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Research Article

Rootlike Morphology of ZnO:Al Thin Film Deposited on Amorphous Glass Substrate by Sol-Gel Method

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Zinc oxide (ZnO) and aluminum doped zinc oxide (ZnO:Al) thin films have been deposited onto a glass substrate by sol-gel spray coating method at atmospheric pressure. X-ray diffractometer (XRD), scanning electron microscopy (SEM), and UV-Vis spectrophotometer have been used to characterize the films. XRD spectra indicated that all prepared thin films presented the wurtzite hexagonal structure. SEM images exhibited rootlike morphology on the surface of thin films and the shortest root diameter was about 0.219 μm. The UV-Vis absorption spectra exhibited the absorption edges that were slightly shifted to the lower wavelength. From this result, the incorporation of aluminum into the ZnO involved a slight increase in the optical band-gap of films. The optical bands of films were 3.102 eV, 3.115 eV, 3.118 eV, 3.115 eV, 3.109 eV, and 3.109 eV for ZnO, ZnO:Al 2%, ZnO:Al 4%, ZnO:Al 6%, ZnO:Al 8%, and ZnO:Al 10%, respectively. Increase of Al doping concentration in ZnO films contributed to the increase of their optical band-gap which can be explained by the Burstein-Moss effect.

1. Introduction

Zinc oxide (ZnO) is the most popular materials that can be used for many applications. Many researchers have studied this material for electronics [1], energy [2], and environment [3] applications. ZnO is of low cost and nontoxic and has high chemical stability which make this material so interesting [4]. ZnO can be used for transparent conductive oxide [5], gas sensors [6], and photocatalyst [7–9]. ZnO has a wide band-gap energy (~3.3 eV) and has been studied in different forms such as powder [10] and thin film [11]. Several techniques can be used to make ZnO:Al thin film, such as DC or RF magnetron sputtering [12, 13], electron beam evaporation [14], pulsed laser deposition [15], chemical vapor deposition [16], spray pyrolysis [17], and sol-gel processing [18]. Sol-gel is the most widely used method because of its easy and low-cost preparation [19].

Substitution of Zn^{2+} ion by group III ions such as B^{3+}, Al^{3+}, Ga^{3+}, and In^{3+} will produce extra electrons and improve optical, electrical, thermal, and magnetic properties. The most commonly used dopant is aluminum (Al) [20, 21]. In this work, we proposed ZnO and ZnO:Al thin films deposited by sol-gel spray coating. The films have been characterized by XRD, SEM-EDX, and UV-Vis. The Al doping concentration in the ZnO:Al films was controlled and its effect on the films properties was investigated.

2. Materials and Method

ZnO and ZnO:Al thin films were synthesized by sol-gel spray coating method. As a starting material, zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) was dissolved in 2-propanol with a concentration of 0.5 mol L^{-1}. Monoethanolamine (MEA) was wisely dropped into solution and was stirred under room temperature for 30 min. For doped films, aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) was added to the solution with a molar percentage, fixed at 0, 2, 4, 6, 8, and 10% moles and were then denoted as ZnO, ZA2, ZA4, ZA6, ZA8, and ZA10, respectively. The precursor solution was deposited onto glass substrate by spray coating at 450°C hotplate temperature

