Results in Physics xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.journals.elsevier.com/results-in-physics

Characterizations of multilayer ZnO thin films deposited by sol-gel spin coating technique

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A R T I C L E   I N F O

Article history:
Received 28 August 2016
Received in revised form 23 November 2016
Accepted 19 December 2016
Available online xxxx

Keywords:
Multilayer films
Semiconductor
ZnO
XRD
SEM
Optoelectronic properties

A B S T R A C T

In this work, zinc oxide (ZnO) multilayer thin films are deposited on glass substrate using sol-gel spin coating technique and the effect of these multilayer films on optical, electrical and structural properties are investigated. It is observed that these multilayer films have great impact on the properties of ZnO. X-ray Diffraction (XRD) confirms that ZnO has hexagonal wurtzite structure. Scanning Electron Microscopy (SEM) showed the crack-free films which have uniformly distributed grains structures. Both micro and nano particles of ZnO are present on thin films. Four point probe measured the electrical properties showed the decreasing trend between the average resistivity and the number of layers. The optical absorption spectra measured using UV–Vis. showed the average transmittance in the visible region of all films is 80% which is good for solar spectra. The performance of the multilayer as transparent conducting material is better than the single layer of ZnO. This work provides a low cost, environment friendly and well abandoned material for solar cells applications.

Introduction

Zinc oxide is a non toxic, abundant, low cost and wide direct band-gap (3.2–3.4 eV) II–VI compound semiconductor [1–3]. This leaves it within the visible region having high optical transmission, suitable for solar spectrum [1]. Therefore, it has vast applications in optoelectronics device because of its structural, electrical and optical properties [4–9]. Due to these promising characteristics, thin films of ZnO have showed the considerable attention in the literature [1,10–12]. It is proposed that Multilayered ZnO thin films can increased the electrical properties of films [2]. Optimized multilayered ZnO films can be designed to have low resistivity and high solar transparencies in the visible region that are needed for the applications in solar cells and light emitting diodes [13].

The low cost and small time require for the synthesis of ZnO thin films for industrial requirements is always a need. Multilayered thin films of ZnO can be deposited by several methods such as magnetron sputtering [14], pulsed laser deposition [15] and spray pyrolysis [16]. Among them sol-gel technique is simple, low cost and large area deposition technique.

The review of literature showed that the properties of stacked ZnO thin films layers, deposited by sol-gel technique, which is cost effective and easy deposition technique, has not been studied yet. Current study will facilitate to fabricate optoelectronic devices with affordable cost. In present work, the structural, morphological, electrical and optical properties of single, three and five layers of ZnO thin films deposited by sol-gel spin coating has been discussed.

Methodology

The stacked layers of ZnO thin films were prepared by using sol-gel method. The ZnO solution was prepared by dissolving 0.88 g of "Zinc acetate dehydrates" in the 20 ml of "2-methoxyethanol". Then this solution was stirred with the help of magnetic stirrer at 60 °C for 30 min. After that the "Mono ethanol amine" as a stabilizer was added in this solution and stirred the solution for 90 min at the temperature of 60 °C. The clear homogeneous solution of ZnO was obtained by aging this solution for 24 h.

The solution is now ready to prepared films. Now the glass substrate is fixed on spin coating system and its disc speed is adjusted at 2400 rotation/min. The rotation time is 30 s per sample. The drops of sol-gel solution are dropped on the glass substrate as per requirement of layers. After 30 s, the glass substrate is removed

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http://dx.doi.org/10.1016/j.rinp.2016.12.029
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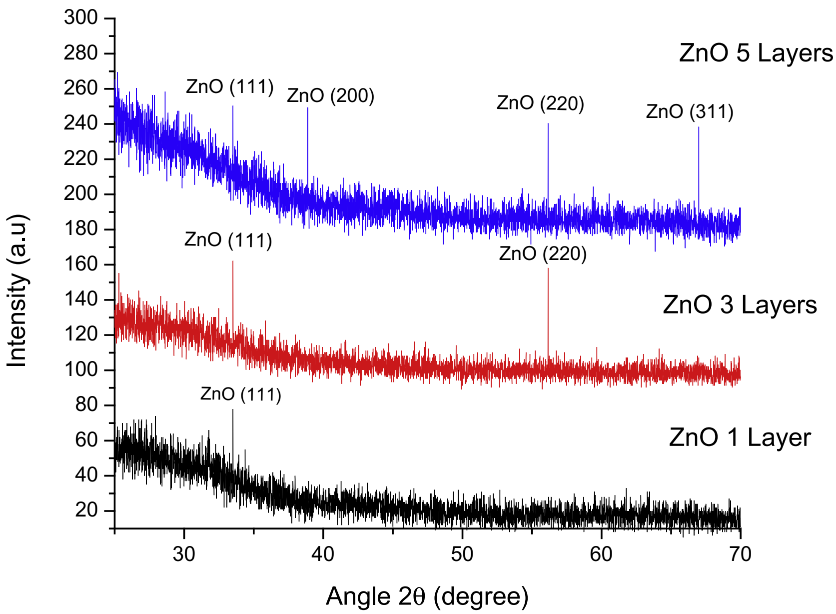

