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OPTICAL PROPERTIES AND SURFACE MORPHOLOGY OF Al-DOPED ZINC OXIDE THIN FILM SOLAR CELL

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ABSTRACT

The undoped and aluminium-doped (1-4) wt% zinc oxide (ZnO) thin films were fabricated at 40 nm, 100 nm and 150 nm thickness using thermal evaporation method onto corning glass substrates and annealed at 450^{o}C in vacuum for 1 hour. The optical properties were studied using the UV-Vis and photoluminescence spectrums measurements. The morphology and the compositions of the films were observed using atomic force microscopy (AFM) and energy dispersive X-rays analysis (EDAX). The annealed crystalline structure was confirmed using X-ray diffraction (XRD). All the annealed Al-doped ZnO thin films were transparent and showed 80% - 95% transmission in the UV and visible light regions. As the doping increased up to 3 wt% , the optical band gap increased from 4.361 eV (undoped), 4.375 eV (1 wt%), 4.486 eV (2 wt%), 4.491 eV (3 wt%) and 4.416 eV (4 wt %). The emission PL spectra showed three main peaks centered at about 390 nm (UV), 420 nm (blue) and 580 nm (green) at excitation of λ = 290 nm. The intensity of the blue and green peaks decreased as the doping increased. The grain-size of the thin films decreased while the surface roughness increased with increasing aluminium doping.

Keywords: Al-doped Zinc Oxide; thermal evaporation; optical band-gap; photoluminescence; thin film solar cell;

INTRODUCTION

Transparent conductive oxide films such as tin oxide, indium tin oxide, cadmium sulphate and Al-doped zinc oxide are being widely studied. This is due to the low series resistance for high electronic conduction and high optical transmission for high light input to ensure high photocurrent. These materials are presently in use and under development for industrial application especially in solar cell [1]. Research on aluminum doped zinc oxide as transparent conductive oxide (TCO) started when industries looking to replace Indium Tin Oxide (ITO). This is due to high costs and limited resource of tin [2]. Zinc oxide is used more at present because of the wide availability of its constituent raw material and its low cost [3].

METHODOLOGY

Undoped ZnO and different compositions of aluminium doped ZnO (1-4 wt%) were prepared on cleaned corning glass substrates by thermal vacuum evaporation method. The correct amount of aluminium and zinc oxide were mixed together and the mixture underwent milling process for 20 minutes. The mixture was then poured into a crucible and heated in the furnace for 2 hours at the temperature of 700ºC and left for slow cooling overnight. Then the compound was pestled to powder form. The operating pressure of the evaporating system was in the range from 10^{-5} to 10^{-6} torr. The distance between the source and substrate were kept constant at 15cm during the deposition process. Then the compound was placed in a molybdenum boat crucible in the glass bell jar. All thin film samples deposition rate and thickness were monitored using quartz film thickness monitor FTM5. The deposition rate and thickness were kept constant at 0.3 nm/s and 100nm respectively. The prepared samples were then annealed at a temperature of 450ºC under vacuum condition using high temperature vacuum tube furnace GSL-1100 for one hour.

The optical properties of the samples were measured using Shidmadzu 3101PC UV-VIS NIR Spectrophotometer in wavelength range from 250nm – 1800nm focussing on the transmittance and absorbance spectra. The photoluminescence was analyzed with a spectrophotometer and the peaks in the spectra represent a direct measure of the energy levels. The determination of surface topology and morphology of undoped and aluminium-doped zinc oxide thin films would be carried out using atomic force microcopy. The grain size and RMS value hence could be obtained.

RESULTS AND DISCUSSION

The undoped and Al-doped ZnO thin films were optically characterized through transmission measurement in the near UV, Vis and IR regions using UV-Vis spectrum measurement. Figure 1 showed the transmittance spectra of undoped ZnO, 1wt%, 2wt%, 3wt% and 4wt% Al-doped. In the application of TCO, high transparency was the most important factor in the application of Al-doped ZnO [4]. For most optical applications a high transmission in visible range was very important [5]. Thus, the optical transmission was determined using UV-Vis spectrophotometer within the range of 250nm to 800nm.

The undoped ZnO and all the Al-doped ZnO thin films regardless of its doping weight percent, all demonstrate transmission above 80% in the UV-Vis range [4]. The transmission of the Al-doped ZnO was higher than that of undoped ZnO. As the weight percent of the Al-doped increased, the average transmission could be seen decreased from 90% to 85% in UV range. This may due to the fact that the film with 1wt% doping presents more voids than the film with 2wt%, 3 wt% and 4wt% Al-doped [6].

