Synthesis and Characterization of ZnO Thin Layers using Sol-Gel Spin Coating Method

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Abstract

The potential of thin layer in many applications has led to research on the development of many new materials and their fabrication methods. This study aimed to synthesize a thin layer of ZnO using the facile and low-cost sol-gel spin coating method. The ZnO thin layer is deposited on a glass substrate and analyzed to observe the influence of the deposition variables such as heating and rotation speed, and its aging. The characterization methods include the identification of the formed phase using X-Ray Diffractometer (XRD), and the microstructure and elemental composition using Scanning Electron Microscopy (SEM) coupled with EDS (Energy Dispersive Spectrometer). The study shows that a thin layer of ZnO is successfully deposited on a glass substrate by heat treatment at temperatures of 300 °C and 500 °C. Furthermore, XRD reveals that higher heating temperatures result in higher diffraction peak intensity. At a heating temperature of 300 °C crystals are formed but are not yet perfectly oriented, while they are at 500 °C. On the other hand, higher spin coating rotation speed gives rise to lower intensity of diffraction peak. The ZnO crystallization is easier to form in the coating process with a lower rotation (1500 rpm). Interestingly, the thin layer is stable over time where there is no significant change in each sample, both in terms of intensity and width of the ZnO crystal peak. The results indicate that gel precursor aged less than two days can form ZnO crystals. Finally, SEM results show that the surface morphology of the ZnO layer heated at 500 °C has an average grain size of 300 nm. Based on the cross-sectional results of SEM shows that the higher the coating rotation speed has resulted the thinner of the ZnO layer, where the thickness of the resulting layer is on order >5 μm.

Keywords: synthesis; characterization; ZnO thin layer; sol-gel spin coating

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INTRODUCTION

In recent decades, as the demand for energy continues to increase, there has been tremendous interest in developing renewable energy sources and environmentally friendly technological device systems (Matsuda & Kawamura, 2016), some of which include fuel-cells, solar-cells, supercapacitors, and efficient batteries (Tan et al., 2021). In accordance with the interest in many fields of application, thin layers of several materials have been developed by the sol-gel method (Soo et al., 2013a, 2013b). Since
being introduced by Groove in 1852, thin layer technology has undergone many developments in terms of manufacturing methods, materials used, and applications (Greene, 2017). In the thin layer processing technique, the material commonly used is metal (Jittiarporn et al., 2017; Mironyuk et al., 2020; Shi et al., 2020; Tan et al., 2020), organic, inorganic, and hybrid organic-inorganic (Kawamura et al., 2010; Nisticò et al., 2017; Takahashi, 2018; Takahashi et al., 2014).

The advancement of thin films by the sol-gel method for various applications is highly dependent on the material used. In fuel-cell applications, for example, PDDA films and microparticles of PhSiO_{3/2} succeeded in increasing proton conductivity to achieve a stable proton supply (Daiko et al., 2008). Likewise, Pt/TiO_2 was demonstrated as an electrocatalyst for fuel-cell electrolyte membrane applications (Nbelayim et al., 2020). The performance of a lightweight, high-capacity battery is developed from the synthesis of Li/Ti double alkoxides in a Li_4Ti_5O_{12} thin film (Mosa & Aparicio, 2020), and LiF/FeF_2 in the form of Li_0.5FeF_3 (Kim et al., 2012; Tawa et al., 2019). Formation of superhydrophobic/superhydrophilic layers in film fabrication including surface design and film coating using Al_2O_3, ZrO_2, and TiO_2 materials (Tadanaga et al., 2004). In addition, the development of thin films by the sol-gel method is used in the extraction technology of waste disposal, especially heavy metal adsorbents, such as electro-spinned flexible Fe_3O_4 fibers (Shi et al., 2020) and yttria-stabilized ZrO_2 membranes (Qin et al., 2020). The most extensively researched is the application of thin layers as solar-cells (dye-sensitized solar cells, DSSC) (Abd-Ellah et al., 2016; Nbelayim et al., 2017, 2018, 2020; Tan et al., 2017; Toe et al., 2020), from zinc oxide material (ZnO) (Khan et al., 2017; Muchuweni et al., 2017; Prasada Rao et al., 2010).

