American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS)
ISSN (Print) 2313-4410, ISSN (Online) 2313-4402

http://asrjetsjournal.org/

Effect of Aluminum Doping on Zinc Oxide Thin Film Properties Synthesis by Spin Coating Method

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Abstract

A sol-gel spin coating method has been successfully used to synthesize pure zinc oxide (ZnO) and Al-doped ZnO thin films. Synthesis of pure phase of ZnO thin films with polycrystalline hexagonal wurtzite structure with the lattice parameters a=3.2568A and c=5.2108A have been revealed using XRD analysis. There is no change in the phase structure with Al doped ZnO thin films and the lattice parameters decreased with increased in Al-doping concentration. The crystallite size, lattice constants and strain are decreased, as the Al dopant concentration increases in ZnO lattice which is attributed to the interstitial substitution of Al ions in Zn sites into ZnO lattice as confirmed by EDX results. SEM studies show that with Al-doping the growth of the films takes place to be nanowire in structure at Al concentration up to 3% wt and the size reduced more at 5% wt. This indicates that Al-doping has an influence on the surface morphology of the films. Bandgap energy of ZnO is 3.37 eV with direct band to band transitions and decreased to 3.25 eV with increased Al-doping concentration. These properties of Al doped ZnO thin films make it a promising materials to be effectively used in many optoelectronic devices and application such as solar cell, photocatalysis, gas sensor and so on.

Keywords: ZnO thin films; Al-doped; crystalline size; spin coating; Nanostructure.

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1. Introduction

Transition-metal oxides and their alloys have been attracted in last few years due to their unique physical and chemical properties such as wide optical band gap energy of 3.37 eV at room temperature, large exciton binding energy of 60 meV and fast electron mobility. ZnO play important role for many optoelectronic devices and applications [1].

For example chemical and gas sensors, optical and magnetic memory devices, UV-light emitting diodes, solar cells, piezoelectric transducers, photodiodes, photodetectors, transparent conductive oxides, biomedical and more [2]. However, ZnO thin film is prepared using various techniques such as spray pyrolysis, radio-frequency (RF) sputtering , sol–gel spin coating, pulsed laser deposition (PLD), chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) [2, 3]. The sol–gel spin coating method is low cost in compared with others and promising one to prepare chemical components with uniform chemically homogenous films, high yield and scalable process [4]. One of the most important problems have to overcome is improvement the electrical conductivity and optical transparency of metal oxides. Among these suggestions the insert of defects using extrinsic doping such as Al, In, and Ga have been considered. Since, Jeong and his colleagues in 2003 have been prepared highly oriented undoped and aluminum-doped ZnO (AZO) films in the (002) direction by RF magnetron sputtering on glass substrates. XRD results showed that AZO (002) crystal grew parallel to the substrate. The as-grown AZO films not only have an average transmittance of 85% in the visible region, but also have an optical band gap between 3.2 and 3.64 eV [5]. Besides, Abbas and Araa have been prepared Al doped ZnO using ethylene glycol as a media at room temperature, the absorption band is between (367-800) nm with energy gap =4.448 eV [6]. After that Jung and his colleagues have been deposited Al-doped ZnO (AZO) thin films on glass substrates at room temperature by using the continuous composition spread (CCS) method. They found that the average transmittance in ranged of wavelength region of 400 to 900 nm was 93% and the optimized composition of the AZO thin film was $Al_{0.05}Zn_1O_{1.05}$ (about 3.13-wt% Al_2O_3) [7]. As well as, Rahman and his colleagues have been deposited Al-doped ZnO thin films on glass substrate successfully by an inexpensive spray pyrolysis method. The optical band gap energy was 3.28 eV of ZnO decreased gradually to 3.05 eV for 4 mol% of Al doping [8]. Additionally, in 2013 Eric and his colleagues have been deposited zinc oxide (ZnO) and aluminum-doped zinc oxide (ZnO:Al) thin films onto glass and silicon substrates by RF magnetron sputtering using a zinc-aluminum target. Their XRD analysis revealed that the ZnO films are polycrystalline with preferential growth parallel to the (002) plane, which corresponds to the wurtzite structure of ZnO. The films exhibit optical transmittances greater than 80% in visible region and red shift in the optical energy gap of prepared films mean increased from 3.28 eV to 3.36 eV with Al doping have been observed [9]. In the same way, have been successfully deposited Aluminum doped ZnO (AZO) thin films by spin coating technique onto glass substrates. X-ray diffraction results reveal that all the films are polycrystalline with a hexagonal wurtzite structure with a preferential orientation according to the direction (002) plane. The crystallite size of ZnO and AZO films was determined from Scherrer's formula and Williamson–Hall analysis. The lattice parameters of the AZO films were found to decrease with increasing Al content. The optical band gap (Eg) of the films is increased with increasing Al concentration. The AZO thin films indicate a high transparency in the visible region with an average value of 86%. These transparent AZO films may be open a new avenue for optoelectronic and photonic devices applications in near future [10]. Later, Alkahlout has been deposited

