

R. HUSSIN^{1,2,5*}, F. HANAFI², R.A. RASHID¹, Z. HARUN^{2,3}, Z. KAMDJ²,
S.A. IBRAHIM^{1,3}, A.R. AINUDDIN², W. RAHMAN^{4,5}, A.M. LEMAN^{1,5}

STRUCTURED ANALYSIS OF NANOSTRUCTURED ZINC OXIDE (ZnO) THIN FILMS DEPOSITED BY SOL-GEL

In this work, zinc oxide (ZnO) thin films are deposited on glass substrate using the sol-gel spin coating technique. The effect of annealing temperature on structural properties was investigated. The ZnO sol-gel was produced from zinc acetate dehydrate as the starting material with iso-propanol alcohol as the stabilizer. The ratio was controlled, distilled water and diethanolamine as the solvent mixing on a magnetic stirrer for an hour under constant heat of 60°C. The ZnO thin film was deposited using the spin coating technique with the speed of 3000 rpm for 30 minutes before the sample undergoes pre-heat in the oven at the temperature of 100°C for 10 minutes. The sample was annealing in the furnace for an hour at 200°C, 350°C, and 500°C. The X-ray diffraction (XRD) analysis confirms that hexagonal wurtzite structure with zincite and zinc acetate hydroxide hydrate composition. The thin films surface roughness was analyzed using an atomic force microscope (AFM) and scanning electron microscope (SEM) for surface morphology observation.

Keywords: Sol-gel; Zinc Oxide (ZnO); Thin films; nanostructured

1. Introduction

The ZnO is a semiconductor material with several favorable properties, including good optical properties such as transparency, high and room-temperature solid [1,2]. The application of thin film has been widely used nowadays in the field of semiconductors [3], oil-water separation [4], and optical application [5]. ZnO thin film is one of the essential types of thin film. ZnO thin film can be grown using various techniques from physical method and chemical method. Many causes can interfere with thin-film growth, such as the environment, the deformation technique, and the method. Different types of emission defects had been recorded, with some of them already been identified as the causes. At the same time, the rest of it remains experimental and study and the study that has been done on how to obtain a thin film with better structural quality with better optical properties, composition, and improves morphological structure. In this study, the ratio of the starting material was iso-propanol alcohol and the heat treatment temperature is tested to obtain a conclusion on a better ZnO thin film besides finding the solution on the

emission defect. Thin-film deposition techniques can generally be classified in three ways: physical process, chemical process, and wetting process. The physical method covers the deposition technique, which depends on the evaporation and ejection of the materials from the source.

In contrast, the chemical method covers the deposition technique, which depends on the physical properties, thermal effects, and thermal growth [6,7]. The film growth generally occurs at the third step, where the unit species lose their velocity component normal to the substrate and are physically absorbed onto the surface of the substrate with a weak bond. The absorbed species are not in equilibrium with each other around the surface until they interact with other adsorbed atoms and form clusters. Finally, the clusters continue to grow until they reach a critical radius that is thermodynamically stable as the nucleus. Various deposition techniques have prepared ZnO thin films, including sol-gel process [1,2,8], spray pyrolysis [9], ultrasonic spray [6], magnetron sputtering [10], pulsed laser deposition [11], and reactive electron beam evaporation. An excellent optical properties quality material shows high transparency within a visible range

¹ UNIVERSITI TUN HUSSEIN ONN MALAYSIA, FACULTY OF ENGINEERING TECHNOLOGY, DEPARTMENT OF MECHANICAL ENGINEERING TECHNOLOGY, JALAN EDU HUB GUNASAMA 1, PAGO HUB, KMI, JLN PANCHOR, 84600 PAGO HUB JOHOR, MALAYSIA

² UNIVERSITI TUN HUSSEIN ONN MALAYSIA, FACULTY OF MECHANICAL AND MANUFACTURING ENGINEERING, PARIT RAJA, 86400 BATU PAHAT, JOHOR, MALAYSIA