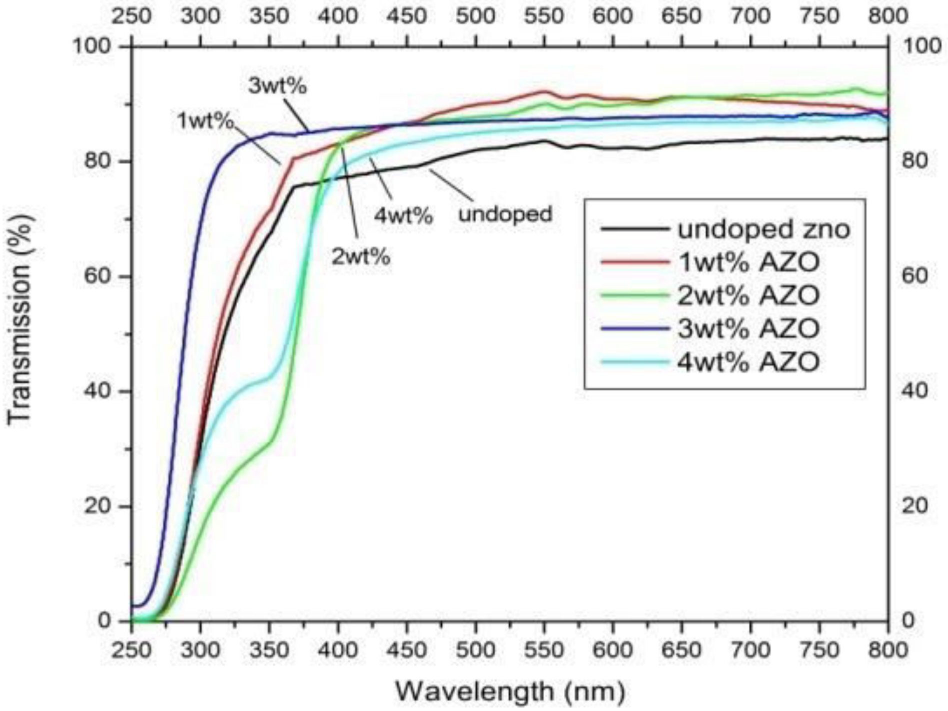
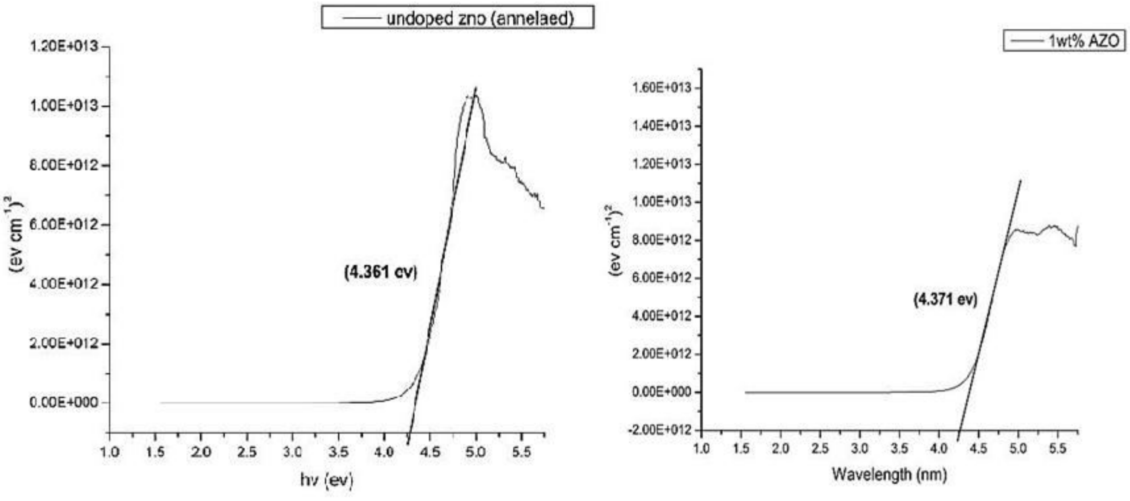
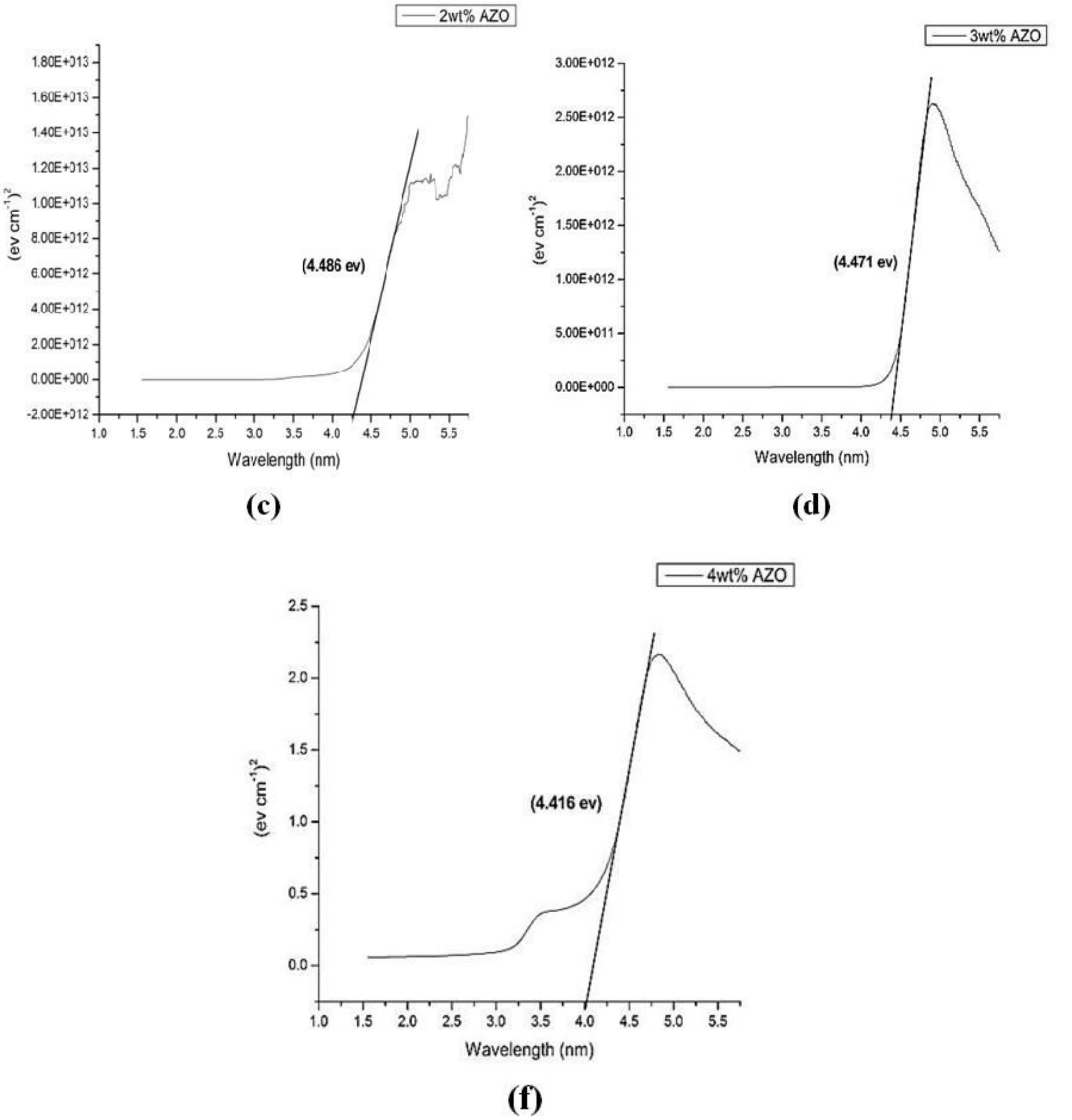


Figure 1: The optical transmittance spectrum of undoped Zno, 1wt%, 2wt%, 3wt%, and 4wt% Al-doped



(a)

(b)



(c) **(d)**

(f)

Figure 2: The optical energy band gap of (a) undoped ZnO (b) 1wt% (c) 2wt% (d) 3wt% and (e) 4wt% Al-doped ZnO

The sharp absorption edge for undoped ZnO revealed at the wavelength of about 275nm. As the weight percent of Al-doped increased, it could be observed from figure 4.1 that the absorption edge decreased to shorter wavelength started from undoped ZnO to 3wt% aluminium doping content [5]. The variation of optical direct band gap could be obtained by plotting $(\alpha hv)^2$ versus hv.

The bandgap energies estimated could be shown in table 1. The absorption edge for direct bandgap given by [6]:

$$\alpha hv = C(hv - E_g)^{1/2}$$

where C is a constant for a direct transition, and α is the optical absorption coefficient. The graph of $(\alpha h v)^2$ versus hv is then plotted. The optical energy gap E_g could be obtained from the x-intercept of the plotted graph for direct transition. The direct energy band gap is shown in Figure 2(a)-(f). The energy gap was obtained by extrapolating the linear absorption edge part of the curve using the equation above [7].

Table 1 shows the optical energy band gap obtained as explained above. As the weight percent of Al-doped increased up to 4wt%, the energy band gap increased. This is due to reason when doping, the density of the electron decreased as the Al^{3+} ion was substituted into Zn^{2+} ion site in the film. This means that the valence level was lowered [5].

