CHAPTER 6

Results and Discussion (Part III): Mg Doped ZnO Films (I)

Deposition and properties of the effects of Mg doping on ZnO films are investigated in this chapter. These films were deposited by the ultrasonic spray pyrolysis technique and the properties such as thickness, crystal structure, morphology, optical properties and electrical properties were measured. In this project, Mg doped ZnO films were prepared in 2 part. The first part was presented in this chapter, the starting solution of films were prepared from 0.2 M Zinc Acetate Dehydrate ($Zn(CH_3OO)_2.2H_2O$) and Magnesium Chloride ($MgCl_2$) as dopant with various 0-9 at.% Mg. The solution was ultrasonic sprayed on glass substrates and heated at 350-450°C. The second part of Mg doped ZnO film will be presented in the next chapter.

6.1 Film preparation

6.1.1 Starting solution preparation

The starting solutions for Mg doped ZnO films were prepared from $Zn(CH_3OO)_2.2H_2O$ and $MgCl_2$ as dopant, which were dissolved in ethanol (C_2H_5OH) and deionized water (DI water) in the volume ratio of 1:3. Hydrochloric (HCl) acid was added to increase the solubility. The compositions of these solutions were a fixed at 0.2 M $Zn(CH_3OO)_2.2H_2O$ while the atomic percentage ratio of Mg/Zn from was varied 0 to 9 at.%, as listed in Table 6.1.

Table 6.1 Specifications materials and compositions of the starting solutions for Mg doped ZnO films used in this study.

Materials	Source	Purity	Solution compositions
$Zn(CH_3OO)_2.2H_2O$	Sigma-Aldrich	≥98%	0.2 M
$MgCl_2$	Sigma-Aldrich	≥98%	0-9 at.% Sn
C_2H_5OH	EMSURE®	absolute	25 % of solution
DI water	-	-	75 % of solution
HCl	EMSURE®	37%	0.01 M

6.1.2 Spray coating

All starting solutions were sprayed on microscope glass substrates heated at 350°C by using ultrasonic spray pyrolysis in air. The distance between the nozzle and the substrate was 20 cm with nozzle frequency of 34 kHz and spray rate of 2.5 ml/min for a total time of 3 min. The schematic diagram of the Mg doped ZnO films fabrication process is shown in Figure 6.1.

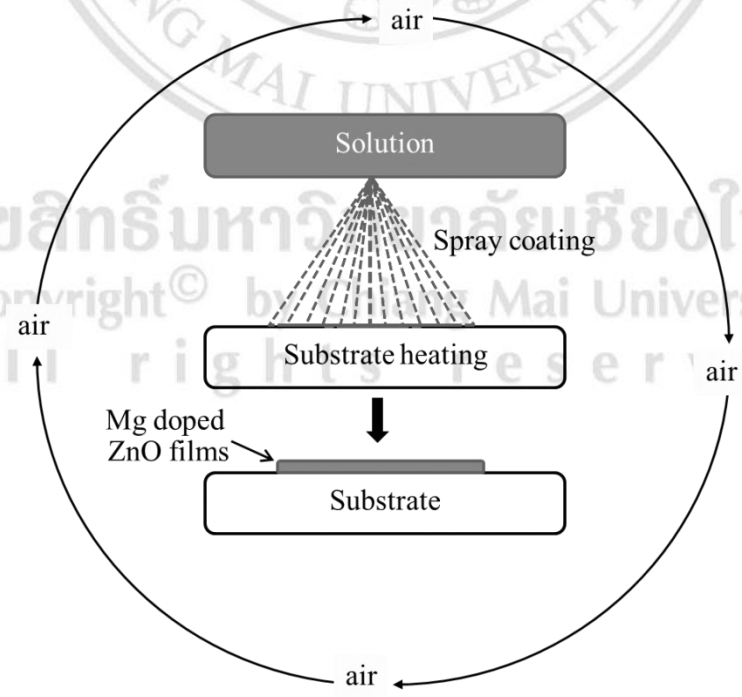


Figure 6.1 Schematic diagram of Mg doped ZnO film preparation.

6.2 Results and discussions

Images of Mg doped ZnO films with different Mg concentrations deposited on glass substrates heated at 350-450°C are shown in Table 6.2. It was found that all films had high transparency. The characterizations of these films such as thickness, crystal structure, morphology optical and electrical properties are described in the following sections.

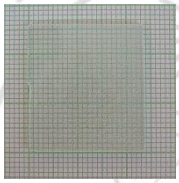
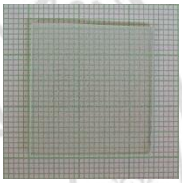
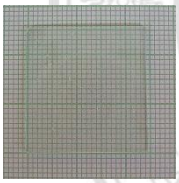
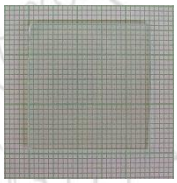
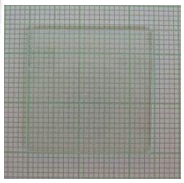
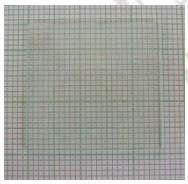
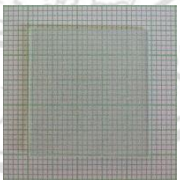
Substrate temp. (°C)	Mg doping				
	0 at.%	3 at.%	5 at.%	7 at.%	9 at.%
350					
400					
450					

Figure 6.2 The appearance of Mg doped ZnO films with different Mg concentrations deposited on glass substrates heated at 350-450°C.

6.2.1 Thickness

Figure 6.3 shows the SEM cross section microstructures of Mg doped ZnO films with different Mg concentrations deposited on glass substrate heated at 350-450°C, which were investigated by SEM technique. It was observed that the films grew well on the glass substrate.

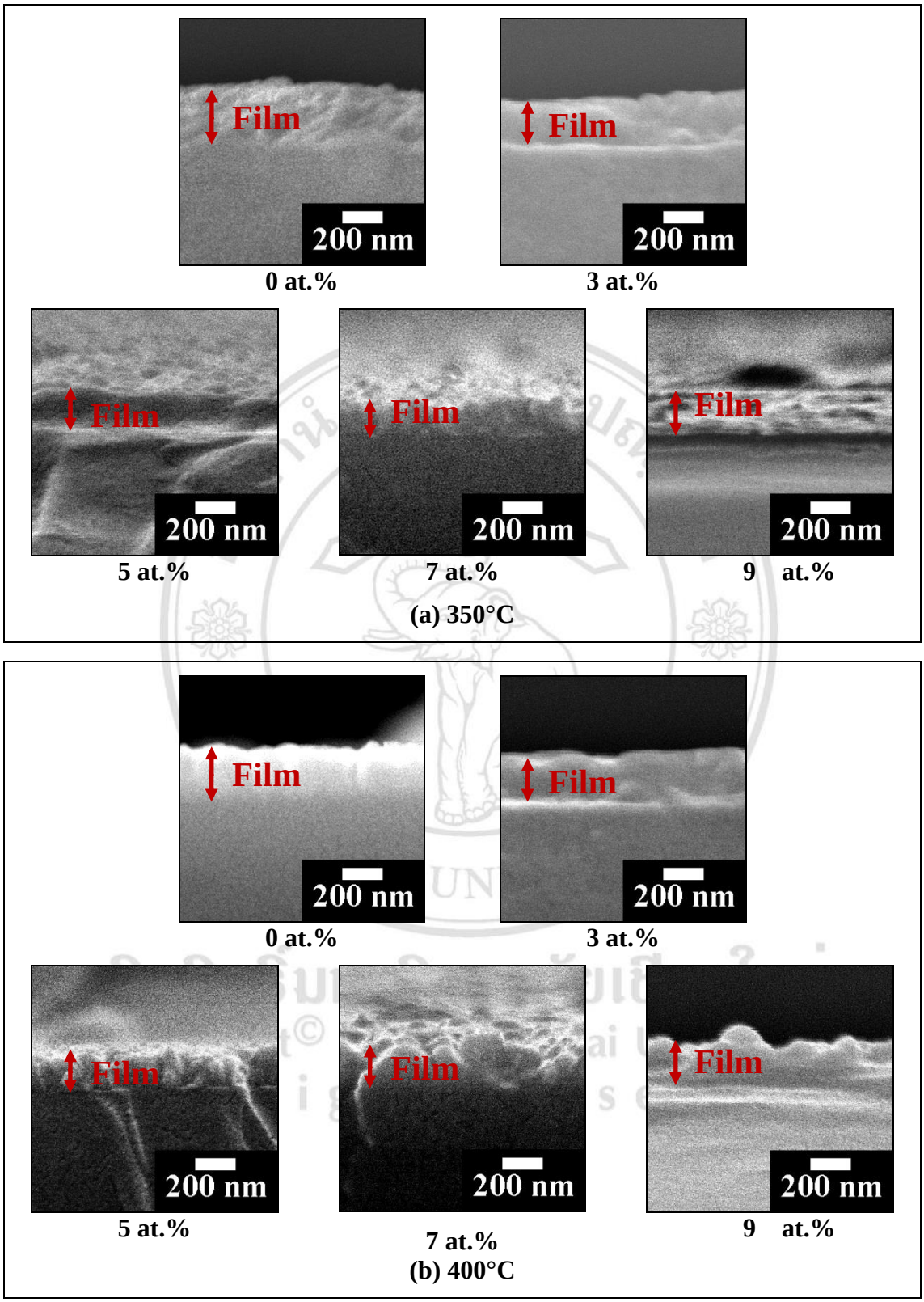


Figure 6.3 SEM cross section microstructures of Mg doped ZnO films with different Mg concentrations deposited on glass substrates heated at 350°C (a), 400°C (b) and 450°C (c)

