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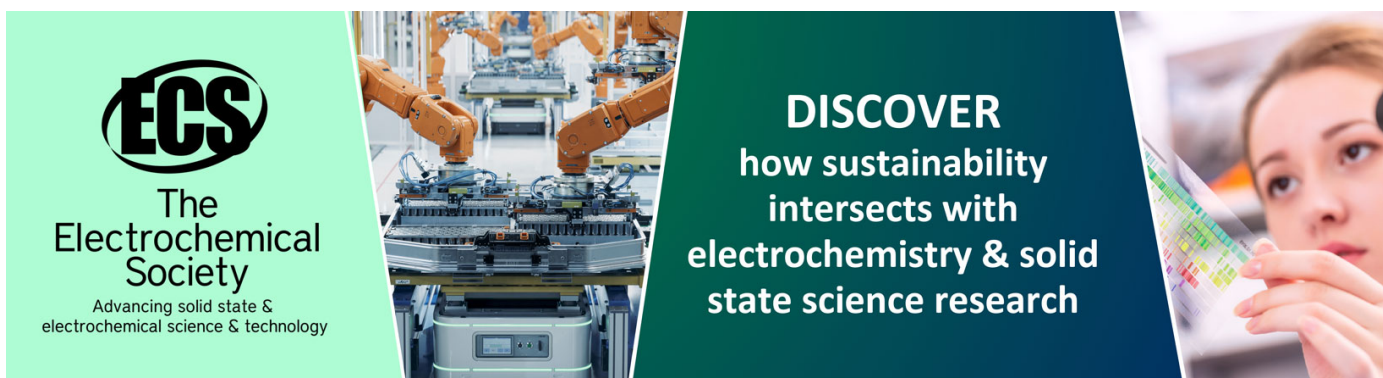
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The Effect of Thickness of ZnO Thin Films on Hydrophobic Self-Cleaning Properties

N Mufti, D Arista, M Diantoro, A Fuad, A Taufiq and Sunaryono

Department of Physics, Faculty of Mathematics and Natural Sciences,
Universitas Negeri Malang (State University of Malang) Jl. Semarang 5, Malang
65145, Indonesia

Email: Nandang.mufti.fmipa@um.ac.id

Abstract. Glass coating can be conducted by using ZnO-photocatalyst based semiconductor material since it is preminent in decomposing organics compound and dangerous bacteria which often contaminates the environment. If there are dirt containing organics compound on the glass, the ZnO photocatalyst coat can be applied as self-cleaning, usually called self-cleaning glass. It depends on the coating thickness which can be controlled by setting the speed of spin coating. In this research, the various rotating speeds of spin coating were conducted at 2000 rpm, 3000 rpm, and 4000 rpm to control the thickness. The raw materials used in this research were $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ (PA 99,5%), Ethylene glycol, Diethanolamine (PA 99%), Isopropanol Alkohol, Glycerol, and Ashton. Synthesis methods used were sol-gel prior to spin coating technic were applied. The results of the film were characterized by using SEM, XRD, and UV-Spectrophotometer. The crystal structure was analyzed by using Highscore plus and GSAS software, the size crystal was calculated by using Scherrer equation, a contact angle with ImageJ software. It was shown that ZnO thin film had been successfully synthesized with the crystal size around 21 nm up to 26 nm. The absorption value is higher due to the increasing of coat thickness with bandgap ± 3.2 eV. The test result of hydrophobic and hydrophilic characteristics show that all samples of ZnO thin film with the thickness $\pm 1.050 \mu\text{m}$, $\pm 0.450 \mu\text{m}$, $\pm 0.250 \mu\text{m}$ can be applied as self-cleaning glass. The best result was gained with the thickness of thin film $\pm 1.050 \mu\text{m}$.

Keywords: Photocatalyst, ZnO, thin film, spin coating, self-cleaning property

1. Introduction

The use of glass has increased in the various field especially in building construction or household property. Glass also used as a decorator for the alternative of energy saving since it can help lighting of building in the day. One of the glass weaknesses is it is easily contaminated by dirt that gradually reduces the room lighting even they can damage the surface of material. Therefore, it needs other alternatives to solve such problem. One of them is surface engineering technology [1,2]. One kind of surface engineering technologies is coating. Glass coating can employ photocatalyst based semiconductor material. Semiconductor photocatalyst has drawn people's attention as it produces free radical (OH) that can mineralize dangerous substances into environment friendly-substance [1-3].