Table 1: The direct optical energy bandgap obtained

No.	wt% Al-doped	Direct band gap (ev)
1.	0	4.361
2.	1	4.375
3.	2	4.486
4.	3	4.491
5.	4	4.416

Photoluminescence spectra were obtained at room temperature for all the prepared ZnO films with different aluminium doping. The excitation wavelength used was 290 nm. Two main peaks could be observed which were the excitation and emission peak. The emission peak was centered between 360 nm and 500 nm. Figure 3 showed the emission spectra of the undoped ZnO and all the prepared Al-doped ZnO.

Three main peaks could be seen located at 390 nm, 420 nm and 485 nm from the emission spectra. As the aluminium doping increased to 4wt%, the intensity of the blue peak (~420 nm) and the green peak (~485 nm) was decreased. The green emission was due to different intrinsic defects such as the zinc vacancy and oxide antisite defects. This result was reported in Ding et al as well. As for the blue peak, it might due to undesired scattering from the laser [8]. The locations of the peaks did not change with the introduction of aluminium into the zinc oxide thin film. The overall intensity of the spectrum with increasing weight percent of aluminium doping could be seen decreased, this might cause by the increase of Zn interstitial and attain summit with the increasing Al^{3+} substitute as ZnO was a self-assembled oxide compound.

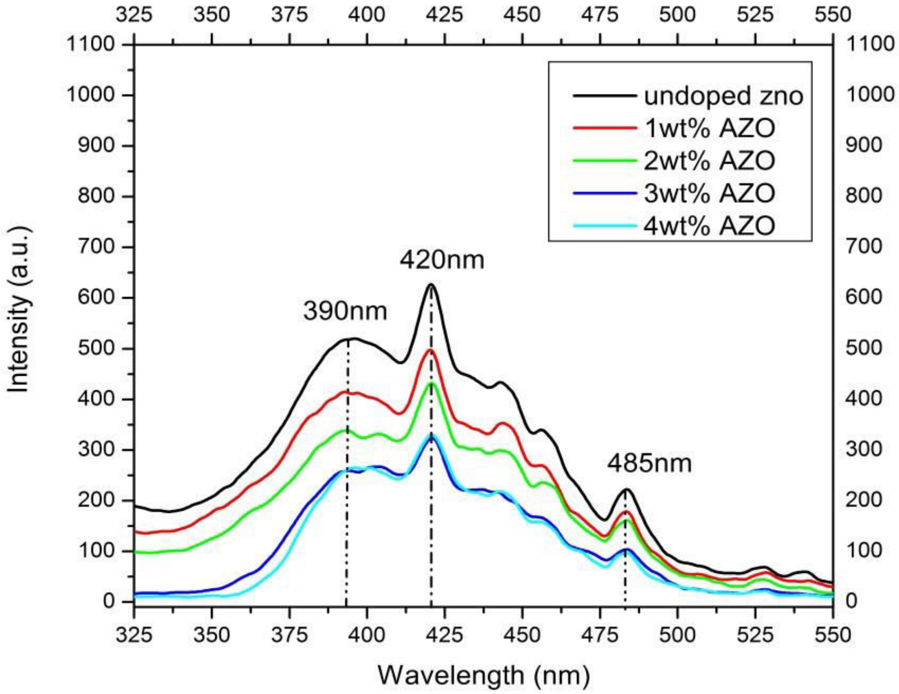
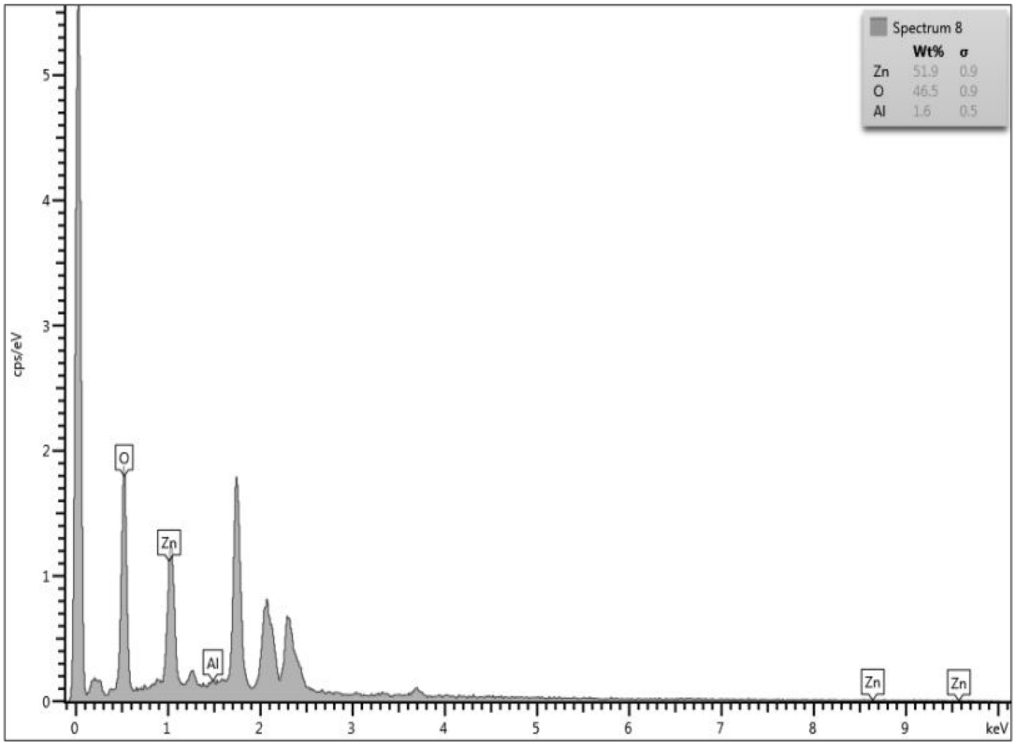


Figure 3: The emission spectra of the undoped ZnO, 1wt%, 2wt%, 3wt%, and 4wt% Al-doped

