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MORPHOLOGY-DEPENDENT OPTICAL TRANSMISSION OF RF-SPUTTERED ZnO:Al FILM ON GLASS SUBSTRATE

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Aluminum doped zinc oxide (ZnO:Al) films with different thickness (360, 410, 850, 1290 and 3230 nm) on glass substrate deposited by RF magnetron sputtering were etched in HCl solutions. All films showed a (HCP) wurtzite phase with (002) preferred orientation.The crystallinity of as-deposited films was increasedwith increasing the film thickness. AFM revealed thatgrain size, shape and distribution are strongly depended on the film thickness. The optical transmission of all films was strongly depended on the surface morphology and film thickness. The transmission spectra of film thickness lower than 500 nm showed a smooth pattern over wide wavelength range and its transmission increased with increasing the film thickness whereas film thickness higher than 500 nm exhibited a fluctuate pattern and wavelength at the maximum transmission strongly depended on surface morphology. Etching process give rises to a higher surface roughness and wide wavelength range of transmission.The 3230 nm-film showed the maximum transmission of 86% in wavelength between 550-650 nm and the etched 360 and 410 nm-films showed an average transmission of about 86% in visible region.

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*Keywords:*ZnO:Al film; Optical transmittance; Sputtering; Atomic force microscopy (AFM); Scanning electron microscopy (SEM).

1. Introduction

Aluminum-doped zinc oxide (ZnO:Al) film is a transparent conductive oxide (TCO) material and an excellent candidatesin applications for transparent and conductive electrodes in thin film solar cell and other optoelectronic devices such as solar cell, LED and solid state display device. The ZnO:Al film has been attracted much attention because of its excellent properties such as nontoxicity, thermal stability, high optical transmission, good conductivity and abundance in nature.The conductivity and optical transmission of the ZnO:Al film are powerfully related to film thickness, structure, crystallite size and morphology.The ZnO:Al film was intensively prepared by many research groups. The film have been preparedby many methods such as sputtering deposition [1-11], sol-gel method [12-14], spray pyrolysis technique [15-16], atomic layer deposition [17] and vacuum thermal evaporation technique [18] on glass[1,3,4,6,7-8,10-18], flexible [2,5,9]and silicon [10,14] substrates. To achieve good conductivity and excellent optical transmission, the structure, surface morphology and roughness of the film were largely manipulated by annealing and etching process. It has been know that surface morphology is an important key to enhance the optical transmission of the film by mean of in light scattering and trapping abilities. The chemical etching process has been generally used to produce textured surface ZnO:Al film. Acetic acid, HCl (hydrochloric), and HF (hydrogen fluoride) solutions are the important etching reagents to texture the film surface. The effects of etching parameters such as etching time, solution concentration and etching method on the film properties have been intensively reported.The acetic acid etched-film on TPT substrate showed that the (200) plane of hexagonal phase ZnO was shifted to higher angle with increasing etching time and surface morphology exhibited pyramidal structure which supported the light trapping and appeared the

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hole after a long etching time [1]. The HCl etched-film on glass substrate achieved a regular distribution on large craters with size of 1-2 μm and 250 nm in depth and all film showed a high average transmission more than 85% [2]. The dependence of working pressure and substrate temperature on surface structure of HCl-etched film on glass has been intensively reported.

In this work, the effects of surface morphology and film thickness on electrical resistance and optical transmittance of sputtered ZnO:Al films on glass substrate were intensively studied to understand the relation between the film morphology and its optical transmittance.