Sol-gel coating techniques commonly used include spray coating, dip coating, roll coating, and spin coating (Tan et al., 2021). Among these, spin-coating method is the most frequently used (Khan et al., 2017). This method combines simple physical and chemical methods and has several advantages compared to other methods, for instance being cost-efficient with relatively simple setup, and excellent control over the thickness (through parameters of time, rotational speed, and viscosity of the solution) and the homogeneity of the layer (Cheng et al., 2003).

Among thin film-forming materials, zinc oxide (ZnO) is the most extensively studied because it is one of the transparent semi-conductive oxides (Zou et al., 2007) with a relatively high exciton binding energy (60 mEV) and a wide band gap around of 3.2 to 3.4 eV (Rwenyagila et al., 2014; Sivaramakrishnan & Alford, 2010; Valverde-Aguilar & Manriquez Zepeda, 2015). These advantages of optical and electrical properties allow ZnO to be applied as optical waveguides, optoelectronic devices (Çopuroğlu et al., 2009; Khan et al., 2017; Rwenyagila et al., 2014), piezoelectricity, conductive gas sensors, transparent conductive electrodes, photocatalysts and DSSC (Djurišić et al., 2010). One of the exciting properties of ZnO is its crystal formation process that occurs at temperatures under 400 °C. This phenomenon depends on the type of deposition and the solvent used. Previous studies showed that crystalline ZnO was formed using ethylene glycol and glycerol as a solvent at a heating temperature of 200 °C (Torres Delgado et al., 2009). Heating at temperatures below 300°C is an early stage of heating, where the crystal structure has been formed but has not been oriented perfectly. Furthermore, with higher heating at 400 °C and 500 °C, the ZnO crystal structure will be perfectly oriented (Raoufi & Raoufi, 2009). Another attractive property of ZnO to observe is aging. Aging is the storage of sol-gel for a certain time.
before being used as a coating material. The aging process affects the physical, electrical, and optical properties of the ZnO thin film (Xu et al., 2009).

Literature surveys reveal that reports on the properties of ZnO thin films deposited by the sol-gel technique is lacking (Khan et al., 2017). Here, we develop a thin layer of ZnO material by the sol-gel spin coating method and assess its crystallization properties and morphology. The variables that are the focus of this study include heat treatment, rotation speed, and aging.

**METHOD**

A thin layer was deposited on a glass substrate of 5 x 10 mm$^2$ using a sol-gel method using zinc acetate dehydrate [Zn(CH$_3$COO)$_2$.2H$_2$O] powder (M: 219.49 g/mol, 99% Merck, Germany) with a molar ratio of 1:1 MEA:ZnAc. Ethanol (C$_2$H$_6$O) (99% technical, Merck) was used as solvent and ethanolamine (MEA: C$_2$H$_7$NO) as stabilizer, each with a purity of 99%. The solution was prepared by magnetic stirring at ±70 °C for 30 minutes. ZnAc was rather difficult to dissolve in ethanol. Therefore the dissolution process must be accompanied by heating, which was carried out on a hot plate with a temperature range of 80 to 100 °C. This was followed by the addition of MEA. After the heating process for 30 to 40 minutes, the solution was then allowed to stand at room temperature to form a gel. The gel was the divided into five parts and each was aged for 0, 10, 24, 48 and 72 hours, in air with a temperature of ±25°C and humidity of 70±5%.

The thermal behavior of ZnO gel was tested using Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA). This analysis aimed to observe changes in energy and mass as function of temperature. The DTA/TGA analysis results are used as a reference in determining the temperature at which the phase transformation occurs.

![Figure 1. DTA-TGA test results of ZnO thin film deposited by spin coat sol-gel.](image)

Based on the results of the TGA (Fig. 1), it can be seen that there is 90% decrease in mass up to a temperature of 280 °C, after which there is no further decrease in mass. This decrease in mass is followed by energy release or endothermic (DTA Graph in Fig. 1). Based on the DTA and TGA graphs, it is estimated that the change of ZnO + H$_2$O into ZnO crystals occurs on heating above 280 °C, so that the ZnO layer pre-heating process can be carried out at a temperature of 300 °C.