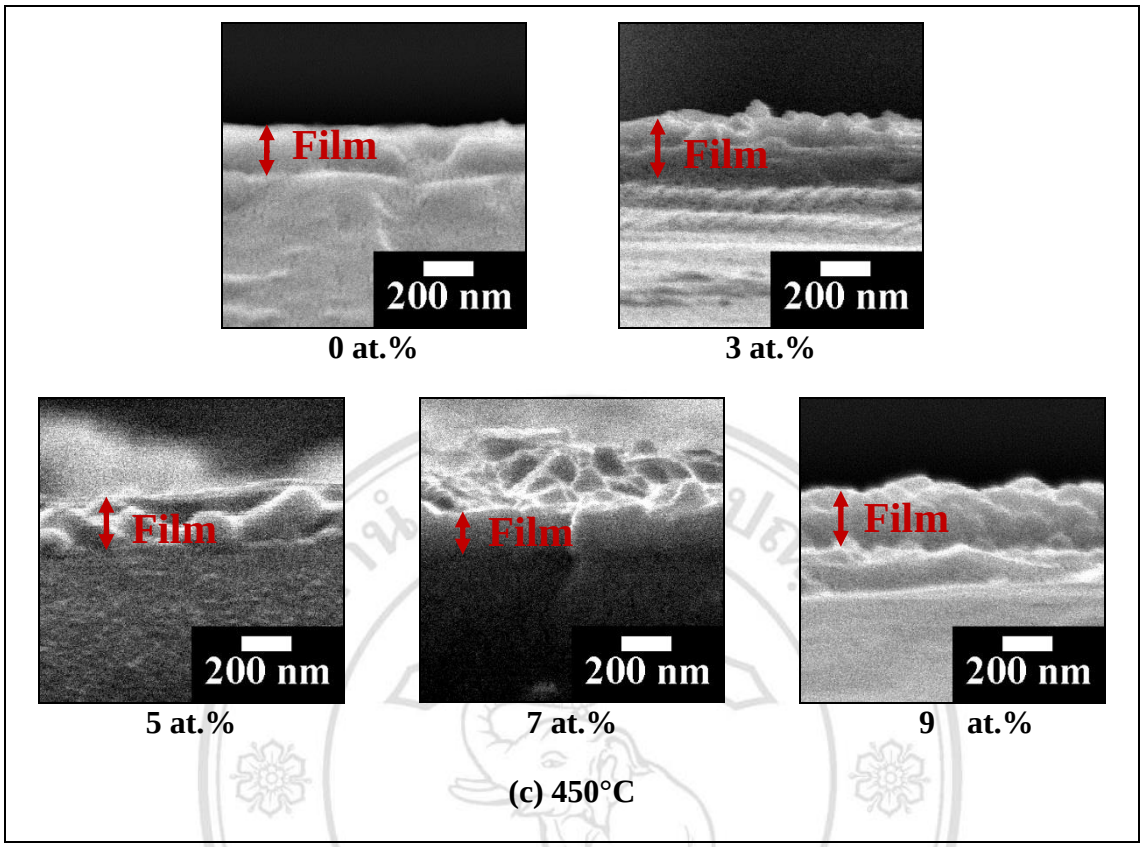


Figure 6.3 SEM cross section microstructures of Mg doped ZnO films with different Mg concentrations deposited on glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) (continued).

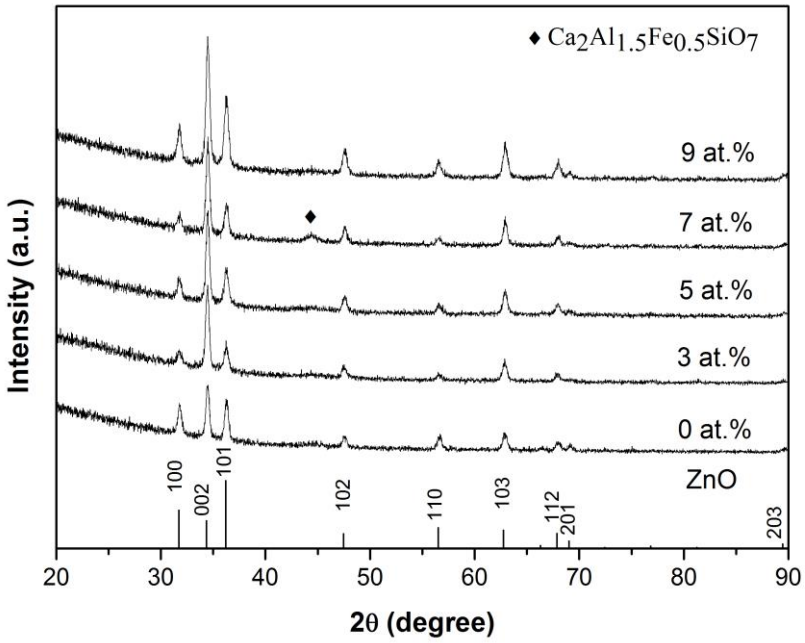
The thicknesses of films were estimated from these SEM images and listed in Table 6.2. The thicknesses of films were similar in the range 200-300 nm. The thicknesses of films depend on the time of spraying and flow rate of solution. It was found that the concentration of Mg dopant does not affect the thickness of the films.

Table 6.2 Thickness of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350-450°C.

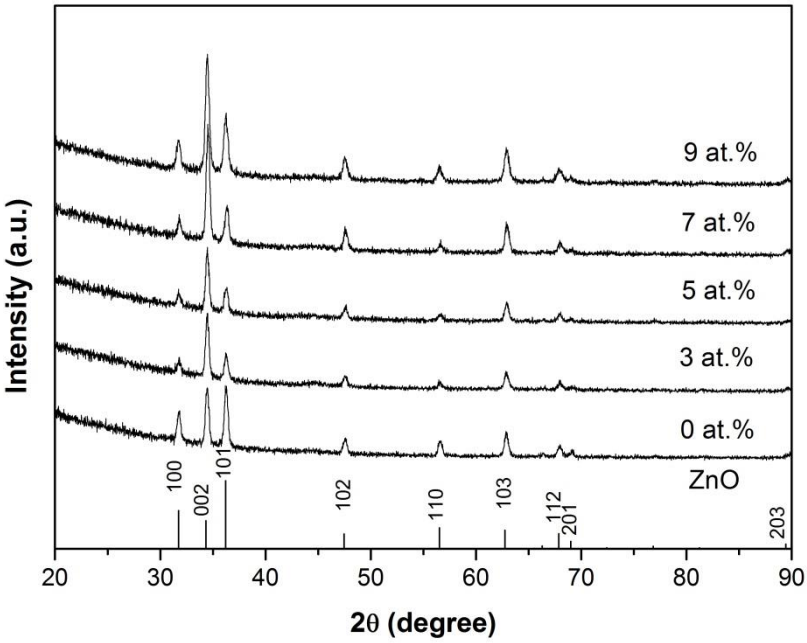
Substrate temperature (°C)	Thickness (nm)	Mg Content (at.%)				
		0	3	5	7	9
350	Value	248.5	244.1	247.8	226.5	237.0
	SD	25.0	11.0	12.2	20.7	15.1
400	Value	241.5	230.8	231.3	235.9	239.0
	SD	13.3	7.0	9.0	21.7	25.72
450	Value	242.5	243.4	225.0	220.8	230.0
	SD	8.9	17.7	21.7	20.0	13.4

6.2.2 Crystal structure

The XRD patterns of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350-450°C are shown in Fig. 6.4. All films were identified as the polycrystalline hexagonal wurtize structure of ZnO with preferred orientation along the (002) plane. The crystallinity of undoped ZnO films was found to increase with increasing substrate temperature. This behavior occurred due to the movement of grain boundaries at high energy of glass substrate heating and observed in ZnO films [86,87] and other TCO films such as ITO and AZO [5, 88]. While, the crystallinity of Mg doped ZnO film was found to decrease with increasing substrate temperatures. Moreover, the crystallinity of these films increased with increasing Mg doping when these films were coated at 350-400°C of substrate temperature. The similar result was reported from other work [56,89]. As the substrate temperature was increased to 450°C, the crystallinity was found to decrease with increasing Mg doping

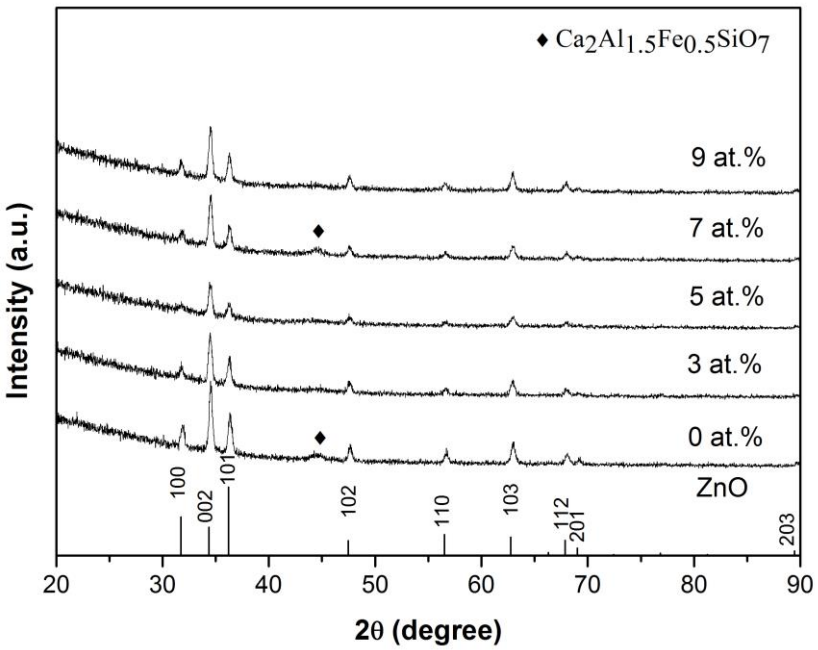


(a) 350°C



(b) 400°C

Figure 6.4 The XRD patterns of Mg doped ZnO films with different Mg concentrations on glass substrate deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c).



(c) 450°C

Figure 6.4 The XRD patterns of Mg doped ZnO films with different Mg concentrations on glass substrate deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) (continued).