2. Experimental Methods

ZnO:Al films with different thickness were deposited by FR magnetron sputtering on glass substrate. The composite ZnO:Al target (ZnO (99.9%) doped with Al_2O_3 (5 wt.%) in a 3-in disk type) was installed at a distance of 4.0 cm away from the glass substrate. The base pressure in the vacuum chamber was around 10^{-5} mbar and Argon pressure during the sputtering process was 10^{-3} mbar. The target was cleaned by glow discharge process before each deposition. The deposition process of the films was carried with a constant sputtering power of 150 W at sputtering time for 10, 20, 30, 40 and 50 min.All thickness of the sputtered ZnO:Al film were following wet-etched in 0.5% of hydrochloric acid (HCl) aqueous solution for 10 seconds. The thickness of both as-deposited and etched films wereexamined by scanning electron microscopy (SEM). Surface roughness and morphology were characterized by atomic force microscopy (AFM) over scan area of 1x1, 5x5 and 10x10 μm^2. X-ray diffraction (XRD) with CuK_α radiation was used to identify the film crystal structure. The chemical composition of some ZnO:Al film was also confirmed by an energy-dispersive spectroscopy (EDS). The electrical resistance of the films was carried out by 4-point probe technique. The optical transmittance of the films was measured by UV-Visible NIR spectrophotometer in the wavelength range of 200-800 nm.

3. Results and Discussions

Fig.1 shows cross sectional SEM images of as deposited ZnO:Al film at sputtering power of 150 W for 10, 20, 30, 40 and 50 min. These images obviously indicate that the deposited films are adhered on the glass substrate with a smooth interface. The averaged thickness from SEM image is 360, 410, 850, 1920 and 3230 nm. The thickness of ZnO:Al film is plotted as function of deposited time representing the exponential increase with increasing the sputtering times as shown in Fig. 1 (f). It can be confirmed that the increase of film thickness with increasing sputtering time because the ion density or the number of atoms sputtered was increased with the time to deposit on the substrate without back diffusion in this interval time of deposition process.

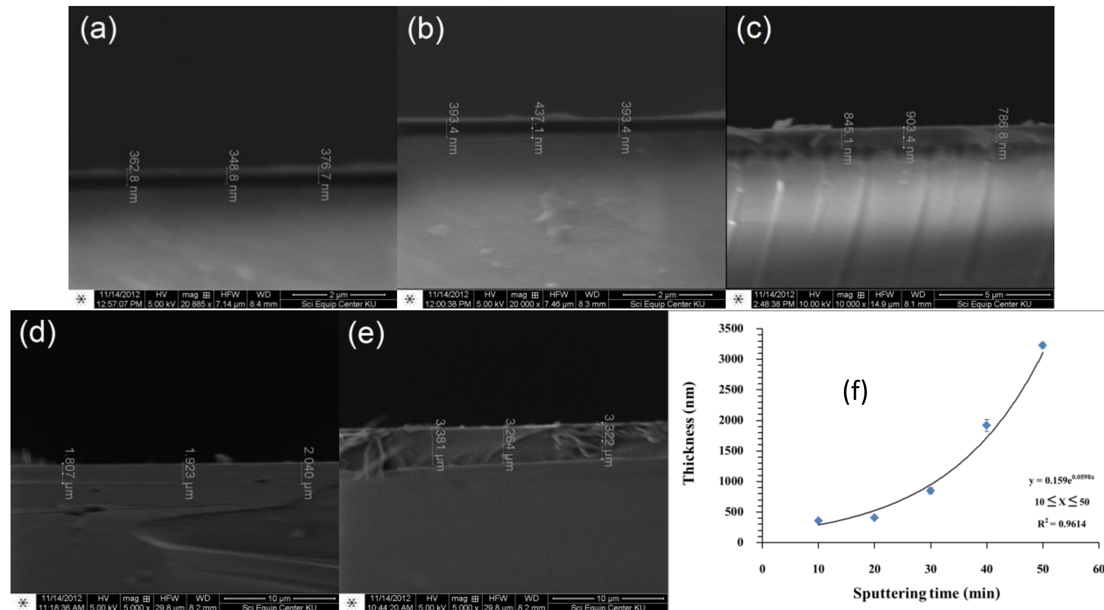


Fig.1 Cross sectional SEM images of as-sputtered ZnO:Al film deposited at power of 150 W for (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50 minutes on glass substrate and (f) thickness at different sputtering times.