The deposition of the thin layer on a glass substrate with spin coating was also carried out at 1500, 2000, and 2500 rpm variations. A thin layer of ZnO was heated
using a furnace. The heating process was carried out in 3 stages. The first heating for 1 hour at a temperature of 100 °C (calcination) aimed to gradually remove the water content and residual solvent in the layer. The second heating at 300 °C, where the temperature was slowly increased from room temperature to 300 °C for 5 hours, was held for 6 minutes. This stage was a pre-heating stage that functioned to remove solvents from ethanol, water, MEA, and facilitated ZnOH conversion to ZnO. The next stage was post-heating or final heating at a temperature of 500 °C. Like the pre-heating process, the temperature rise was set slowly from room temperature to 500 °C in 10 hours, then held for 10 minutes. This post-heating functioned to form ZnO particles with uniform crystal orientation and eliminate the pores.

The characterization of the coating results included identification of the formed phase using X-ray Diffractometer (XRD) with the help of a search match and refinement program using Rietica software with the comparison is standard data (CPI ZnO 1011259), layer microstructure, and elemental composition observed by Scanning Electron Microscopy (SEM) coupled with EDS (Energy Dispersive Spectrometer).

**RESULTS AND DISCUSSION**

**Effect of heating on the ZnO crystal layer**

The X-ray diffraction pattern of the ZnO layer deposited at 2000 rpm at various heating temperature and aged for 24 hours is shown in Figure 2.

![Figure 2. XRD pattern of ZnO layer with the variation of heating temperature](image)

Based on Figure 2, it can be seen that the layer heated at a temperature of 100 °C forms two peaks at an angle of 33.15° and 59.30°. These peaks correspond to zinc propianate (C₆H₁₀O₄Zn) phase and zinc salicylate dihydrete {(C₆H₁₀O₆Zn).2H₂O} phase, respectively. These peaks clearly originate from the solvents on the layer.

At a heating temperature of 300 °C crystals are formed but are not yet perfectly oriented. At 500 °C, the ZnO crystals are perfectly oriented. This is consistent with the results of DTA-TGA (cf. Fig. 1) in that the formation of ZnO occurs above 280 °C. With the help of the Rietica program, hexagonal ZnO has been formed with lattice parameters for a temperature of 300 °C (a = 3,245 Å, c = 5,209 Å) and a temperature of 500°C (a = 3,249 Å, c = 5,205 Å). In the range of 2θ of 25° to 60°, crystal plane peaks are formed, indicating that the layer obtained is polycrystalline.

Pre- and post-heating affect the ZnO layer in the form of solvent evaporation and reaction material decomposition. At low pre-heating temperature (< 300 °C), the (100), (002), and (101) diffraction peaks appeared with random preferential growth. This
happens because at this temperature, the reagents have completely evaporated, and the thermal decomposition of the precursors has not yet occurred. Still, they occur at post-heating temperatures above 500 °C (Suwanboon et al., 2008). The increase in the intensity of the diffraction peak at higher temperatures is due to greater energy available to increase the movement of atoms, which increases the quality and crystallization of the layer (Mandal et al., 2008).

**Effect of spin coating speed on ZnO layer**

![Figure 3](image)

**Figure 3.** The XRD pattern of the ZnO layer with variations in spin coat rotational speed.

Figure 3 shows XRD results for ZnO layers made with variations in rotational speed of 1500, 2000, and 2500 rpm. The XRD peaks of the three samples show a decrease in intensity as rotation speed increases. This happens because ZnO crystallization is easier to form in the coating process with a lower rotation (1500 rpm).

**Effect of aging on ZnO crystal layer**

The XRD pattern of the synthesized ZnO layer with variations in aging of the precursor gel is presented in Figure 4.