³ UNIVERSITI TUN HUSSEIN ONN MALAYSIA, FACULTY OF MECHANICAL AND MANUFACTURING ENGINEERING, INTEGRATED MATERIAL AND PROCESS, ADVANCED MANUFACTURING & MATERIALS CENTRE, PARIT RAJA, 86400 BATU PAHAT, JOHOR, MALAYSIA

⁴ UNIVERSITI MALAYSIA PERLIS, FACULTY OF MECHANICAL ENGINEERING TECHNOLOGY, PERLIS, MALAYSIA

⁵ UNIVERSITI MALAYSIA PERLIS, CENTER OF EXCELLENCE GEOPOLYMER AND GREEN TECHNOLOGY (CEGEGOTEC), PERLIS, MALAYSIA

* Corresponding autor: rosniza@uthm.edu.my



with an average transmittance between 80 and 90% due to low scattering or absorption loss [12]. Typically the reflectance decreases while the transmittance increase depending on the doping materials. For a better quality of optical properties closely related to the characteristic of the bandgap of the material as the wider bandgap brings the better optical properties [12]. Optical properties were studied using a UV-Vis spectrophotometer to determine the absorbance, transmittance percentage, and concentration of materials. In this study, the ratio of the starting material and the sintering temperature was variable to growth on a better ZnO thin film besides finding the solution on deposition effect parameters.

2. Methodology

The detailed procedure to grow ZnO thin film on glass substrates and each characterization process with analysis procedure on X-ray diffraction (XRD), Atomic Force Microscope (AFM), and Scanning Electron Microscope (SEM).

Sol-gel preparation and characterization

The ZnO thin films were prepared by using the sol-gel method. The glass substrates were cleaned by using acetone, ethanol, and distilled water in the ultrasonic bath. Then, the glass substrate was put into acetone solution and cleaned using an ultrasonic bath for 10 minutes. The ZnO sol-gel was prepared by dissolving zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) in iso-propanol ($\text{C}_3\text{H}_8\text{O}$). The diethanolamine (DEA) ($\text{C}_4\text{H}_{11}\text{NO}_2$) and distilled water which both act as a catalyst. The zinc acetate dihydrate powder was dissolved in iso-propanol with a concentration of 0.06 mol/L to form the ZnO precursor solution. The precursor solution was stirred for 30 minutes and heated at 60°C on a hotplate magnetic stirrer until a homogenous ZnO precursor solution was formed. Then, diethanolamine and distilled water were added drop by drop until the solution changed from milky white to a clear transparent solution. The solution was thoroughly stirred and heated for 2 hours before being kept for 24 hours aging process at room temperature at 23°C. The sol-gel synthesis parameter was set at ratios 1 and 10 of Iso-Propanol, as shown in Tables 1 and 2.

TABLE 1

Chemical composition for solution ratio 1

Name of chemical	Chemical formula	Ratio
Zinc acetate dehydrate	$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	1
Iso-Propanol	$\text{C}_3\text{H}_8\text{O}$	1
Distilled water	H_2O	1
Diethanolamine	$\text{C}_4\text{H}_{11}\text{NO}_2$	1

TABLE 2

Chemical composition for solution ratio 10

Name of chemical	Chemical formula	Ratio
Zinc acetate dehydrate	$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	1
Iso-Propanol	$\text{C}_3\text{H}_8\text{O}$	10
Distilled water	H_2O	1
Diethanolamine	$\text{C}_4\text{H}_{11}\text{NO}_2$	1

Spin coating technique

The ZnO films were deposited on glass substrates by using the spin coating technique. The spin coating technique has been conducted by dripping sol-gel dropped onto a substrate and spin at 3000 rpm for 30 seconds. The droplet of ZnO sol-gel spreads rapidly on the substrate. Spin coater (VTC-50A, MTI Corporation) was used to deposit thin films. The substrate was placed on the spin coater rotating plate center with a few drops of ZnO sol dripped onto the substrate. Then, the spin coater was switched on to deposit the thin film. The deposition was run for ten cycles for one type of ZnO sol until the resulting thin film form on the glass substrate. The thin film deposition was conducted in a control fume hood at room temperature. After each deposition cycle, the substrate was taken out from the spin coater and dried in the oven at 100°C for 3 minutes to evaporate the ZnO sol-gel and remove organic residual. One deposition cycle is considered as one time of deposition with a one-time drying process. After the drying process in the oven was done, the substrate should be cooled to room temperature before other deposition cycles can be done on the substrate. The deposited substrate was then calcined at 200°C, 350°C, and 500°C in the furnace for the resulting ZnO thin film.

