZnO. K. [16][17]. To overcome this drawback and thus as an effort to increase the zinc oxide capability below the visible region, modifications in the synthesis of zno thin films need to be developed.

Several studies have reported that there is a way of modifying the making of a thin ZnO film such as the addition of doping, annealing after the thin layer process, and varying the concentration of ZnO precursors [17]. The results of previous studies have reported that The optical properties of thin films are affected
by differences in precursor concentrations. A study on the manufacture of thin films with optimum precursor concentrations needs to be carried out in order to obtain the most optimum concentration of precursors which produces an energy band gap that is suitable for its application for photocatalysts, because the film properties are reported to deteriorate at certain precursor concentrations. The results showed that at a concentration of 0.015M the band gap energy reached 3.64\,eV and has low crystal quality [18].

In this research, ZnO thin film was made with variation of ZnO precursor concentration 0.1M, 0.3M, 0.5M with sol-gel spray coating method. The reason for choosing this concentration is based on the results of previous studies showing that concentrations below 0.2 M indicate decreasing crystal quality and has a wider energy band gap, not suitable for photocatalyst applications. So that researchers are interested in depositing thin films with precursor concentrations above 0.2 M [18]. So in this article, we will examine the differences in the optical properties of ZnO thin films due to differences in the concentration of ZnO precursors.

2. Experiments Procedure

Making a thin film with The sol-gel method has several advantages. Among other things, the cost is cheap, no use space with a vacuum high, homogeneous composition, thickness layer can be controlled and its microstructure good enough, so this method a lot used as an alternative in thin layer production. Thin film manufacturing research with the sol-gel method already a lot done because of the many advantages this method.

In this research using the sol-gel spray coating method to know the characteristics and optical properties from a ZnO thin film with various precursor concentrations. From this research, it will be known the effect of precursor concentration on the measurement results of the energy band gap of the ZnO thin film.

Materials

In this research, the manufacture of ZnO thin films using several materials include Zinc acetate dehydrate powder (Zn (COOCH$_3$)$_2$.2H$_2$O), isopropanol solution ((CH$_3$)$_2$CHOH), monoethanolamine solution (HOCH$_2$CH$_2$NH$_2$), acetone, methanol, DI water and gas nitrogen (N$_2$).

**Preparation of ZnO precursor ZnO**

The process of making ZnO precursors begins by dissolving two of the ingredients, namely zinc acetate dehydrate and isopropanol solvent, then adding a monoethanolamine solution. This mixing is done by stirring which lasts for 30 minutes using a temperature of 70°C, produced using 0.1, 0.3, and 0.5 M precursor concentrations. **Deposition of ZnO precursor on glass substrate** the deposition process was carried out using the spray coating method, where the ZnO precursor was deposited on a glass substrate using a temperature of 400 °C on a hot plate. Finally, the thin films were ZnO annealed 450°C for 2 h.

**Optical band gap measurements**

Measurement of the optical properties of the ZnO coating was carried out using a set of tools using a UV-Vis 1240 SA spectrophotometer measured at wavelengths ranging from 200 nm to 800 nm. To obtain the energy band gap, optical absorption measurements were carried out to produce the energy band gap of the ZnO thin film. The band gap energy of ZnO thin film is calculated using the following formula [19]:

$$\alpha h\nu = B (\hbar \nu - E_g)^n$$  \hspace{1cm} (1)
where B denotes the value of the constant coefficient, α is the absorption coefficient value, $E_g$ is the energy band gap, $h\nu$ is the energy of the photon, $n$ is the index of determines the character of optical absorption. graphed the relationship between the absorption coefficient ($\alpha$) and the photon energy ($h\nu$) for the direct transition is $(\alpha h\nu)^2 = h\nu - E_g$. The $E_g$ value indicates the energy band gap of the thin film.

3. Result and Discussion

Figure 1 shows the transmittance spectrum for a ZnO thin film in various concentrations. The increasing concentration of ZnO precursors causes the edge of absorption in the thin film to shift to a longer wavelength (redshift). The increasing concentration of ZnO absorbance may increase. Sharp absorption occurs at wavelengths around 380 nm. This shows that the absorption of ZnO thin films is influenced by the concentration of ZnO precursors. There is a strong absorption capacity for the process of excitation of electrons from the valence band to the conductor material band, this is the basic principle of photocatalyst.

Figure 2, 3, and 4 shows the ZnO thin film energy band gap. The value of the energy band gap of ZnO thin film at various concentrations are tabulated in Table 1. which shows that there is an effect of molarity concentration on the value of energy band gap. the increase of molarity causes the value of energy band gap of ZnO thin film is decreased.
Figure 4. The energy band gap of ZnO thin film with a concentration of 0.5 M.

The value of the energy band gap of ZnO thin film at various concentrations are tabulated in Table 1, which shows that there is an effect of molarity concentration on the value of energy band gap. The increase of molarity causes the value of energy band gap of ZnO thin film is decreased. This is in accordance with the results of previous study which showed that increasing the molarity will decrease the energy band gap of the thin film [20]. The optical band gap and the work function of ZnO nanobars are analyzed by UV-Vis absorption spectra and photo-electron in air spectroscopy (PESA). The results show that there is an effect of solution concentration on the band gap value. As the solution concentration increases, the band gap decreases [21].

| Sample ZnO (M) | Celah pita energi(eV) |
|----------------|-----------------------|
| 0.1            | 3.11                  |
| 0.3            | 3.07                  |
| 0.5            | 3.06                  |

4. Conclusion

ZnO thin films were synthesized using the sol-gel spray coating method. ZnO precursor was prepared by dissolving dehydrated Zinc acetate in Isopropanol solvent then added Monoethanolamine and stirred for 30 minutes at 70°C, the precursor was prepared with concentrations of 0.1, 0.3, and 0.5 M. ZnO precursor deposited on the substrate glass is blown at 400 °C. Optical properties are carried out by recording the transmittance and absorbance which are affected by increasing concentrations. The optical transmission spectra show that the transmission increases with decreasing concentration and the maximum transmission in the visible region is about 90% for ZnO thin films prepared with 0.1 M. The extrapolated value of the optical band gap, for example, is 3.11 eV; 3.07 eV; 3.06 eV for the produced ZnO thin films using precursor concentrations of 0.1, 0.3, and 0.5 M, respectively.

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