IOP Conf. Series: Journal of Physics: Conf. Series **817** (2017) 012025 doi:10.1088/1742-6596/817/1/012025

Preparation and structural characterization of ZnO thin films by sol-gel method

D Aryanto[1], W N Jannah[1], Masturi[2], T Sudiro[1], A S Wismogroho[1], P Sebayang[1], Sugianto[2] and P Marwoto[2]

[1] Research Center for Physics, Indonesian Institute of Sciences, Serpong 15314, Tangerang Selatan, Banten, Indonesia
[2] Physics Department, Faculty of Mathematics and Natural Science Universitas Negeri Semarang, Sekaran-Gunungpati 50229, Semarang, Indonesia

E-mail: didik.aryanto@lipi.go.id

Abstract. ZnO thin films were prepared on glass substrate by sol-gel spin-coating method using zinc-acetate dihydrate as precursor. Effect of precursor concentration on the morphological and structural of the films was investigated. The diffraction patterns of X-ray diffraction (XRD) characterization indicated that all of ZnO thin films were polycrystalline with a hexagonal wurtzite crystal structure. The peaks were indexed to (100), (002) and (101) planes. Intensity of all diffraction peaks increased and became broader in full width at half maximum (FWHM) values with increasing precursor concentration. The calculation of texture coefficient (*TC*) indicated that ZnO thin films exhibited the preferential orientation growth along the *c*-axis. Increasing precursor concentration resulted in decreasing crystalline size and crystallization of the film. The lattice constants (*a* and *c*) and *d*-spacing also changed as function of precursor concentration. It was demonstrated by the bond length, volume per unit cell, lattice strain and dislocation density. The scanning electron microscopy (SEM) images of surface morphology of the films confirmed the results of XRD characterization. The grain size of ZnO thin films decreased as result of increasing precursor concentration. Cross-section of SEM images showed that the thickness of ZnO thin film increases from 149.4 nm to 447.7 nm with increasing precursor concentration. This works shown that morphological and structural of ZnO thin films prepared using sol-gel spin coating methods were strongly influenced by precursor concentration.

1. Introduction

In recent years, many researchers have been studied extensively wide-band gap materials such as zinc oxide (ZnO) because of their application in optoelectronic devices. ZnO has a wide and direct band gap (3.37 eV) at room temperature with hexagonal wurtzite structure [1-3]. Besides that, it has much larger exciton binding energy (60 meV) compared to gallium nitride (26 meV) at room temperature [1]. The other advantage of ZnO is simpler crystal-growth technology, resulting in a potentially lower cost for ZnO-based devices [4]. Therefore, ZnO is very interesting for various fields of industrial and high-technological applications.

ZnO thin films have elicited much interest due to their application, as transparent conducting oxides (TCO) [5] and the window layer in solar cell [6]. Applications of ZnO thin films as the film bulk acoustic resonator (FBAR) filter [7] and surface acoustic wave (SAW) device [8] have also been

investigated. This is due to an excellent piezoelectric property of ZnO thin film and a high optical transmittance in the visible region. ZnO thin films can be prepared using various methods, such as magnetron sputtering technique [5, 9], molecular beam epitaxy (MBE) [10], metal-organic chemical vapour deposition (MOCVD) [11], pulsed laser deposition (PLD) [12], spray pyrolysis [13], ultrasonic spray [2] and sol gel process [3, 14]. However, the sol-gel method is more convenient among other methods, such as low cost, accurate compositional control, low crystallization temperature, homogeneity at the molecular level, and easy reproducibility [2].