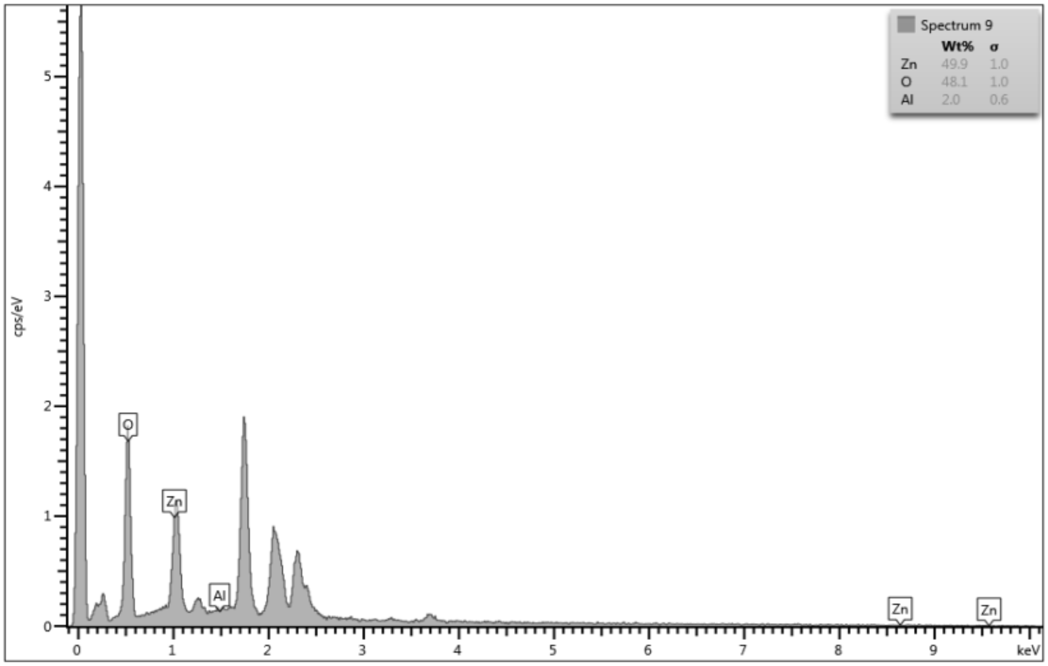
The compositions of the aluminium doped ZnO thin film was estimated by using the energy dispersive X-rays analysis (EDAX). Figure 4 and figure 5 show the EDAX results of the annealed and not annealed 2wt% Al-doped ZnO film on corning glass. From the EDAX analysis, it confirms the composition of Al, Zn and O in the Aluminium doped ZnO films. The Al composition was then well proven to be present in the samples which act as the doping element in ZnO film. Besides the composition of the three elements, the presence of several peaks in the spectrum could be seen from the EDAX result. This is due to presence of silicon in the corning glass substrate, the molybdenum boat and carbon coating on the sample during test.



Spectrum 8

	Wt%	σ
Zn	51.9	0.9
O	46.5	0.9
Al	1.6	0.5

Figure 4: The EDAX results for the annealed 2wt% Al- doped ZnO thin film deposited on corning glass



Spectrum 9

	Wt%	σ
Zn	49.9	1.0
O	48.1	1.0
Al	2.0	0.6

Figure 5: The EDAX results for the not annealed 2wt% Al- doped ZnO thin film deposited on corning glass

Table 2 shows the elemental composition in weight percent of Zn, O and Al in annealed and not annealed 2wt% Al-doped ZnO thin film obtained from the EDAX analysis. We could see from figure 5 that the weight percent of aluminium doping dropped from 2.0wt% to 1.6% after annealed. The weight percent loss was associated to the heat treatment in the sample.

Table 2: The elemental compositions in weight percent of Zn, O and Al

2wt% Al-doped ZnO	**Zn(%)**	**O(%)**	**Al(%)**
annealed	51.9	46.5	1.6
not annealed	49.9	48.1	2.0

Energy dispersive X-rays analysis spectroscopy (EDAX) mapping were provided in addition to the SEM image as shown in figure 6 and figure 7 for the elemental analysis on the surface of the thin films. The taken SEM image showed dense and uniform thin films which deposited on a corning glass substrate. The grains of the thin films could be seen tightly packed to the substrate.