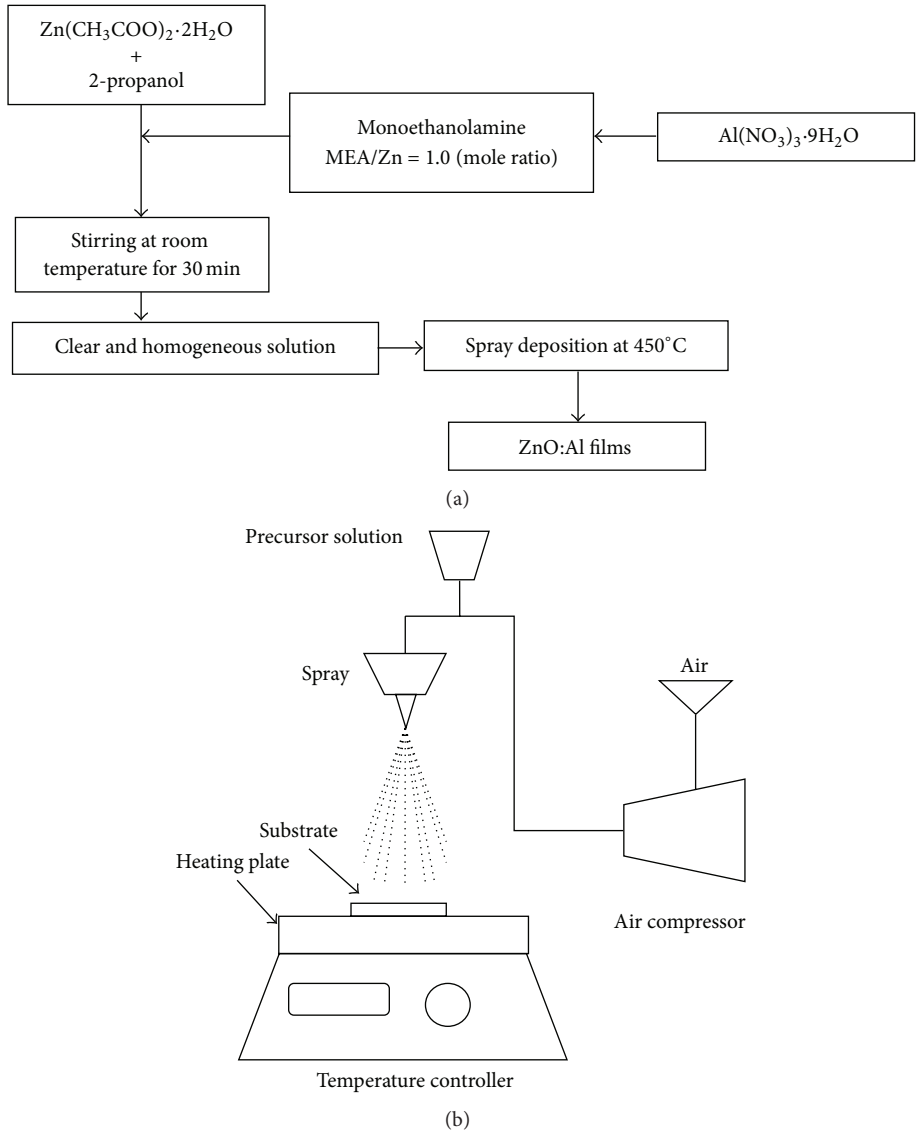

Figure 1: (a) The flow chart shows ZnO:Al preparation by sol-gel technique. (b) Diagram of spray coating system.

and allowed for 1 hr. Figure 1(a) showed the flow chart of preparation and (b) diagram of spray coating system that was used in this study. Prior to a deposition, the glass substrate was cleaned by ultrasonic cleaner using acetone, methanol, and bidistilled water. The prepared thin films were characterized by X-ray diffraction (XRD) using Shimadzu Maxima 7000 (Cu-Kα wavelength: 1.5405 Å). The detection angles were ranging from $2\theta = 10$ to 90°. The morphology of thin films was shown by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) using JEOL-JSM 6510 LA. The optical transmission of the films was measured by a UV-Vis spectrophotometer (Shimadzu 1240 SA).

3. Results and Discussion

3.1. Microstructure. Figure 2 depicts the polycrystalline diffraction pattern for all prepared samples. The pattern clearly showed the hexagonal wurtzite structure of ZnO and matched with the reported data on JCPDS 36-1451. The pattern also demonstrates that the obtained thin films have sharp and narrow peaks, indicating that the materials exhibit high crystallinity. The high crystallinity film can be achieved on amorphous glass surface under high temperature deposition. In our deposition method, the hotplate temperature was adjusted at 450°C which enable making polycrystalline of ZnO. In the ZnO:Al spectra, only ZnO phase was detected and there is no Al or Al oxide phase. This result suggests that the thin films do not have any phase segregation or secondary phase formation because of Al incorporation into ZnO lattice. It also might be caused by Al content which was so small to be detected. We can see that ZA4 and ZA10 exhibited amorphicity due to the glass substrate. The pattern also demonstrates a preferential *c*-axis-orientated structure with the most intense peak at (002). This preferential growth is dependent on the deposition temperature. Ali et al. [22]

