International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:8, No:5, 2014

Physical and Electrical Characterization of ZnO Thin Films Prepared by Sol-Gel Method

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***Abstract*—**In this paper, Zinc Oxide (ZnO) thin films are deposited on glass substrate by sol-gel method. The ZnO thin films with well defined orientation were acquired by spin coating of zinc acetate dehydrate monoethanolamine (MEA), de-ionized water and isopropanol alcohol. These films were pre-heated at 275°C for 10 min and then annealed at 350°C, 450°C and 550°C for 80 min. The effect of annealing temperature and different thickness on structure and surface morphology of the thin films were verified by Atomic Force Microscopy (AFM). It was found that there was a significant effect of annealing temperature on the structural parameters of the films such as roughness exponent, fractal dimension and interface width. Thin films also were characterizied by X-ray Diffractometery (XRD) method. XRD analysis revealed that the annealed ZnO thin films consist of single phase ZnO with wurtzite structure and show the c-axis grain orientation. Increasing annealing temperature increased the crystallite size and the c-axis orientation of the film after 450°C. Also In this study, ZnO thin films in different thickness have been prepared by sol-gel method on the glass substrate at room temperature. The thicknesses of films are 100, 150 and 250 nm. Using fractal analysis, morphological characteristics of surface films thickness in amorphous state were investigated. The results show that with increasing thickness, surface roughness (RMS) and lateral correlation length (ξ) are decreased. Also, the roughness exponent (α) and growth exponent (β) were determined to be 0.74±0.02 and 0.11±0.02, respectively.

***Keywords*—**ZnO, Thin film, Fractal analysis, Morphology, AFM, annealing temperature, different thickness, XRD.

I. Introduction

ZnO is a very useful and important material for multiple applications in both microelectronic and optoelectronic devices. Zinc oxide is a group II-VI wide direct band-gap semiconductor (3.4 eV at room temperature) that has been extremely investigated for many years [1]. ZnO has been usually used in its polycrystalline form for over 100 years in a wide range of applications: facial powders, ointments, sunscreens, catalysts, lubricant additives, paint pigmentation, piezoelectric transducers, and transparent conducting electrodes [2], [3]. Various techniques can be adapted to the growth of ZnO thin films on various substrates, such as reactive or magnetron sputtering, electron beam (e-beam) evaporation, laser ablation, metal-organic chemical vapor deposition (MOCVD) and sol-gel process [4]-[11]. It is very important to grow c-axis oriented ZnO thin films on substrates which can provide quasi single-crystal property coefficients, namely, piezoelectric, electro-optic, and permittivity, which are necessary for active devices in integrated optics [12]-[14]. In this paper, the ZnO thin films were prepared in various thicknesses by sol-gel spin coating method and annealed at different temperatures. The effect of annealing temperature and different thickness on the structural properties of ZnO thin films deposited on microscope glass was considered by AFM [15].

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II. Materials and Methods

A. Thin Film Preparation

All the chemicals were analysis from reagents without more purification. Nano-crystalline ZnO thin films were prepared on microscope glass slide (75 mm × 25 mm × 1 mm) substrate (washed with ethanol and dilute acid) by a sol-gel method. Sol solution was obtained by adding 3.10 g zinc acetate dehydrate ($Zn(CH_3COO)_2 2HO_2ZnAc.2H_2O$), 0.86 g mono-ethanolamine (MEA) and adequate deionized water to 15 mL isopropanol alcohol, then heated to 60°C with continuous stirring for 60 min [16]. The coating substrate (microscope glass slid) was preheated at 275°C for 10 min in air after each coating. The sol-gel coating was made often a day after the sol solution was prepared and the molar ratio of MEA to zinc acetate was maintained at 1:1.Then the films were covered by spin coating method.

The films of ZnO were prepared by sol-gel spin coating method onto glass substrate with 3000 rpm for 45 sec. Film deposition was carried out in air at room temperature by a rate 3000 rpm for 30 sec [17]. After each coating, the films were preheated at 275°C for 10min and post-heated at 350°C, 450°C and 550°C, for 80 min. Also films have been prepared in 100, 150 and 250 nm thicknesses. The deposition was repeated to gain a film with suitable thickness.