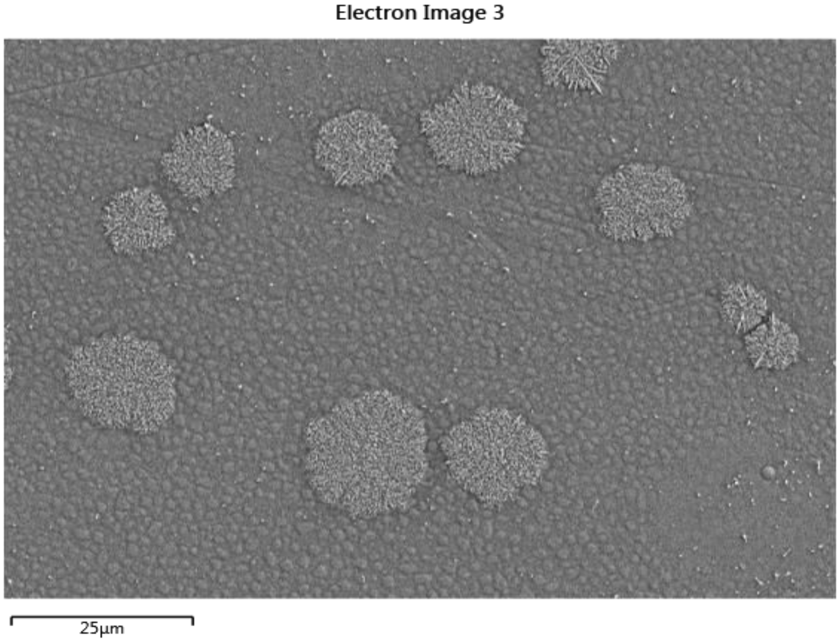


Figure 6: The SEM image of annealed 2wt% Al-doped ZnO thin film

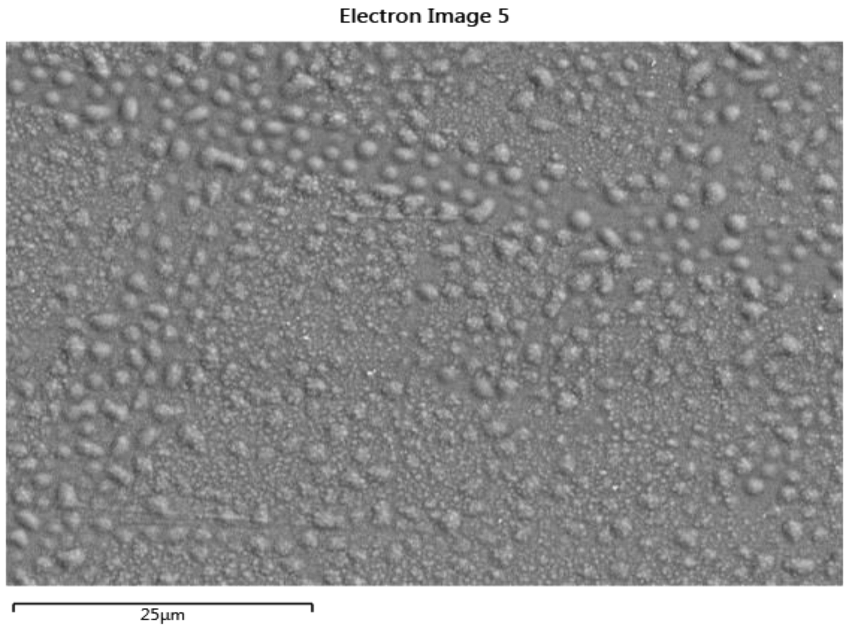
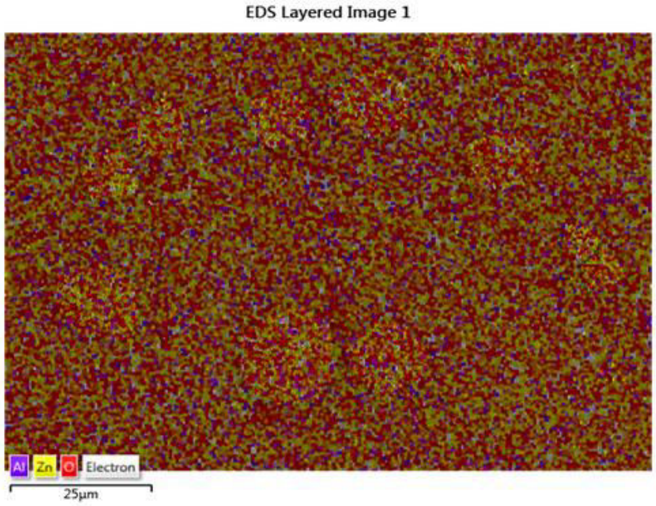
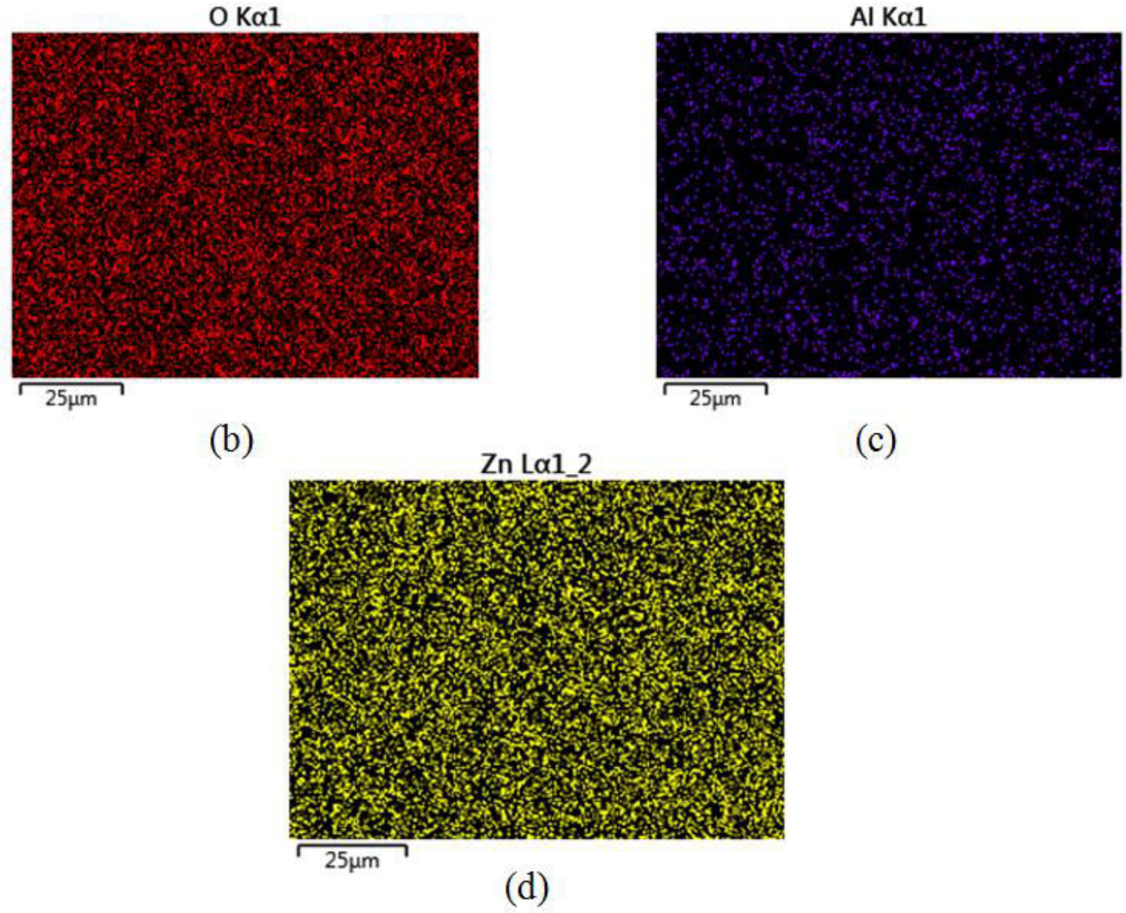


Figure 7: The SEM image of not annealed 2wt% Al-doped ZnO thin film

The EDAX mapping on annealed and not annealed of O, Al and Zn are shown in figure 8(a)-(d) and figure 9(a)-(d) respectively. From the elemental analysis, it could be seen that the aluminium which acts as a dopant was distributed evenly on the surface of the thin film. The elemental mapping could be confirmed by the weight percentage in EDAX analysis.

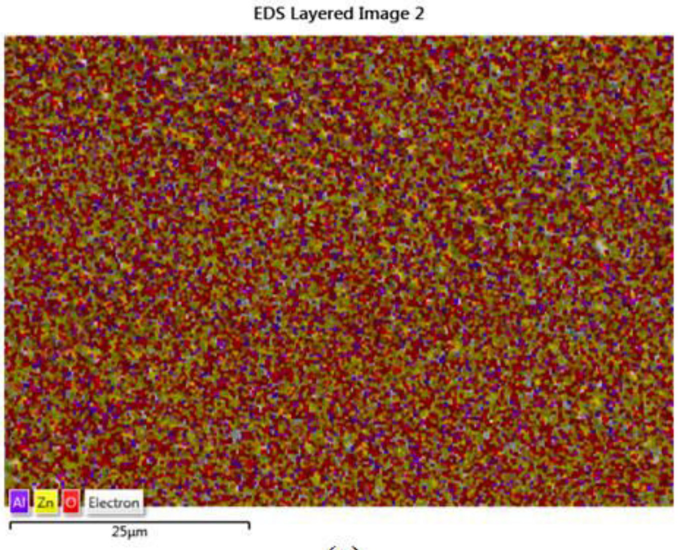


(a)

