Effect of ZnO Precursors Molarity on Structural, Morphological and Antibacterial Activities of ZnO Thin Films Prepared by Sol–gel Spray-coating Method

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**Abstract.** ZnO Thin film had been deposited on glass substrate with sol-gel spray coating method. The ZnO precursor was prepared by dissolving Zinc acetate dehydrate (Zn (COOCH3)2.2H2O) into isopropanol ((CH3)2CHOH) and then stirring with a magnetic stirrer at 70°C and then adding monoethanolamine (MEA: HOCH2CH2NH2) by titration. The precursor was stirred for 30 minutes until the homogeneous ZnO precursor was done. ZnO precursors have been synthesized with various precursor molarity variations of 0.1 M, 0.3 M, 0.5 M, and 0.7 M. Deposition ZnO precursor on glass substrate using spray coating technique at 400°C and annealing was done on the thin film at 450 oC for 2 hours. The results of this study indicate that there is an influence of the precursor molarity toward crystallinity, morphology and energy band gap of the ZnO thin Film. XRD measurement results show that crystallite size increases with increasing ZnO precursors molarity. The results of SEM measurements showed that the thin film samples with ZnO 0.5 M and 0.7 M precursor molarity obtained uniform grain on the thin film surface. The increase of precursors molarity can cause the decreased value of band gap energy of ZnO thin film. The increase in ZnO precursor molarity can also improve the ability of ZnO thin films to degrade Escherichia coli bacteria for better. For the best perfect degradation (100%) was obtained for ZnO thin films at a molarity of 0.5 M and 0.7 M.

Keywords: Zinc Oxide, Thin Film, *Sol-gel*, *Escherichia coli*

1. Introduction

Semiconductor materials have been the attention of researchers as photocatalyst material. In addition, the semiconductor material can be used as an antibacterial. Some semiconductors are used as antibacterials among others TiO2[1], Ag[2], Fe2O3[3], CuO[4], MgO[5] and ZnO[6]. ZnO can be one antibacterial material, this is because ZnO has some properties such as nontoxic, high purity level, direct energy band gap of 3.37 eV, electron excitation energy of 60 eV, and high transmittance in the optical region [7][8][9]. The application of ZnO to bacteria degradation can be made in form of thin film.

The thin film is a material with a thickness of not more than 10 μm that laminates a substrate [10]. The advantages of using a thin film such as can modify the material composition, good degree of homogenety and allows producing a thin layer with a larger area [11]. A Thin Film of ZnO can synthesize by various methods such as laser deposition[12], spray pyrolysis[13], the magnetron sputtering method[14], and the sol-gel method[15]. Sol-gel method has advantages such as low manufacturing cost, a simple deposition technique, and is easy to adjust composition as it can add dopant material and can fabricate layers with large area [7].

Several studies have used a ZnO thin film to degrade bacteria and have a significant decrease in the number of bacteria when added by using some doping material [16] [17][18]. In addition, it can be used by varying the of ZnO precursors molarity. The effect of different of ZnO precursors molarity on the ability of bacterial degradation has not been done by some researchers. Most of the effect of ZnO molarity on the thin film is only discussed in the morphological structure and optical properties [11] [19].

In this research, the preparation of ZnO thin films by varying the ZnO precursor molarity. Then, the ZnO precursor is deposited on a glass substrate by using a sol-gel spray coating method. The ZnO thin film characterized based on Structure and Morphology properties and applied to degrade Escherichia coli bacteria as organic pollutants.

1. Methods

The ZnO precursor solution is prepared by dissolving zinc acetate dehydrate (Zn(COOCH3)2.2H2O) (Merck KgaA, Darmstadt, Germany) into isopropanol ((CH3)2CHOH) (Merck KgaA, Darmstadt, Germany) and then stirring with a magnetic stirrer at 70 °C for 30 minutes on hot plate (Yellow MAG HS7, France). The solution has been added by monoethanolamine (MEA: HOCH2CH2NH2) (Merck KgaA, Darmstadt, Germany) with the titration method. The precursor is stirred for 30 minutes to obtain a transparent and homogeneous ZnO precursor. ZnO precursors have been synthesized with various precursor molar variations of 0.1 M, 0.3 M, 0.5 M, and 0.7 M. The glass substrate is cleaned from its impurities by immersing the substrate in acetone for 5 minutes. The glass substrats put in methanol for 5 minutes. Then, the substrate glass has been put into the aquadesfor 5 minutes and disposed of with an ultrasonic bath (Krisbow, Indonesia).