Characterization Analysis

The ZnO thin films have been characterized with various methods such as XRD, FESEM, AFM, EDX, and UV-Vis. Different methods are used to study different analyses of ZnO thin film characteristics. The X-Ray Diffraction (XRD, Bruker D8 Advanced) analyzed thin films' crystal structure and lattice parameters. The characterization was obtained with Cu-K α radiation at a wavelength range is 0.15406 nm and scan angle 2 θ . The analysis is carried out at 2 θ (20° to 70°). The results obtained from XRD were analyzed using EVA software to match with a standard pattern. The Scanning Electron Microscope (SEM) was used to observe the morphology of the thin film sample at high magnification, high resolution, and depth of focus. Atomic Force Microscope (AFM) (XE-100 Park System) was used to scan surface topographies and RMS values. In this study, the scan size used was 3 μm \times 3 μm . The results obtained were analyzed using XEC software.

3. Results and Discussion

Structure analysis of ZnO thin film

The crystal structure of ZnO thin film was studied using X-ray diffraction (XRD). Fig. 1 shown the XRD analysis of ZnO thin films with two different ratios of Iso-Propanol and three calcination temperatures at 200°C, 350°C, and 500°C. Fig. 1 shows the XRD spectra of ZnO thin film based on the sol-gel ratio (1 and 10). The XRD spectra match two types of structure, zinc acetate hydroxide hydrate from the reference spectra file no PDF2007:00-056-0569 and zinc oxide with the spectra file no of PDF2007:00 036-1451. Through the analysis from Fig. 1 at the highest diffraction peak resulting at ZnO (101) followed by (002) and (100) respectively. In contrast, the higher peak and intensity was formed at the sample with calcination temperature of 500°C compare to the sample with calcination temperature of 350°C and 200°C. The results have shown that the diffraction for samples with calcination temperature of 350°C and 200°C has a very low intensity. It is shown that the intensity increases if the sol-gel ratios decrease. The sample with calcination temperature of 350°C with the sol-gel ratio one and the sample with calcination temperature of 200°C detected the composition of zinc acetate hydroxide hydrate caused by contamination to