In addition, there is some small phase found in every condition. It may be assumed that this phase is a Calcium Aluminium Iron Silicate phase ($Ca_2Al_{1.5}Fe_{0.5}SiO_7$: JCPDS No. 039-0282) precipitated in the glass substrate. From SEM image in Fig 6.5, the occurrence of small crystal growing in the glass matrix could be observed which may be corresponded to the $Ca_2Al_{1.5}Fe_{0.5}SiO_7$ phase.

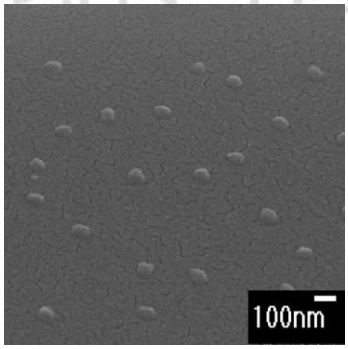


Figure 6.5 Fracture surface of microscope glass substrate.

Table 6.3 Crystallite size of (002) and (101) plane of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350-450°C.

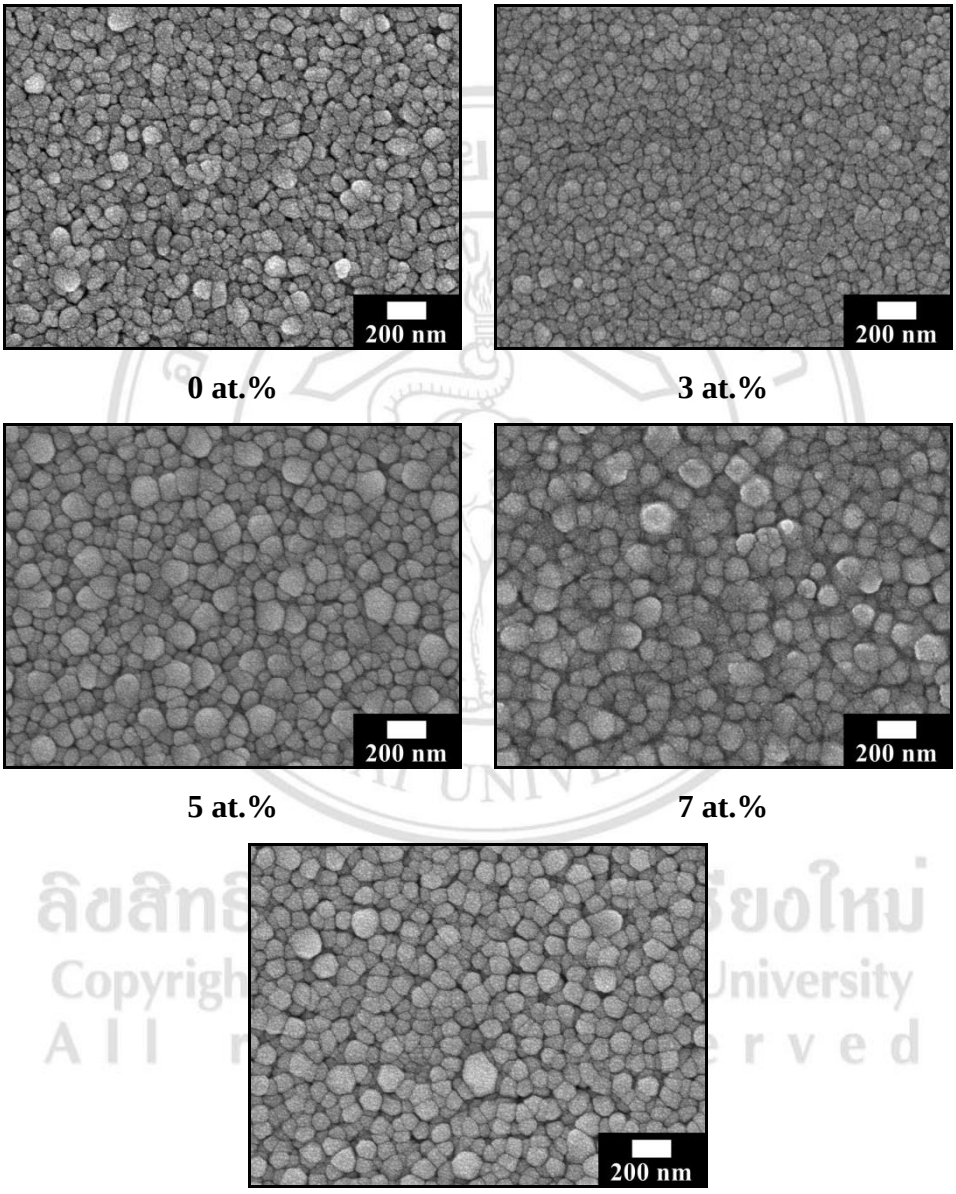
Properties	Substrate Temp. (°C)	Plane	Mg Content (at.%)				
			0	3	5	7	9
Crystallite size (nm)	350	(002)	35.56	34.35	34.78	34.38	32.78
		(101)	29.94	25.16	26.87	27.75	27.08
	400	(002)	36.26	36.62	36.04	35.94	32.81
		(101)	31.75	29.42	30.21	28.76	27.02
	450	(002)	37.43	35.72	36.78	36.98	36.65
		(101)	30.38	30.57	30.84	31.45	33.01

The crystallite sizes of Mg doped ZnO films with different Mg concentrations are listed in Table 6.3. The crystallite sizes of these films can be calculated from FWHM values of the (002) and (101) peaks by equation 3.2 and the FWHM values were obtained from the XRD patterns. The crystallite size variation of the (002) and (101) peaks was found to increase with increasing substrate temperature. While, the crystallite size variation of the (002) peak decreased with increasing Mg concentration and the (101) peak increased with increasing Mg concentration.

6.2.3 Morphology

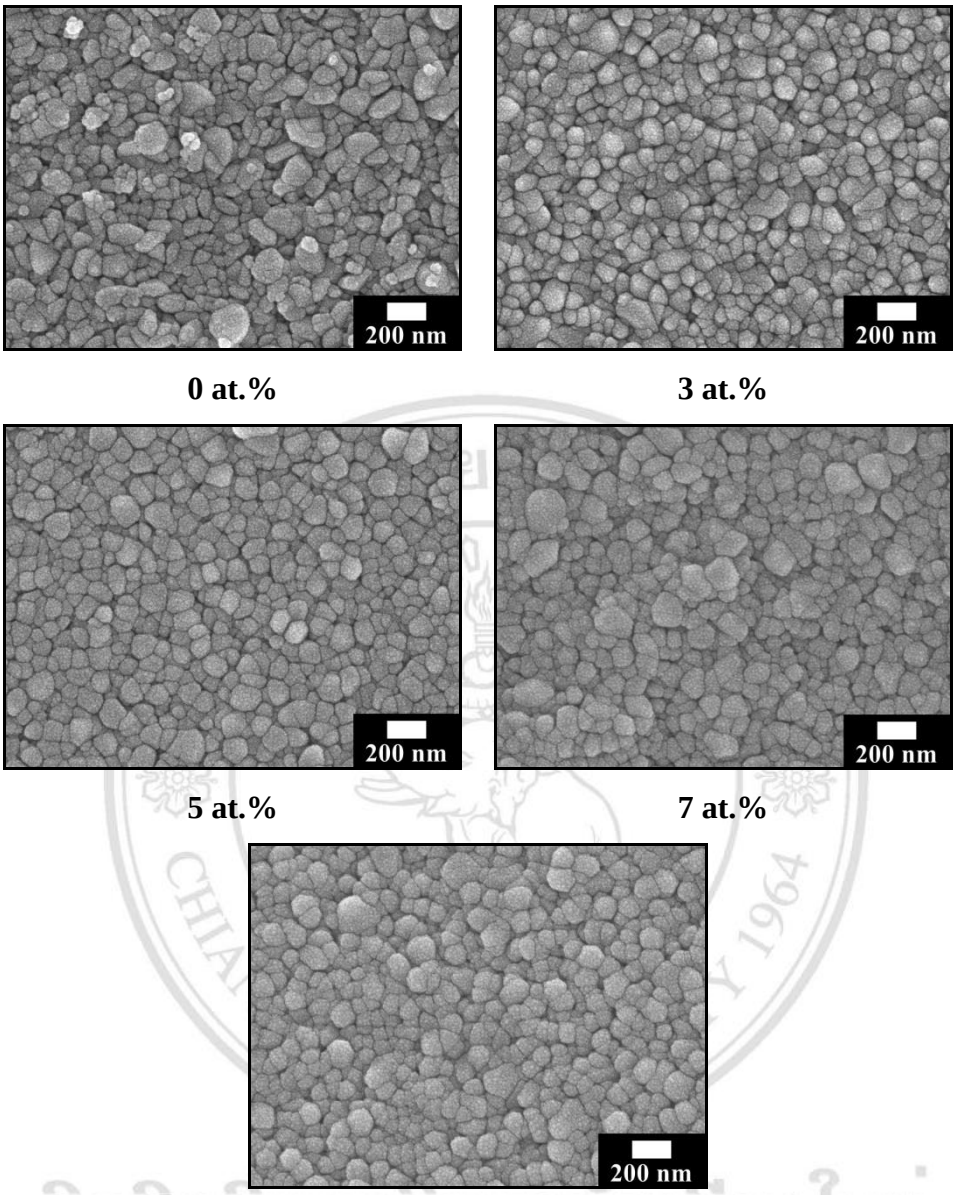
Surface morphologies of Mg doped ZnO films with different Mg concentrations deposited on a borosilicate glass substrates heated at 350-450°C were investigated by SEM and AFM techniques and are shown in Figures 6.6 and 6.7, respectively. It can be seen that the substrate temperature and Mg doping concentration both affected the microstructure of the films. The undoped ZnO films were loosely packed film with irregular shape and changed to homogeneous film with hexagonal shape with addition Mg concentration. However, the films coated at 450°C were not homogeneous films. The behavior of ZnO grain shape that changes with

Mg doping was oalso bserved in Mg doped ZnO powders, synthesized by microwave processing, as studied by *Vijayalakshmi et al* [90], Moreover, the morphology of films were loosely packed with increasing substrate temperature to 450°C, this results may be due to the decreasing crystallization of the films, coated at this temperature (Figure 6.4 (c)).