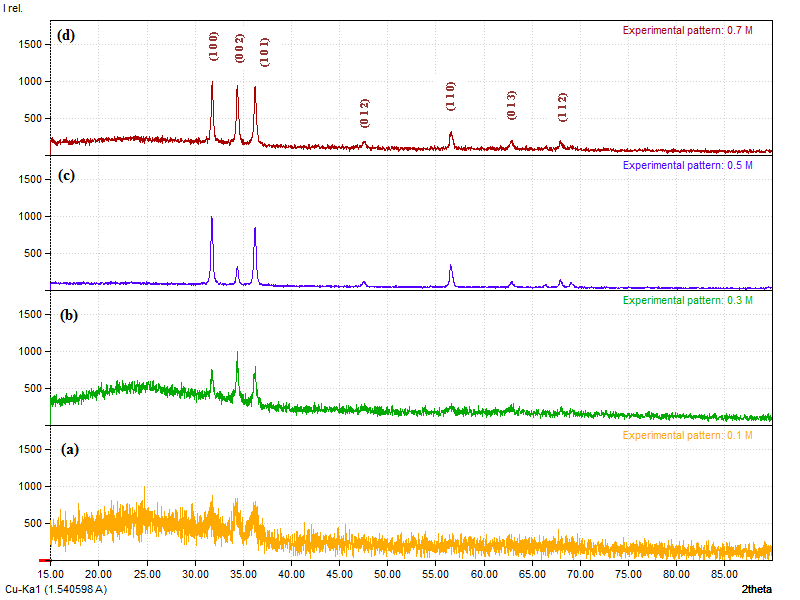
Deposition process of ZnO precursor solution into the glass substrats done firstly by coating ZnO precursors using a spray coating technique. The first step is a cleaned glass substrate placed on a hot plate at a temperature of 70 °C to increase the bonding strength of the solution with the substrate for 60 minutes. The second step, the hot plate temperature is increased to 400 °C. Next, ZnO precursor solution is inserted into the spray gun device (Krisbow HS-80, Indonesia), and ZnO precursor is sprayed evenly over a glass substrate. Then, the glass substrate stays on the hot plate with a temperature of 400 °C for 30 minutes. The hot plate temperature is slowly lowered into room temperature, and the thin film is performed annealing at 450 °C for 2 hours.

ZnO thin film is characterized by morphology and structures properties. X-ray Diffraction (XRD) is used to measure crystal quality (Shimadzu, Japan). Characterization of morphology is using scanning electron microscope (SEM) (Shimadzu, Japan).

ZnO thin film is used to degrade Escherichia coli bacteria. The Escherichia coli bacteria used had an initial molarity of 108 CFU/ml and is prepared in a petri dish. The thin films 0.1 M, 0.3 M, 0.5 M, and 0.7 M were placed into each petri dish already contained Escherichia coli bacteria. All samples were irradiated under UV C Lamp (Electronic Ballast) with a lamp with the power of 21-40W for 2 hours. The tested bacteria were validated by total plate count test (TPC) to determine the presence of Escherichia coli bacteria after treatment with a thin layer of ZnO on a various variation of precursor molarity.

1. Results and Discussion
   1. **Structural, Morphological and Optical Properties ZnO Thin Film**

Figure 1 shows the XRD pattern of ZnO thin film with the various of ZnO precursors molarity. The XRD pattern shows that the crystalline ZnO thin film can form well on the glass substrate shown by the emerging crystalalite phases of ZnO

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**Figure1.** XRD pattern of ZnO thin film on a variation of ZnO precursor molarity of (a) 0.1 M, (b) 0.3M, (c) 0.5M, (d) 0.7M

The XRD spectrum results show that the ZnO formed is hexagonal Wurtzite with the orientation of the plane (100), (200), (101), (012), (110), (013), and (112). The dominant peak is seen at the Bragg angle between 21o-70o. XRD results show that the ZnO precursor molarity can increase the angular value of 2θ shifts to higher angle. XRD peak in ZnO thin films with ZnO precursor molarity of 0.5 M and 0.7 M show better crystallinity than ZnO precursor molarity of 0.3M and 0.1 M. Table 1 shows that the full width at half maximum (FWHM) value decreases with increasing of ZnO precursor molarity. This shows that the crystallinity of thin films with high molarity (0.5M and 0.7M) has good crystallinity. This result shows that ZnO thin film with highest concentrate is able to narrow the full width at half maximum (FWHM) value [19].

Furthermore, the average size of thin film crystals is calculated using the Scherrer formula [19]:

|  |  |
| --- | --- |
|  | (1) |

Where D is the size of the crystal, K is the constant (for the oxide material = 0.94), λ is the wavelength of the X-ray source used (in this study λ = 1,5406 Å) β is the FWHM value and θ is the top of Crystal diffraction. Based on the results of the size calculation of the crystal shows that the increased of ZnO precursors molarity causes the increasing size of crystals. The thin film which has the largest crystal size is a thin film with a molarity of 0.7M. Similar results have shown that the crystal quality of the ZnO thin film increased significantly with increasing molarity of ZnO precursors [20].