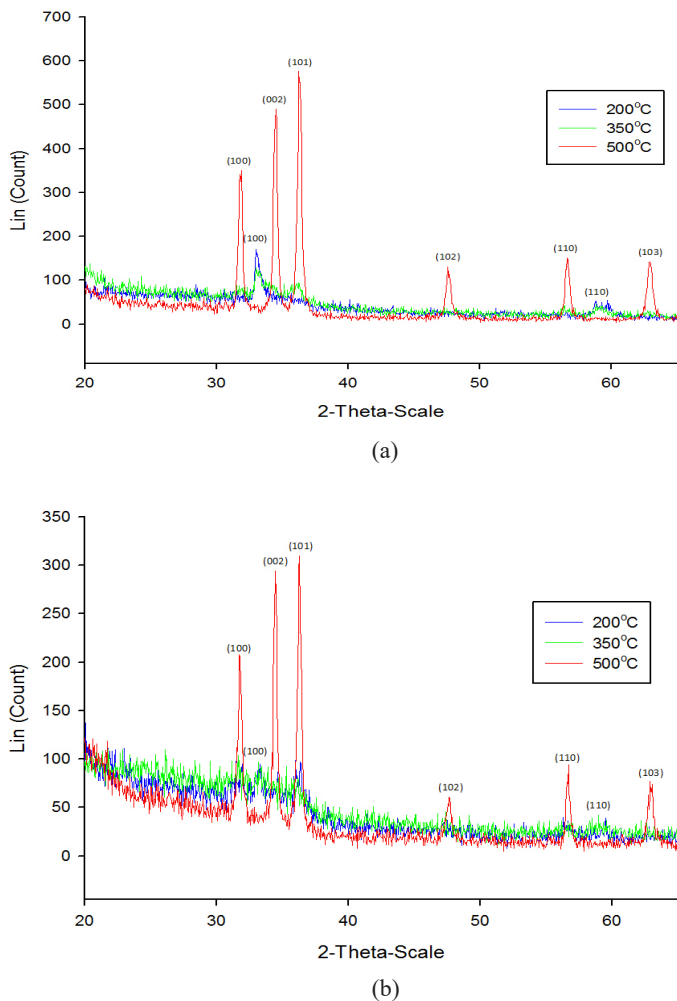


Fig. 1. XRD pattern for the sample with sol-gel (a) ratio one and (b) ten

the sol-gel during sol-gel preparation. The XRD result demonstrated that all the film is polycrystalline wurtzite hexagonal structure. The findings are similar to Vaseem and Shaivalini findings, where the similar composition detected on XRD analysis with the same highest peak plane also obtain from the graph [8,13].

Surface roughness analysis of ZnO thin film

The surface roughness of ZnO thin film was characterized using AFM. The surface's mean roughness (Ra) is calculated for a $3 \mu\text{m}^2 \times 3 \mu\text{m}^2$ scan area. Fig. 2 shown the root mean square (RMS) vs. temperature (°C), while Fig. 3 shows AFM topographies of ZnO thin films. Based on Fig. 2 and Fig. 3, the sol-gel ratio and calcination temperature affect the surface roughness and morphology of the thin film. The morphology of the ZnO thin film shows that a higher ratio of solvent and higher calcination temperature gave the smaller grain size compared to all the samples. Mouet T [13] found a similar result where the temperature directly effects the sample roughness and grain size. According to Fig. 2, the sample with an annealing temperature at 350°C has a smoother surface than sample calcination at 200°C and 500°C because the temperature effects the roughness and grain size. Fig. 3 shows that the sample with the higher ratio of the sol-gel given a smaller roughness value compared with the lower ratio of solvent. It is known that the increase in surface roughness may cause deterioration of the optical properties [14].

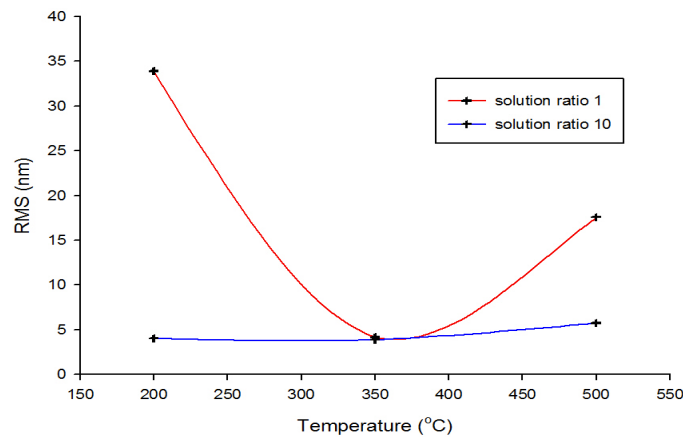


Fig. 2. RMS table on surface roughness for samples

Surface morphology analysis of ZnO thin film

The micrograph of ZnO thin film was observed using a scanning electron microscope (SEM). Fig. 4 shows the micrograph of the ZnO thin film using the SEM at the magnification of 1000 times based on the sol-gel ratio. The micrograph shows the thin film's surface morphology given the different grain boundary sizes at 500°C with ratios 1 and 10. Fig. 4 shows the ZnO thin films micrograph with a ratio 1 has a smoother surface than