![Figure 4](image)

**Figure 4.** XRD pattern of deposited ZnO layer with an aging variation.

Based on Figure 4, there is no significant change in each sample, both in terms of intensity and width of the ZnO crystal peak. These results indicate that gel precursor aged less than two days can form ZnO crystals. The results of another study reported that after aging for seven days, the peak intensity (002) of ZnO increased compared to samples aged for up to two days (Maldonado et al., 2010). This may occur because
Aging can cause further condensation of active groups and ZnO aggregation in solution and cause significant growth at peak intensity (002) of ZnO (Fathollahi & Amini, 2001).

**Surface morphology of ZnO thin layer**

SEM photos of the ZnO layer surface heated at 100, 300, and 500 °C, respectively, are presented in Figure 5.

![Figure 5. SEM photos of the ZnO layer surface heated at: (a) 100°C, (b) 300°C, and (c) 500°C.](image)

At a temperature of 100°C (Fig. 5a), the layer is still coarse and porous, with a pore size of approximately 6–8 μm. This is because the layer still contains water molecules and solvents that have not completely evaporated at this temperature. When the layer is heated at 300 °C (pre-heating), the remaining organic matter can evaporate completely, and ZnO grains begin to grow (Fig. 5b), but the distance between the particles is still relatively large. When the ZnO layer is heated at 500 °C (Fig. 5c), the atoms in the existing grains receive sufficient driving force energy to diffuse to form new, larger grains. As a result of this inter-grain diffusion, necking will be formed, resulting in the shrinking of the boundary between grains and porosity (Fig. 5c). The average grain size at this temperature is about 300 nm.

To this end, the morphology and crystal structure of the ZnO layer made by the sol-gel process is influenced by the solvent, pre-heating and post-heating temperatures, sol concentration, substrate, and coating process (Habibi & Khaledi Sardashti, 2008). The ZnO layer's nucleation thermodynamics and crystal growth showed a transformation from an amorphous to crystalline state. The growth of crystals with the dominant c-axis orientation depends on the surface energy of the layer and the glass substrate and the interfacial energy between them. In crystal growth, the growing fields depend on the loss of slow-growing fields, with lower surface energies.

In addition to heat treatment, the morphology and thickness of the ZnO layer are also affected by the spin coating speed. Figure 6 shows the surface morphology of the coated layer at 1500, 2000, and 2500 rpm.
Figure 6. SEM photos of the ZnO layer surface coated with variations in rotation speed: (a) 1500 rpm, (b) 2000 rpm, and (c) 2500 rpm.

Based on Figure 6, it can be seen that the higher the rotation speed, the smoother the coating obtained, with smaller average grain size. The ZnO layer coated at 1500 and 2000 rpm has similar average grain size of 300 nm, while the ZnO layer coated at 2500 rpm has an average grain size of 100 nm. The results are consistent with previous studies that reported that the higher the rotational speed used to make the ZnO layer, the smaller of grain size produced (Ilican et al., 2008). The cross-sectional analysis of the coated ZnO layer with variations in rotational speed is presented in Figure 7.

Figure 7. Cross-section of the coated ZnO layer with variations in rotational speed: (a) 1500 rpm, (b) 2000 rpm, and (c) 2500 rpm. (1 = air, 2 = ZnO layer thickness, 3 = substrate)

The results show that the thickness of the ZnO layer coated with 1500 rpm rotation is about 30 µm (Fig. 7a), while the layer coated with 2000 rpm rotation is about 20 µm (Fig. 7b), 2500 rpm at about 5 µm (Fig. 7c). Therefore it is confirmed that the thickness of the ZnO layer gets thinner as the rotation speed increases. In forming a coating on the substrate, it takes a large enough centrifugal speed to distribute the gel over the entire surface and remove the excess gel to the outside of the substrate. If the rotational speed is increased, the previously attached gel will be thrown out of the substrate, and the layer will thin out, or it can also disappear. This is because the binding force between the substrate and the gel is not strong enough to withstand the centrifugal force, which is too high. So, the faster the coating rotation, the more gel will leave the substrate so that the resulting layer is thinner.