Fig. 1. XRD pattern of ZnO single, three and five layers thin films.

Table 1
XRD summery of single layers, three layers and five layers ZnO thin films.

Number of peaks	Peak position (2 theta)	Counts (intensity)	*hkl*	d spacing [A°]	FWHM	Crystallites size × 10^{-9} (m)	Phase	Dislocation line density × 10^{15}
Single layer of ZnO thin film								
1	33.504	29.0697	111	2.672	0.0182	7.96	ZnO	15.8
Three layers of ZnO thin films								
1	33.498	39.9174	111	2.672	0.013	11.15	ZnO	8.05
2	56.154	20.0368	220	1.636	0.0083	18.9	ZnO	2.79
Five layers of ZnO thin films								
1	33.509	34.8908	111	2.672	0.0082	17.7	ZnO	3.2
2	38.875	38.033	200	2.314	0.0089	16.5	ZnO	3.66
3	56.149	33.9489	220	1.636	0.0081	19.4	ZnO	2.65
4	66.994	37.9591	311	1.395	0.008	20.8	ZnO	2.31

from spin coating disc and placed on the hot plate for almost 10 min to dry at 100 °C. The experiment is repeated to make thin films with multilayer.

The thin films are put in Furnace and the temperature is raised gradually until the temperature reached 400 °C. Then the furnace is switched off and each sample is left to cool down until it reaches room temperature. Then samples are taken from the furnace and now they are ready to analyze.

Results and discussion

XRD results

Fig. 1, shows the XRD pattern of 1, 3 and 5 layers ZnO thin films. In single layer thin film of ZnO, one peak of ZnO having hexagonal phase having (1 1 1) planes of reflection (PDF # 65-2880). In three layers of ZnO thin film, two peaks of zinc oxide with hexagonal phases (1 1 1) and (2 2 0) planes of reflections, respectively, were observed according to PDF card number 65-2880. In five layers of ZnO thin film, four peaks of hexagonal phase of zinc oxide having (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of reflection, respectively, were observed (PDF # 21-1272). This XRD pattern confirms the presence of ZnO in these films. Also, it confirms the synthesized ZnO powder is pure, because of absence of any other impurities peaks in the XRD pattern [17].

XRD – particle/grain size calculation

In grain atoms are in periodic order. If the grain size is large then it improved electrical, piezoelectric etc. properties of material.d-spacing is calculated by using Bragg's Law [18]

$$2d\sin\theta = n\lambda \tag{1}$$

The grain size is measured by the using the Scherer's formula [19].

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{2}$$

where, 'D' = "Grain size", λ = "CuK_{alpha} radiations having 1.54 Å wavelength" [20]. In single layer, one peak is obtained at 2θ values of 33.504°; the particle size at this value is 11.15 nm. The calculated particle size of three layers of ZnO thin films at 2θ values of 33.504, 56.154 degrees are 7.96 nm and 18.9 nm, respectively. The calculated particle size of five layers film at 2θ values of 33.504, 38.875, 56.154 and 66.994 degrees are 17.7, 16.5, 17.9 and 20.8 nm, respectively.