ZnO is one of the photocatalytic semiconductors. ZnO has been applied as the main material of light transmitter diode, cathode ray tube, electroluminescence thin film, and a gas sensor [4,5] ZnO



gives better efficiency rather than TiO_2 as the photodegradation in water solution [5]. Besides, the combination of hydrophobic photocatalytic effectivity and super hydrophilic allows ZnO becoming a good candidate for self-cleaning glass application.[1,5]. ZnO has some such preeminences as stable to the light (it is not degraded when it does light absorption), non-toxic, photosensitive, cheap cost, and it is able to decompose organical compound and harmful bacteria that often contaminates [6,7].

The thin ZnO Films can be created through some methods such as vapor deposition, pulsed laser deposition, molecular beam epitaxy, metal organic chemical vapor deposition, sputtering, electron beam evaporation, spray pyrolysis and spin coating [4,8]. The sol-gel spin coating is a method to form a coat from photoresist polymer material which is positioned on the surface and other flat materials. After the sol-gel solution is dripped on the substrate, the rotary speed is set by centrifugal force to produce homogeneous thin coat. This sol-gel spin coating method combines physics and chemistry methods. This method is considerably easy and effective to make thin coat only by setting the time parameter, rotation speed as well as solution viscosity. Sol-gel spin coating method has some benefits, for examples, cheap cost, low annealing temperature, easy-controlled composition and structure, homogeneous composition, no need high vacuum, the coating thickness is controllable and shows good microstructures. This method, therefore, is frequently used in this recent years (Foo, 2013). This method is easy and effective to form thin coat only by setting the time, rotation speed as well as solution viscosity parameters [8,9]

There two types of the self-cleaning coating, i.e. hydrophobic and hydrophilic which has getting interested for daily application [1,5,5]. Hydrophilic is a condition when water touches the glass; the particle spreads out the water over the glass so that it cleans the glass automatically [5]. Hydrophobic is a condition in which the surface cannot hold the water and has big contact angle size when it can not do irradiation. The physical surface might influence the hydrophobic characteristic of the material, the substance coated by the material is in nano size and has wider surface rather than bulk material [2]. When the glass is touched by water, the glass surface will be brighter. The glass will look cleaner for a longer time, and the maintenance cost is cheaper. Self-cleaning glass helps to reduce the use of glass cleaner products which are not environmentally safe, so the environment pollution might reduce as well [1–3]. The photocatalytic coating of ZnO can be applied as self-cleaning. However, the appropriate of ZnO film thickness to self-cleaning properties is still rarely investigated. Therefore, in this study, we investigate the effect of ZnO film thickness to self-cleaning properties. The thickness ZnO Films controlled by setting the speed of spin coating. The crystal size, crystal structure, of ZnO films were characterized by XRD, while effectivity of self-cleaning glass of ZnO films was characterized by hydrophobic and hydrophilic behaviors.

2. Experimental Method

This sample has prepared by glass cleaning route before coating process. The glass was washed with soap, soaked in alcohol 96% for 15 minutes and soaked in acetone for 15 minutes. The glass, subsequently, was put into an oven at temperature of $105\text{ }^{\circ}\text{C}$ for one hour. Before using the glass, it was cooled to room temperature. After that, the making process of the solution with sol-gel method and solution of ZnO was prepared by using the raw material of zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}]$. Firstly, 5.488 g zinc acetate dihydrate was mixed into 3 mL of ethylene glycol. It was then heated at a temperature of $150\text{ }^{\circ}\text{C}$ for 30 minutes. After that, 20 ml of isopropyl alcohol (IPA) was added and stirred at room temperature for 30 minutes. When the solution was whitish, 0.5 mL glycerol was added and following by adding 1.5 mL of diethanolamine (DEA) as a stabilizer. Subsequently, it was stirred for 60 minutes to obtain a homogeneous sol solution. The coating synthesis was, then, conducted by using spin coating method to get thin coat deposition on a substrate which subsequently. The ZnO created was then shaken and dripped on glass surface to cover the entire surface. The spin coating was set at rotation speed of 2000, 3000, and 4000 rpm for 30 seconds. The resulted film was then heated at a temperature of $300\text{ }^{\circ}\text{C}$ for 10 minutes and subsequently annealed at a temperature of $550\text{ }^{\circ}\text{C}$ for one hour. The ZnO thin films were characterized by using X-ray Diffractometer, SEM, and UV-VIS Spectrometer. The characteristics of hydrophobic and

hydrophilic of ZnO thin films was conducted by dripping water on the coated surface. For hydrophilic, the sample was irradiated under sunlight for 30 minutes, and then the water was dripped on it.