Surface morphology in 2 and 3 dimensions of sputtered ZnO:Al film with different thickness was shown in Fig. 2. All as-deposited films clearly show that the surface morphology is film thickness dependent. A 360 nm-film exhibits the fine grain size of a small columnar structure. The 850 and 3230 nm-films show a columnar structure with a moderate grain size and narrowest size distribution. However, the 850 nm-film shows a slightly larger grain size than that of the 3230 nm-film. It can be observed that the 850 nm-film displays the largest columnar structure with a regular size. The 1920 nm-film exhibits the granular structure with broad grain size distribution. Moreover, the morphology of the 410 nm-film shows the larger grain size of columnar structure in comparison to the 360 nm-film. These results refer that the morphology of sputtered film is strongly thickness dependence or growth mechanism because the sputtered atoms usually tend to agglomerate invertical direction corresponding to the columnar structure of the film.

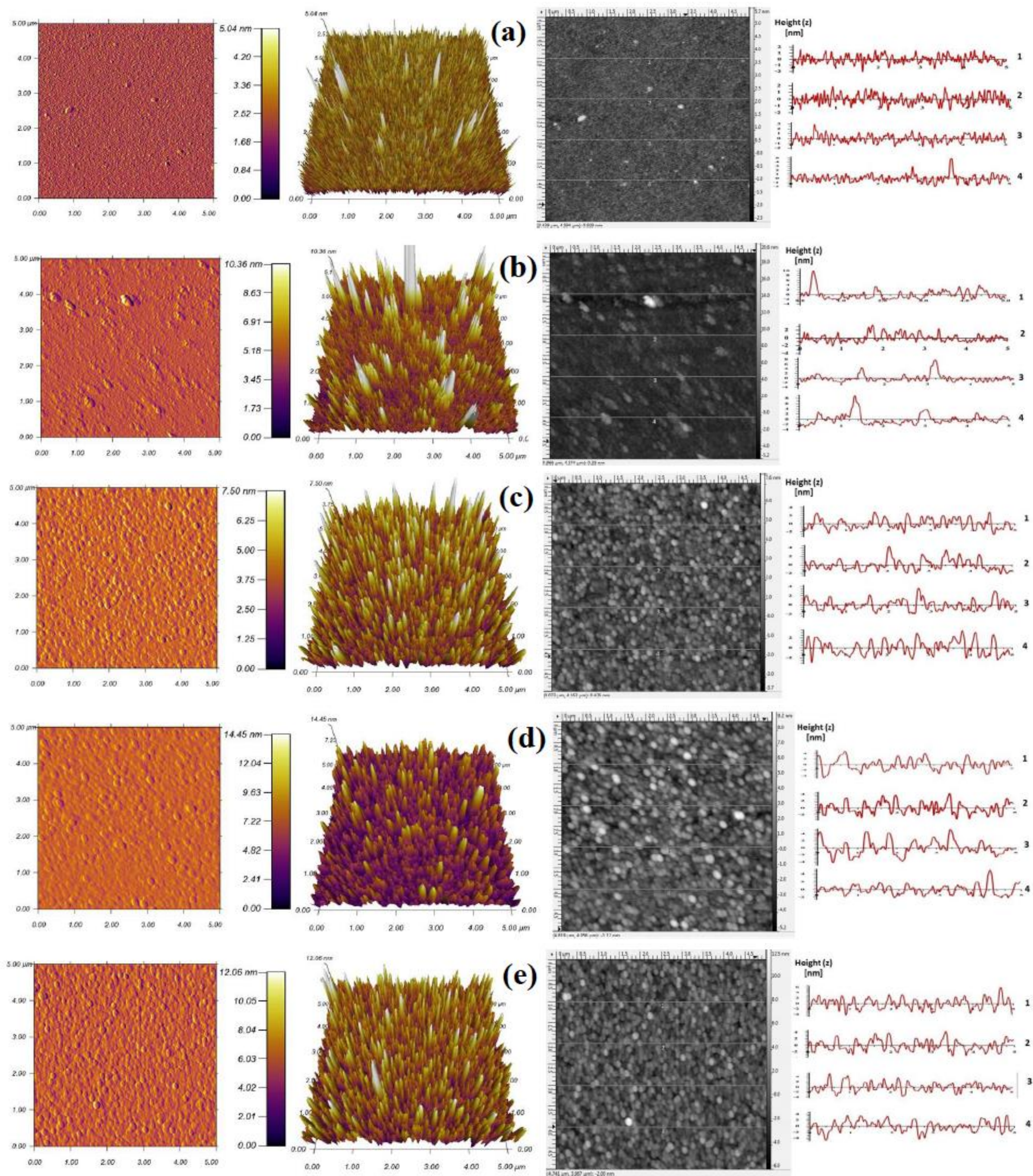


Fig.2 AFM images in 2D, 3D and cross section of as-deposited ZnO:Al film on glass substrate with the thickness of (a) 360, (b) 410, (c) 850, (d) 1920 and (e) 3230 nm over an area of 5x5 μm^2.