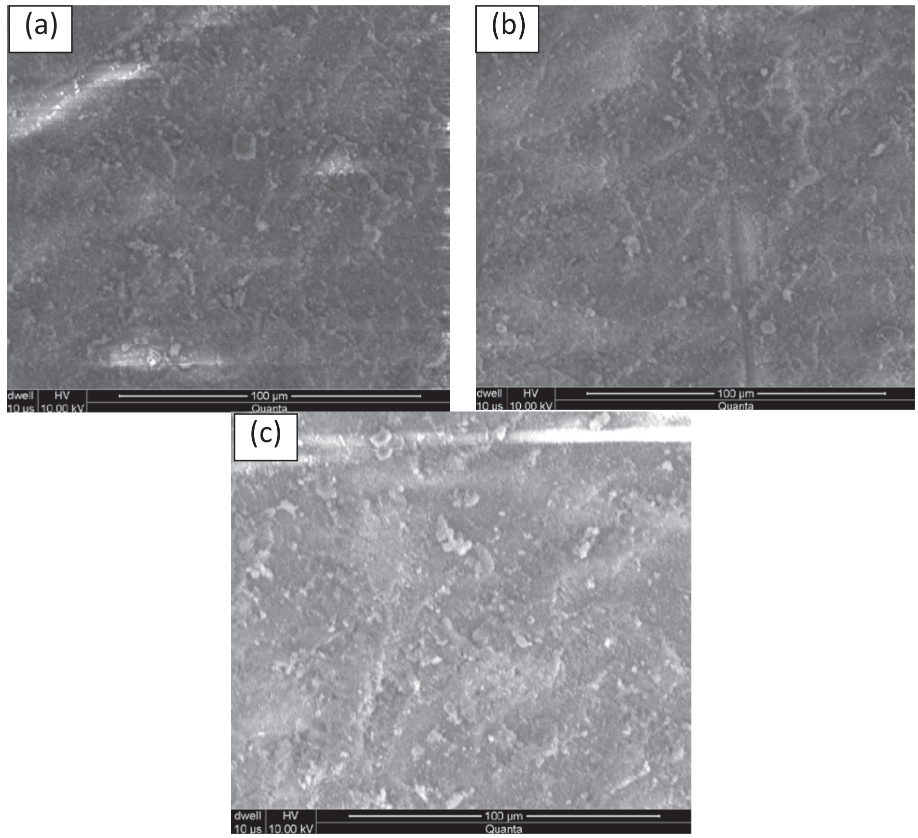

Fig. 2. SEM micrographs of (a) Single layer (b) Three layers (c) Five layers ZnO thin films.

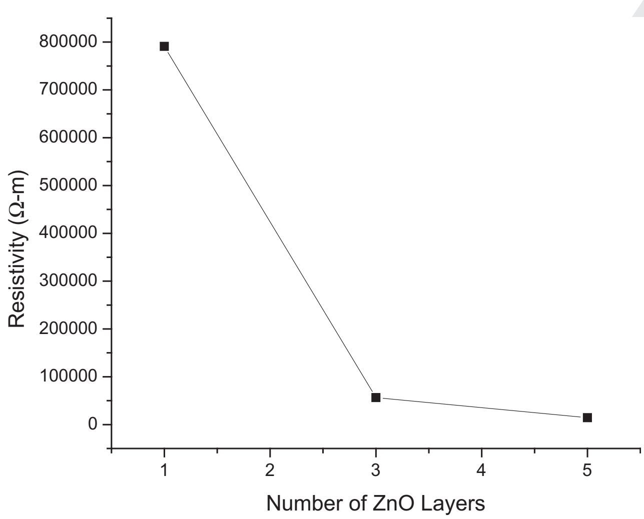

Fig. 3. Graph between average resistivity and number of layers of ZnO.

XRD – dislocation density

The term "dislocation" refers to a crystallographic defect in material sciences. It has inverse relation with grain size and is calculated by using the relation [21].

$$\sigma = \frac{1}{D^2} \tag{3}$$

The dislocation line density of single layer ZnO thin film at 2θ values of 33.504° is $8.05 \times 10^{15}\,(\text{nm})^{-2}$. In three layers of ZnO film, the dislocation line density at 2θ values of 33.504, 56.154 degrees are 15.8×10^{15} and 2.79×10^{15}, respectively. The dislocation line density of five layers of film at 2θ values of 33.504, 38.875, 56.154 and 66.994 degrees are 3.2×10^{15}, 3.66×10^{15}, 3.13×10^{15} and 2.31×10^{15}, respectively.

The summery of different structural parameters of three layers, five layers and seven layers of 20% Cu doped TiO_2 thin films are explained in Table 1.

XRD – crystallinity index

It is generally agreed that the peak breadth of a specific phase of material is directly proportional to the mean crystallite size of that material. Quantitatively speaking, sharper XRD peaks are typically indicative of larger crystallite materials.

When the grain size is large then more atoms are in order and there is less grain boundaries. Therefore, atoms easily move from grain to grain and electrical properties are improved. In these ZnO multilayer thin films, the grain size is increased with the layers due to which the average relative intensity was increased. This means that the crystallinity of films were improved. Therefore, the atoms easily move from grain to grain. Thus electrical properties have improved. These results matched with the four point probe results, where the electrical conductivity increased by increasing the number of layers.

