Effect of spinning rate on structure and morphology of ZnO:Cu thin film prepared using a sol gen spin coating method

by Budi Astuti

Effect of Rotation Speed on Structural and Morphology of Cu-ZnO Thin Films Prepared using Sol-gel Spin Coating Method

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ABSTRACT

Cu doped ZnO (Cu-ZnO) thin film were deposited on glass substrate using sol-gel spin coating method. The various rotation speed of 2600, 2800, 3000, 3200, and 3400 rpm was sintered at $250\ ^0C$ for 10 m and annealed at $350\ ^0C$ for 2 hours. The effect of rotation perminutes on structural properties was investigated by x-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray (EDX). The result of XRD indicated that Cu-ZnO thin fims has strong c-axis orientation, (002) plane peak at $2\theta = 34.42^o$ corresponding to hexagonal wurtzite crystal. Increases of the rpm was resulted Cu-ZnO thin films with high homogeneous. Its proved by SEM and EDX result.

Key word: Cu-ZnO, thin film, rpm, sol-gel spin coating

INTRODUCTION

Thin film technology continues to develop towards materials that are cheap and environmentally friendly and easy in large-scale production (Harish *et al*., 2019). In addition, thin films must also have a good structure, optical, electrical and magnetism properties (Ammaih *et al*., 2014). The development of thin film technology has been applicated to solar cells (Tumbul *et al*., 2019), transparent conduct oxide (TCO) (Mughal *et al*., 2017), photocatalysts (Kaviyarasu *et al*., 2017), transistors (Ruzgar *et al*., 2019), super capacitors (Hassan *et al*., 2019) and others . At present, one of the materials being developed is zinc oxide (ZnO). ZnO material is included in II-VI inorganic semiconductors compounds. ZnO has a wurtzite crystal structure with a lattice spacing a = 3.25 Å and c = 5.21 Å, has a bandgap width of 3.4 eV and has a melting point of 2248 K (Arif *et al*., 2018). Beside it, ZnO have weaknesses in their electrical properties. To improve these properties, the addition of doping from transition metals is an efective method (El-Hilo, Dakhel, & Ali-Mohamed, 2009) such as Cu (Marwoto *et al*., 2012).

Several methods of growing thin films have been developed such as RF magnetron sputtering (Samavati *et al*., 2016), DC magnetron sputtering (Zhu *et al*., 2015), spray pyrolysis (Mimouni *et al*., 2015), metalorganic chemical vapor deposition (MOVCD) (MOVCD) (Li *et al*., 2019), molecular beam epitaxy (MBE) (Darma *et al*., 2019), and pulsed laser deposition (PLD) (Zawadzka *et al*, 2016) and sol-gel spin coating (Leela *et al*., 2019). Sol-gel spin coating method has advantages in the manufacturing process that is easy, inexpensive and can be applied to large scale production (Arif *et al*., 2018; Nimbalkar *et al*., 2017). The spin coating sol-gel method is also influenced by several factors such as rotation speed and rotation time. This rotational speed per minute (rpm) can affect surface morphology, subsurface defects and impurities (Ilican *et al*., 2008).

ZnO doped Cu thin film are grown on glass substrates and sintered to form new compounds and dialing to form crystal structures. The effect of rotation per minutes (rpm) on the surface morphology structure was investigated by using x-ray diffraction (XRD), and Scanning Electron Microscopy (SEM) - Energy Dispersive X-ray (EDX).

EXPERIMENTAL PROCEDURES

Zinc acetate dihydrate $[Zn\,(CH_3COO)_2.2H_2O, ZAD]$ and Copper (II) acetate monohydrate $[Cu(CH_3COO)_2.H_2O, CAM]$ were of analytic grade with purity around 99.99% from Merck KGaA, 64271 Darmstandt (Germany) was utilized as main percursor. Then, 2-propanol $[CH_3CH(OH)CH_3]$ as solvent and monoethanolamine $[NH_2CH_2CH_2OH$, MEA] as stabilizer. There are from Merck KGaA, 64271 Darmstandt (Germany). The solution was formed at 0.5 M by mixing2.17 g ZAD and 0.02 g CAM in 20 mL 2-propanol solvent and stirred using a magnetic stirrer. After stirring for 15 minutes at 60 °C ,0.62 mL MEA was added to solution under stirring at constant rate. The final solution was stirred at same temperature (60 °C) for 60 minutes. Finally, the solution has higly homogeneous and transparent blue color. The solution was then left for 24 hours at room temperature to find out there is no sediment in the solution. In the same time, cleaning process for subtrate was done using acetone for 15 minutes and methanol for 5 minutes with ultrasonic bath. Then, the glass substrate were dried using Nitrogen gases. Afterward, the solution was droped on glass substrate and rotated at various speed 2600, 2800, 3000, 3200, and 3400 rpm for 15 second. The last, ZnO:Cu thin films were thermally sintered a 250 °C for 15 minutes and annealed at 350 °C for 2 hours. The structural properties of ZnO:Cu thin films were characterized by x-ray diffraction (XRD) analysis with wavelength monochromatic $Cu\,K_\alpha$ radiation (λ = 1.542 Å). The surface morphology was investigated by scanning electron microscopy (SEM) and energy dispersive x-ray (EDX).