After wet-chemical etching process in a dilute hydrochloric acid, the surface morphology of etched ZnO:Al film are shown in Fig. 3. AFM result exhibits that surface of ZnO:Al film was extremely scratched for the thinner films such as 360, 410, and 850 nm-films contrast with the surface of the thick film such as 1920 nm and 3230 nm-films were displayed the rectangular column morphology. The etched 3230 nm-film displays a regular size and distribution whereas the etched 1920 nm-film shows a continuously columnar morphology with a random texture.

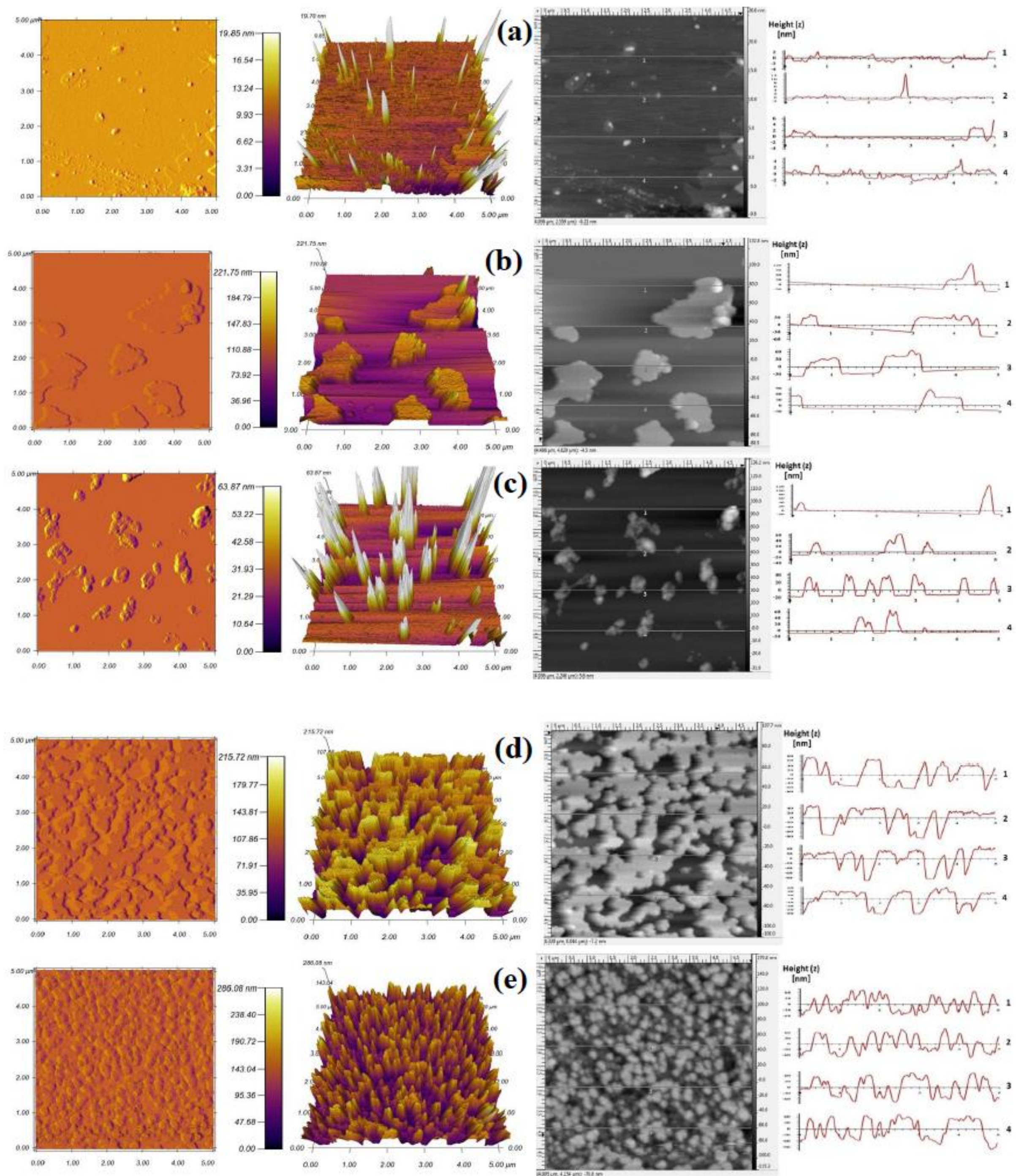
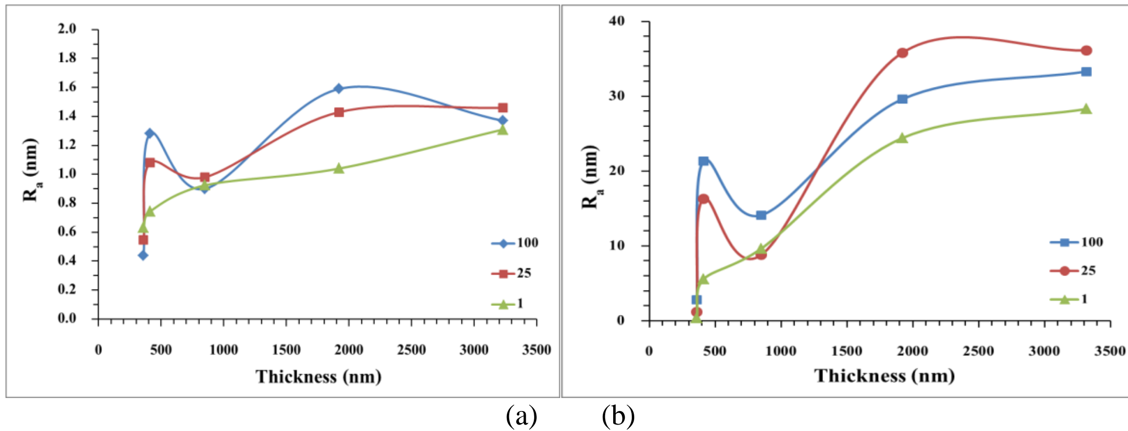


