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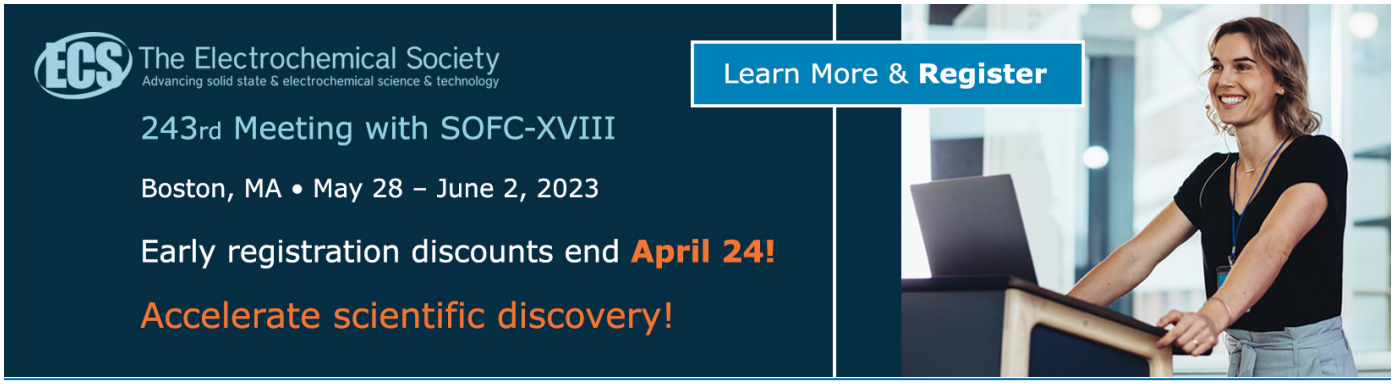

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X-ray diffraction studies of ZnO:Cu thin films prepared using sol-gel method

B Astuti[1]*, A Zhafirah[1], V A Carieta[1], N Hamid1, P Marwoto[1], Sugianto[1], U Nurbaiti[1], F D Ratnasari[1], N M D Putra[1] and D Aryanto[2]

[1]Physics Department, Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang, Indonesia
[2]Research Center for Physics, Indonesian Institute of Sciences, Indonesia

*Corresponding author: b_astuti79@mail.unnes.ac.id

Abstract. ZnO:Cu thin films were deposited on corning glass substrate using sol gel method with different concentration of Cu (0, 1, 3, and 5%) has been done. The effect of the different Cu concentration on the structural properties of these films was studied in detail. Based on the XRD result, the ZnO thin films undoped and doped Cu are polycrystalline with hexagonal wurtzite structure and has preferred orientation is c-axis. All peaks of ZnO thin films undoped and doped Cu shows that reflection peaks associated with (100),(002) and (110) planes. The film quality was improved with the increasing of the Cu concentration. The value of the lattice constant a and c was found to be increased with increases of the Cu concentration. Changes in the lattice constant affect the bond length of ZnO (L) and the volume of one hexagonal system unit (V). The lattice parameter also affects to the crystallite size. The crystallite size was increased with Increasing of the Cu concentration and the lattice parameter. Furthermore, the strain value of the film decreases with increases of the Cu concentration. Lattice strain that has decreased is due to the cavity around of the formed film. Cavities between atoms also affect the density of the dislocation. The larger cavity between atoms on the films that makes the dislocation density becomes smaller.

1. Introduction

Zinc Oxide (ZnO) is a good semiconductor material for various application variations based on the nature of low fabrication costs, environmentally friendly, compatibility and also simple fabrication processes [1]. ZnO crystal has a hexagonal wurzite structure with a wide direct band gap of 3.37 eV, and high exciton binding energy (60 meV) at room temperature [2]. ZnO material which is supported by metal transition material such as Cu has been verified as an effective method to adjust its function including its electrical and optical properties [3]. Cu doped ZnO (ZnO:Cu) showed a significant increase in the properties of electrical, magnetic, photocatalytic performance [4] and gas sensing properties [5]. Practically, ZnO based thin film can be grown by various techniques including radio frequency magnetron sputtering [6], DC magnetron sputtering [7], pulse laser , deposition, laser molecular beam epitaxy [8], pyrolysis spray [9], metalorganic chemical vapor deposition [10], sol-gel spin coating [11] and etc. Oxide materials are the basis of various smart and functional materials such as for transparent conducting oxide (TCO).