3. Results and Discussion

The microstructure of ZnO thin films were analyzed by using SEM to obtain the samples' thickness and morphology. Table 1 shows the average coat thickness of each ZnO thin film from the different speed of spin coating.

Table 1. The Thickness of ZnO Thin Films

Rotation speed (rpm)	Average film thickness (μm)
2000	1.050
3000	0.450
4000	0.250

From Table 1, we can see that the lower speed of spin coating resulted in bigger film thickness and vice versa. The decrease of film thickness may caused by the high rotation speed which leads to higher centrifugal force. The force brings the liquid distribution at a higher rate and spread out more to cover a larger area on the glass substrate. Figure 1 shows the morphology of ZnO thin films with 50.000 times magnification.

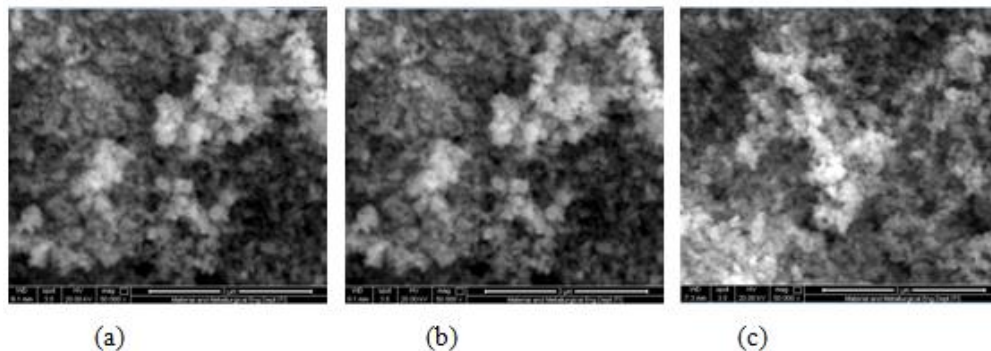


Figure 1. Morphology of ZnO thin films with the rotation speed (a) 2000 rpm (b) 3000 rpm (c) 4000 rpm

The diffraction pattern of ZnO thin film sample with an average thickness of 0.250, 0.450, and 1.050 μm are shown in Figure 2. From Figure 2, we can see that when a coat was being thicker, the crystal orientation of thin film will preferably grow on (002) plane. The films with lower thickness tend to grow with less preferred orientation. The later exhibits more randomly showing the existence of (100), (002) and (101) Bragg's planes.

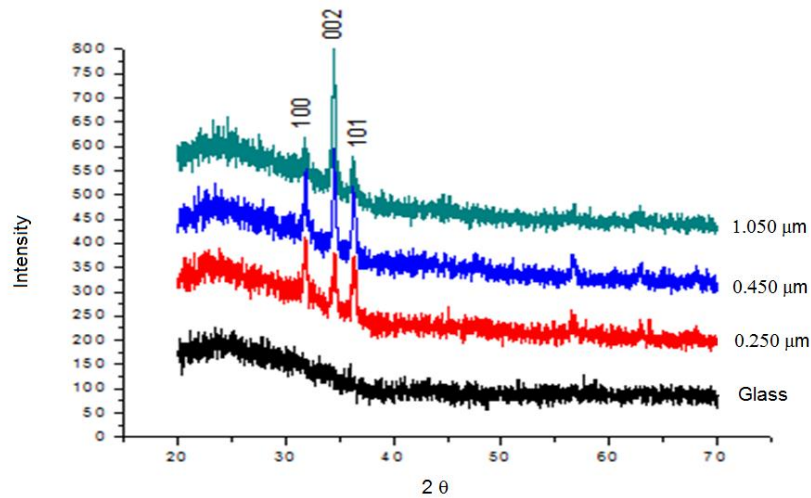


Figure 2. Diffraction patterns of ZnO thin films with various thicknesses

Table 2. The Analysis Result of Crystal Structure of Thin Film ZnO

Parameter	Model	$\pm 1.050 \mu\text{m}$	$\pm 0.450 \mu\text{m}$	$\pm 0.250 \mu\text{m}$
$a = b \text{ (\AA)}$	3.250	3.249	3.249	3.248
$c \text{ (\AA)}$	5.250	5.206	5.203	5.203
$\alpha = \beta \text{ (}^\circ\text{)}$	90	90	90	90
$\gamma \text{ (}^\circ\text{)}$	120	120	120	120
c/a	1.6	1.6	1.6	1.6