(a) 350°C

Figure 6.6 SEM images of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c).



(b) 400°C

Figure 6.6 SEM images of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) (continued).

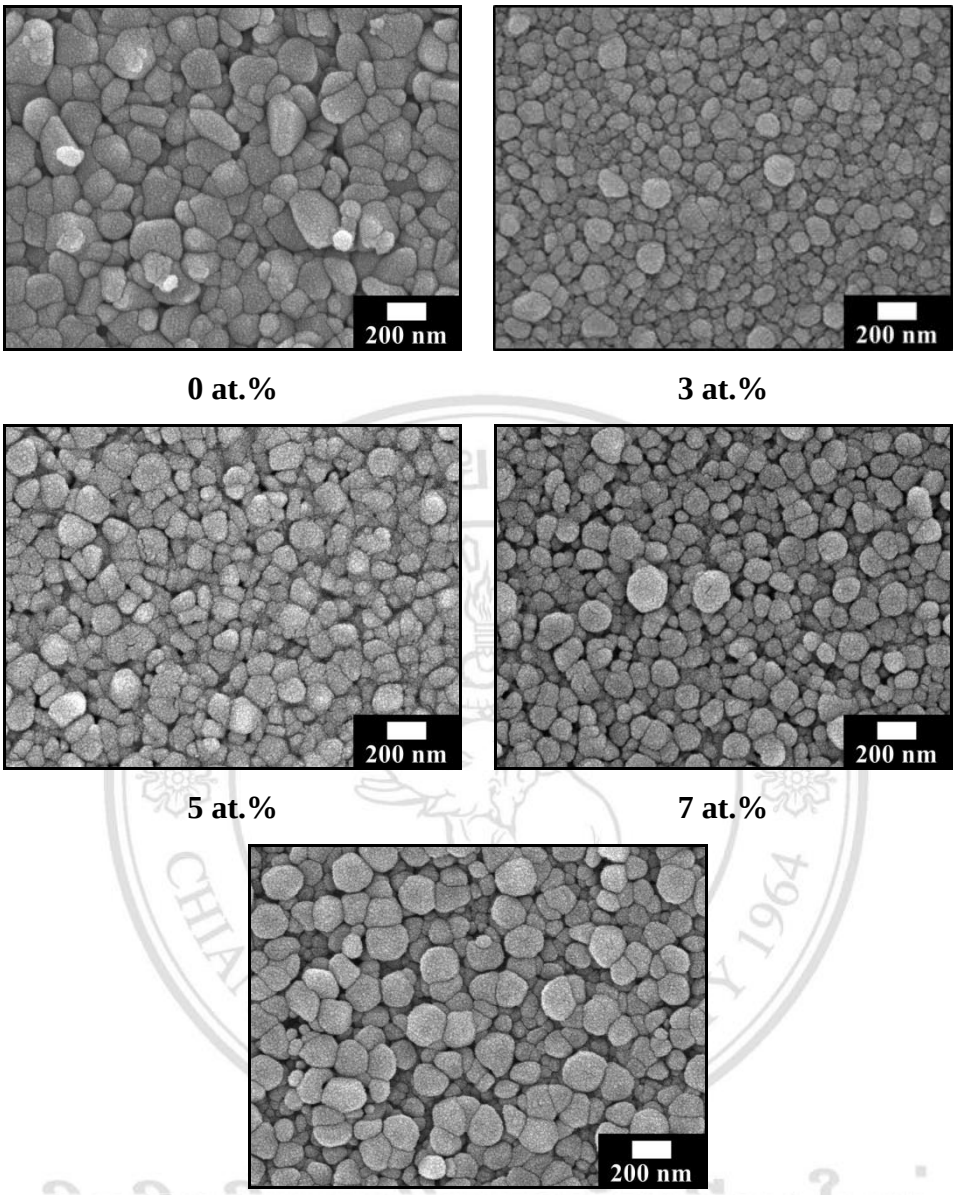
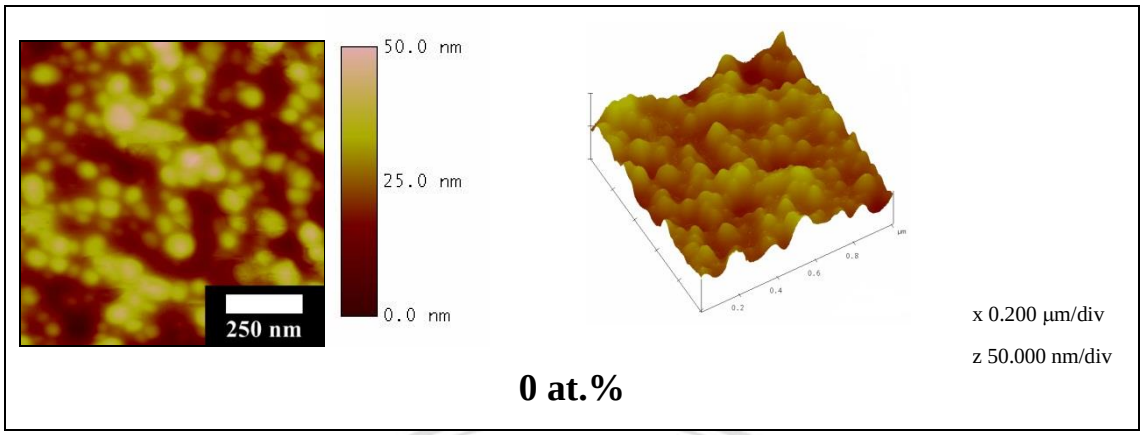
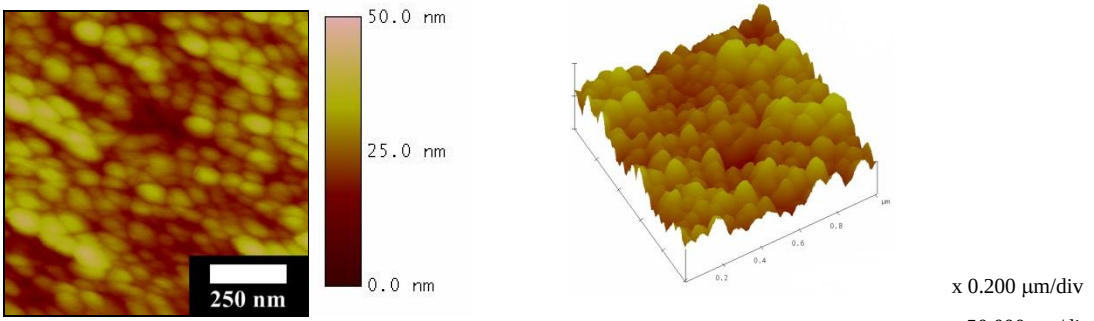


Figure 6.6 SEM images of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) (continued).

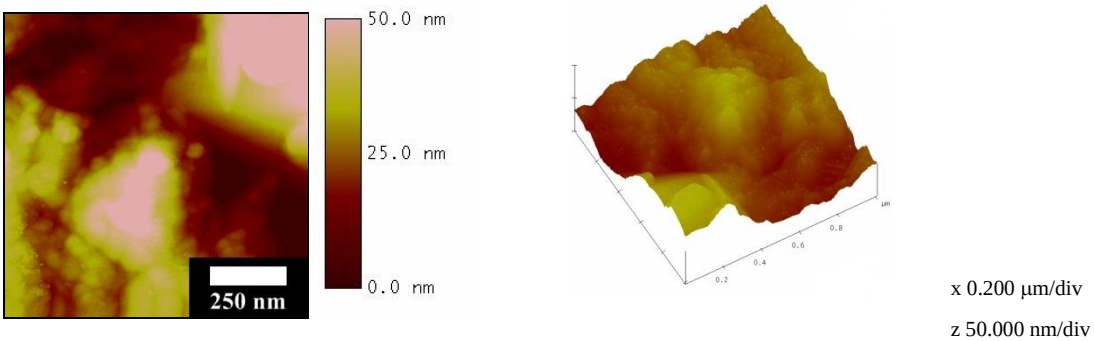


(a) 350°C

Figure 6.7 AFM images of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c).