B. Atomic Force Microscopy

Ex situ measurements of surface morphology of the films were carried out following heating process. For obtaining surface morphology of thin films we used an Atomic Force Microscopy (AFM) instrument (TM Microscope Veeco Metrology Group) on contact mode. A commercial standard pyramidal Si_3N_4 tip was used. AFM images were acquired in ambient air and digitized in to 256×256 pixels and 512×512 pixels. AFM images of ZnO thin films annealed at different thicknesses are shown in the Fig. 1.

C. X-Ray Diffraction

The phase composition of ZnO thin layers (amorphous and post-heated at different temperatures) was measured by XRD method with X-ray diffractometery (D8 Advance Bruker X-ray) at room temperature, with monochromated CuK α (

$\lambda = 1.54$), in the scan range 25°<2θ<70° with scan rate of (2θ /s) 0.08.Spectrum of post-heated layers were studied by spectrometer (SHIMADZU UV-3100).

III. Results and Discussion

Fig. 1 shows 3D-Images of atomic force microscopy (AFM) in various thicknesses in contact mode and scan distance (3µm ×3µm). Useful numeral data from sample surface was extracted by a sharp Si_3N_4 probe and with constant force mode in the ranges of 512×512 pixels. By converting images of topography to ASCII data, their analysis was investigated.

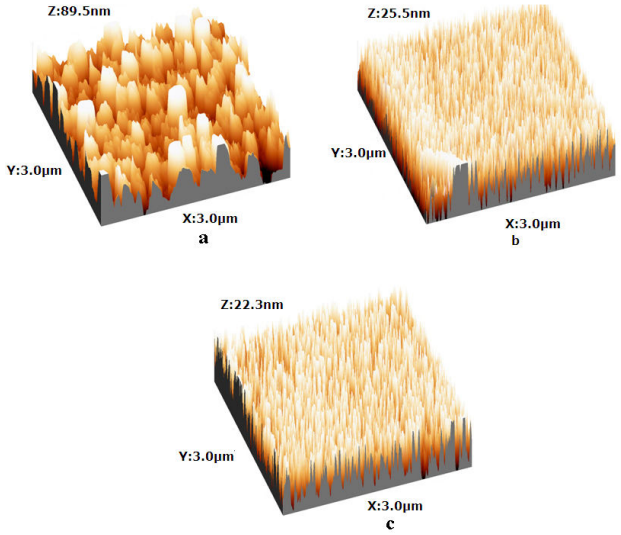


Fig. 1 Image of ZnO thin layers in the scale of 512×512 pixels in thickness of a-100 nm, b-150, and c-250 nm

The concept of fractal dimensionality, in contrast with traditional, has proven very successful both in applying to a wide range of complex surface geometries and in advancing our understanding of how the geometry affects the physical properties of the system.

In order to study the fractal properties of ZnO thin films, we calculated the height-height correlation functions of both samples from AFM images.

Denoting by h(i,j),the height of the surface measured by AFM at the point (i,j),N×N the total number of points at which the surface heights have been measures and d the horizontal distance between two adjacent pixels then the interface width w(or rms)value of the surface roughness is evaluated by this formula :

$$W = \frac{1}{N}\sqrt{\sum_{i-j-1}^{N}(h(i,j)-<h(i,j)>)^2} \quad (1)$$

where, h <i,j> is the average overall surface points:

$$\prec h(i,j) \succ = \frac{1}{N^2}\sum_{i-j-1}^{N} h(i,j) \quad (2)$$

The height-height correlation function H(r) is evaluated along the fast scan direction (x direction) by this formula [18]:

$$H(r=md) = \frac{1}{N(N-m)}\sum_{j-1}^{N}\sum_{i-1}^{N-m}[h(i+m,j)-h(i,j)]^2 \quad (3)$$

For self-affine surfaces, the dynamic scaling hypothesis suggests that the height-height correlation function H(r) has the scaling form:

$$H(r) = \begin{cases} \rho^2 r^{2\alpha} & for \quad r << \xi \\ 2w^2 & \quad\quad r >> \xi \end{cases} \quad (4)$$

ρ is average slope and α is the roughness exponent which describes how locally "wiggly" the sample surface is. Parameter ζ is the lateral correlation length which is defined as the largest distance in which the height is still correlated. ζ prepares a linear measure which separated the treatment of rough surface in low-rang and high-range.