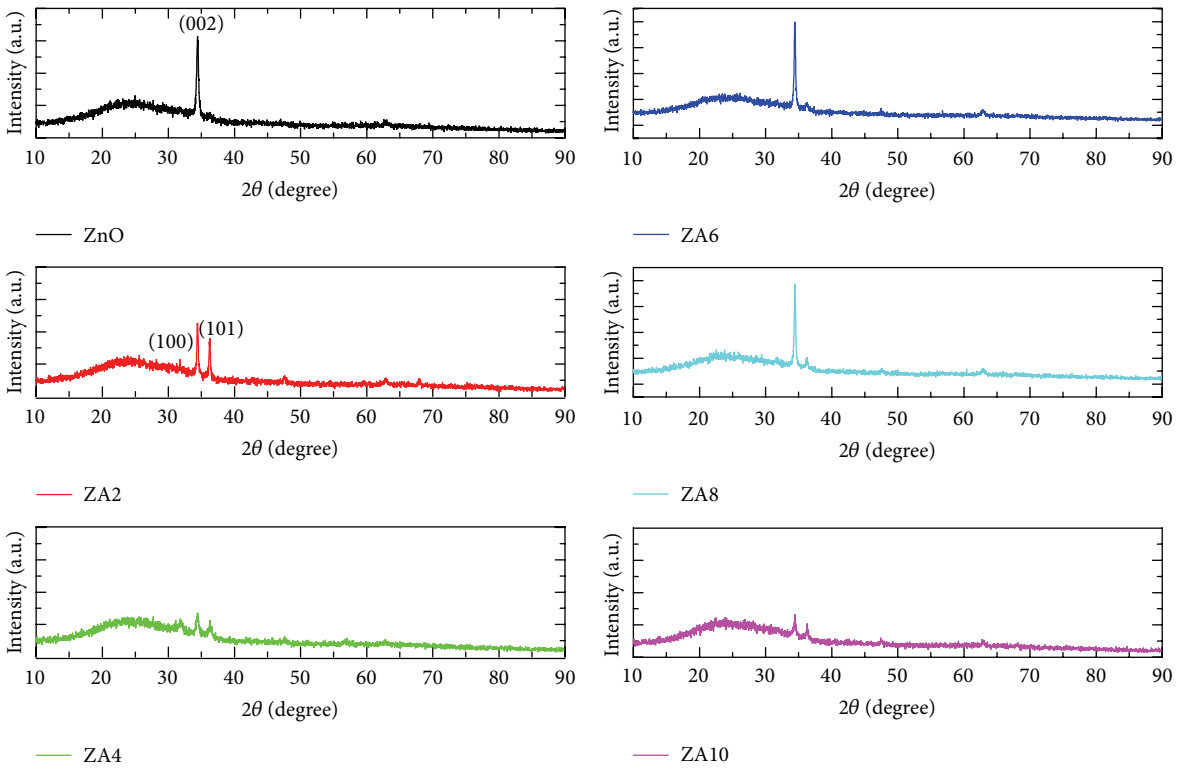

Figure 2: XRD spectra of ZnO and ZnO:Al thin films.

have reported that the optimal growth temperature for the RF-sputtering technique was 400°C. In our study with a sol-gel method and a small temperature difference, we still get high quality of polycrystalline of ZnO:Al. The crystallite size can be estimated by the Scherrer formula (see equation (1)) using (002) peak. The crystallite size of ZnO:Al became bigger than pure ZnO thin film and is shown in Table 1:

$$D = \frac{k\lambda}{\beta_{1/2}\cos\theta}, \quad (1)$$

where $k = 0.90$ is the Scherrer constant, $\beta_{1/2}$ is the full width at half maximum and $\lambda = 1.5405$ Å is the wavelength of Cu-Kα radiation.

We can note that the lattice parameter c decreased; it might be affected by the substitutional replacement of Zn^{2+} (ionic radius 0.072 nm) ions by Al^{3+} (ionic radius 0.053 nm) [23]. The estimated value of crystallite size from (002) plane was found to increase from 18.85 nm for ZnO to 25.37 nm for ZA10. Normally, it was expected that the crystallite size should also decrease due to replacement of Zn^{2+} ions by Al^{3+} ions [24]. The same result has been obtained by Abd-Lefdil et al. [25]. The increase in crystallite size may be due to the enhanced thickness of Al-doped films. During deposition process, the lower surface energy grains may become larger as film thickness increase [26].