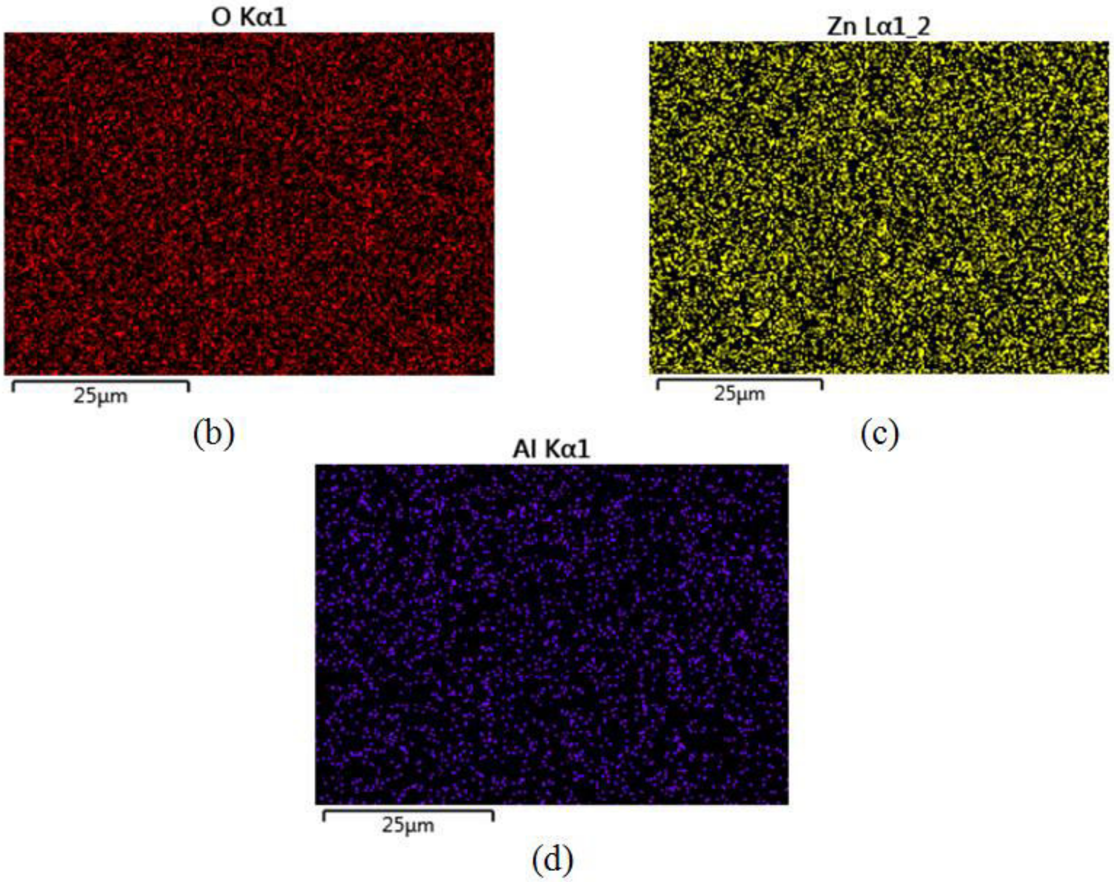


(b) (c) (d)

Figure 8: EDAX maps of annealed (a) Al-doped ZnO (b) O (c) Al (d) Zn



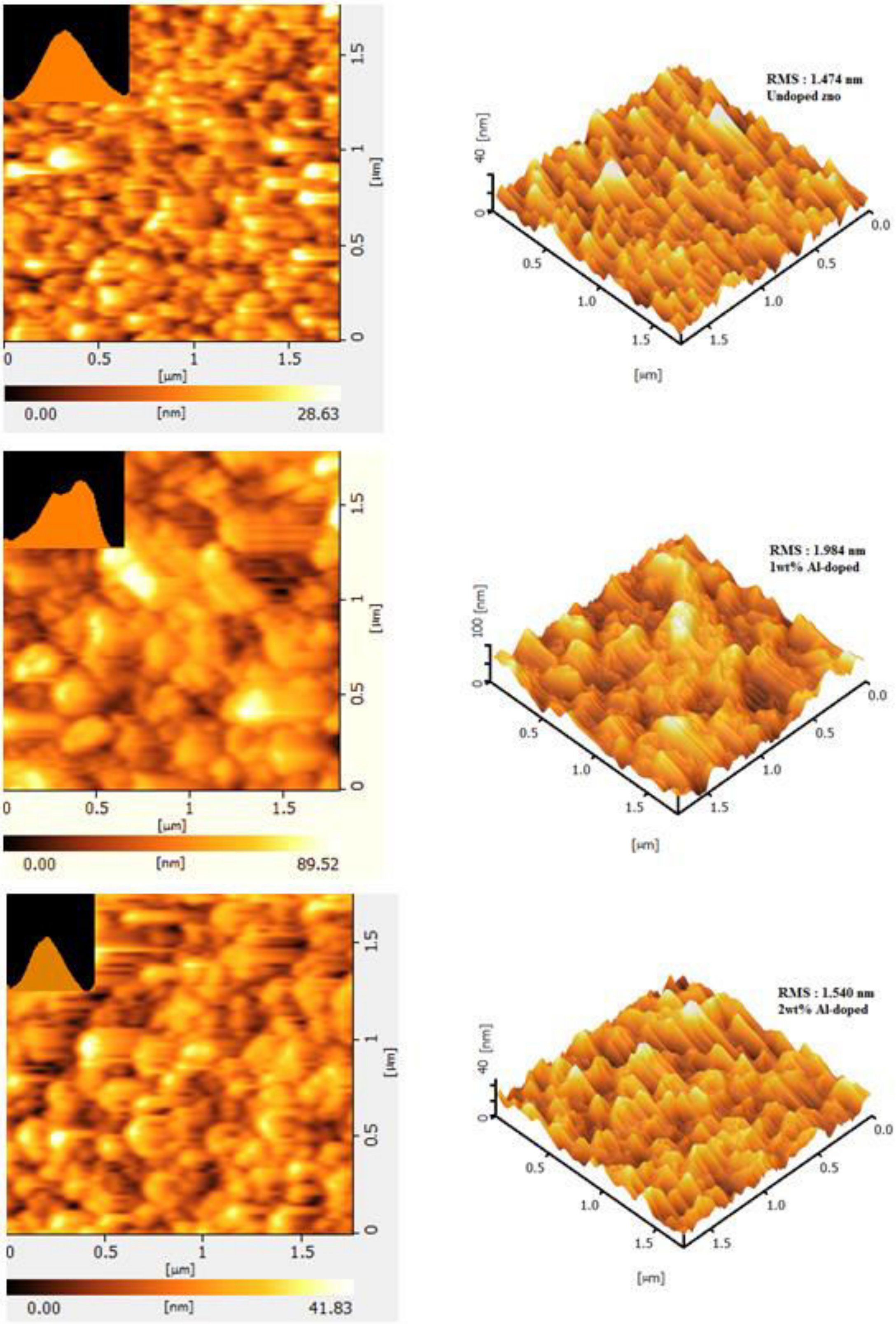
(a)



(b) (c) (d)

Figure 9: EDAX maps of not annealed (a) Al-doped ZnO (b) O (c) Al (d) Zn

Atomic force microscopy is one of the effective ways to study the surface analysis. This is due to its high resolution and powerful software analysis. By using the AFM technique, the morphology of all the prepared samples was characterized. The information about the grain size and surface roughness were obtained from the AFM analysis. Figure 10 shows the two and three-dimensional representation of 1 cm × 1 cm area of the prepared samples ranging from 1wt% to 4wt% Al-doped by thermal evaporation method. From the images, we could observed that the deposited films are uniform and densely packed. The morphology of all the prepared films are homogenously distributed and have larger grain size, this illustrates the crystallinity nature of the film.