The relationship between roughness exponent (α) and fractal dimension (D_f) is D_f=E+1-α with 0<α<1 . E+1 is the dimension of embedded space where layers grow in it.

For profile E=1 and for plan E=2.The value of α corresponds to surface structure. In the scale of low-rang, curve ln H(r) based on ln(r), is a direct line [19], [20]. It means that H(r) adapts to $r^{2\alpha}$. Roughness exponent can be extracted by slope H(r) in this scale (that slope is 2α). The flat part of curve depends on interface width (w).The value of ζ can be calculated by curve H (r) in the following formula:

$$H(r) = 2w^2\left\{1-\exp\left[-\left(\frac{r}{\xi}\right)^{2\alpha}\right]\right\} \quad (5)$$

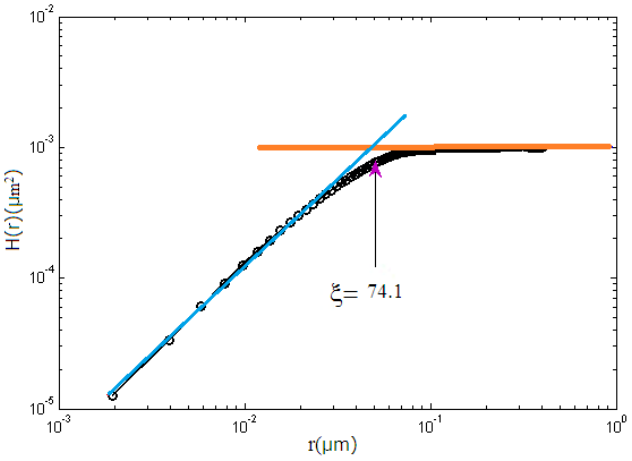


Fig. 2 The height-height correlation function H(r) based on r for layer with thickness of 100 nm

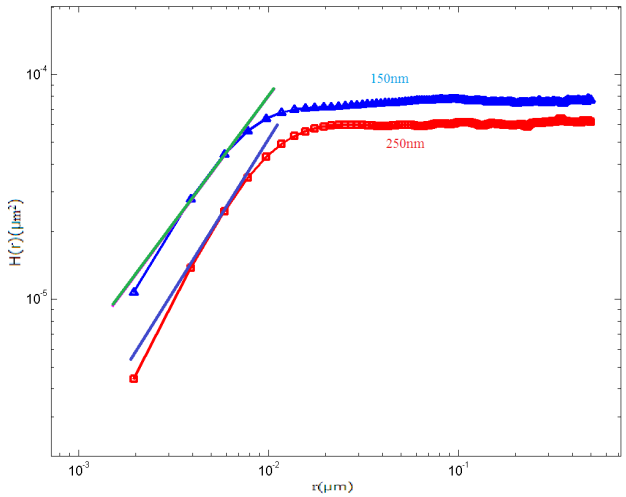


Fig. 3 The height-height correlation function H(r) based on r with thickness of 150 nm and 250 nm

Comparing the results of Table I shows that interface width and correlation length extremely depend on increase of thickness in Amorf mode. By increasing the thickness, their value was extremely decreased and also roughness exponent (α) of all layers are correlated with each other [21]. This subject shows that by increasing the thickness, roughness dynamic structure of thin layers is possibility the same as each other in Amorf mode [22].

TABLE I
AVERAGE HEIGHT (R_a), INTERFACE WIDTH (w), LATERAL CORRELATION LENGTH (ξ), ROUGHNESS EXPONENT (α) AND FRACTAL DIMENSION OF ZNO LAYERS

Sample	Thickness	R_a	W(nm)	ζ	α	D_f
a	100 nm	17.7	22.7	74.1	0.71	2.29
b	150 nm	14.6	16.9	43.1	0.74	2.26
c	250 nm	4.7	5.9	37.2	0.78	2.22

The other parameter is growth exponent (β).If time of deposition (t) and layer thickness (d) was commensurated to deposition rate (r) by this formula: d=rt, then for evaluating the growth rate, interface width(w) do as a function of thickness in growth samples with various time of deposition.