SEM results

The morphological properties are another essential property like crystal structure. SEM images of multilayer thin films of ZnO, deposited by sol-gel spin coating technique is depicted in Fig. 2 (a–c). All the deposited films were crack less, and had uniformly distributed grain structure. It may be observed from the SEM micrographs that there is mixed structures of the films in which some particles are in nano size and some are in micro size. This

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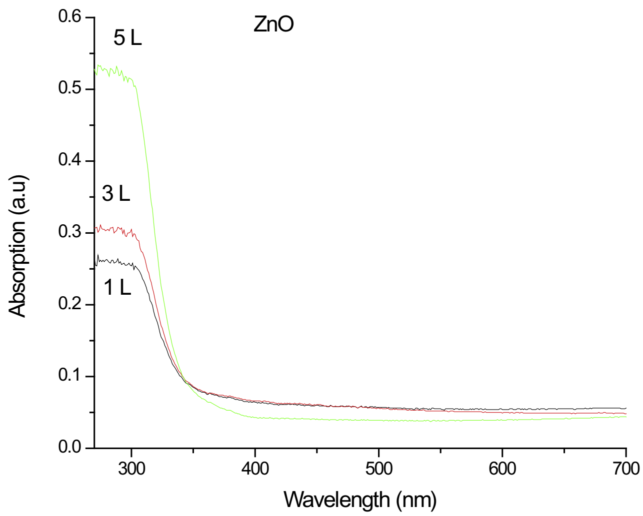

Fig. 4. Absorption spectra of single, three and five layers of ZnO thin films.

is because of the high viscosity of the sol [22]. In all films, ZnO particles were dispersed onto the ZnO thin films. This dispersion is increased by increasing the number of layers. This would be useful to enhance the optical and electrical properties of films as the ZnO particles have high mobility.

Four point probe results

The electrical properties of ZnO layers were studied by using four point probe technique. Thin film's resistivity is calculated by using the relation [18].

$$\rho = \frac{\pi}{\ln 2} \cdot \frac{V}{I} \tag{4}$$

The average resistivity as a function of number of layers of ZnO thin films is shown in Fig. 3. The average resistivity of single, three and five layers of ZnO thin films were found to be 7.91×10^5 (ohm-m), 5.65×10^4 (ohm-m) and 1.43×10^4 (ohm-m) respectively. From the Fig. 1, it is clear that the average resistivity decreases by increasing the number of layers of ZnO, therefore the conductivity is increased and hence electrical properties are improved by increasing the number of layers. The free carrier concentration in the five layers of ZnO increased which decreased the resistivity [23]. In addition, the large grain size reduced the grain boundaries which improved electron's mobility and as a result the resistivity of films is reduced [24–26].

Optical properties

Fig. 4, shows the optical absorption of single, three and five layers of ZnO thin films in the wavelength range of 270–300 nm. This graph has two regions; one is strong absorption region ($\lambda \leqslant 300$ nm) and other is strong transmittance region ($\lambda \geqslant 348$ nm). In strong absorption region, when the numbers of