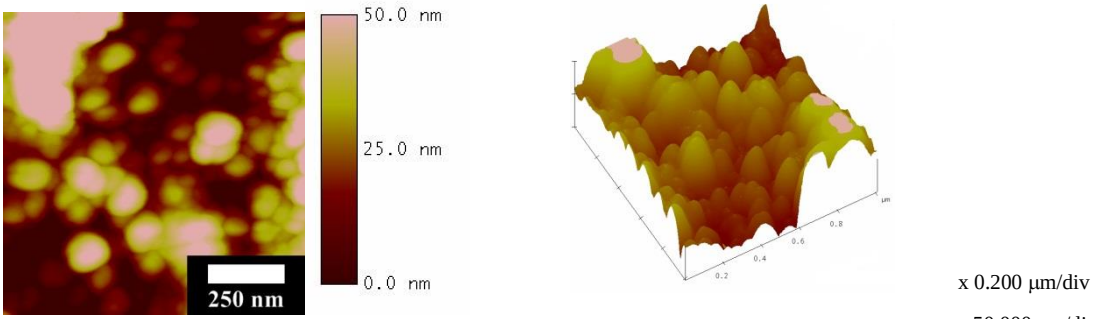
7 at.%



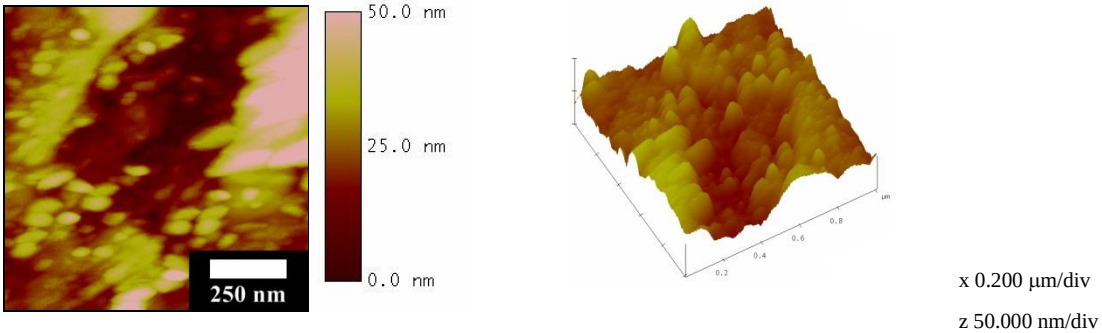
9 at.%

(a) 350°C

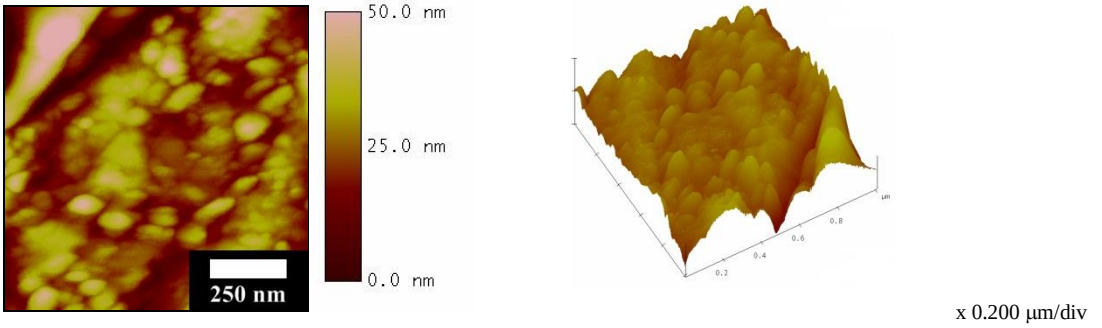
Figure 6.7 AFM images of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) (continued).



0 at.%



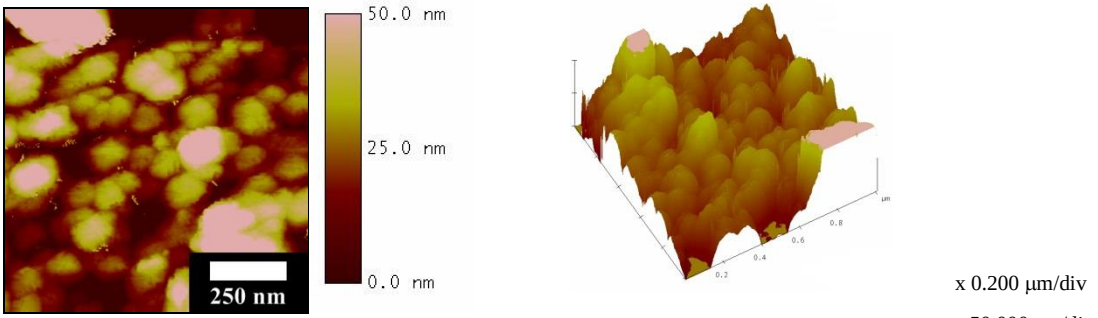
3 at.%



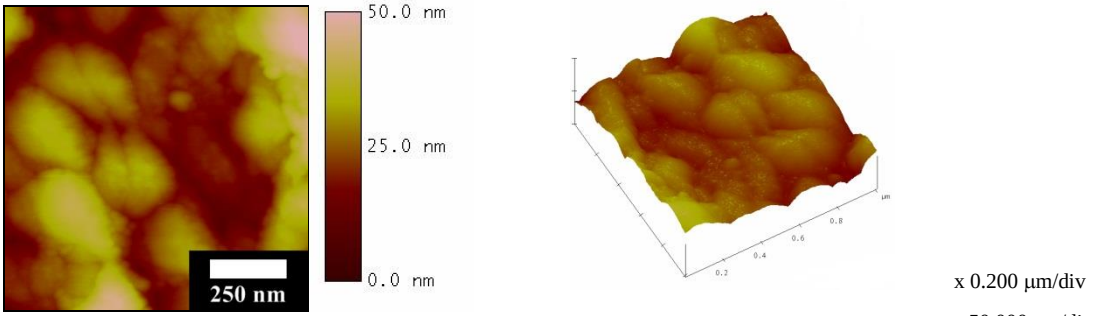
5 at.%

(b) 400°C

Figure 6.7 AFM images of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) (continued).



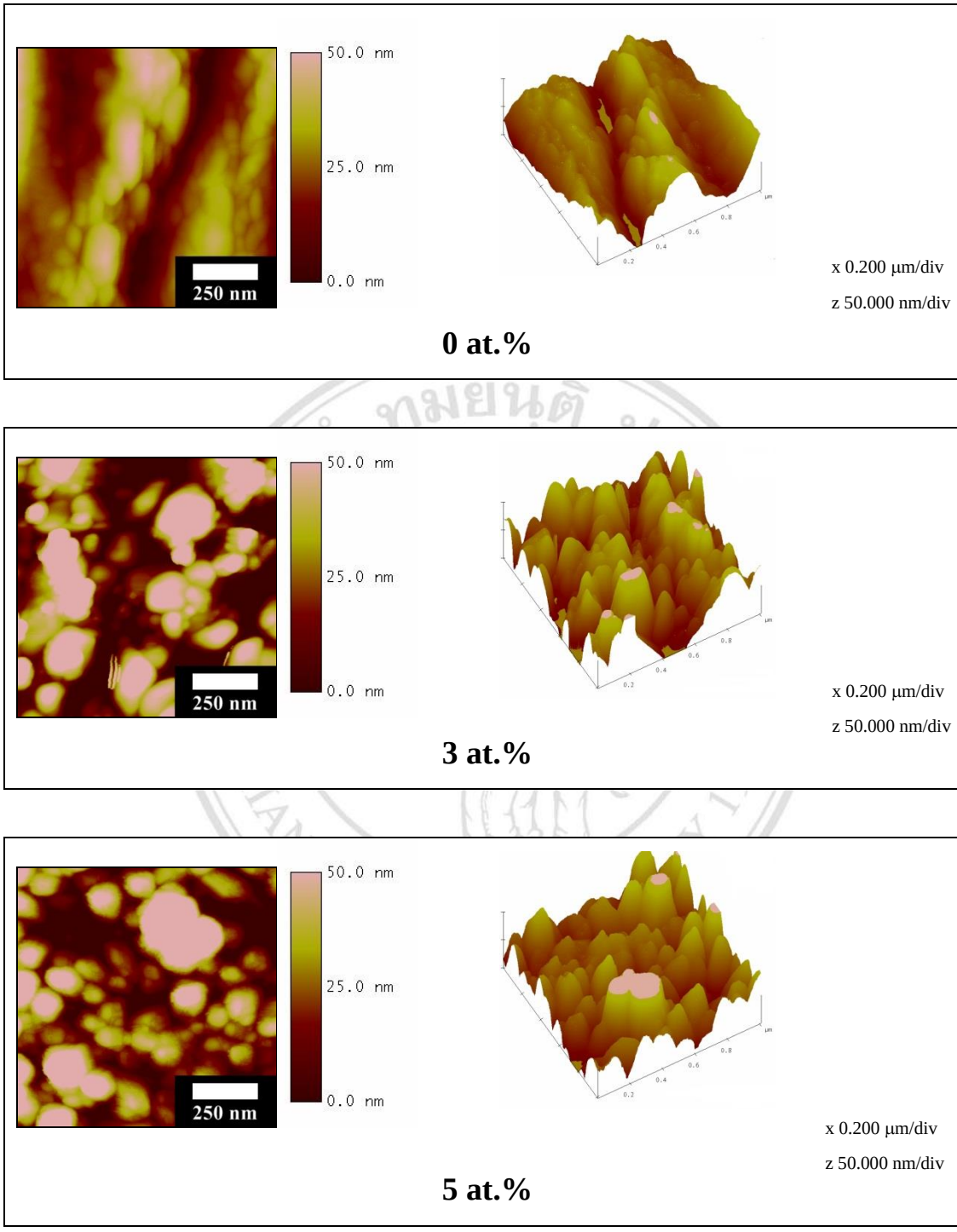
7 at.%



9 at.%

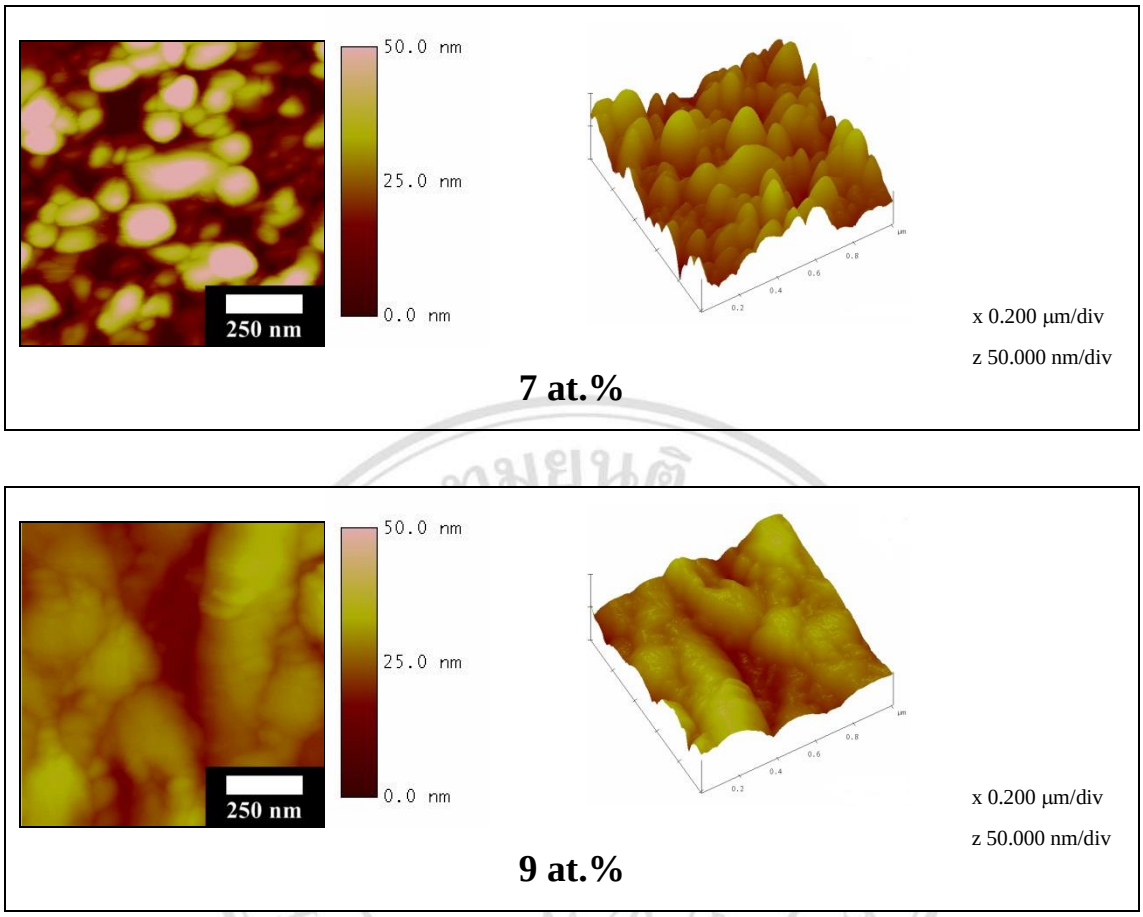
(b) 400°C

Figure 6.7 AFM images of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) (continued).