0
0.5
1
1.5
[µm]
0.00
[nm]
28.63
RMS : 1.474 nm
Undoped zno
40 [nm]
0.0
[µm]
89.52
RMS : 1.984 nm
1wt% Al-doped
100 [nm]
41.83
RMS : 1.540 nm
2wt% Al-doped

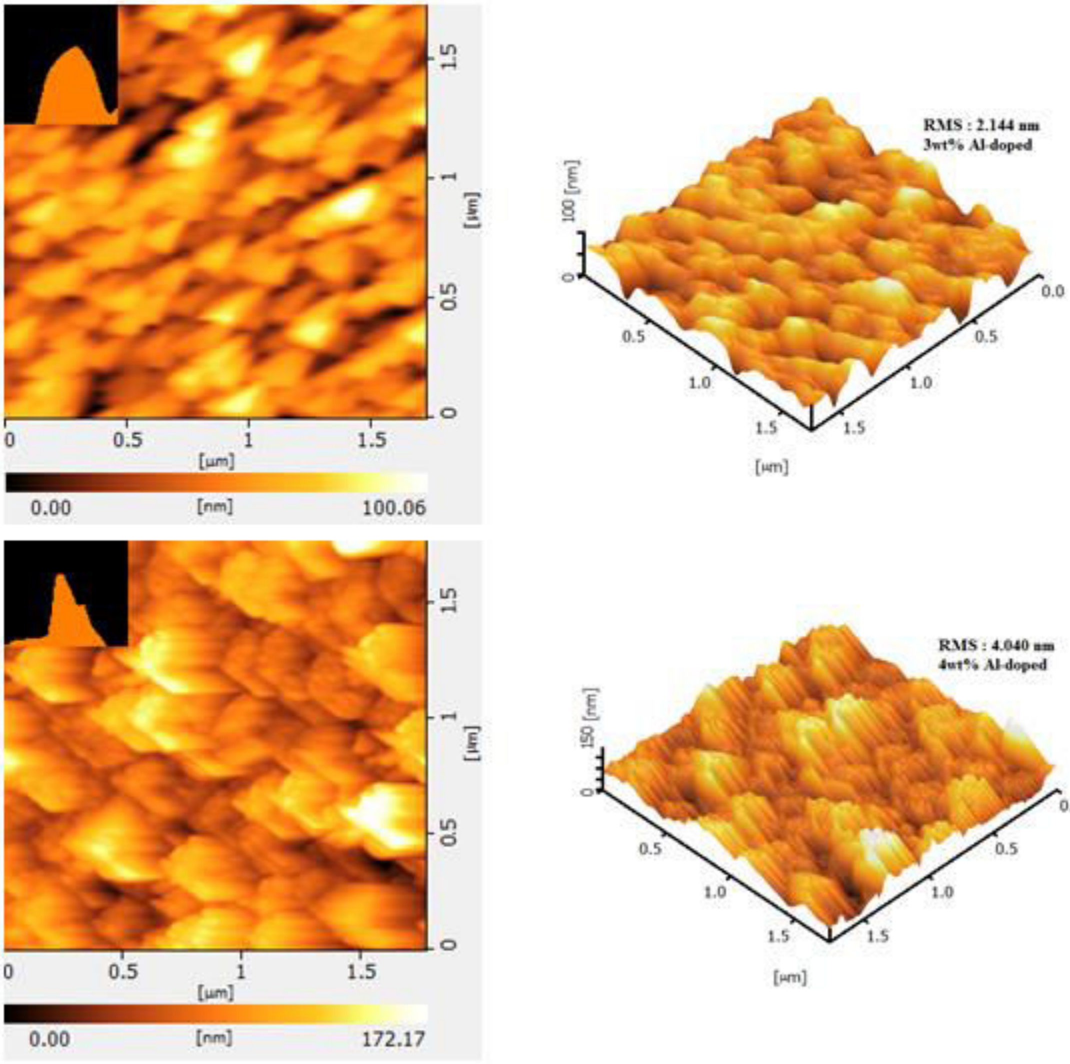


Figure 10: 2D and 3D of AFM images of undoped, 1wt%, 2wt%, 3wt% and 4wt% Al-doped ZnO thin films respectively

The grains are made of different sizes varying from 75.22 nm-78.07 nm. From figure 10, it could be seen that the grain size of undoped ZnO thin film is larger than the 4wt% Al-doped. As the weight percent of the Al-doped increased to 4wt%, the value of the grain size decreased. This results agrees well with Jeong et al [5]. The value of the grain size was calculated from the mean size of 5 grains from all the prepared samples respectively as shown in table 4.3.

Table 3: The mean grain size of the prepared thin films

wt% Al-doped	1 (nm)	2 (nm)	3 (nm)	4 (nm)	5 (nm)	Mean (nm)
0	78.47	77.26	77.67	78.47	78.46	78.07
1	76.39	77.23	77.87	76.77	77.39	77.13
2	76.10	76.75	76.46	76.75	77.39	76.69
3	75.80	75.80	76.48	76.48	75.80	76.07
4	76.20	75.59	74.93	74.33	75.07	75.22

The Root Mean Square (RMS) indicates the surface roughness which is due to presence of different sizes of grains measured using AFM technique. The surface roughness is defined as the standard deviation of the surface height profile from the average height was the most commonly reported measurement of surface roughness [9]. The surface roughness increased with the increasing of Al-doped into the zinc oxide thin films [10];[5]. The values of the RMS are listed in table 4. The RMS values versus Al weight percentage is shown in figure 11.

Table 4: The grain size and roughness from AFM analysis

wt% Al-doped	Grain size (nm)	RMS (nm)
0	78.07	1.474
1	77.13	1.984
2	76.69	1.540
3	76.07	2.144
4	75.22	4.040

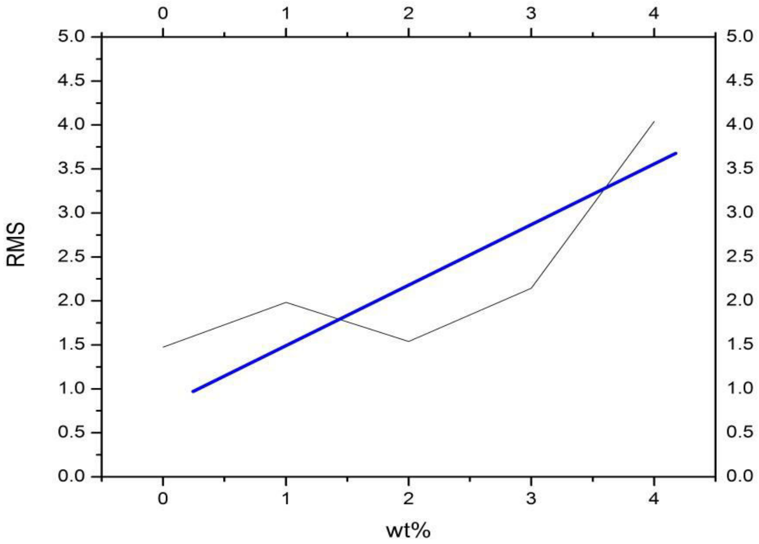


Figure 11: The RMS value against Al weight percentage of all samples

The crystal structure of the 2wt% Al-doped ZnO that was annealed at the temperature of 450ºC deposited on corning class substrate could be studied from the X-rays diffraction (XRD) analysis. At the annealing temperature of 400ºC, the not annealed amorphous zinc oxide thin films would transform to polycrystalline structure according to Tang & Cameron. Figure 12 shows that the annealed sample are polycrystalline [6]; [11] and exhibit typical spectra from the wurtzite structure of zinc oxide. Three main peaks are pointed from the XRD result at 2q =31.85º [100], 2q = 34.5º [002] and 2q =36.35º [101] which showed the structural of zinc oxide. It could be seen that from figure 11 the highest peak is at 2q =34.5º which coincides with crystal plane [002]. The result is agreeable with Starbov et al.[12].