3.2. Morphology. Figure 3 represents the SEM observation of all prepared samples. It can be seen that all films have rootlike morphology. In ZnO image, the root surface had the longest diameter of all other samples. ZnO:Al thin films had shorter root diameter and the shortest root diameter was obtained by ZA6. The root diameter was shown in Table 2. The rootlike morphology was rarely found in other ZnO thin film studies.

Table 1: FWHM and crystallite size parameters of thin films.

Sample name	2θ (002)	FWHM (deg)	D (nm)	c (Å)
ZnO	34.42	0.45816	18.85	5.206797
ZA2	34.48	0.36741	23.52	5.198011
ZA4	34.42	0.44695	19.33	5.206797
ZA6	34.44	0.33876	25.50	5.203865
ZA8	34.42	0.34697	24.90	5.206797
ZA10	34.44	0.34048	25.37	5.203865

Figure 4 depicts the suggested ZnO growth mechanism using sol-gel spray coating method at 450°C. During deposition, the layer of crystalline grains is built onto glass substrate. There is a different temperature from the first layer and other layers that affects the interaction among them. Many particles merge with other particles to make a long structure of ZnO which is called rootlike morphology.

EDX result exhibited Al composition in the thin film sample which was different from Al composition in the precursor solution as shown in Table 2. This might be caused by only a small percentage of Al ions that enable substituting Zn ion. Another reason was the high loss of Al during spray deposition. We can see the saturation result of Al/Zn incorporation at higher percentage of Al doping. This result