(c) 450°C

Figure 6.7 AFM images of Mg doped ZnO films with different Mg concentration deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) (continued).

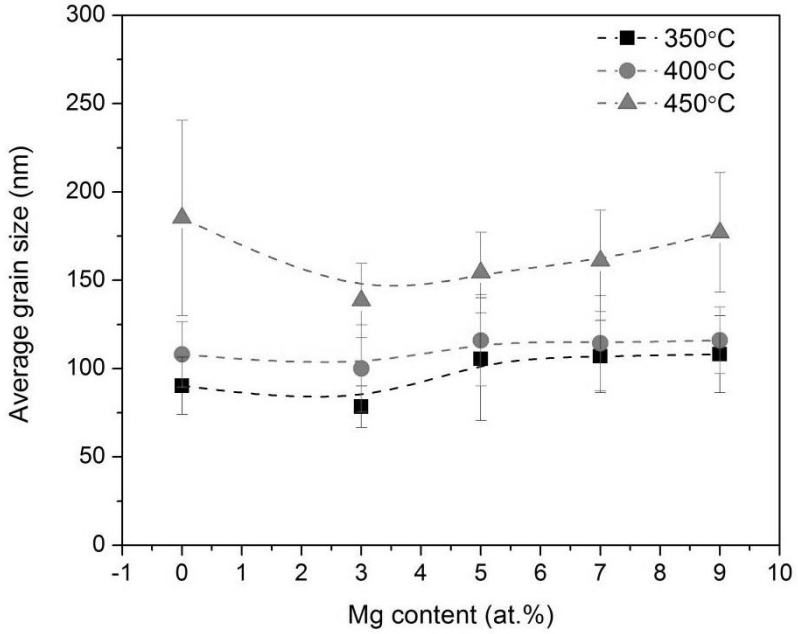


(c) 450°C

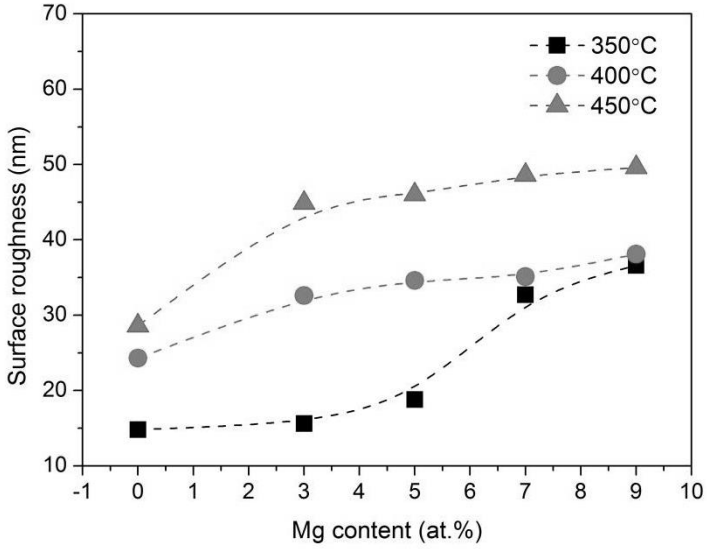
Figure 6.7 AFM images of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) (continued).

The average grain size and surface roughness of films were obtained from these SEM and AFM images, respectively and the trends of these values are shown in Fig. 6.8. It was found that the increasing substrate temperature produced increasing average grain sizes of films, this behavior were observed in other research [5,87]. While the average grain size of films decreased with doping a little Mg concentration (3 at.%). Then increasing Mg concentration (> 3 at.%) produced increasing average grain size of films, this similar results of surface morphology of Mg doped ZnO flms are studied by Huang et al. [61] and Kumar el al. [ถึ] In addition, surface

roughness of film increased with increasing substrate temperature and Mg doping.



(a) Average grain size

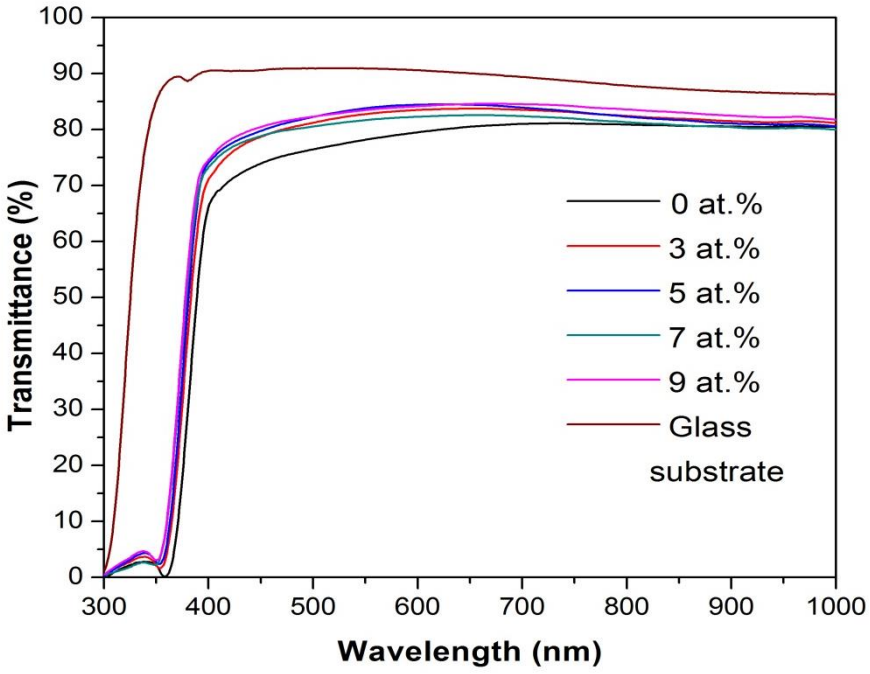


(b) Surface roughness

Figure 6.8 Average grain size and surface roughness of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350 - 450°C.

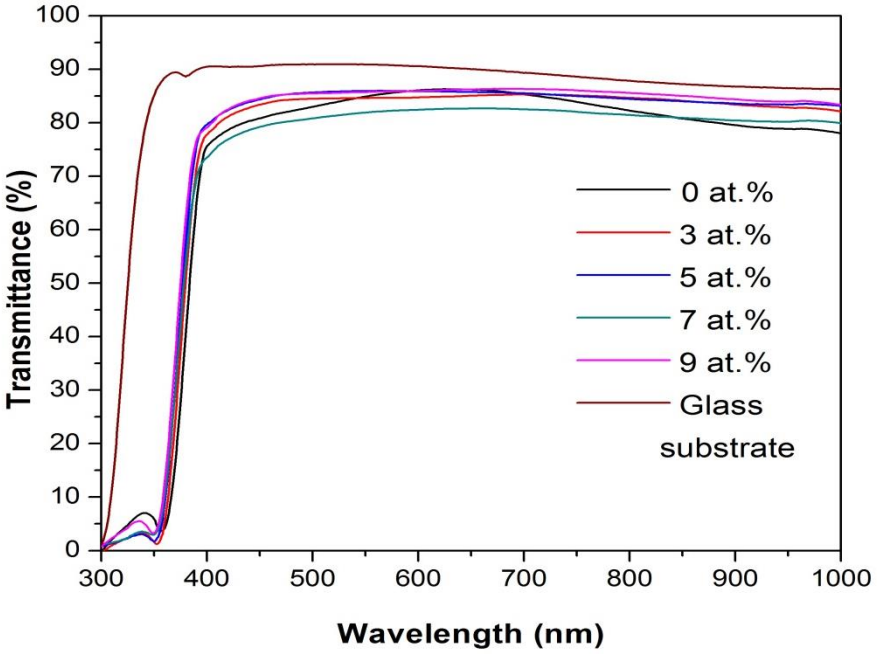
6.2.4 Optical properties

The transmittance and absorbance spectra over the wavelength range 300-1000 nm of glass substrate and Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350 - 450°C are shown in Figures 6.9-6.10. It was found that the glass substrate showed highest transmittance as about 90% and lowest absorbance as about 0.035. Then, the transmittance decreased and the absorbance increased with coating films. The transmittance and absorbance of undoped and Mg doped ZnO films are similar as about 85% and 0.1, respectively and all films showed a sharp ultraviolet cutoff. Moreover, a shift of the absorption edge occurred with added Mg content shifting to lower wavelengths (blue-shift).