Fig.3 AFM images in 2D, 3D and cross section of etched ZnO:Al film on glass substrate with the thickness of (a) 360, (b) 410, (c) 850, (d) 1920 and (e) 3230 nm over an area of 5x5 μm^2.

The average surface roughness of as-deposited ZnO:Al films over different scanning areas is revealed as in Fig. 4 (a). All scanning area, the as-deposited film shows that the film roughness is in the range between 0.545 and 1.600 nm.It clearly shows that the 360, 850 and 3230 nm-films display the narrow roughness distribution whereas the 410 and 1920 nm-films show the broader roughness distribution. This result is consistent with the surface roughness of the etched film as shown in Fig. 4 (b).The etched film displays that the roughness is in the range from 1.13 to 36.10 nm. The roughness isslightly inclined to increase with increasing film thickness. The roughness result indicates that etching process makes the deeper texture on the film surface. The narrow roughness distribution is observed on 360, 850 and 3230 nm-films and the broader roughness

distribution is found on the 410 and 1920 nm-films. These results attribute that surface morphology of the film can be divided two regular and irregular textures depending on the difference of surface roughness in all scanning areas. The regular texture or homogeneous morphology can be observed on the 360, 850 and 3230 nm-films, on the other hand, the irregular texture or inhomogeneous morphology can be found on the 410 and 1920 nm-films. It could be attributed that the increment of surface roughness of etched-film easily raises the oxidation process at the film surface.



(a) (b)

Fig.4 Surface roughness (R_a) of (a) as-sputtered and (b) etched ZnO:Al films with different thickness on glass substrate.