From Table 2, it can be shown that there is almost no difference between lattice parameters at various thicknesses, where the a and c parameters are 3.250 and 5.250, respectively with c/a is around 1.6. These lattice parameters are similar as reported by Li et al. [8]. The crystal size was calculated by using Deye Scherer equation. We firstly inferred the FWHM and 2θ values of the X-ray diffraction data. The size of crystal size as a function of film thickness is summarized in Table 3.

Table 3. The Crystal Size of ZnO Thin Film on Various Speed of Spin Coating

Average Film Thickness (μm)	Bragg planes (hkl)	Crystallite Size (nm)
1.050	100	32.15
	002	24.30
	101	22.89
Average		26.45
0.450	100	26.07
	002	27.99
	101	22.73
Average		25.59
0.250	100	22.32
	002	21.62
	101	19.61
Average		21.18

These results were in line with the early prediction related to the width of the peak in X-Ray diffraction pattern. The wider the peak, the higher the value of FWHM leads the smaller of crystal size. It is clearly seen that the thinner the film, the smaller the crystal size. The results were in line with the research conducted by Gayen (2011), the increase of crystal size was parallel with the increase of coat thickness.

Based on the UV-Vis measurement, we are able to know the transmission value of ZnO thin film as a function of different wavelengths with the various of thickness as shown in Figure 3.

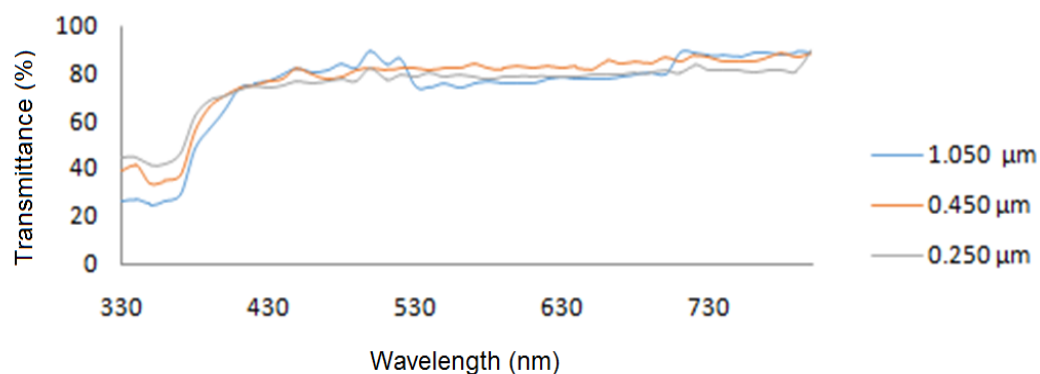


Figure 3. The percentage of transmittance of ZnO thin films as function of wavelength with various of the film thickness

Based on Figure 3, generally, the absorption values of all samples decreased for longer wavelength and this was the characteristic of ZnO semiconductor absorption. The thicker the film, the bigger the absorption value. If the sample was not gradually transparent, the more coats were formed and more molecules of ZnO were included in the process of visible light absorption. The calculation of optical bandgap was begun by deciding the maximum and minimum transmittance values, thickness, the coefficient of thin coat absorption. It was ended by the calculation applying Tauc method by doing extrapolation from the correlation graph $(h\nu)$ as the x-axis and $(\alpha h\nu)^n$ as y-axis so it cut the energy axis and the bandgap value was gained. Transmittance measurement was conducted at the wavelength 330 nm – 800 nm. Our results indicate that the coating thickness did not influence the bandgap value. In all variations of thickness, the results were similar, that was 3.2 eV. This result was suitable for the range of bandgap value of ZnO, that was 3.2-3.5 eV [4,8]. The small value of bandgap might allow electron was easily excited from valence band to the conduction band.