In Fig. 4 shows ZnO layer roughness depended on thickness. By measuring slope in this diagram, value of growth exponent was determined:

$$\beta = 0.11 \pm 0.02 \quad (6)$$

Also average of roughness exponent was calculated by height-height correlation function and it equals:

$$\alpha = 0.74 \pm 0.02 \quad (7)$$

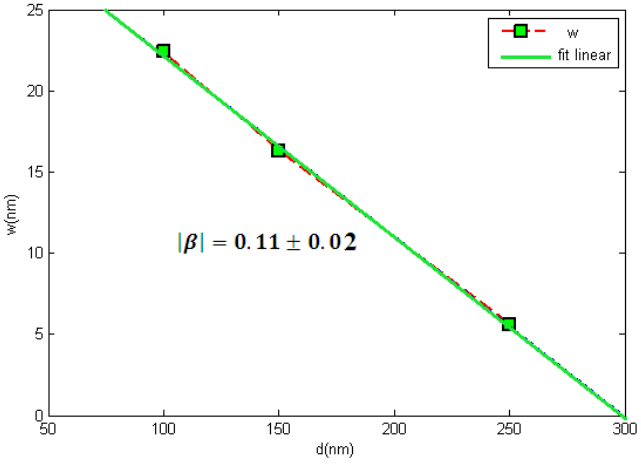
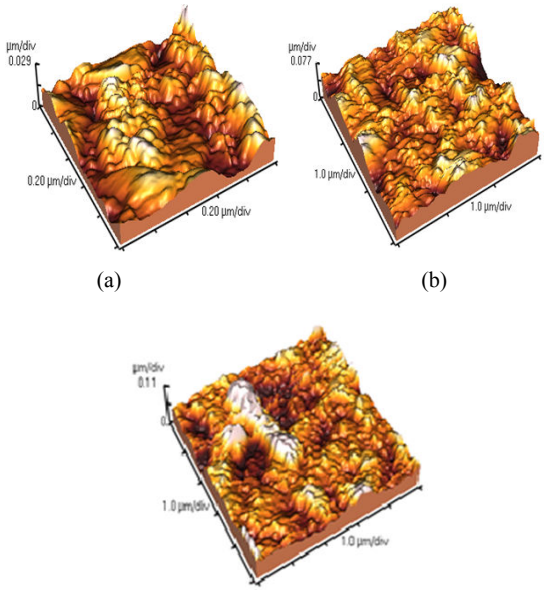


Fig. 4 ZnO layer roughness based on thickness of curve slope, it equals growth rate (β)

Fig. 5 shows 3D-Images of atomic force microscopy (AFM) in various annealing temperature in contact mode. Useful numeral data from sample surface was extracted by a sharp Si_3N_4 probe and with constant force mode in the ranges of 256×256 pixels. By converting images of topography to ASCII data, their analysis was investigated.



(a) (b)

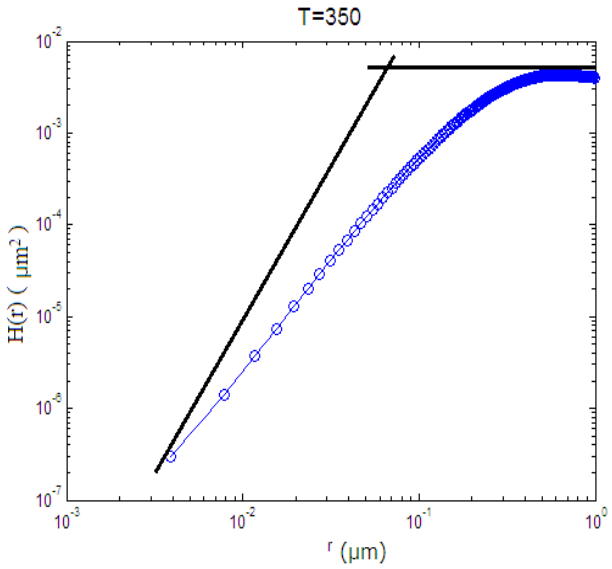
(c)

Fig. 5 AFM images of ZnO thin films (annealed at (a)-350°C, (b)-450°C, (c)- 550°C).