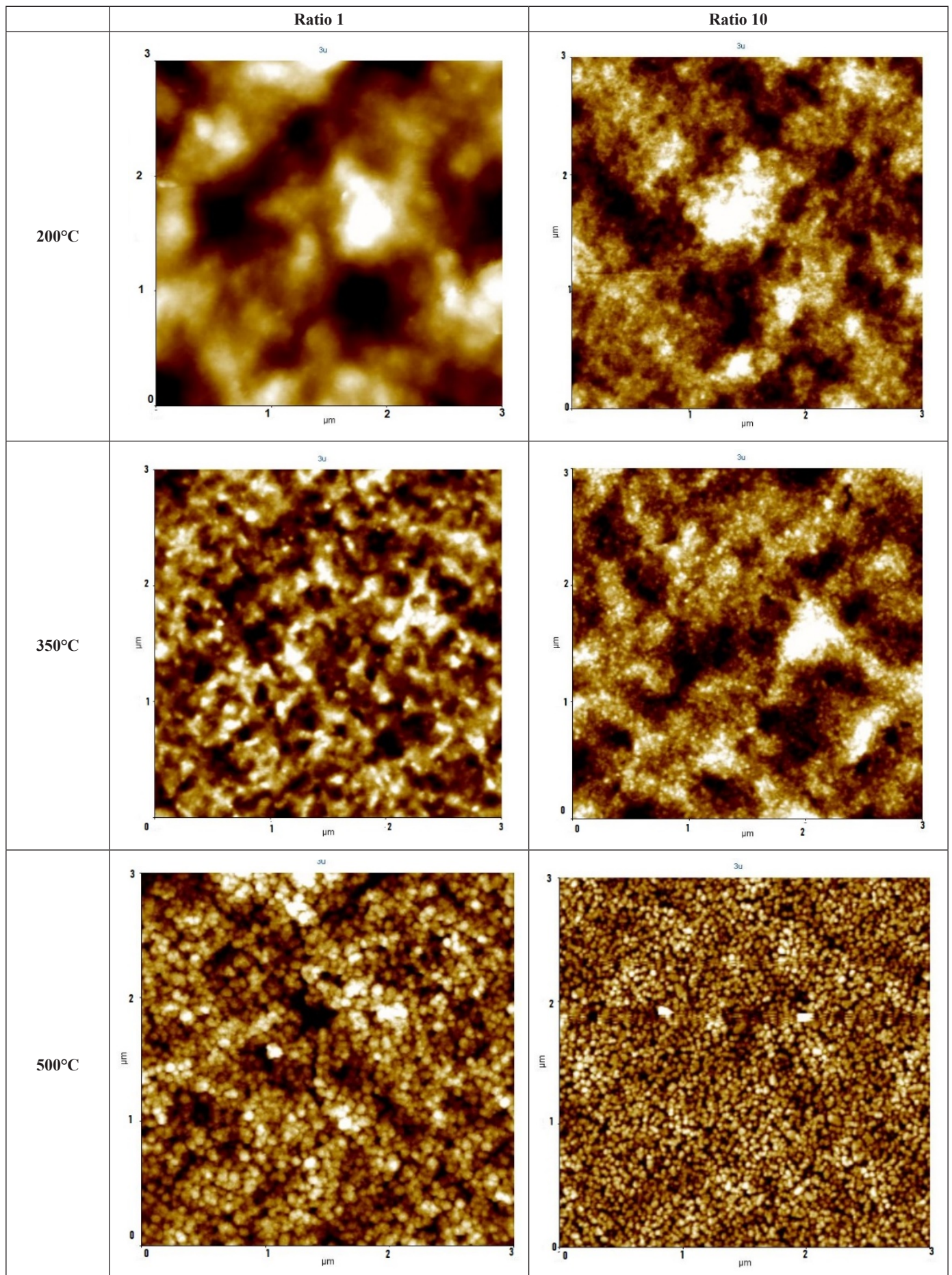
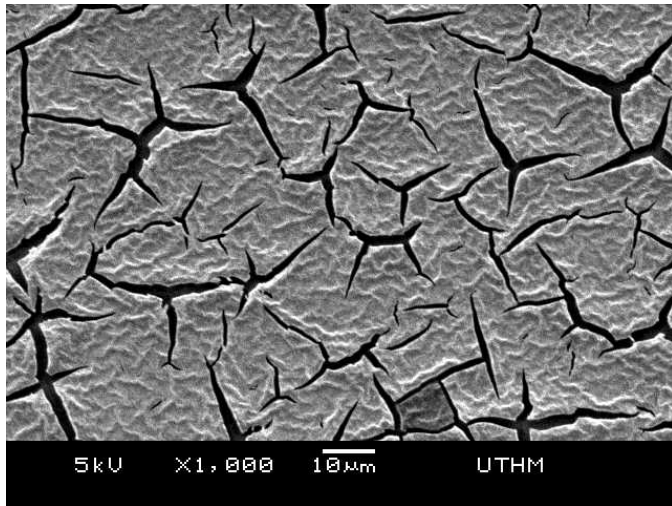
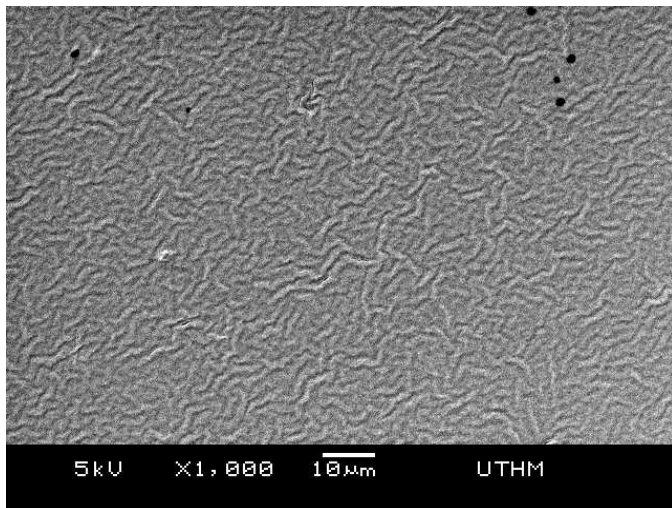