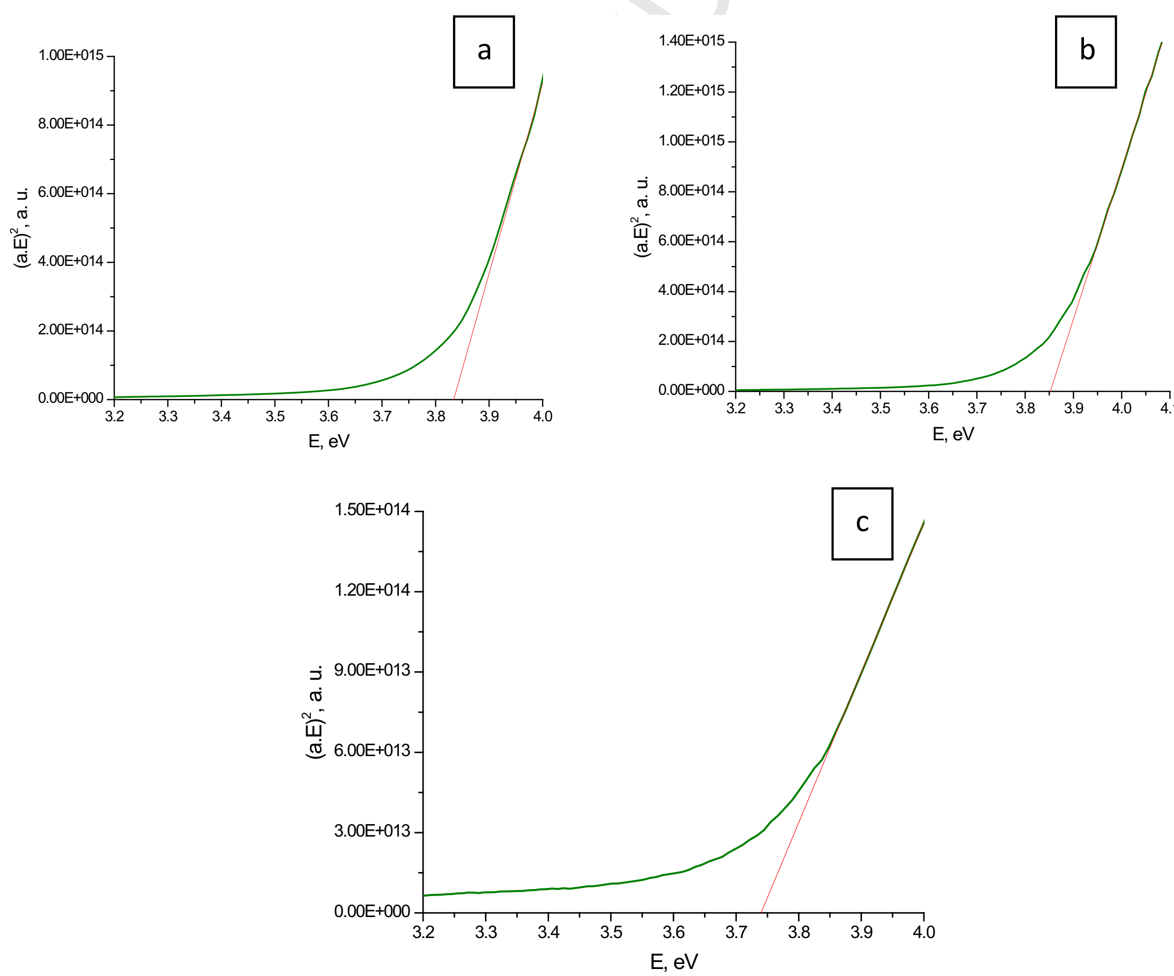

Fig. 5. Band gap of ZnO (a) Single (b) Three and (c) Five layers thin films.

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layers were increased then the absorption increases. When the wavelength increased above 300 nm, then absorption decreases and transmittance increased. The 90% transmittance is obtained in the visible region of five layers ZnO film. These films can be use as UV-protected films for optoelectronic devices because these films have less than 40% transmittance in the UV region [27]. The absorption edges show the transformation from absorption to transmittance regions. In the visible region, the average transmittance of all films is 80%.

A graph is plotted between photon energy and $(\alpha h\upsilon)^2$ to find out the band gap energy is shown in Fig. 5, [28]. Tauc's relation is use to calculate the optical band gap energy is given by in equation [3].

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^n \tag{5}$$

where α, E_g and $h\upsilon$ are "absorption coefficient", "band gap energy" and "photon energy", respectively. 'n' is equal to 2 for "indirect" and 1/2 for "direct band-gap" semiconductor, respectively [29,30]. The band gap energies of single, three and five layers of ZnO thin films are 3.85 eV, 3.81 eV and 3.72 eV respectively. As the reported optical band gap value of ZnO thin film is less than the calculated value, this might be the thermal stress effects produced in films [31]. The decrease in band gap is accordance to the results obtained in literature in which the thickness of ZnO multilayer thin films increased and band gap and electrical resistivity decreased [29].

Conclusion

In summary, ZnO multilayer thin films were prepared by sol-gel method. XRD confirms the hexagonal wurtzite structure. There is increasing trend between the grain size and the number of layers because of the absence of extra phases among the layers. The average resistivity is decreased by increasing the number of layers because of the increasing grain size with layers, grain boundaries reduced which improved the electron's mobility and as a result, reduced the resistivity of films. 90% transmittance is obtained in the visible region of five layers film. The optical band gap energies of single, three and five layers of ZnO thin films are 3.85, 3.81 and 3.72 eV respectively. This decrease in energy is attributed to the increase in thickness of films.

Acknowledgements

This project is partially supported by King Saud University, Deanship of Scientific Research, College of Science Research Center, Saudi Arabia.

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