X-ray measurement techniques are widely used to characterize various thin film materials. Thin film material is a two-dimensional material formed on the surface of the substrate and is usually anisotropy [12]. Anisotropy means that the thin film material grows parallel along the stacking direction (thickness) or in the plane direction (within the surface plane). Based on these reasons, many researchers discuss the nature of thin film materials, and characteristics of the direction of the field owned by thin films. What is often discussed as an example of the nature of anisotropy is the crystal structure, crystallinity, and other properties of the thin film itself which is adapted to what application will be achieved. These subjects include constant lattice, crystal orientation, crystallite size etc. Furthermore, a frequent discussion is about the crystal phase of thin films, where the presence of unstable phases in the Bulk state, also the distortion or relaxation of the epitaxial thin film process. Additionally, the X-ray reflectivity method can also be used to determine various properties of thin films such as the thickness and density of the film.

In this paper, we employed a simple and easy sol gel process to prepare ZnO: Cu thin film. Furthermore, the deep exploration based on structural properties was discussed using X-ray diffraction technique such as crystallinity, crystallite size, lattice parameter, Zn-O length bond (L), volume of unit cell of hexagonal system (V), strain dan dislocation. And also morphology of the ZnO doping Cu thin film as affecting concentration of dopan are elaborated with the XRD analysis.

2. Methods

The precursors, dopants, solvents and stabilizers in the manufacture of this sol gel are zinc acetate dehydrate (Zn (CH3COO) 2.2H2O), Copper acetate monohydrate (Cu (CH3COO) 2.H2O), propanol (CH3CH2CH2OH) and ethanonlamine (C2H7NO) from Merck. Sol solution is prepared by dissolving Zinc acetate dihydrate and adding Copper acetate monohydrate with variations of 0, 1, 3, and 5% to isopropanol solvent then stirred using magnetic stirrer at 60 ° C for 15 minutes. Next add the ethanolamine stabilizer to the sol solution, then stir again for 60 minutes. After that, the sol solution was cooled and left for 24 hours. At the same time, cut the corning glass substrate with dimensions of 1.5 x 1.25 cm. The substrate is then washed using ethanol and acetone in an ultrasonic bath for 10 minutes. Then substrate is rinsed with DI water and dried with nitrogen gas. Next step, the deposition process using spin coating technique. After substrate was placed on the spin coater then a solution of 0.075 mL was dropped onto the glass substrate and rotated at a rate of 3000 rpm for 15 minutes. Then the preheating is done at a temperature of 300 °C for 15 minutes. The purpose of the preheating process is to vaporize the solvent and organic components on the resulting thin film. To get a good film and no cracks, then annealing is done at a temperature of 500 °C for 2 hours. After that, the ZnO:Cu sample is left until room temperature. ZnO:Cu thin film samples that have been produced, then characterized using X-ray diffraction (XRD) from Rigaku smartlab. The XRD data will then be discussed in detail about the relationship of full width at haft maximum (FWHM) and crystal size, lattice parameters. Length of bond between atoms, volume of the plane of the thin film formed. The lattice strain and dislocation density that occur in the thin film formed will also be discussed as the effect of increasing the concentration of Cu doping. ZnO doping Cu thin film morphology will be characterized using a scanning electron microscope (SEM) from Hitachi High-Tech Co. Ltd., Japan.

3. Results and Discussion

To determine the crystal structure which includes the type, grain size, lattice constants or parameters, d spacing and FWHM X-ray diffraction can be used. X-rays are electromagnetic waves with wavelengths between 400-800 nm. XRD provides diffraction data and quantization of diffraction intensity at the corners of a material. XRD spectrum is presented in a graph between intensity versus Bragg angle, 2θ. Each peak diffracted in the XRD spectrum shows a crystal field with a certain orientation (anisotropic property)[13]. Rays that hit the sample will be scattered by particles forming thin films. There are scattered rays that eliminate each other (destructive interference) and some are mutually reinforcing (constructive interference). The more rays that reinforce each other, the peaks of intensity that are

formed are also increasingly sharp. Figure 1 shows the diffraction pattern of ZnO doping Cu thin films with different doping concentrations.