RESULT AND DISCUSSION

1. Structural Study

The direction of crystal orientation and the structure of ZnO:Cu thin film crystals were examined using XRD. The XRD spectrum of ZnO:Cu thin films made by the sol-gel spin coating method is then rotated with variations in the speed of 2400, 2600, 3000, 3200 and 3400 rpm as shown in Figure 1. Based on Figure 1, there are 3 dominant peaks that correspond to fields (100), (002), and (101) so that this ZnO:Cu film has a polycrystalline structure. Then, based on the direction of the dominant plane orientation (002) it shows that the ZnO:Cu structure is hexagonal wurtzite. The values of the ZnO:Cu thin film constant can be seen in Table 1 which has been matched with JCPDS data with numbers (01-078-3315) and (76-0704). The results of the lattice constant *a* and *c* based on calculation are similar to JCPDS reference number. Crystal size, *D* is calculated by the Debye-Scherrer's equation

$$\boldsymbol{D = \frac{K\lambda}{\beta \cos\theta}} \quad (1)$$

where K is the Scherrer constant (0.89), λ (1.542 Å) is the wavelength of radiation, β is FWHM and θ is the peak position of XRD.

Then, the dislocation density, δ was obtained using equation (2),

$$\boldsymbol{\delta = \frac{1}{D^2}} \quad (2)$$

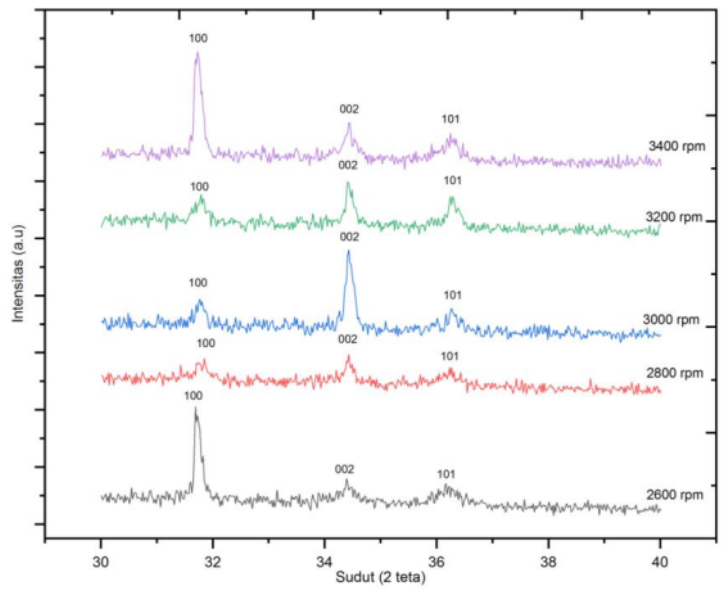


Figure 1. XRD patterns for ZnO:Cu thin films spinned at different rotation per minutes.

The variation of rotation per minutes (rpm) affects the orientation of the crystal planed was produced. It is clear on the Figure 1, three diffraction peaks was appear at $2\theta =$ 31.69°; 34.42° and 36.21° according to (100), (002) and (101), respectively. Crystal orientation (002) plane on ZnO:Cu thin films has the highest intensity at a rotational speed of 3000 rpm compared to the other rpm (lower than and higher than 3000 rpm). That can be said, the 3000 rpm is the optimum rotation to growth ZnO:Cu thin film using spin coating method.