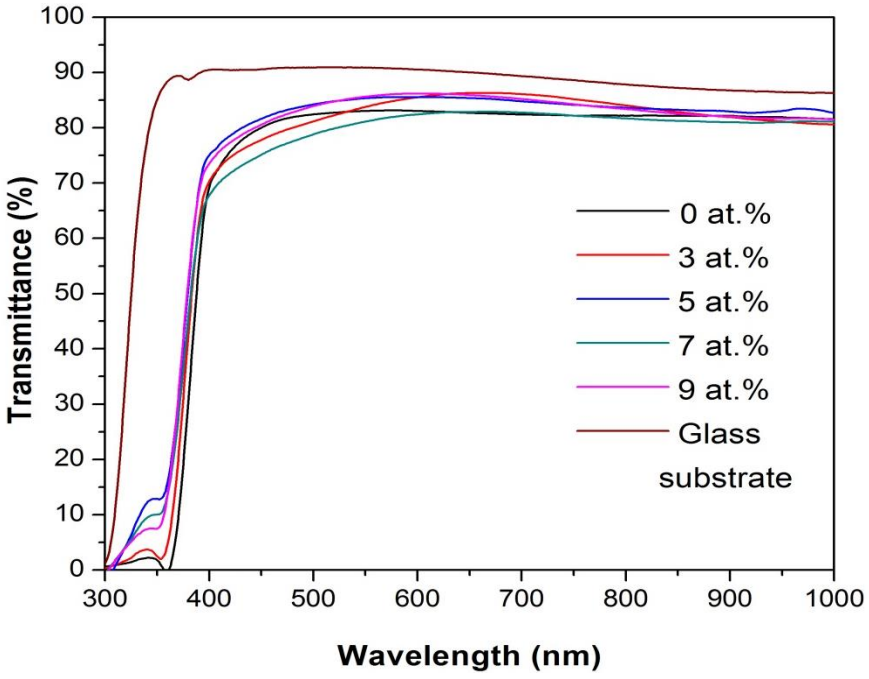


(a) 350°C

Figure 6.9 Transmittance spectra of Mg doped ZnO with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c).

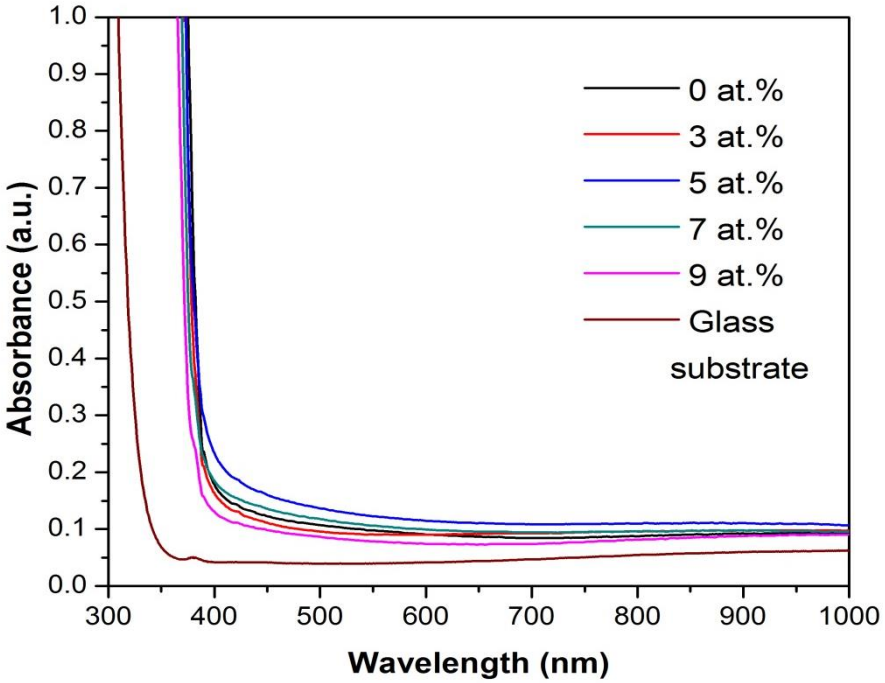


(b) 400°C

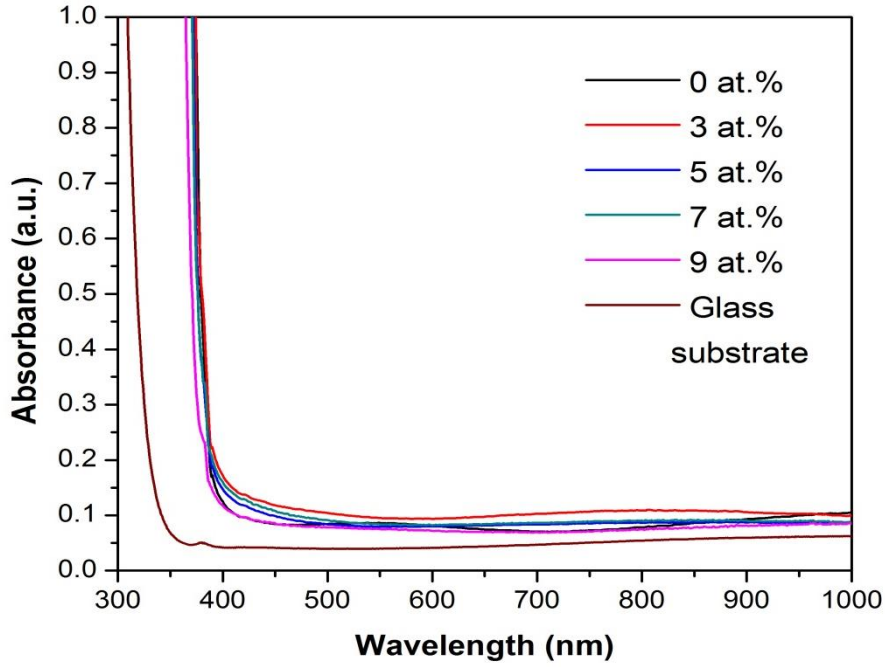


(c) 450°C

Figure 6.9 Transmittance spectra of Mg doped ZnO with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) (continued).

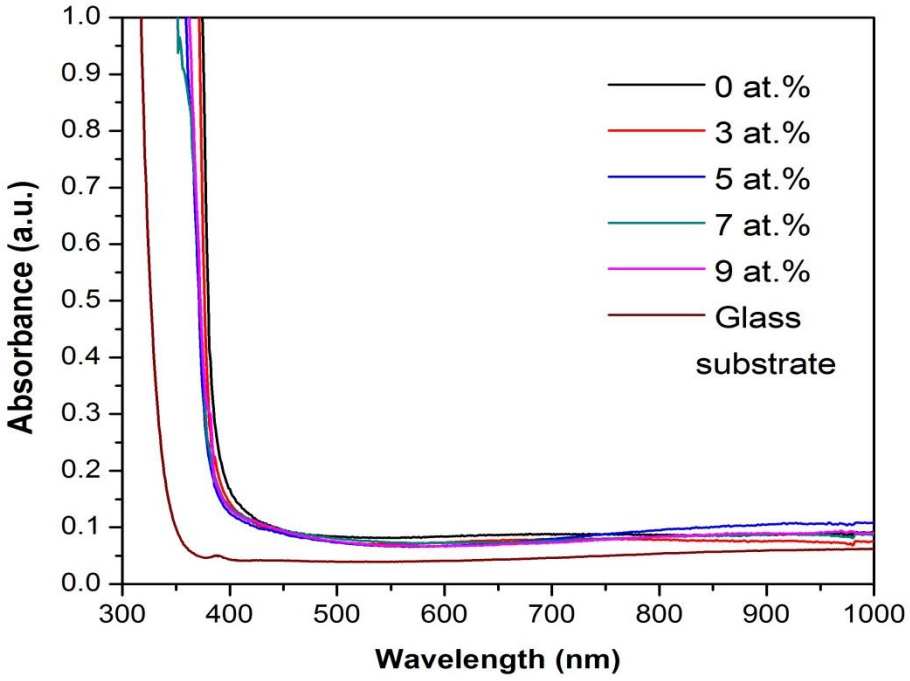


(a) 350°C



(b) 400°C

Figure 6.10 Absorbance spectra of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c).

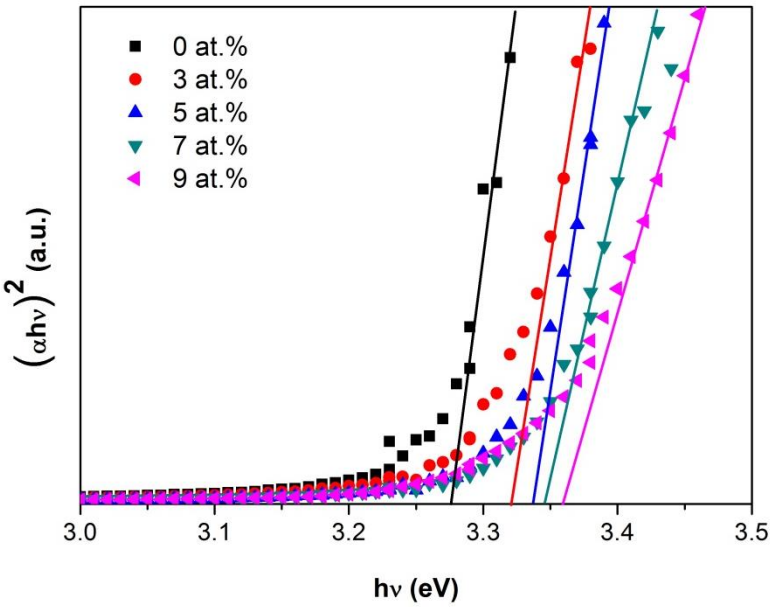


(c) 450°C

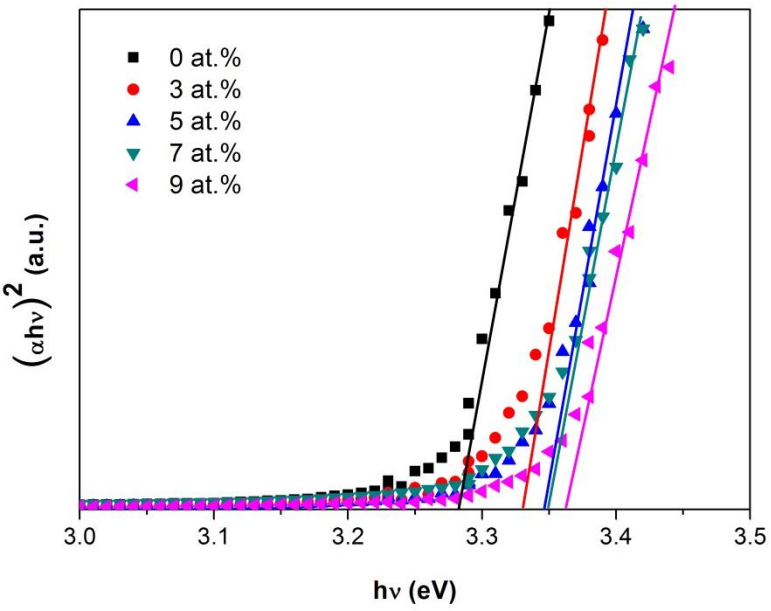
Figure 6.10 Absorbance spectra of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) (continued).