Transparent conducting Ga:ZnO (GZO) and Al:ZnO (AZO) layers by spin coating on glass substrates using crystalline nanoparticles redispersed in 1-propanol. Both films were found to be crystalline with a hexagonal structure and the visible transmission of both layers is high (T > 80%).

In this paper, Al doped ZnO with different concentrations using sol–gel approach have been synthesized to obtain highly conductive and transparency films. Furthermore, the structural and optical properties have been studied.

2. Materials and Methods

Undoped ZnO precursor solution was prepared using zinc acetate dehydrate [ZnAc:($Zn(CH_3COO)2\square 2H_2O$)] as solvent and menoethanolamine (MEA) as stabilizer. ZnAc was first dissolved in ethanol and followed by addition of MEA to increase the solubility. The molar ratio of MEA/ZnAc was chosen as 0.25 [1.1 gm] corresponding to a solution with 0.5 M concentration. In addition, to prepare Al doped ZnO (AZO) precursor solution, aluminum acetate basic hydrate [$(CH_3CO_2)AlOH\square H_2O$] was used as doping agent. To obtain AZO thin films with different Al doping concentrations, the solutions with different Al/Zn molar ratios of 1%, 2%, 3%, 4%; and 5% were prepared by adding aluminum acetate basic hydrate to the precursor solution prepared for ZnO. The prepared precursor solutions were stirred at 80 C for 2 h to prepare clear and homogenous solution. The glass substrate were cleaned in ethanol for 10 min using an ultrasonic bath and then cleaned with deionized water and dried. The gel solution was deposited onto glass substrate at 3000 rpm for 30 s using a spin coater model (KW-4A. CHEMAT TECHNOLOGY) and a hot ^{plate} model (KW-4AH, CHEMAT TECHNOLOGY) were used to fabricate the ZnO/glass thin films. The prepared films were preheated at 250 C for 10 min with dry furnace to evaporate the solvent and remove organic residuals. The structural properties have been characterized using X-ray diffraction (XRD) with PAnalytical diffractometer using Cu Kα radiation at 45 kV and 30 mA. The surface morphology of the thin films was characterized using scanning electron microscopy (SEM) and the element chemical compositions of the films were investigated by an energy dispersive X-ray spectrometer (EDX) which associated with SEM. In addition, the optical properties of the films were examined with the normal incident transmittance measured using UV/VIS spectrophotometer.

3. Results and discussion

3.1 Structural properties

Figure 1 show the typical X-ray diffraction spectra for un-doped (pure) and Al-doped ZnO thin films with various wt% Al of 0, 1, 2, 3 and 5. The diffraction peaks are observed at 34.46, 36.19, 47.54, 54.59, corresponding to (002), (101), (102), and (110) respectively, which belongs to a hexagonal structure.

Crystal structure with lattice parameters of a = 3.258 Å and c = 5.2108 Å and coincide with the peaks JCPDS Card No. 89-7102 [11]. There is no peaks change related to Al and other related impurities alumina phases have been characterized and seen in the X-ray pattern which supports that Al ions were substituted by Zn sites entire the lattices of ZnO crystal. In addition, no significant differences in regarding of peak position were observed for pure ZnO and Al-doped ZnO thin films which that mean the Al incorporation into ZnO without any new

sorts of stress from the differences in the ion size between Al and Zn [4, 12].