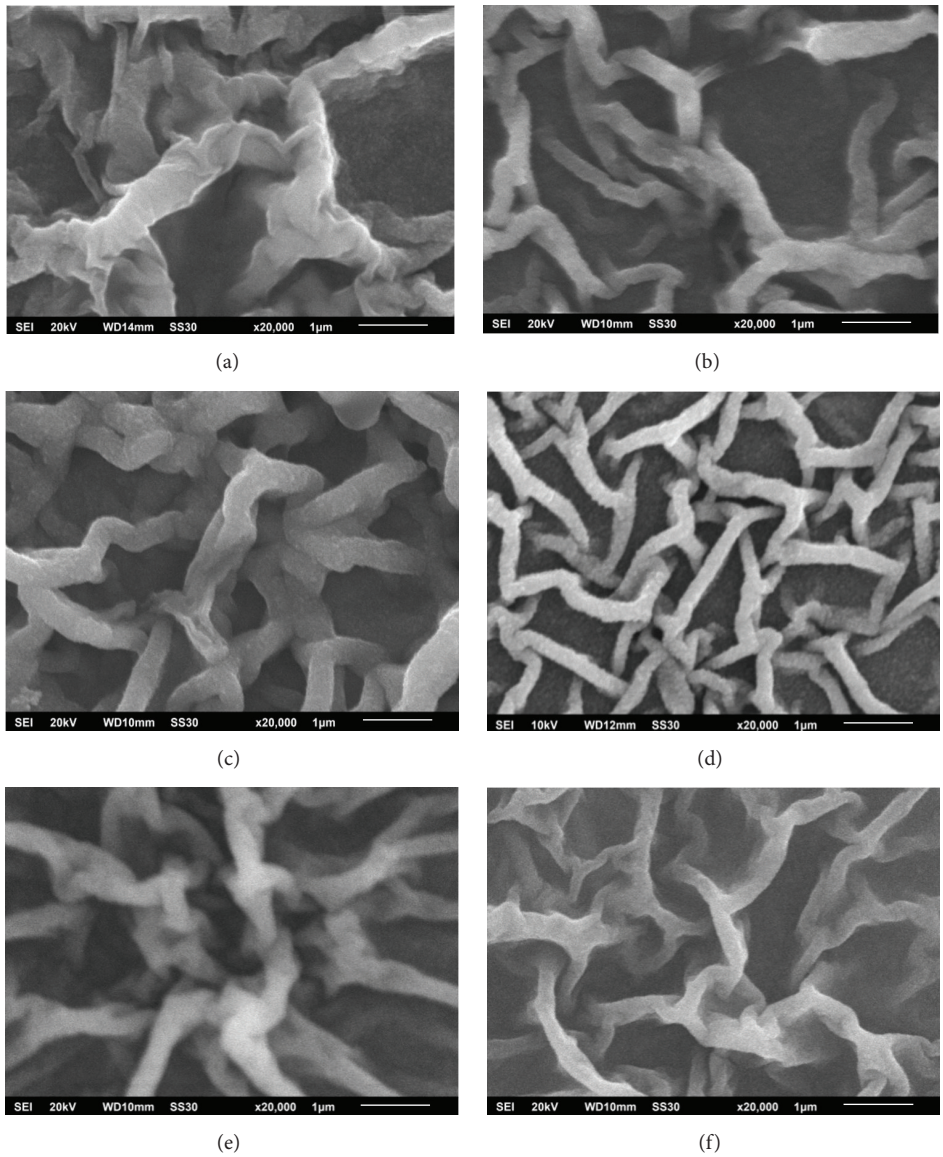

Figure 3: SEM images of ZnO (a), ZA2 (b), ZA4 (c), ZA6 (d), ZA8 (e), and ZA10 (f) thin films.

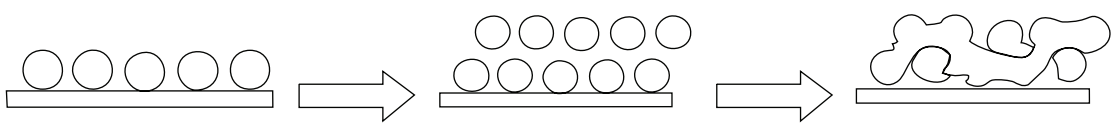

Figure 4: Rootlike morphology of ZnO:Al mechanism.

Table 2: Root diameter, Al/Zn composition, and energy gap of thin films.

Sample name	Root diameter (μm)	Al/Zn in solution	Al/Zn incorporated	Energy gap (eV)
ZnO	0.482	0	0	3.102
ZA2	0.227	0.02	0.01	3.115
ZA4	0.377	0.04	0.02	3.118
ZA6	0.219	0.06	0.03	3.115
ZA8	0.375	0.08	0.03	3.109
ZA10	0.288	0.10	0.03	3.109

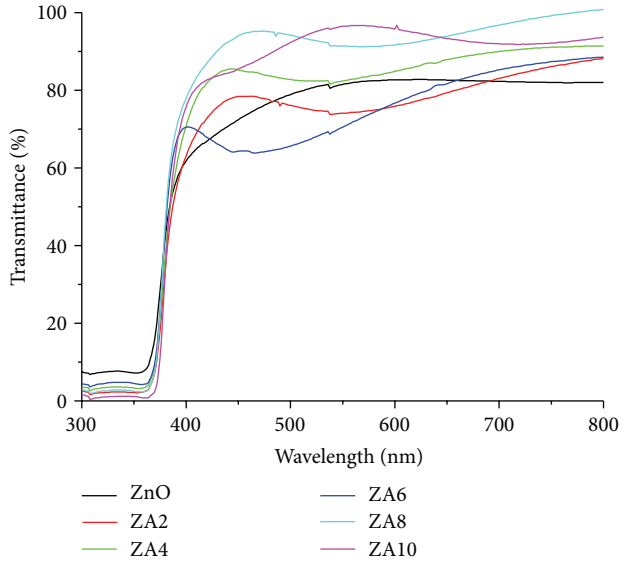

Figure 5: Optical transmittance spectra of thin films.

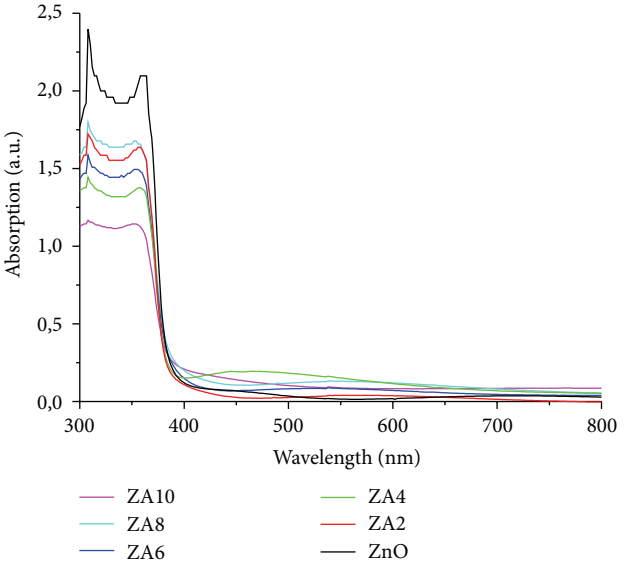

Figure 6: Absorbance spectra of thin films.