Fig. 3. AFM surface Morphology of ZnO Thin Films with different parameter with magnifications $3 \mu\text{m}^2 \times 3 \mu\text{m}^2$

10 ratio. From the perspective of the sol-gel ratio, the grain boundary of samples with a sol-gel ratio of 1 is more significant than samples with a sol-gel ratio of 10 higher intensity thin film, causing it harder to close the gap between grains. The findings made by P. Hosseini Vajargah and Shaivalini Singh show the same type of grain, and boundary conditions prove that temperature directly effects the grain condition of the thin film and the surface roughness [1,13]. Our finding can be concluded that the ratio of solvent, i.e., Iso-Propanol, also given a different surface structure.



(a)



(b)

Fig. 4. Micrograph image of SEM on sample at 500°C with ratio (a) 1 and (b) 10

5. Conclusion

In conclusion, the different structured of ZnO thin films were obtained using the different ratios of iso-propanol alcohol at ratios 1 and 10 on composition. The other parameter were controlled are calcination temperature process at 200°C, 350°C, and 500°C. The XRD spectra showed the existence of ZnO with the

crystal structure with hexagonal wurtzite of the highest diffraction peak resulting at ZnO (101) followed by (002) and (100) with calcination temperature at 500°C. It is proved that the intensity of thin film can be controlled by the calcination temperature and the ratio of sol-gel. The intensity of thin-film increases with the increase of the calcination temperature. The result of AFM shows that the chemical ratio and calcination temperature affect the thin film surface roughness and morphology. It proved that the sample with a higher ratio of sol-gel has a smaller roughness value than the sample with a lower ratio of sol-gel. The sol-gel ratio and calcination temperature also can control the surface condition and grain boundary shown with the SEM image. The smaller sol-gel ratio has the more extensive grain boundary because higher intensity thin film causing it harder to close the gap between grains. The in-depth analysis of influences temperature and solvent maybe will be extended to include in further studies.