In the sol-gel spin coating process, the characteristic of ZnO thin films was influenced by solvent, precursor concentrations, chemical for stabilizer, pre-annealing, post-annealing, annealing atmosphere and film thickness [1-3, 15]. Kim et al. prepared ZnO thin films using sol-gel spin coating method at various precursor concentrations (0.3-1.3 M) [16]. The pre-heating and post-heating temperatures of samples were 250°C and 650°C, respectively. The ZnO thin films with precursor concentration of 0.7 M have a higher peak intensity on the (002) orientation compared to the other samples. Another work by Kamaruddin et al. showed that ZnO thin film deposited on a glass by sol-gel spin coating method at different precursor concentrations (0.3-0.7M) and then followed by annealing at 450°C for 1 h [1]. The result showed that the grain size, root mean square (RMS) roughness, crystalline size, crystallinity and transparency of ZnO thin films increased with increasing precursor concentration. Both of previous studies used Isopropanol and 2-Methoxyethanol as solvent and monoethanolamine (MEA) for stabilizer. However, fabrication of ZnO thin films derived from sol-gel spin coating method with methanol and ethanolamine as solvent and stabilizer, respectively is still rare. The effect of precursor concentration on the thickness of films has also not been reported.

In this work, ZnO thin films from zinc acetate-dihydrate-methanol-ethanolamine solution were deposited on glass by sol-gel spin coating method. The concentration of precursor solutions was varied from 0.5 to 1 M. All films were pre-heated at 150°C for 1 hour and post-heated (annealed) in the furnace at 800°C for 1 hour. The influence of precursor concentrations on the morphology and structural of ZnO thin films was discussed.

2. Experimental Details

ZnO thin films were deposited onto glass substrate using sol-gel spin coating methods. The solution for ZnO thin films was prepared using zinc acetate dihydrate ($Zn(CH_3COO)_2 \bullet 2H_2O$), ethanol and ethanolamine ($NH_2CH_2CH_2OH$) as a precursor, solvent and stabilizer, respectively. The concentration of the precursor solutions containing zinc acetate dehydrate, ethanol and ethanolamine was varied from 0.5 M to 1 M and the molar ratio of zinc acetate dehydrate ethanolamine ($NH_2CH_2CH_2OH$) was maintained at 1:1. The resulting solution was stirred at room temperature for 1 h using a magnetic stirrer at 300 rpm. Finally, the solution was aged for 3 days before it was spin coated onto glass substrate. Prior to the deposition process, a glass substrate was cleaned sequentially with acetone, methanol and DI water in an ultrasonic bath. The deposition was carried out using a spin coater with a speed of 3000 rpm for 60 s. After coating, ZnO thin films were pre-annealed at 300°C for 1 h, followed by post-annealing at 800°C for 1 h in air atmosphere. The structural analysis of ZnO thin films was carried out using a Smartlab Rigaku X-ray diffractometer with a CuK_α (λ = 1.5406 Å) as an X-ray source. The lattice parameters, *d*-spacing, texture coefficient (*TC*), crystalline size (*D*), lattice strain (ε), dislocation density (ρ) were calculated from the XRD data. Morphology studies were carried out using a scanning electron microscope (SEM) (Hitachi High-Tech Co. Ltd, Japan).

3. Results and Discussion

The XRD patterns of ZnO thin films deposited on glass substrates using sol-gel spin coating method with various precursor concentrations are shown in the figure 1. The XRD patterns reveal that the three main diffraction peaks belong to ZnO with (100), (002) and (101) planes according to a JCPDS card No. ICDD-01-078-3315. No impurity peaks of Zn metallic are detected in the XRD patterns. The result indicates that the ZnO thin films are polycrystalline in nature with a hexagonal wurtzite crystal structure [1, 9]. Based on figure 1, all diffraction peak of ZnO thin films with the precursor

concentration of 0.5 M have the lowest intensities. In general, the intensity of all diffraction peaks increases with increasing precursor concentration, as shown in figure 1. However, further analysis of XRD results indicates that the preferential crystal growth orientation is along (002) plane. The preferential crystal orientation can be obtained from texture coefficient (*TC*), which is calculated using the Equation as shown below, [9].