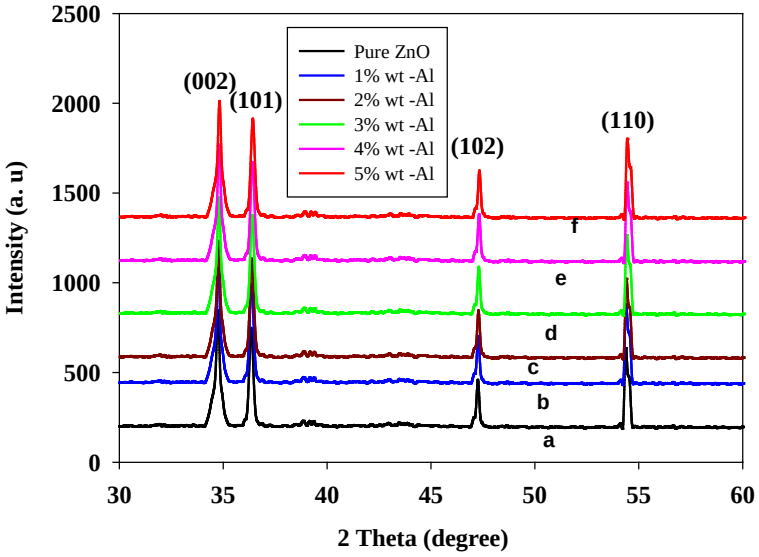


Figure 1: X-ray diffraction spectra for un-doped and Al-doped ZnO thin films with various wt% Al of a- pure ZnO thin film, b- 1 % wt, c-2% wt, d- 3% wt, e- 4% wt and f- 5% wt

The sharp peaks and high peaks intensity revealed that the synthesized Al-doped ZnO nanoparticles are well crystalline. The average crystalline size and lattice constant (c) of the films were calculated using the full width at half maximum (FWHM) of all peaks from the Scherrer's equation [13-17] as following:

$$(1)\ D = \frac{0.9\lambda}{B\cos\theta}$$

where λ is the X-ray wavelength, θ is Bragg angle of (002) peak, and *B* is FWHM value. The grain size and the average uniform strain e_{zz} for the lattice along the c-axis of ZnO and AZO on glass substrate has been estimated from the lattice parameters using the Eqn. below [13-17].

$$(2)\ \varepsilon_{zz} = \frac{c - c_o}{c_o} \times 100\%$$

where c_o is the lattice constant for the unstrained ZnO. The numerical value of c is calculated from XRD data according to the following equations:

$$(3)\ 2d_{hkl}\sin\theta = \lambda$$

where d_{hkl} is the lattice spacing of (*hkl*), λ is the X-Ray wavelength and θ is Bragg angle. At the same time, ZnO is a hexagonal structure which follows the formula [15]:

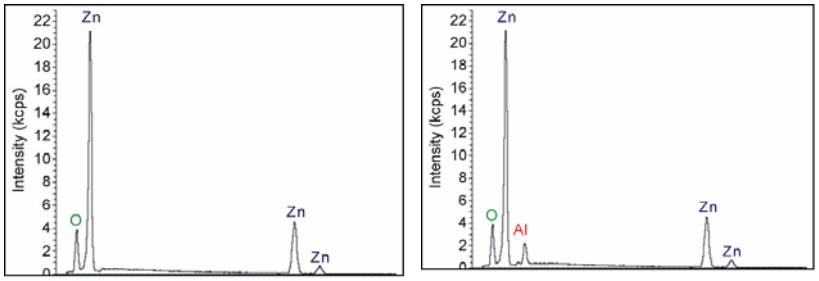
$$(4)\ d_{hkl} = \frac{1}{\sqrt{4/3(h^2 + hk + k^2)/a^2 + l^2/c^2}}$$

where *a* and *c* are the lattice constants, thus using c_o for ZnO of 0.521 nm [13]. The crystalline size and the average uniform strain e_{zz} for the lattice along the c-axis of ZnO and AZO on glass substrate has been summarized in Table 1. From this Table, it is clear that the crystallite size, lattice constants and strain are decreased, as the Al dopant concentration increases in ZnO lattice. The decrease in crystallite size, lattice constants and strain with increasing Al concentration in ZnO is attributed to the interstitial substitution of Al ions in Zn sites into ZnO lattice as confirmed by EDX results [3, 18] (shown in Figure 2 below) .