REFERENCES

- [1] P.H Vajargah, H. Abdizadeh, R. Ebrahimi-fard, M.R Golobostan-fard, Sol-gel derived ZnO thin films: Effect of amino-additives, *Appl. Surf. Sci.* **285**, 732-743 (2013). DOI: <https://doi.org/10.1016/j.apsusc.2013.08.118>
- [2] I. Lorite, J.Wasik, T. Michalsky, R. Schmidt-Grund, P. Esquinazi, Hydrogen influence on the electrical and optical properties of ZnO thin films grown under different atmospheres, *Thin Solid Films* **556** 18-22. (2014). DOI: <https://doi.org/10.1016/j.tsf.2013.12.057>
- [3] F. Challali, D. Mendil, T. Touam, T. Chauveau, V. Bockelée, A.G. Sanchez, A. Chelouche, M.P. Besland, Effect of RF sputtering power and vacuum annealing on the properties of AZO thin films prepared from ceramic target in confocal configuration, *Mater. Sci. Semicond. Process* **118**, 105-217 (2020). DOI: <https://doi.org/10.1016/j.mssp.2020.10521>
- [4] J. Wang, A. Wang, W. Wang, Robustly superhydrophobic/superoleophilic kapok fiber with ZnO nanoneedles coating: Highly efficient separation of oil layer in water and capture of oil droplets in oil-in-water emulsions, *Ind. Crops. Prod.* **108**, 303-311 (2017). DOI: <https://doi.org/10.1016/j.indcrop.2017.06.059>
- [5] S.D. Yang, Y.X. Zheng, L. Yang, Z.H. Liu, W.J. Zhou, S.Y. Wang, R.J. Zhang, L.Y. Chen, Structural and optical properties of highly (110)-oriented non-polar ZnO evaporated films on Si substrates, *Appl. Surf. Sci.* **421**, 891-898 (2017). DOI: <https://doi.org/10.1016/j.apsusc.2017.02.069>
- [6] A.R. West, *Solid State Chemistry*, 2003. John Wiley & Sons, Singapore.
- [7] K.L. Chopra, *Thin Film Phenomena*, 1969, McGraw Hill, New York.
- [8] M. Vaseem, A. Umar, Y.B. Hahn, (2015). *ZnO Nanoparticles : Growth, Properties, and Applications* **5** (1-36), American Scientific Publishers.
- [9] C. Jagadish, V.A. Coleman, *Basic Properties and Applications of ZnO*, Elsevier (2006).

- [10] H. Morkoc, U. Ozgur, Zinc Oxide: Fundamentals, Materials and Device Technology, Wiley-VCH (2009).
- [11] S. Singh, P. Chakrabarti, Comparison of the structural and optical properties of ZnO thin films deposited by three different methods for optoelectronic applications, *Superlattices Microstruct.* **64**, 283-293 (2013). DOI: <https://doi.org/10.1016/j.spmi.2013.09.031>
- [12] K. Vijayalakshmi, K. Karthick, D. Gopalakrishna, Influence of annealing on the structural, optical and photoluminescence properties of ZnO thin films for enhanced H₂ sensing application, *Ceram. Int.* **39** (5), 4749-4756 (2013). DOI: <https://doi.org/10.1016/j.ceramint.2012.11.061>
- [13] T. Mouet, T. Devers, A. Telia, Z. Messai, V. Harel, K. Konstantinov, I. Kante, M.T. Ta, Growth and characterization of thin ZnO films deposited on glass substrates by electrodeposition technique, *Appl. Surf. Sci.* **256** (13), 4114-4120 (2010). DOI: <https://doi.org/10.1016/j.apsusc.2010.01.093>
- [14] A. Taabouche, A. Bouabellou, F. Kermiche, F. Hanini, S. Menakh, Y. Bouachiba, T. Kerdja, C. Benazzoux M. Bouafia, S. Amara, Effect of Substrates on the Properties of ZnO Thin Films Grown by Pulsed Laser Deposition, *Adv. Mater. Phys. Chem.* **3** (4), 209-213 (2013). DOI: <https://doi.org/10.4236/ampc.2013.34031>