$$TC = \left(\frac{I_{(hkl)} / I_{r(hkl)}}{\left[1/n \sum I_{(hkl)} / I_{r(hkl)} \right]} \right) \quad (1)$$

where $I_{(hkl)}$ is the XRD intensity from the thin film, n is the number of reflections observed in the XRD pattern, and $I_{r(hkl)}$ is the intensity of the reference. A detail of the *TC* coefficient with variation of precursor concentrations is shown in Table 1. The value of *TC* indicates the maximum preferred orientation of the films along diffraction plane [9, 17]. As show in Table 1, all ZnO thin films have texture coefficients relatively (>1) higher value along the (002) plane. It was confirmed by the preferential orientation along the *c*-axis. The minimization of surface energy and internal stress influences the preferential orientation of the crystal [18]. The growth of the film along the *c*-axis as a result of the highest atomic density was found along the (002) plane. This could be related to the dominant crystal growth on the c-orientation. Previous work by Kamaruddin et al. shows a different result that the ZnO thin film has preferential growth along (101) planes with increasing precursor concentrations (0.3-0.7) [1]. This may be due to the different in the annealing temperature.

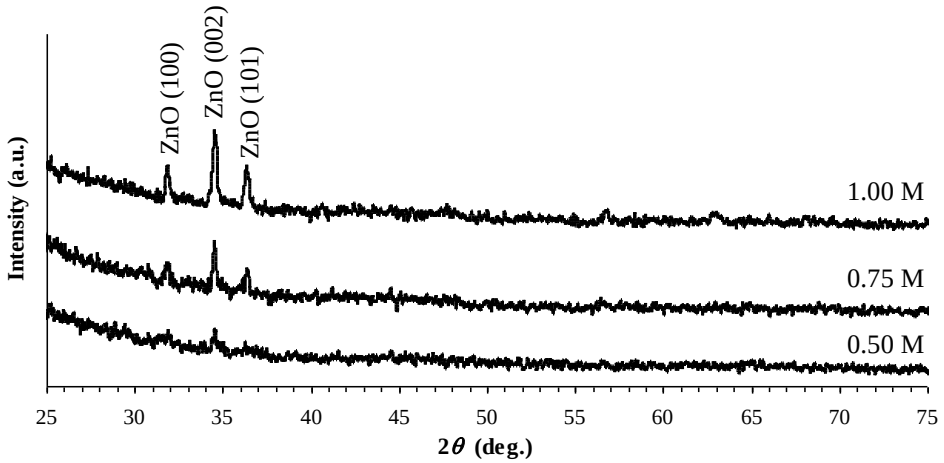

Figure 1. XRD patterns of ZnO thin films with various precursor concentrations and annealed at 800°C.

The lattice parameters, *a* and *c*, of hexagonal phase was estimated according to the peak position of phases and the following equation [15],

$$a = \frac{\lambda}{\sqrt{3}\sin\theta} \sqrt{h^2 + hk + k^2} \quad (2)$$

$$c = \frac{\lambda}{2\sin\theta} l \quad (3)$$

where λ is the X-ray wavelength of 1.5418 Å, θ is a Bragg diffraction angle of the (002) peak and *h k l* is Miller indexes. The results are given in Table 1. The value of lattice constants (*a* and *c*) in this work changes as increasing precursor concentration with the variation different in the range of 0.004-0.027

Å, while the theoretical values (ICDD-01-078-3315) of *a* and *c* are 3.249 Å and 5.205 Å, respectively. The stress occurrence in the thin film was attributed to the different in the lattice constant [18].

The *d*-spacing of different crystal plane (*h k l*) for the hexagonal structure is determined using the equation [9, 15]

$$\frac{1}{d^2} = \frac{4\left(h^2 + hk + l^2\right)}{\left(3a^2\right)} + \left(\frac{l^2}{c^2}\right) \tag{4}$$

The values of *d*-spacing in this work (as shown in Table 1) are larger than un-stress ZnO bulk (2.602 Å) [15], which indicate the presence of strain fields within the non-equilibrium grain boundaries inside of crystallite.