Table 1: The FWHM, crystalline size, the calculated lattice constant *c* and the strain of ZnO thin films prepared Sol-Gel method

Orientation (002)	2θ (degree)	FWHM (2θ°)	Crystalline size (d)	Lattice constant (*c*)	Strain
Pure-ZnO	34.25	0.1367	38	5.31	-0.01868
1% wt Al-ZnO	34.27	0.1954	27	5.29	-0.01497
2% wt Al-ZnO	34.28	0.2936	18	5.27	-0.01123
3% wt Al-ZnO	34.30	0.4279	12	5.26	-0.00935
4% wt Al-ZnO	34.32	0.5786	9	5.24	-0.00557
5% wt Al-ZnO	34.33	0.7993	7	5.22	-0.00176

To assess the elemental composition of the synthesized un-doped ZnO and AZO (contains 5 wt% – Al) thin films, the EDX analysis was done and the result is shown in Figure 2- a and b, respectively. In EDX spectrum, numerous well-defined peaks were evident concerned to Zn, O, and Al which clearly support that the AZO nanoparticles are made of Zn, O, and Al. No other peaks related to impurities were detected in the spectrum, which further confirms that the synthesized nanoparticles are Al doped ZnO.



-a- **-b-**

Figure 2: EDX analysis of pure and doped ZnO thin films: a- Pure ZnO (left), b- 5 % wt-Al (right),

Figure 3 show that SEM images of pure and doped ZnO thin films. SEM images revealed that the Pure ZnO not recognized well (Figure 3-a) and become more crystalline and look like ball (Figure 3.3 b) after that the structure become nanowire and the diameter decrease with increase in Al concentration (Figures c, d, e, and f)