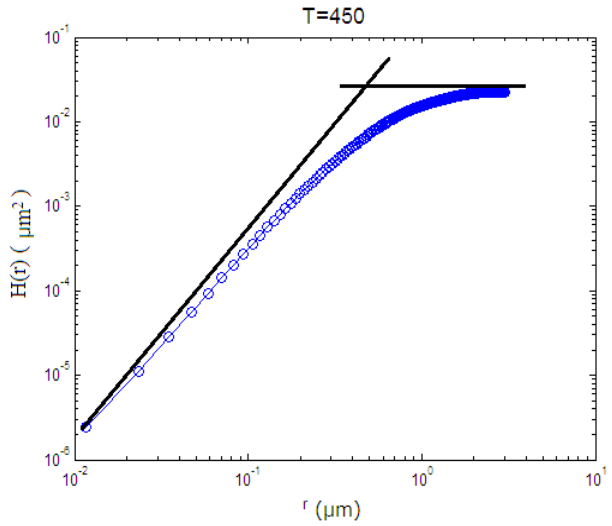
Table II shows the roughness value (rms), roughness exponent, fractal dimension, and correlation length in different temperatures.

TABLE II
THE RMS OF ROUGHNESS, ROUGHNESS EXPONENTS, FRACTAL DIMENSIONS AND CORRELATION LENGTHS OF SAMPLES (ANNEALED AT DIFFERENT TEMPERATURE)

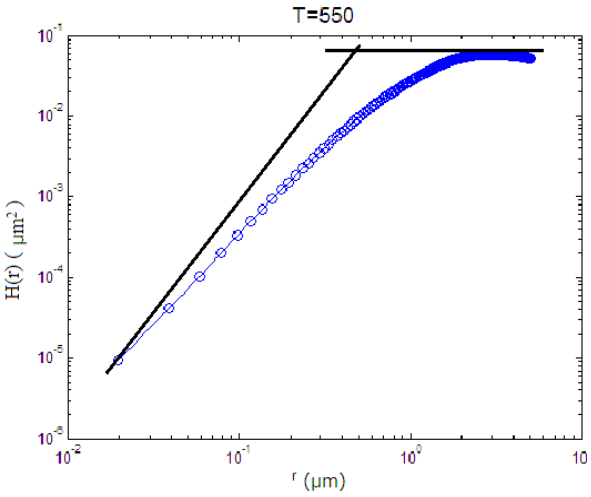
Annealing temperature	W(nm)	α	D_f	ξ (nm)
350°C	7.1	0.59	2.41	53
450°C	21	0.30	2.70	330
550°C	41	0.21	2.79	550



(a)



(b)



(c)

Fig. 6 Correlation functions of ZnO thin films (annealed at (a)-350°C, (b)- 450°C, (c)- 550°C)

Fig. 7 shows the XRD diffraction patterns of ZnO thin film on glass, pre-heated at 275°C and annealed at 350°C, 450°C and 550°C.

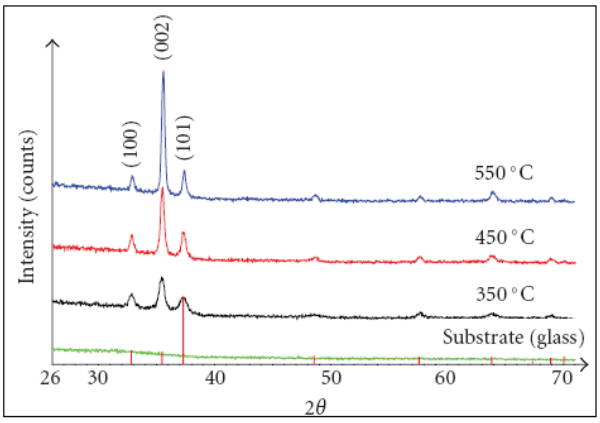


Fig. 7 The XRD pattern of ZnO thin film on glass (annealed at 350°C, 450°C, and 550°C)