XRD patterns of the as-deposited ZnO:Al film with different thickness on glass substrate are shown as in Fig. 5. All as-deposited films showed only the (002) peak of a hexagonal wurtzitestructure with c-axis oriented perpendicular to the substrate surface and the intensity of the peak was increased and position was gradually shifted to higher diffraction angle with increasing film thickness. The peak shift implied that the lattice parameter of ZnO was decreased because the Al3+ ions substituted in Zn2+ ions in lattice site[19]and the intrinsic stress during growth process was increasingly induced. As-deposited films showed that the crystallite size calculated from FWHM of the peak was decreased with increasing film thickness as an inset of **Fig. 5**. The calculated grain sizes of the films were more or less uniform for all films, ranging from 23.6 – 38.0 nm. The calculated crystallite size was in the same range in comparison to the previous works. [20, 21] The crystallite size reached the maximum value of 38 nm in a 360 nm-film and thenquickly decreased to the minimum value of 23.6 nm in a 410 nm-film and showed value of 25.5, 24.0 and 24.3 nm in 850, 1920 and 3230 nm-films, respectively. After HCl-etching process, the intensity of the (002) peak of the etched-360 and 410 films in XRD result was disappeared. However, EDS analysis confirms that atomic percent of Zn element is less than 1% atomic the etched-360 and 410 films and increased with the film thickness and then reached about 5% in etched-3230 film. It could be considered that the HCl-etching mainly removes the ZnO phase of the film.Calculated crystallite size of etched 850, 1920 and 3230 nm-films are 22.0, 21.4 and 19.7 nm, respectively. The size was decreased with increasing film thickness. It can be referred that the percentage of Zn element significantly entailed the properties of in ZnO:Al films.

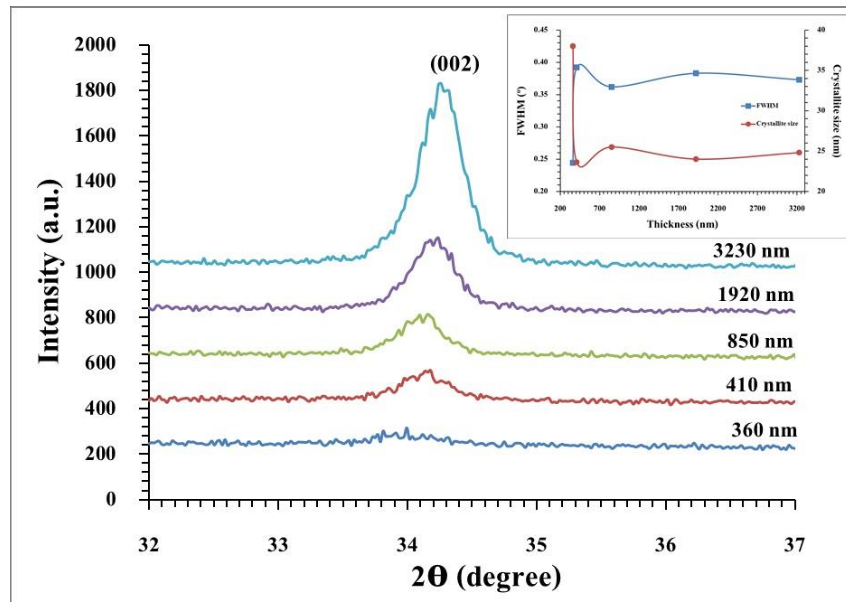


Fig.5 XRD patterns of as-deposited ZnO:Al film with different thickness and an inset of FWHM (Full width at haft maximum) and crystallite size.

Electrical resistance and film thickness correlated with sputtering timeof as-deposited films was presented as in Fig. 6. The electrical resistance of the 360 nm-film cannot be measured because of the low crystallinity and amorphous phase in an initial stage of growing process. The resistance of the film was steeply decreased with increasing sputtering time and thickness. The maximum and minimum resistances of 2884 and 224 Ω were observed on the 410 and 3230 nm-film, respectivelywhereas the 850 and 1290 nm-film exhibited the resistance of 2503 and 241 Ω. The precipitous decrease of electrical resistance attributed that the electrical properties is not only depended on the film thickness and structure but also related to surface morphology and roughness.