The band gap was evaluated from this transmittance spectra and thickness (Table 6.3) using Tuac's relationship in equation 3.8. The $(\alpha h\nu)^2$ versus $h\nu$ plots of all films are shown in Figure 6.11 (a-c) The intercept of $(\alpha h\nu)^2$ on the *x*-axis gave the value of the direct band gap and the band gap of all films showed in Figure 6.11 (d). It was found that the band gap of undoped and doped ZnO films increased slightly with increasing temperature (350 to 400°C). After that, the band gap of these films reduced with increase of substrate temperature to 450°C. These results are close to the pure ZnO film data from the work of *Benramache et. al* [91]. In addition, the band gap of doped ZnO films was higher than that of the undoped ZnO films and increased with increasing Mg content. This behavior was described by Huang et al. [61], Mg^{2+} induced a new defect after substituting Zn^{2+} because of the electronegativity and ionic radius difference of Zn (0.60 Å)

and Mg (0.57 Å), which can be located at a higher Fermi level. This defect may create a higher Fermi level than for the initial ZnO films.

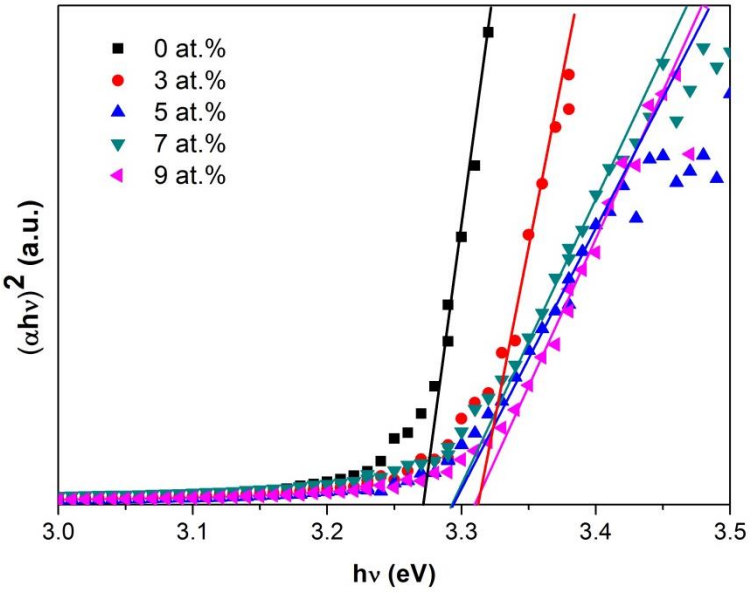


(a) 350°C

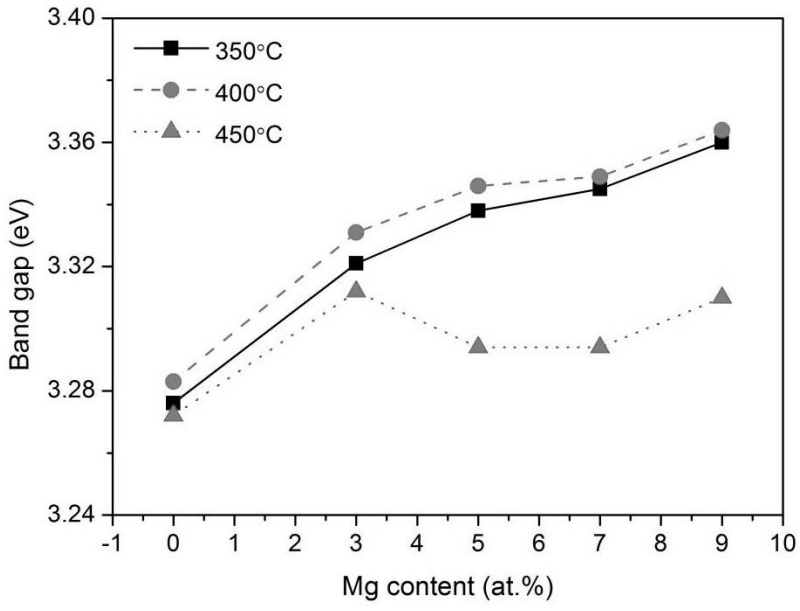


(b) 400°C

Figure 6.11 The $(\alpha h\nu)^2$ versus $h\nu$ plots of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) and band gap (d) of these films



(c) 450°C

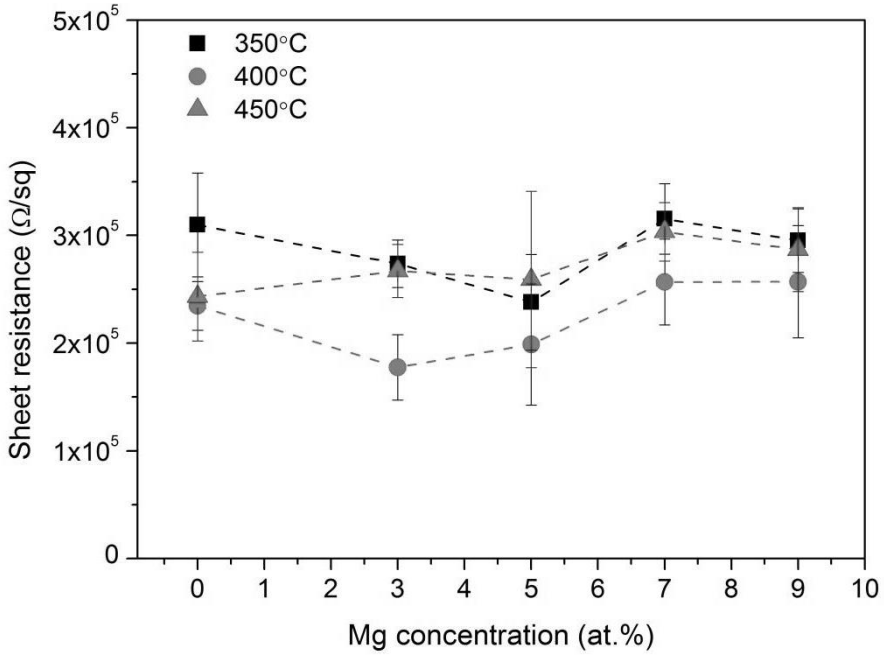


(d) Band gap

Figure 6.11 The $(\alpha h\nu)^2$ versus $h\nu$ plots of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C (a), 400°C (b) and 450°C (c) and band gap (d) of these films (continued).

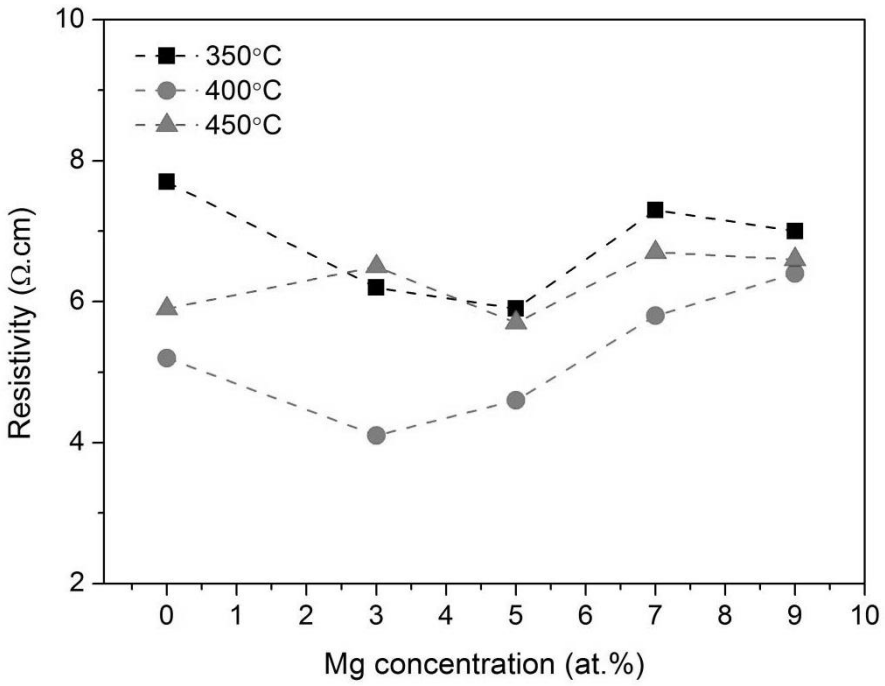
6.2.5 Electrical property

The sheet resistance and the resistivity of of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350°C - 450°C are shown in Figure 6.12. The resistivity is calculated from resistance and thickness of films by equation 3.10, the thickness was listed in Table 6.2. It was found that the similar resistivity values of undoped and Mg doped ZnO films were obtained. For the Mg doped ZnO films this similarity was attributed to the partial substitution of Zn^{2+} ions by the same valence Mg^{2+} ions [58]. Hence, Mg^{2+} do not generated carriers in ZnO lattice [61].



(a) Sheet resistance

Figure 6.12 Sheet resistances (a) and resistivity (b) of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350-450°C.



(b) Resistivity

Figure 6.12 Sheet resistances (a) and resistivity (b) of Mg doped ZnO films with different Mg concentrations deposited on a glass substrates heated at 350-450°C (continued).