The Zn–O bond length (*L*) has been calculated using the following relationship [19],

$$L = \sqrt{\left(a^2/3\right) + \left((1/2) - u\right)^2 c^2} \tag{5}$$

where u = (a^2/3c^2) + 0.25 is the potential parameter of the hexagonal structure. The volume (*V*) of unit cell of hexagonal system has been calculated from the equation [19].

$$V = 0.866 \times a^2 \times c \tag{6}$$

As can be seen in Table 1, the Zn-O bond length increases with increasing the precursor concentration, which is the value in the range of 1.9651-1.9745Å. Compared to the results of previous studies, this Zn-O bond length is slightly smaller. Ilican et al., [20] reported that the Zn-O bond length is 1.9767 Å in the unit cell of ZnO and neighbouring atoms. The other work by Fang et al. [14], reported the Zn-O bond length is 1.9781 Å. In this work, the lattice volume of ZnO thin film increases with increasing precursor concentration. The volumes of ZnO thin films in this work are smaller than the result by Fang et al. [14]. Higher post-annealing temperatures affect the crystal volume of ZnO thin films. These also result in volume shrinkage of grain size, affecting the bond length and the lattice volume of ZnO thin films. The parameter process (pre- and post-annealing) during fabrication of ZnO thin film by sol-gel spin coating methods strongly influences the structure of ZnO thin films.

Table 1. Calculated parameters crystal of ZnO thin films with various precursor concentrations after annealing at 800°C.

Precursor concentration (M)	*h k l*	*TC*	*d*-spacing (Å)	*a* (Å)	*c* (Å)	*L* (Å)	*V* (Å^3)
0.50	(002)	1.00	2.5953	-	5.1907	-	-
0.75	(100)	0.88	2.7901	3.2217	-		
	(002)	1.50	2.5990	-	5.1980	1.9651	46.7237
	(101)	0.62	2.4663	-	-		
1.00	(100)	0.85	2.8088	3.2434	-		
	(002)	1.55	2.6004	-	5.2009	1.9745	47.3809
	(101)	0.60	2.4735	-	-		

Figure 2 shows the full width at half maximum (FWHM), crystalline size, lattice strain and dislocation density of (002) peak of ZnO thin film as function of precursor concentration. The FWHM increases from 0.14° to 0.26° with increasing the precursor concentration from 0.50 M to 1.00 M. This indicates that the crystal quality of ZnO thin film decreases with increasing precursor concentration. A smaller FWHM value indicates a better crystallization of the thin films [26]. The result of FWHM attributed to decrease in crystalline size. The crystallite size (*D*) of ZnO thin films was calculated using Scherrer's formula [5, 9]:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \tag{7}$$

where β is the FWHM of the ZnO (002) diffraction peak. As shown in Figure 2, the crystalline size of ZnO thin films decreases with increasing precursor concentration. This might ~~be~~ due to the presence of internal stress and defects in the film. The stress relaxation at the grain boundaries results in the smaller crystalline size. This result is in close agreement with the results of SEM characterization which will be discussed later.

The lattice strain (ε) along the c-axis was calculated using the tangent formula [9]

$$\varepsilon = \frac{\beta}{(4\tan\theta)} \tag{8}$$

It affects the length of dislocation lines per unit volume of the crystal. The dislocation density (ρ) due to lattice strain can be expressed by the relation below [9].