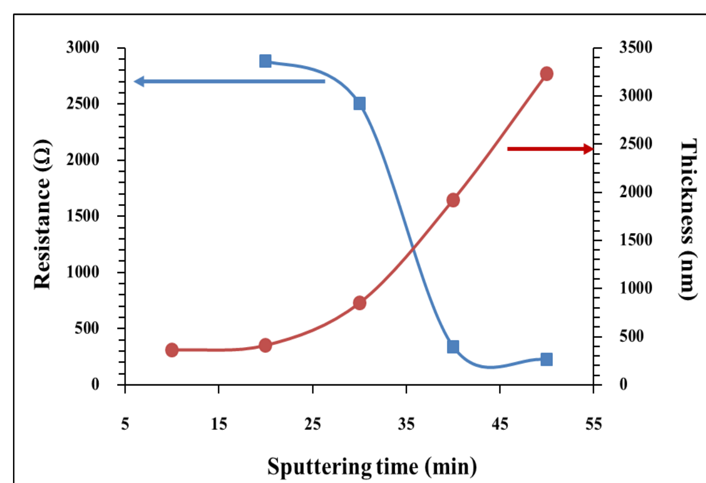
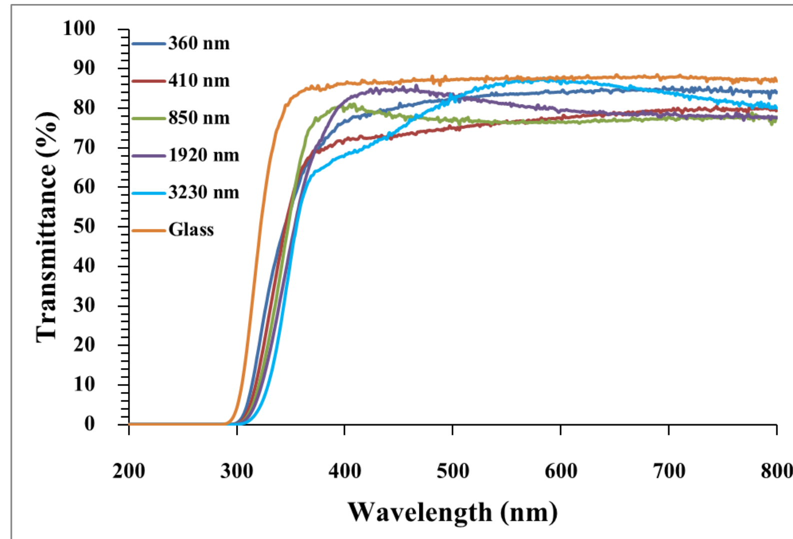
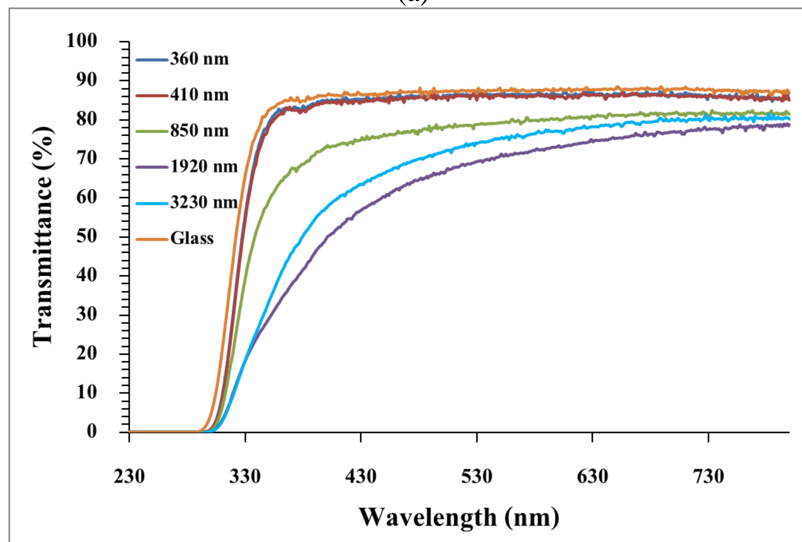


Fig.6 Electrical resistance (R) and film thickness of ZnO:Al film on glass substrate plotted as a function of sputtering time.