IV. CALCULATION OF THE ELECTRICAL RESISTIVITY

Usually for measuring the electrical resistance of thin layers, four-point probe method can be used. In this method the effect of contact points resistance and interface wires was minimized and usually constant electrical current is applied between two points then the potential between two other is measured. Electrical resistance for thin layer was defined as:

$$R_s = \frac{CV}{I} \tag{8}$$

In Fig. 8 current I was applied between two probes (1,4) (outside points and contacted with layer) and the potential is measured between two others (2,3) [23]. C is correction factor

that is obtained by length and width of thin layer and the space between contacted probes (Table III).electrical resistivity is calculated through this formula (it is layer thickness):

$$\rho = R_s t \quad (9)$$

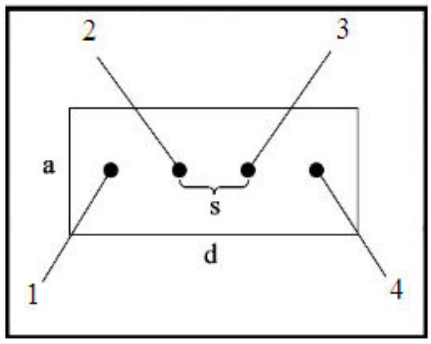


Fig. 8 Arrangement of four-point probe for measuring electrical resistance of thin layer

TABLE III
CORRECTION FACTOR OF RESISTANCE IN VARIOUS RANGES

$\frac{d}{s}$	$\frac{a}{d}=1$	$\frac{a}{d}=2$	$\frac{a}{d}=3$	$\frac{a}{d}>3$
1	-	-	0.9988	0.9940
1.5	-	-	1.4893	1.4893
3	2.7000	2.7003	2.7005	2.7005
∞	4.5224	4.5324	4.5324	4.5324

In materials and energy research center of Meshkin Dasht samples surface resistance is measured by four-point probe device. Increasing thickness decreased surface electrical resistance of samples. Surface resistance of samples equals 0.282×10^4, 1.416×10^2 and 1.319×10^1 in thickness of 200 nm, 280 nm and 360 nm. By surface resistance and thickness of films, electrical resistivity can be calculated [24]. In Fig. 9 electrical resistivity of samples in various thicknesses is shown:

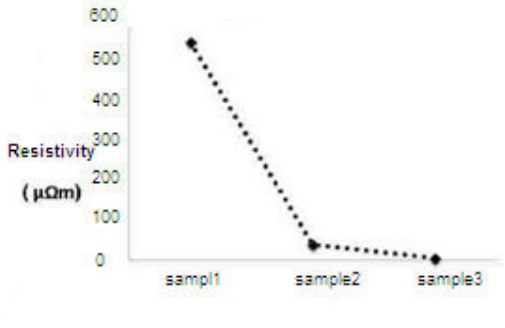


Fig. 9 Electrical resistivity of films

V. CONCLUSION

In this study Atomic Force Microscopy (AFM) and X-ray Diffractometery (XRD) techniques investigated the various characteristics of ZnO thin film (prepared by sol-gel method in various thickness and different temperatures). Fractal analysis of AFM data for extracting surface parameter of ZnO thin film is done. The results show that with increasing thickness, surface roughness (rms) and lateral correlation length (ξ) are decreased. Roughness exponent of all layers was correlated with each other. Increasing annealing temperature increased the crystallite size of the thin film. In this study we showed that by changing post-heated temperature in specific temperature range (550°C), obtained suitable surface roughness. Morphology and layer (prepared from sol-gel method) depended on preheated temperature. Layer thickness was increased by increasing time of deposition ,also By increasing thickness, the grains size are increased, and also increasing of grains size decreased samples' electrical resistivity.

XRD pattern of ZnO thin film showed in all films increasing temperature made crystal quality better than last sample. In AFM analysis, size average and grain height was maximized by increasing temperature.

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