$$\rho = \left[\frac{\sqrt{12}\,\varepsilon}{D\,d}\right] \tag{9}$$

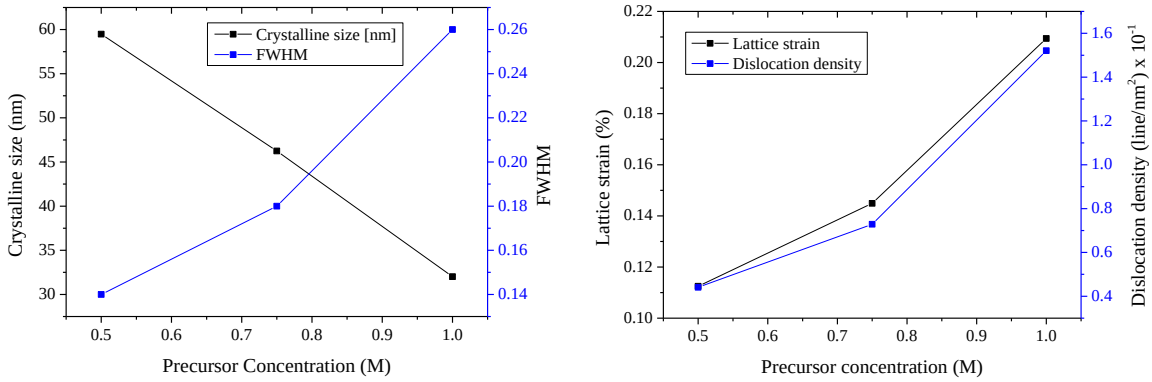

Figure 2. FWHM, Crystalline size (D), lattice strain (ε) and dislocation density (ρ) of ZnO (002) as function of precursor concentrations after annealing at 800°C.

According to XRD data, the lattice strain and dislocation density value increase as the precursor concentration increases from 0.50 M to 1.00 M. The increase in Zn content may lead to the stretch of lattice constant during annealing treatment. This can increase the strain, lattice energy and also diminish the driving force of the growth, resulting decrease in the particle size and crystallization. The results are enhanced by XRD results (Figure 1) and SEM image (Figure 3). Lattice mismatch between the substrate and film also contribute in the lattice strain and dislocation densities.

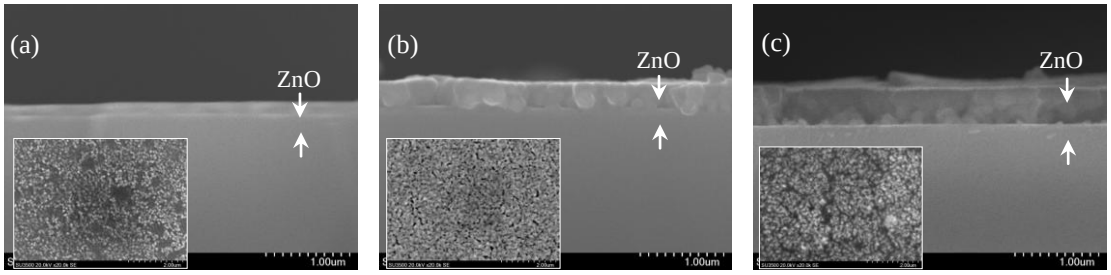

Figure 3. Cross-sectional and surface morphology images of ZnO thin films with precursor concentration of (a) 0.50M, (b) 0.75M and (c) 1.00 M.

The typical SEM surface and cross-sectional morphology of ZnO thin films deposited on a glass with different precursor concentrations are presented in Figure 3. The surface morphology and cross-sectional of SEM images shows that the grains of ZnO thin films becomes smaller and denser with increasing precursor concentrations, as shown on the work by Baneto et al. [21]. The different result is shown by Kamaruddin et al. [1], which the grain size of ZnO thin films increases slightly when the precursor concentration is increased from 0.3 to 0.6 M. In this work, the decrease in grain size seems to be related to a micro-densification effect. The number of nuclei of metal centers increases as an effect of increasing precursor concentration [13], which leads to the formation of a denser and compact structure of the ZnO thin film on the substrate surface. In addition, as show in Figure 3, an increasing precursor concentration causes an increase in the film thickness. The ZnO thin film with precursor concentration of 0.50, 0.75 and 1.00 M has an average thickness of around 149.4, 326.0, and 447.7 nm, respectively. The small crystallites were gathered to form a layer with increasing precursor concentration. Another reason, the increasing Zn^{2+} ions concentration as function of precursor concentration affects the formation of film thickness. The result of cross-sectional SEM images supports the XRD patterns that increasing the intensity of all diffraction peaks are influenced by the thickness of film.