was affected by the limitation of Al doping in ZnO thin film. The thermodynamic solubility limit of Al in ZnO has been reported to be in the 2-3 at. % range [27]. According to the phase diagram of Al/Zn mixture in the previous study [28], the mixture only shows Zn phase at our temperature treatment. The limitation of Al is the maximum Al content in the ZnO at a given temperature. The substitution of Al in ZnO remains quite difficult because of the difference in ionic radius, coordination preference, and oxidation state [29].

3.3. Optical Properties. The optical transmittance spectra were shown in Figure 5 and, in these spectra, an improvement of the film transparency at high Al doping concentration can be seen. The highest transparency was obtained by ZA8 about 95% in the visible wavelength region. The increase can be explained by the reduction of light scattering in the film which was caused by the lower thickness [18]. It also exhibited the fringes pattern that indicated the high quality and homogenous surface [30]. Figure 6 shows the absorbance spectra of all prepared thin films. We can see that ZnO:Al thin films have a slight shift to lower wavelength (blue shift).

The optical band-gap can be estimated from the transmission spectra. Prior to calculation, the absorption coefficient should be calculated using the formula below:

$$\alpha = \ln\left(\frac{1}{T}\right) \times \left(\frac{1}{e}\right), \quad (2)$$

where T is the transmittance spectra and e is the thickness of the thin film. We can use α from the calculation to get the optical band-gap and obey the following equation:

$$(\alpha h\nu)^2 = A\left(h\nu - E_g\right), \quad (3)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, A is a constant, and E_g is the optical band-gap [31]. The optical band-gap E_g can be obtained by extrapolating the linear part of the curve to $(\alpha h\nu)^2 = 0$ if one plots $(h\nu)^2 \sim h\nu$.

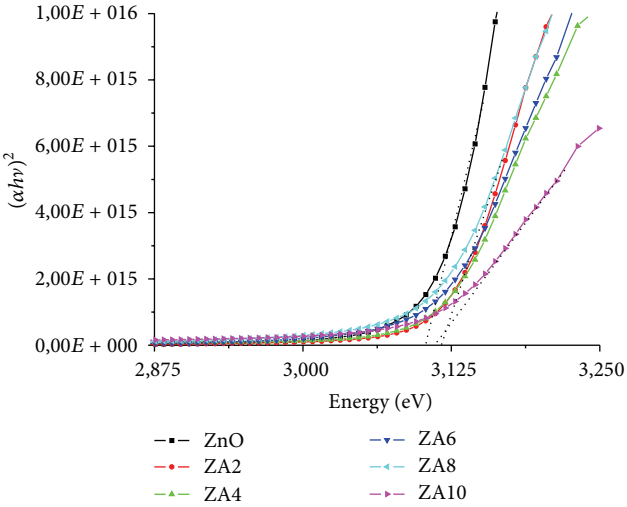

Figure 7: Optical band-gap of thin films.

The optical band-gap of ZnO and ZnO:Al thin film was presented in Figure 7. The ZnO:Al thin films had bigger optical band-gap than pure ZnO thin film; the same result has been obtained by some papers [32–35]. The increase of band-gap was caused by the Moss-Burstein effect [36]. The effect stated that the blue shift of the optical band-gap of semiconductors is affected by impurity in the conduction band [37]. ZnO:Al films are semiconductors in which the Fermi level lies in the conduction band which means that electrons occupy the levels at the bottom of the conductivity band [37, 38].

4. Conclusions

The pure and the aluminum doped ZnO films were successfully deposited by the sol-gel spray coating technique. XRD

spectra showed the hexagonal wurtzite structure of ZnO. The estimated crystallite size increases with addition of Al due to replacement of Zn^{2+} ions by Al^{2+} ions. The surface of all prepared thin films showed rootlike morphology and the diameter decreased with increase of Al content. The transmittance spectra showed high transparency of ZnO:Al thin films about 95%. The absorbance spectra exhibited that ZnO:Al had a slight shift to higher wavelength than pure ZnO. The optical band-gap resulted in slight increase for the Al-doped films as explained by the Moss-Burstein effect.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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