|  |  |
| --- | --- |
|  | (2) |

Where is interplanar spacing for planes with Miller indices (hkl). The calculation of lattice parameters at peak (002) is tabulated in Table 1. The standard value for ZnO polycrystalline powder is c = 5.201 Å [21][22]. The results of the calculation of lattice parameters in the direction of c obtain the value of 5.2409 Å, 5.2276 Å, 5.2231 Å, and 5.2070 Å for the molarity of thin film ZnO 0.1 M, 0.3 M, 0.5 M, and 0.7 M, respectively. All of ZnO crystals in each molarity obtained a larger lattice parameter value compared to standard ZnO lattice parameters c = 5.201 Å.Which means the lattice on the ZnO crystal has a lattice strain in the direction c. The value of the lattice strain is calculated using the formula [23]:

|  |  |
| --- | --- |
|  | (3) |

The calculation results obtained increasing of ZnO precursor molarity lattice strain value decreased. A lattice strain on the ZnO crystal causes the dislocation density (δ). Calculation of dislocation density (δ) is using formula [23]:

|  |  |
| --- | --- |
|  | (4) |

Table 1 shows the relationship between particle size and molarity. The quality of the crystal size has increased significantly by adding of ZnO precursors molarity.

**Table 1.** Detailed peak position (θ), full width at half maximum (FWHM), average crystallite size (D), lattice constant (cf), Average strain (ε) and dislocation density (δ) for the different films.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sampel ZnO | (0 0 2) Peak | | D (nm) | cf (Å) | Average strain (ε) (10-3) | Dislocation density (δ) lines/m2 |
| Position | FWHM |
| 0.1 M | 34.19 | 0.56 | 15.46 | 5.2409 | 7.67 | 1.42 x1016 |
| 0.3 M | 34.28 | 0.24 | 36.08 | 5.2276 | 5.11 | 0.40 x1016 |
| 0.5 M | 34.31 | 0.2 | 43.30 | 5.2231 | 4.24 | 0.28 x1016 |
| 0.7 M | 34.42 | 0.2 | 43.32 | 5.2070 | 1.15 | 0.076 x1016 |

Figure 2 shows the SEM image on ZnO thin film with various precursor molarity. The morphology results of the ZnO thin film show that the ZnO precursor molarity increases better result. This is indicated with a uniform grain formed on a ZnO thin film with high molarity (0.7 M and 0.5 M). The morphology of a ZnO thin film of 0.1M has a surface like a cavity. While on a ZnO thin film with a molarity of 0.3M has a surface like ganglia that is not evenly distributed on the surface of thin film. ZnO thin film with a high molarity (0.5 M and 0.7 M) has a uniform grain on the surface of a thin film. This can be explained, as the molarity increases, the amount of Zinc acetate dissolved more which causes the electrostatic interaction between the solute particles to become larger so that many of the solutes that are assembled form a uniform grain on the surface of thin film[19].

|  |  |
| --- | --- |
| D:\PKPT DATA AKU\sem\ZnO 0,1m 450c\sem 20000x.bmp | D:\PKPT DATA AKU\sem\ZnO 0,3m 450c\sem 20000x.bmp |
| (a) | (b) |
| D:\PKPT DATA AKU\sem\ZnO 0,5M 450C\sem 20000x.bmp | D:\PKPT DATA AKU\sem\ZnO 0,7 m 450c\sem 20000x.bmp |
| (c) | (d) |
| **Figure 2.** SEM image on a ZnO thin film (a) 0.1 M, (b) 0.3M, (c) 0.5M, (d) 0.7M | |

The value of the band gap energy of ZnO thin film at various molarity can be seen in Figure 3. Based on Figure 3, there is an effect of molarity molarity on the value of the energy band gap. The increase of molarity can cause the decreased value of the energy band gap of ZnO thin film. The results of this research are consistent with the results of the Soylu et al [11] this is because the energy band gap changes are affected by the size of the crystal, the strain, and the precursor molarity [24].

Figure 3. Band gap energy value for ZnO thin films with various precursor molarity

* 1. **Bacteria *E.coli* Degradation**

The ability of ZnO thin film to degrade *Escherichia coli* bacteriais using total plate counter (TPC). TPC is a quantitative measurement of the total number of bacteria. These measurements are used to provide an image of the bacterial population within a medium. The total *Escherichia coli* bacteria and percentage degradation after UV irradiation to sample for 2 hours shown in Table 2. Table 2 shows a decrease in the number of *Escherichia coli* bacteria after treatment of the photocatalyst process using a ZnO thin film with UV irradiation for 2 hours. Increased of ZnO precursors molarity causes better degradation ability. The best degradation perfectly (100%) is obtained for a ZnO thin film at a molarity of 0.5 M and 0.7M.

This photocatalyst activity is related to the ZnO band gap energy. Increased degradation can be correlated with a decrease in the band gap energy of ZnO. The increasing of ZnO precursors molarity causes a decrease in energy band gap from the ZnO thin film. the decrease in the band gap of energy can reduce the minimum energy required for excitation of electrons so that more energy ranges can be used to generate electron pairs and holes. *E.coli* bacteria that have been decomposed due to the photocatalyst process. This corresponds to the theory that ZnO produces hydroxyl radicals that can damage *E.coli* membranes that can kill bacterial cells [25].

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