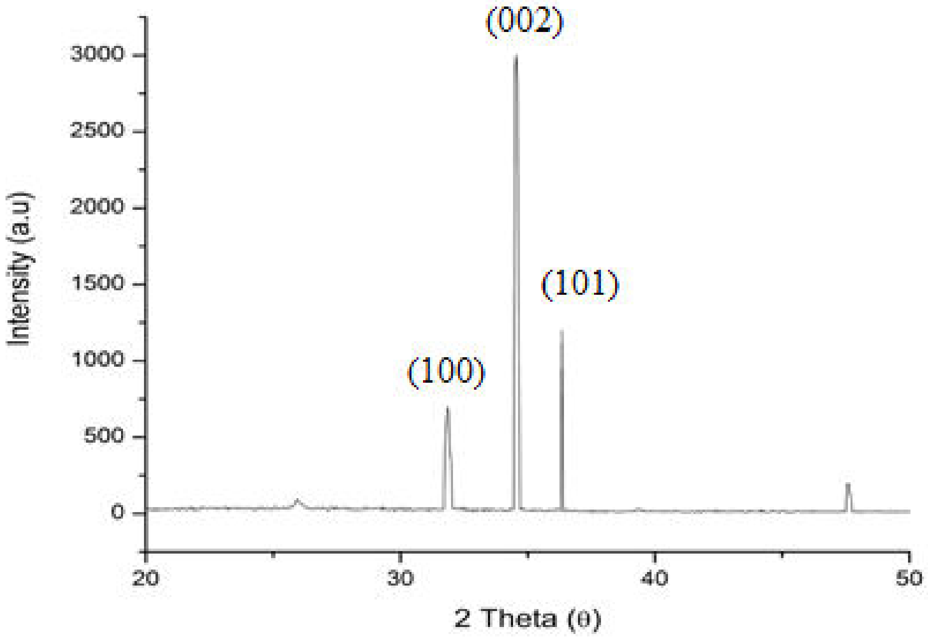


Figure 12**:** XRD spectrum of 2wt% Al-doped ZnO

CONCLUSIONS

All the work reported was based on the various analyses that had been carried out on the prepared samples. The main objective of this study is to prepare the Al-doped zinc oxide and to investigate the structural and optical properties of the prepared samples. These objectives had been successfully achieved by the experiments and various analyses that had been done.

The presence of aluminium which acted as a doping in the zinc oxide thin films had been successfully confirmed from the study of the elemental composition by the energy dispersive of X-rays analysis (EDAX). All the prepared samples were annealed at the temperature of 450ºC. From the X-rays diffraction (XRD) analysis, the post annealed samples showed a transformation to polycrystalline structure from amorphous zinc oxide before annealing.

In the atomic force microscopy (AFM) analysis, the surface roughness which were determined by the RMS value and grain size were obtained. The results showed that the grain size was decreased while surface roughness increased with increasing doping in weight percentage of Al-doped.

The investigation of the optical properties had been done through the photoluminescence and UV-Vis spectrum measurement. The transparency of all the prepare samples are higher than 80% in the UV to visible light (300 nm – 800 nm). This result has displayed its application as transparent conductive oxide (TCO) in solar cell as TCO requires high transmission within 350 nm - 800nm. The Al-doped zinc oxide thin films have direct band gap energy. The optical band gap energy was obtained from extrapolating the linear absorption edge. As the weight percent of Al-doped increased up to 3wt%, the energy band gap increased which are undoped (4.361ev), 1wt% (4.371ev), 2wt% (4.375ev), 3wt% (4.486ev) and 4wt% (4.416ev).

Results indicated that in photoluminescence spectrum analysis, all the emission energy from the prepared samples was lower than the excitation energy. This might due to the heat energy for the phonon excitation. The excitation used was l = 290 nm. The intensity of the Al-doped zinc oxide thin films linearly decreasing with the increasing of dopants. The emission PL spectra showed three main peaks centered at about 390nm (UV), 420nm (blue) and 580nm (green).

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REFERENCES

[1]. McEvoy, A., Castañer, L., & Markvart, T. (2nd Edition). (2012). *Solar Cells: Materials, Manufacture and Operation*. USA: Academic Press.
[2]. Jiménez-González, a. *Journal of Crystal Growth*, *192*(3-4), 430–438 (1998)
[3]. Faÿ, S., Kroll, U., Bucher, C., Vallat-Sauvain, E., & Shah, a. *Solar Energy Materials and Solar Cells*, *86*(3), 385–397 (2005)
[4]. Jeong, S. H., Kho, S., Jung, D., Lee, S. B., & Boo, J. H. *Surface and Coatings Technology*, *174-175*(03), 187–192 (2003)
[5]. Zhou, H., Yi, D., Yu, Z., Xiao, L., & Li, J. (2007). *Thin Solid Films*, *515*(17), 6909–6914 (2007)
[6]. Ziegler, E., Heinrich, A., Oppermann, H., & Stöver, G. *Physica status solidi (a)*, *66*(2), 635-648 (1981)

[7]. Kuo, S.-Y., Chen, W.-C., Lai, F.-I., Cheng, C.-P., Kuo, H.-C., Wang, S.-C., & Hsieh, W.-F. *Journal of Crystal Growth*, *287*(1), 78–84 (2006)

[8]. Lin, B., Fu, Z., & Jia, Y. *Applied Physics Letters*, *79*(7), 943-945 (2001)

[9]. Nasir, E.M, *International Journal of Innovative Research in Science and Technology, 3*(1), 8117 (2014)

[10]. Mihaiu, S.M., Toader, A., Anastasescu, M., Gabor, M., Jr, T.P., Stoica, M., & Zaharescu, M. *Processing and Application of Ceramics, 3*(1-2), 79-84 (2009)

[11]. Tang, W., & Cameron, D. C. *Thin Solid Films*, *238*(1), 83–87 (1994)

[12]. S. Zhang and S. Cheng, “Thermally evaporated SnS : Cu thin films for Solar,” no. 61076063, pp. 889–892, 2011.

[13]. Starbov, N., Balabanov, S., Bineva, I., Rachkova, a, Krumov, E., & Starbova, K. *Journal of Physics: Conference Series*, *398*, 012019 (2012)