The picture of the contact angle of ZnO thin film with the different thickness was taken by using a camera and then it was measured by using ImageJ software. The result of contact angle was shown in Figure 4. Kenanakis et. al [5] found that self-cleaning glass application should be hydrophobic and superhydrophobic. In table 6, we can see that the contact angle resulted $\geq 90^\circ$ when it was in the room and $\leq 10^\circ$ after got sunlight in 30 minutes. The hydrophobic characteristic caused the water rolling down, so it did not stamp to the glass by bringing the dirt. With hydrophilic characteristics, the water would spread out the surface of glass cleaning the dirt and the gravitation forces caused the spread water dropped, so the glass remained clean and bright although it was affected by water.

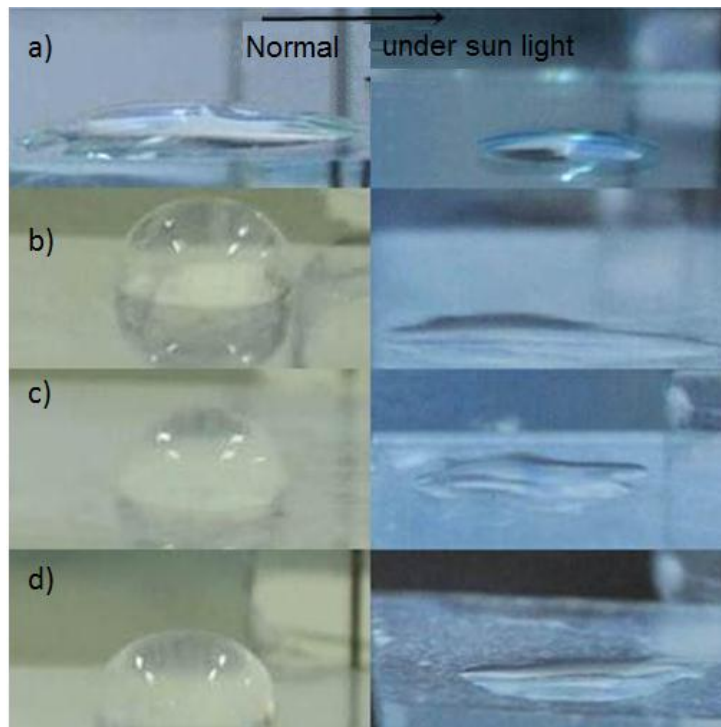


Figure 4. Contact angel of ZnO thin film with various thickness (a) uncoated, (b) 1.050 μm (c) 0.450 μm , (d) 0.250 μm

Table 4 shows the contact angle value of ZnO thin film with a various thickness of speed of spin coating. It shows that ZnO thin film with $\pm 0.250 \mu\text{m}$ thickness had the biggest contact angle, that was 96.32° when it was inside a room. ZnO thin film had the smallest contact angle – 20.61° – when it was under sunlight in 30 minutes. On the contrary, ZnO thin film with $\pm 1.050 \mu\text{m}$ thickness had the biggest contact angle, that was 99.99° when it was inside a room. It had the smallest angle – 6.03° – after it was lighted by the sun in 30 minutes. The variation shows good hydrophobic characteristic since it had contact angle above 90° . it also shows good super hydrophilic characteristic since it had contact angle under 10° .

Table 4. Contact Angel of ZnO Thin Film with Various Coat Thickness

Average Thickness (μm)	Normal Contact Angle ($^\circ$)	Sunlight Contact Angle ($^\circ$)
Uncoated	16.81	17.83
1.050	91.03	6.03
0.450	97.84	8.54
0.250	99.74	10.44

The contact angle increased based on the coating thickness. It was because the thicker the coat, the more particles of ZnO were deposited. The role of ZnO was detaining liquid on the surface, so there of material contact with liquid was narrower, so the number of ZnO deposition influenced the hydrophobic characteristic of material.

4. Conclusion

Based on data analysis and discussion, it can be concluded that coat thickness did not influence crystal structure of ZnO thin films. The thicker the coat, the bigger the coat crystallite size of ZnO thin film was. The thicker the coat, the higher the UV absorption value of ZnO thin film, however, it did not influence the bandgap value, that was 3.2 eV. Besides, the thicker the coat, the bigger the hydrophobic characteristic of ZnO thin film. It was because of the thicker the coat, the more particles were deposited and it influenced hydrophobic characteristic since the material contact area was narrower. Sun lighting caused hydrophilic characteristic of ZnO thin film smaller since sunlight could produce a pair of electron and hole on the surface of ZnO resulted by hydroxyl cluster that caused the contact angle decreased.

5. References

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