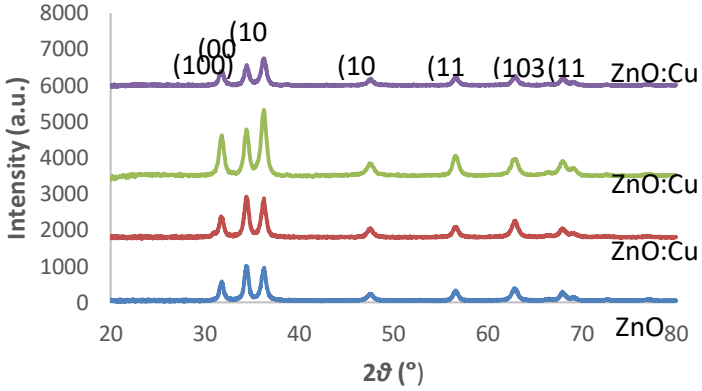

Figure 1. XRD pattern of ZnO and ZnO doping Cu thin films

The XRD spectrum from ZnO doping Cu thin film obtained, then matched with ICDD (International Center for Diffraction Data) data no. 00-005-0664. From the XRD spectrum in Figure 1, it can be seen that there are three diffraction peaks that are dominant at 2θ = 31.7, 34.5, and 36.3, which are fields (100), (002) and (101), respectively. These results indicate that the thin film formed has a hexagonal wurtzite type polycrystaline structure [14]. Based on the XRD spectrum results do not show any preferred orientation of the crystallization formed. This can be seen from the diffraction peak intensities (100), (002) and (101) which are almost the same. The low intensity of the diffraction peaks produced is due to the thickness of the thin film formed quite thin. Furthermore, to determine the preferred orientation of the resulting thin film can be determined by calculating the value of the texture coefficient (TC) shown in equation (1) [15]. The TC value indicates the preferred orientation of the thin film along the crystal plane direction. A film is said to have a preferred orientation if the TC value > 1 [16].

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

where *TC* is texture coefficient, $I_{(hkl)}$ is XRD intensity of the film samples, *n* is the number of reflections observed in XRD pattern, and $I_{r(hkl)}$ is reference intensity. The complete of *TC* calculation results are shown in Table 1.

Table 1. TC values for ZnO doping Cu thin films with different doping concentrations

Variation of Cu concentration	*hkl* (100)	(002)	(101)
0	0.784457	1.840593	0.763366
1	0.683254	1.910785	0.778267
3	1.000456	1.486962	0.923553
5	0.861052	1.501359	0.937357

Based on Table 1, it can be seen that all ZnO thin films without and doped Cu have TC values > 1, for the crystal plane (002). Thus it can be said that ZnO thin films that have been grown have a preferred orientation throughout the field (002). In other words, the resulting ZnO:Cu thin film grows along the c axis. The next deep discussion will focus on the crystal field (002). Its because for the window layer application on solar cell was used crystal plane of (002) [17]. For the average crystallite size value of

ZnO:Cu thin films can be calculated from full width at haft maximum (FWHM) using the Scherrer formula [9,18]:

$$D = \frac{0.89\,\lambda}{\beta \cos\theta} \quad (2)$$

Where D is the crystallite size, k is the shape factor, λ is the X-ray wavelength of Cu Kα (0.154 nm), β is the full width at haft maximum (FWHM) and θ is the Bragg angle. The results of the calculation of crystallite size can be seen in Table 2. Based on Table 2, its clear the introduction of copper action is not shifted the diffraction peaks of the film compared to ZnO undoped. This means the copper ion is not replace the Zn ions on the structure of the thin films, but the copper ions are just interstitials on the ZnO structure of the films. That can be seen from the XRD spectrum not new diffraction peak was apperaed. Other reason, also can show from the d-spacing and lattice parameter value, c is not change between ZnO undoped and ZnO doping Cu.

Table 2. Structural parameter of ZnO:Cu thin film with variation of Cu concentration

Doping Cu	2θ	FWHM	D (nm)	d-spacing(Å)	Lattice parameter c (Å)	L (Å)	V(Å^3)
0	34.39	0.50945	28.1988	1.3166	5.2161	2,2723	47.9712
1	34.39	0.56344	25.4968	1.4870	5.2161	2.2725	48.0743
3	34.44	0.61932	23.1994	1.3078	4.9753	2.1642	45.7130
5	34.42	0.57061	25.1784	1.3195	5.2117	2.2707	48.1799

The crystallite size values of undoped and ZnO doped Cu decreased with the addition of Cu doping concentrations as shown in Table 2. Increased doping Cu concentrations decreased the crystallinity properties of the resulting thin films. This is related to the positioning behavior of the doping atoms in the ZnO crystal structure. Almost all doping atoms may substitute with the Zn atoms in low Cu content [19]. Because the amount of Cu doping is low and the ionic radius is almost the same as Zn2+ (0.060 nm) and Cu (0.057 nm), the crystal structure of ZnO does not distort severely. In addition to reasons for ionic radius, Madelung's energy is also likely to influence the substitution of Zn atoms by dopants. Substitution of dopant atoms in Zn atoms continues to occur with the addition of dopant concentrations until the limit of the solubility of the host material occurs.