From the results in Figure 6, although the layer looks smooth, most of the areas in the layer have many micron-sized cracks. These cracks are caused by the uneven heating rate on the surface of the coating layer and the different thermal coefficient between the substrate and the coating layer. Cracks also occur in the area between the
layer and the substrate (Fig. 6). Based on the cross-sectional photo of the ZnO layer (Fig. 7), it can be seen that the layer is not completely attached to the substrate. This condition makes the coating to peel off easily when exposed to scratches or friction from the outside. Cracks can also be seen from the EDX results (see Fig. 8). From the Figure we also see existence of Ca (0.98% wt) in the cracks, that originates from the substrate (from XRF results). Although the Ca content is small, this still indicates that the cracks are intense they penetrate the ZnO layer. Based on the Figure 8, it is estimated that the thickness of the ZnO layer formed with heating at 500 °C is about 5 μm to 20 μm.

![Figure 8. EDX results of ZnO layer on a glass substrate: (a) surface topography, and (b) elemental content.](image)

Microcracks may occur on the ceramic coating surface with the cracks spreading along the grain boundaries (Sakka, 2018). This phenomena happens because the layer and the substrate have a huge difference in the coefficient of thermal expansion. The spread of microcracks along the grain boundaries is formed before the crystallization process. These microcracks can be prevented by equalizing the coefficient of thermal expansion (α) between the coating and the substrate. For example BaTiO3 (α =140 x 10^{-7} K^{-1}), the layer has microcracks when deposited on a SiO2 glass substrate (α = 5 x 10^{-7} K^{-1}), but BaTiO3 has no microcracks on a single crystal substrate of MgO (α = 135 x 10^{-7} K^{-1}) (Sakka, 2018). Microcracks can occur during the heating process at low temperatures (100°C - 400°C). In another study (Kozuka & Hirano, 2000) reported that in the production of the titania layer, the crystal structure appears at a temperature of 500°C, while cracks appear at temperatures below it. This means that the crack occurs before the crystallization process.

Microcracks can also occur due to variations in the thickness of the gel layer. In the titania layer made with variations in thickness, the thicker layer is obtained, which tends to crack at low temperatures (Kozuka & Hirano, 2000). This happens because the thickness affects the occurrence of intrinsic stress during the heating process. The crack formation also depends on the heating rate. Cracks appear at higher temperatures when the coating is heated at a low heating rate. At low heating, the rate will produce a smaller porosity. This indicates that the low heating rate allows sufficient time for the coating to solidify during heating resulting in high tensile stresses in the substrate plane.
CONCLUSION

The ZnO layer was successfully deposited on a glass substrate by heat treatment at 300 °C and 500 °C. At a heating temperature of 100 °C, the ZnO structure has not yet been formed, and when the heating temperature is 300 °C, crystals have started to form but have not been oriented perfectly. ZnO crystals are perfectly oriented at 500 °C. XRD results show that the higher heating temperature has resulted in higher diffraction peak intensity. At a heating temperature of 300 °C crystals are formed but are not yet perfectly oriented while at 500 °C they are. On the other hand, higher spin coating rotation speed gives rise to lower intensity of diffraction peak. The ZnO crystallization is easier to form in the coating process with a lower rotation (1500 rpm). Interestingly, the thin layer is stable over time where there is no significant change in each sample, both in terms of intensity and width of the ZnO crystal peak. The results indicate that gel precursor aged less than two days can form ZnO crystals. SEM results show that the surface morphology of the ZnO layer heated at 500 °C has an average grain size of 300 nm. The cross-sectional results of SEM show that the higher the rotation speed, the thinner the resulting ZnO layer, where the thickness of the resulting layer is on the order of > 5 μm.

RECOMMENDATION

The XRD results of the ZnO layer deposited on the glass substrate were all polycrystalline in structure. Efforts to make ZnO layer single crystal must be continued, by proper selection of substrate and higher post-heating. In addition, the SEM results show that the surface morphology of the ZnO layer is not homogeneous, there are many cracks and the size is still thick. For this reason, it is necessary to carry out more in-depth experiments in terms of the use of appropriate concentrations, speeds, and rotation times, as well as the selection of a substrate that has a heat capacity and plane orientation in accordance with the ZnO layer, for example alumina ceramic material.

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