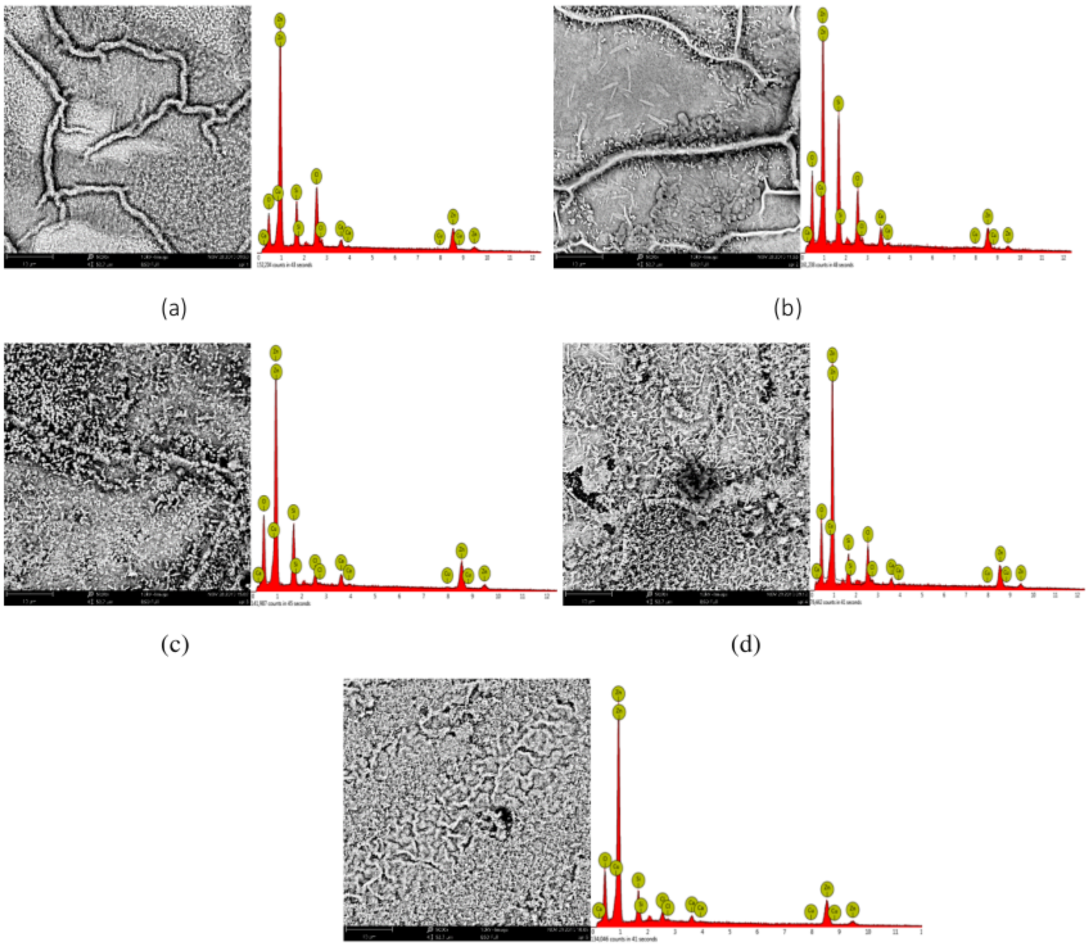
As we known, the crystal orientation (002) plane is can be applicated as Window layer on the solar cell technology. Requirement of window layer material is should have high transmittance and wide band gap energy. Previous researcher reported that (002) ZnO thin films have a high transferability of 80-90% (Bedia *et al*., 2015; Rahmane *et al*., 2015).

Table 1. Structural and lattice parameters of ZnO:Cu thin films

Rpm	2θ		FWHM (°)		Lattice constants (Å)		*d* (*nm*)	*D* (*nm*)	σ (nm^2)	Lattice constants from JCPDS (Å)	
	100	002	100	002	a (100)	c (002)	(002)	(002)		a (100)	c (002)
2600	31.70	34.42	0.16	0.20	3.26	5.21	2.61	42.30	0.00056	3.25	5.21
2800	31.76	34.46	0.20	0.16	3.26	5.21	2.60	52.89	0.00036	3.25	5.21
3000	31.80	34.43	0.12	0.12	3.25	5.21	2.60	70.49	0.00020	3.25	5.21
3200	31.8	34.44	0.16	0.16	3.25	5.21	2.60	52.89	0.00036	3.25	5.21
3400	31.73	34.47	0.2	0.31	3.26	5.20	2.60	26.44	0.00143	3.25	5.21

2. **Surface Morphology**

The surface morphology of ZnO:Cu thin films with rpm variations (2600, 2800, 3000, 3200, and 3400) was analyzed by SEM-EDX. Figures 1 and 2 shows the surface morphology of ZnO:Cu thin films changing following increases on rpm. Based on the SEM result that identify the structure inhomogeneous, dense, and particles agglomerate occur (Arif et al., 2018). It is clearly also, ZnO:Cu thin film samples that are rotated at 3000 rpm have a higher uniformity compared to the other samples. This was confirmed by the analysis data based on the XRD characterization. The EDAX Study of the prepared sample is shown in Figure 3.



(a) (b) (c) (d) (e)

Figure 2. SEM-EDX micrograph for ZnO:Cu thin films (a) 2400 (b) 2600 (c) 3000 (d) 3200 and (e) 3400 rpm

The EDX is used to analyze the chemical purity and stoichiometries of thin films samples. Based on Figure 3,Its shows that the sample of ZnO:Cu thin film not only contain zinc and oxygen, but have impurity are present in the sample. Impurity contain on this film such as Si, Cl, and Ca element. For Si element was expected come from the substrate, that because the samples are quite thin. According to

Figure 2 also can be seen the Cu element has high intensity peak at the same place with Zn. It can assume the Cu atom substitutes several Zn atoms in the ZnO matrix (Hanh *et al*., 2019). All samples have Cu atoms but ZnO:Cu thin film samples rotated at 3000 rpm have the highest concentration of Cu atoms.

CONCLUSION

ZnO:Cu thin film grown using sol gel spin coating has been done with variation of rotation. Based on the XRD result, the ZnO:Cu thin film was obtained has hexagonal wurtzite structure with dominant orientation (002) plane. Morphology of the film with rotation at 3000 rpm is higher uniformity compared to the other samples. From EDX analysis on ZnO:Cu thin films have shown the presence of Cu atoms along with the concentration of atoms and the weight of Zn and O on ZnO:Cu thin films. The Cu atom substitutes several Zn atoms in the ZnO matrix. All samples have Cu atoms but ZnO:Cu thin film samples rotated at 3000 rpm have the highest concentration of Cu atoms.

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