The lattice parameters c are calculated using the equation [2, 20]:

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

and

$$c = \frac{\lambda}{\sin\theta} \quad (4)$$

To calculate the distance between atoms or q-spacing, use the formula as follows [21]:

$$\frac{1}{d^2} = \frac{4\left(h^2 + hk + l^2\right)}{3a^2} + \frac{l^2}{c^2} \quad (5)$$

Zn-O bond lengths can be calculated using formulas

$$L = \sqrt{\left(a^3/3\right) + \left(\left(1/2\right) - u\right)^2 c^2} \quad (6)$$

with $u = a^2/3c^2 + 0.25$ is a potential parameter of hexagonal structure. Next to the volume of unit cells of hexagonal structure can be obtained as follow this equation [16]:

$$V = 0.868\; x\; a^2 x\; c \quad (7)$$

Based on Table 2, it can be seen thats changes in parameters affect the bond length of ZnO (L) and the volume of one hexagonal system unit (V). The greater volume starts ZnO undoped to ZnO doping Cu because the lattice parameter is also increasing. Bond length also increased in ZnO undoped to 1% Cu doping. This is in accordance with previous research by Aryanto et al.[16].
Furthermore, from the XRD data we can also obtain information about the lattice strain, stress and dislocation density. The lattice strain, ε along the *c*-axis can be calculated as follow the formula [22].

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

For stress value of the film can be calculated using formula [23].

$$\sigma = -233\ \varepsilon \tag{9}$$

Where σ is the stress value of the thin film and a negative sign indicates a compressive stress. Lattice strain of the film can also affecting to the length of dislocation lines per unit volume of the crystal. As known as dislocation density of the crystal can be calculated as follow the formula [16, 24].

$$\rho = \frac{\sqrt{12}\ \varepsilon}{D\ d} \tag{10}$$

The calculation result of lattice strain, stress and dislocation density can be seen on Table 3.

Table 3. Calculation result of lattice, stress and dislocation density of ZnO:Cu thin film

Doping Cu	Lattice strain, ε	Stress, σ	Dislocation density, ρ (line/nm^2)
0	0.4116	-95.8956	0.00384
1	0.4552	-106.0583	0.00416
3	0.4996	-116.3970	0.00504
5	0.4606	-107.2992	0.00482

From Table 3, its clearly seen the lattice strain of the ZnO thin film was increased with increases of the Cu dopant concentration up to 3% and then decreases. It can be said the stress of the film was decreased with increases concentration of Cu dopant. Stress values indicate the state of the forces between the constituent atoms of the crystal. Stress is proportional to the magnitude of the bonding forces between atoms, so the smaller stress will be affected on the bonding force of the atom. The binding force between atoms is proportional to the binding energy of a crystal, this energy is needed to separate the atoms in a crystal. Lattice vibrations that play a role in the formation of energy in crystals shows a homogeneity of the arrangement of atoms in the crystal. The atoms in this arrangement are not free to move due to the force. The atoms that make up the crystal always vibrate to the equilibrium position, so that the stress value in the film become high, then the arrangement of the atoms in the film more homogeneous. In other word, the film with inhomogeneous structure can be seen from the dislocation density value.

4. Conclusion

The deposition of Cu doping ZnO thin films using the sol gel spin coating method has been successfully carried out. ZnO:Cu thin film was studied using X-ray diffraction (XRD). ZnO: Cu thin films have a hexagonal wurzite structure with a preferred c-axis orientation. The addition of Cu doping concentration resulted in increased FWHM so that the crystallite size decreased. Thus it can be said that crystalinity decreases with the addition of Cu. Furthermore, the lattice parameter changes with the addition of Cu doping. Change of parameters affect the bond length of ZnO (L) and the volume of one hexagonal system unit (V). The greater the volume starts ZnO without doping to ZnO doping because the lattice parameter is also greater. Bond length also increased in ZnO without doping to 1% Cu doping. According to lattice strain of the film was also affects the length of dislocation lines per unit volume of the crystal. The lattice strain of the ZnO thin film was increased with increases of the Cu dopant concentration up to 3% and then decreases. It can be said the stress of the film was decreased with increases concentration of Cu dopant. Stress values indicate the state of the forces between the constituent atoms of the crystal.

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