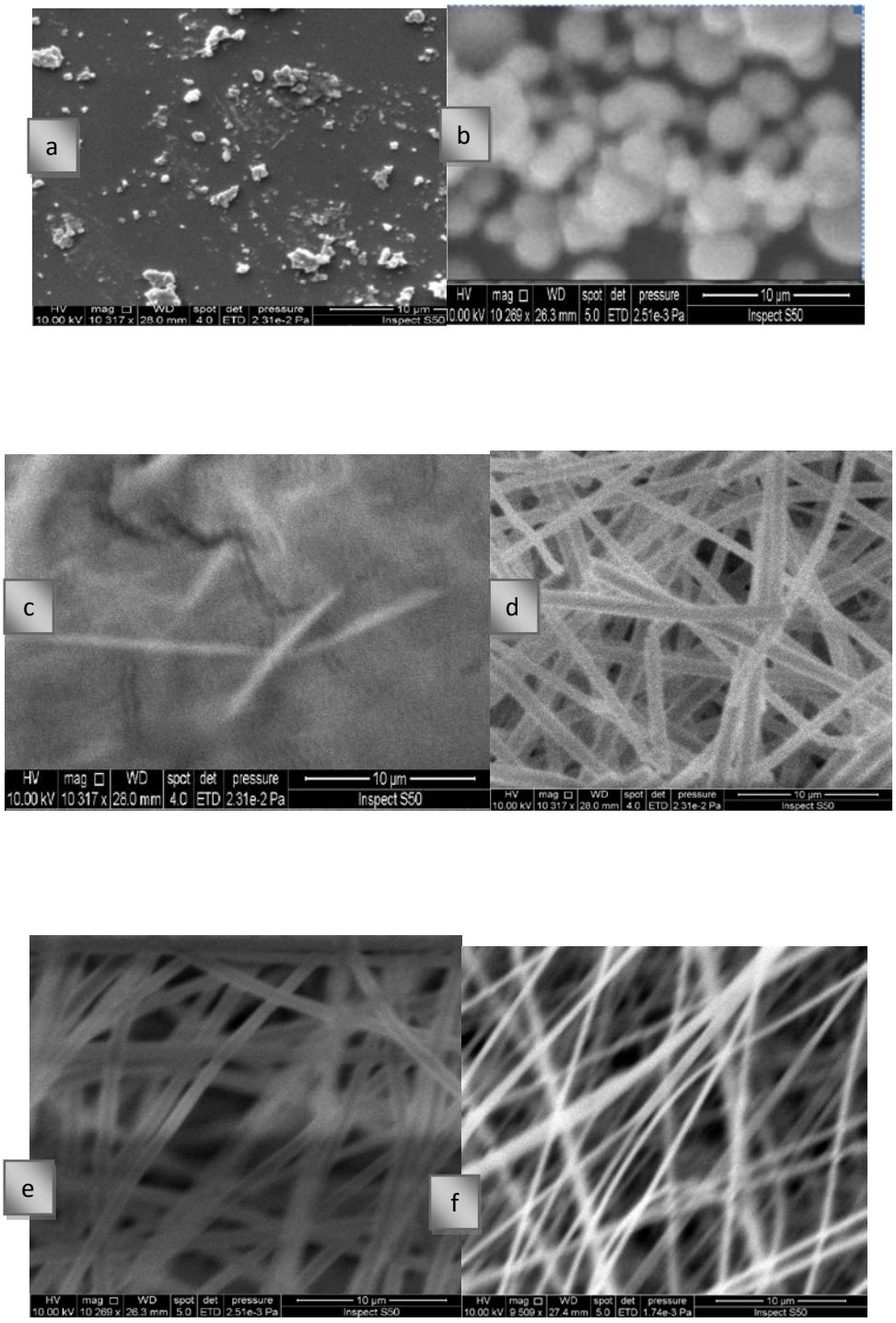


Figure 3: SEM images of pure and doped ZnO thin films: a-Pure ZnO, b- 1 % wt-Al, c- 2 % wt-Al, d- 3 % wt-Al, e- 4 % wt-Al, f- 5 % wt-Al

3.2 Optical properties

Figure 4 shows the optical transmittance spectra obtained for the pure and Al-doped ZnO films deposited onto glass substrates. The optical transmittance of the films was obtained by averaging in the range 450 - 650 nm, as indicated by the vertical dashed lines. In the visible region the pure ZnO thin film had an optical transmittance of greater than 80% and by inserted the Al doping it is reduce to half with increase the Al doping to be 5% wt.

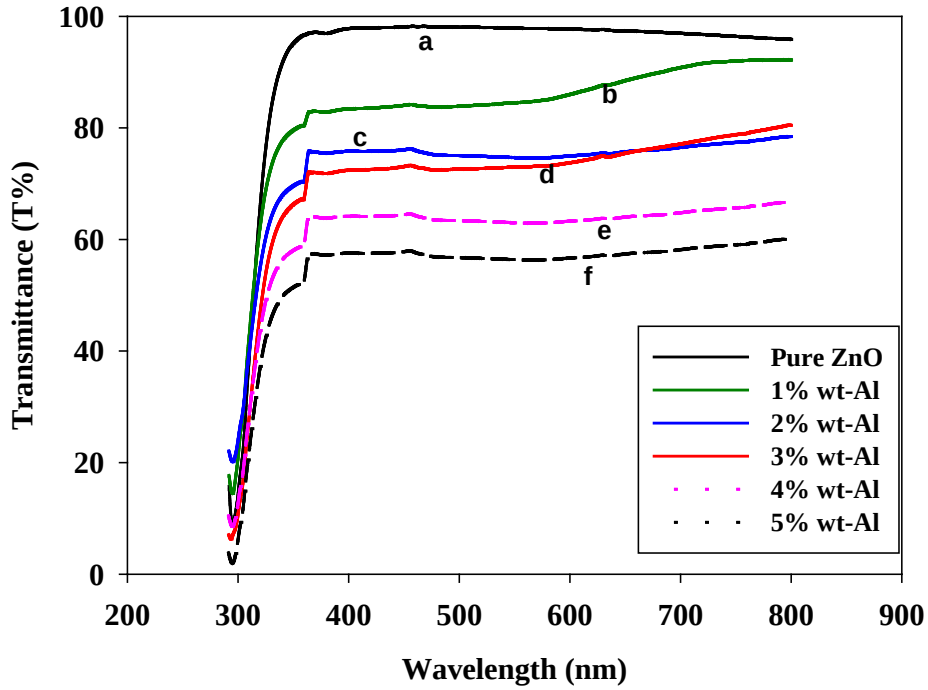


Figure 4: The optical transmittance spectra for the pure and Al-doped ZnO films deposited onto glass substrates: a-Pure ZnO, b- 1 % wt-Al, c- 2 % wt-Al, d- 3 % wt-Al, e- 4 % wt-Al, f- 5 % wt-Al

In addition, one can see that the absorption band of the Al-doped film shifts to lower wavelengths, i.e. there is an increase in the optical band gap of the film. The optical energy gap can be determined using Equation (5) as shown below, which relates the absorption coefficient (α) and the gap energy (E_g) [16].

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \qquad (5)$$

where hυ is the photon energy, E_g is the optical gap energy for direct allowed transitions and B is a constant dependent on the refractive index of the material, the electron effective mass and the speed of light in vacuum.