(a)



(b)

Fig.7Transmittance spectra of (a) as-deposited and (b) etched ZnO:Al films with different thicknesson glass substrate at sputtering power of 150 W.

The optical transmission of as-deposited films with different thickness compared to glass substrate was shown in Fig. 7 (a). The 360 and 410 nm-films showed the smooth transmission spectrum and exhibited the average of 84% and 76%, respectively in visible region. The transmission spectra of the 850, 1290 and 3230 nm-films were oscillated with the transmission wavelength. The 3230 nm-film showed the maximum transmission of 86% in wavelength between 550-650 nm and the minimum transmission of 68% in wavelength between 350-450 nm. The 1290 nm-film showed the maximum and minimum transmissions of 84% and 80% in wavelength between 400-450 nm and 450-800 nm, respectively. The maximum and minimum transmissions of 80% and 76% in wavelength between 350-400 nm and 450-800 nm, respectively were observed in the 850 nm-film. These results suggested that transmittance pattern of the film was thickness dependence for the thin films (360 and 410 nm) and thickness independence for the thick films (850, 1920 and 3230 nm). It can be defined that the filmsthickness less than 500 nm showed the smooth pattern and widespread range with the moderate value of optical transmission in visible region.The thickness beyond 500 nm exhibited the oscillate pattern with the narrow range with the high transmission and the wavelength range at the maximum transmission of these films was increased with increasing the thickness. The maximum transmission of 850 and 3230 nm-film

indicated that the optical transmission of sputtered ZnO:Al film is not only related to film thickness but also closely connected to surface morphology and roughness. The regular morphology and smooth reduced the oxygen absorption at the surface decreasing the electrons traps and increasing efficiency of the optical transmission. The results confirmed that random morphology encouraged the light trapping at the film surface. The optical transmission of etched-films shown in Fig. 7 (b) showed that transmission of the 360 and 410 nm-films was similarto patternof the glass substrate but slightly lower transmission percentage. It can be attributed that the etching process mainly moved the ZnO phase from the deposited film give rise to ZnO clusters dispersed on the glass substrate.The etched 360 and 410 nm-films showed an average transmission of about 86% in visible region. The transmission of etched 850, 1920 and 3230 nm-films were 80, 78 and 76% in visible region, respectively and their transmission were decreased with increasing film thickness. It may be due to the dense and deep morphology of the etched-film. The all results confirmed that the surface morphology as well as film thickness played an important roleinthe optical transmission of the ZnO:Al film in visible region.Our resultssuggested that the thickness played an important key in optical transmission for thin film (thickness < 500 nm) whereas the surface morphology played an important role in transmission for thick film (thickness > 500 nm). The deep-etched, roughness and dense morphology give rise to a lower transmission because of a higher rate of electron trapping. The smoothmorphology withregular shape and optimum size distribution encouraged a higher transmission. The morphological shape and size were also significantly related to the wavelength range of optical transmission. To reach the highest transmission, the clusters of the ZnO:Al film patterned on glass substrate is proposed to be an alternative way.

4. Conclusion

The ZnO:Al film with different thickness of 360, 410, 850, 1290 and 3230 nm on glass substrateprepared by RF-sputtering methodwere etched by HCl solution. Both as-deposited and etched films exhibited a hexagonal wurtzite structure with (002) direction and its intensity were increased with increasing film thickness. Optical transmission of all filmswas strongly dependent on the surface morphology and film thickness. Thin films (thickness < 500 nm) displayed smooth pattern of transmission over a wide wavelength range and its percentage of transmission strongly was depended on film thickness. Thick film(thickness > 500 nm) exhibited an oscillate pattern of transmission and the wavelength at the maximum transmission was significantly be influenced by surface morphology.The 3230 nm-film showed the maximum transmission of 86% in wavelength between 550-650 nm and the etched 360 and 410 nm-films showed an average transmission of about 86% in visible region.

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