4. Conslusion

ZnO thin films with various precursor concentrations were successfully deposited on glass substrates using sol-gel spin coating methods. All ZnO thin films are polycrystalline in nature with hexagonal wurtzite structure and have a preferential orientation along (002) plane. The lattice constant (*a* and *c*), d-spacing, bond length, volume per unit cell, crystalline size, FWHM, lattice strain and dislocation density of ZnO thin films changes are affected by the precursor concentration. An increase in the precursor concentration leads to increases in the thickness of ZnO thin film and the grain size of film becomes smaller. In summary, the structural and morphological of ZnO thin films strongly depend on the precursor concentration.

Acknowledgement

This work was supported by Indonesian Institute of Sciences under Competitive Research Grand Program. The authors are grateful to Laboratory of High Temperature Material and Coating-Research Center for Physics, Indonesian Institute of Sciences, Indonesia.

Reference

[1] Kamaruddin S A, Chan K-Y, Yow H-K, Sahdan M Z, Saim H & Knipp D 2011 *Appl. Phys. A* **104** 263
[2] Gahtar A, Rahal A, Benhaoua B and Benramache S 2014 *Optik* **125** 3674
[3] Jena I, Das S N, Mishra D K and Bose G 2014 *Int. J. Nano and Biomaterials* **5** 287
[4] Özgür Ü, Alivov Y I, Liu C, Teke A, Reshchikov M A, Doğan S, Avrutin V, Cho S-J and Morkoç H 2005 *J. Appl. Phys.* **98** 041301-1

[5] Yang W, Liu Z, Peng D-L, Zhang F, Huang H, Xie Y and Wu Z 2009 *Appl. Surf. Sci.* **255** 5669
[6] Tanaka K, Minemoto T and Takakura H 2009 *Solar Energy* **83** 477
[7] Dutta J, Singh A V, Singhal S and Upadhayay M D 2015 *IETE J. Res* **62**(1) 3-8
[8] Magnusson E B, Williams B H, Manenti R, Nam M-S, Nersisyan A, Peterer M J, Ardavan A and Leek P J 2015 *Appl. Phys. Lett.* **106** 063509-1
[9] Aryanto D, Marwoto P, Sudiro T, Birowosuto M D, Sugianto and Sulhadi 2016 *AIP Conf. Proc.* Vol 1729 No1 (New York: AIP Publishing) p 020039
[10] Ying M, Wang S, Duan T, Liao B, Zhang X, Mei Z, Du X, Gerriu F M, Fox A M and Gehring G A 2016 *Mater. Lett.* **171** 121
[11] Boukadhaba M A, Fouzri A, Sallet V, Hassani S S, Amiri G, Lusson A and Oumezzine M 2015 *Superlattices and Microstruct.* **85** 820
[1] Kodu M, Arroval T, Avarmaa T, Jaaniso R, Kink I, Leinberg S, Savi K and Timusk M 2014 *Appl. Surf. Sci.* **320** 756
[2] Shinde V R, Gujar T P and Lokhande C D 2007 *Sens.Actuators B* **120** 551
[3] Fang D, Lin K, Xue T, Cui C, Chen X, Yao P and H Li 2014 *J. Alloys and Compounds* **589** 346
[4] Lupan O, Pauporte T, Chow L, Viana B, Pelle F, Ono L K, Cuenya B R and Heinrich H 2010 *Appl. Surf. Sci.* **256** 1895
[5] Kim Y-S, Tai W-P and Shu S-J 2005 *Thin Solid Films* **491** 153
[6] Kim D-K and Kim H-B 2015 *Superlattices Microstruct.* **85** 50
[7] Raoufi D and Raoufi T 2009 *Appl. Surf. Sci.* **255** 5812
[8] Thirumoorthi M and Prakash J T J 2015 *Superlattices Microstruct.* **85** 237
[9] Ilican S, Caglar Y, Caglar M and Yakuphanoglu F 2008 *Appl. Surf. Sci.* **255** 2353
[10] Baneto M, Enesca A, Lare Y, Jondo K, Napo K and Duta A 2014 *Ceram. Int.* **40** 8397