Figure 5 shows the ultra violet-Visible (UV-Vis) light absorptions of pure and Al-doped ZnO thin films. In UV region, the emission peak of pure ZnO thin film is at about 376 nm, while, the peak of ZnO doped with Al is at about 378 nm, which are generally originated from the near-band-edge (NBE) exciton transition in wide band gap of ZnO. The shift in peak position illustrates that the Al-doping can slightly tune the structure of energy level and band gap of ZnO nanomaterials.

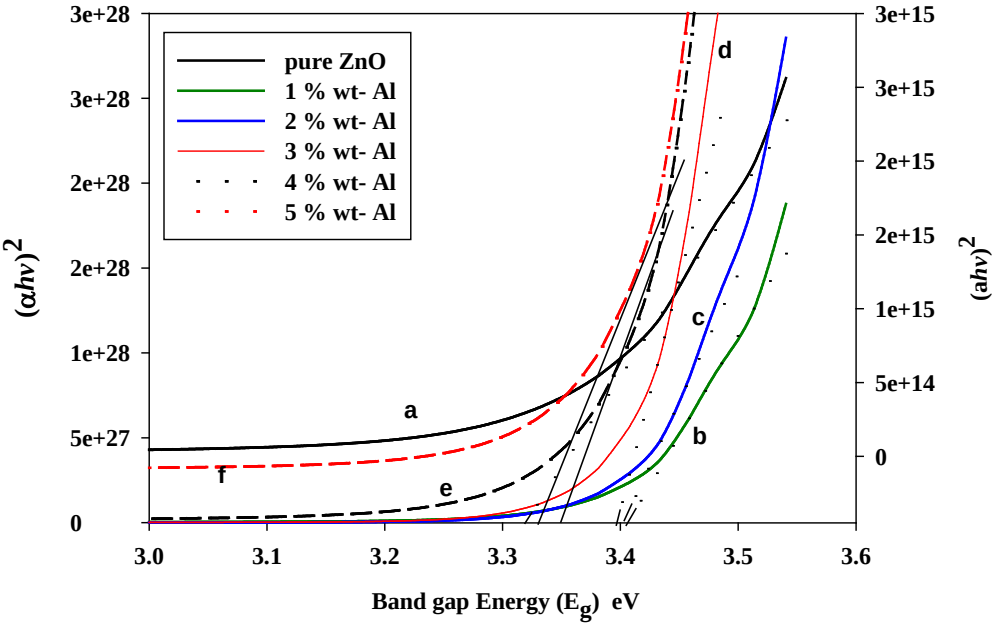


Figure 5: The ultra violet-Visible (UV-Vis) light absorptions of pure and Al-doped ZnO thin films: a-Pure ZnO, b- 1 % wt-Al, c- 2 % wt-Al, d- 3 % wt-Al, e- 4 % wt-Al, f- 5 % wt-Al

Table 2: The FWHM, crystalline size, the calculated lattice constant *c* and the strain of ZnO thin films prepared Sol-Gel method

Region		**ZnO thin film on glass substrate**					
		Pure	1% wt Al	2% wt Al	3% wt Al	4% wt Al	5% wt Al
UV emission	Wavelength (nm)	~ 375	363	364	365	370	373
	Energy band gap (eV)	3.31	3.408	3.403	3.396	3.35	3.32

4. Conclusions

Pure and Al-doped ZnO films were deposited onto glass and silicon substrates using spin coating technique. The pure and Al-doped ZnO films are polycrystalline hexagonal wurtzite structures with preferential growth in the (002) plane. It is clear that the crystallite size, lattice constants and strain are decreased, as the Al dopant concentration increases in ZnO lattice. The decrease in crystallite size, lattice constants and strain with increasing Al concentration in ZnO. The SEM images revealed that the structure of ZnO became in nano behavior with Al doping up to 3% wt which indicated that the optimum condition make this materials promising to used in many optoelectronic applications. Optical transmittance of pure ZnO thin films is greater than 80% in the visible region and it's decreased with decreasing of Al doping. The optical energy band gap of the ZnO thin film decreased from 3.408 eV to 3.32 eV with increasing in Al doping.

Acknowledgment

The authors thank Ministry of higher education and scientific research by Al-Nahrain University, and Thi Qar University, Science College, Iraq to their supports of this research.

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