PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 3, 03TF20(4pp) (2012)

Structural Properties of ZnO Thin Films Obtained by Chemical Bath Deposition Technique

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(Received 03 July 2012; published online 07 August 2012)

Zinc oxide thin films have been deposited onto glass substrate from zinc sulfate, ammonia and thiourea aqueous solution by chemical bath deposition. In the work this were specified solution preparation procedure and optimized the composition of the solution and content of component in it. X-ray difraction and high-resolution scanning electron microscopy were used to characterize structure formation of obtaining ZnO films. As a result of investigation was determined the effect of time deposition on the structural and substructural properties such as lattice parameters, texture quality, coherent scattering domain size.

Keywords: Zinc oxide, Chemical bath deposition, Morphology, Structure, Substructure.

PACS numbers: 81.05.Dz

1. INTRODUCTION

Zinc oxide thin films have attracted special attention of researchers due to its wide range of applications. It is used as a key material for light-emitting diodes [1], cathode-ray tubes [2], thin film electroluminescence [3], gas sensors and etc. [1-3]. ZnO thin films are widely used as conductive and optical cover layers of large area solar cells [4-5].

Recently much attention of researchers has been attracted to fabrication the semiconductor thin layer by chemical method [6-12]. Along with this chemical bath deposition (CBD) technique is the most promising method of thin films deposition [6-10]. Compared to the vapor deposition method, the chemical deposition method is generally economical, simple, doesn't require high temperature and pressure and convenient for large-area deposition. Moreover, this method can also be used to obtain thin films with contolable structural properties such as nanocrystalline layers, nanowires and nanobelts [7-8]. Along with this, the CBD method is suitable for making films of any shape, such as flat-panel, spherical, and porous structures. Main feature of this method is that for the deposition of thin films there can be used a solution with different chemical compounds. By the authors of works [6-8] ZnO films were obtained from zinc nitrate and hexamethylene tetramine (HMTA) solution [7], hexamethylene tetramine and ammonia solution [8], ethylenediamine and triethanolamine [6] solution. In contrast to that, for deposition films, we have used more available solutions of zinc sulphate ($ZnSO_4$) and thiourea ($CS(NH_2)_2$). In the work were specified solution preparation procedure and optimized the composition of the solution and content of component in it, investigated structural features of obtained from this solution thin films.

2. EXPERIMENTAL DETAILS

The details of the procedure are: appropriate amounts of zinc sulfate $ZnSO_4$ solution and ammonia solution (NH_4OH) were separately prepared. Formed mixture is thoroughly stirring for several minutes in order to dissolve the formed precipitate and solution to become homogeneous. Then in obtaining solution there was adding thiourea $CS(NH_2)_2$. These solutions were mixed in a beaker and stirred well for a few minutes. Thoroughly cleaned substrates were mainted in a glass reaction vessel. Substrate mounted in a solution within a specified time (usually 15 - 120 minutes) in order to obtain the required film thickness.

Two series of samples have been investigated in this work. In the first case the solution was maintained at room temperature, in the second case - after placing the substrate the solution was heated to 85 ^{0}C. A schematic diagram of the deposition set up is shown in Fig 1.

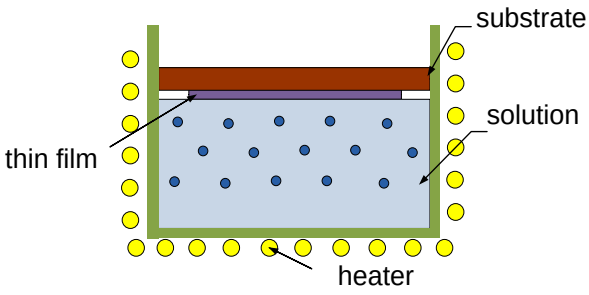

Fig. 1 – Schematic diagram of the chemical deposition system

Structural investigations were carried out with using X-ray diffractometer DRON 4-07 (Ni-filtered K_a – radiation of Cu-anode). The spectra were registered in the angle range 2θ from 20^0 to 80^0, where 2θ is the Bragg angle. X-ray radiation was focused according to the Bragg-Brentano method. The phase analysis was carried out by comparing interplane distances and specific intensities of diffraction patterns from the investigated samples and JCPDS etalon [13].

The quality of the film texture had been estimated by the Harris method. It is especially convenient when plane specimens with the axis of the texture that is oriented normal to the surface tested [14-15]. The pole density was calculated as:

$$P_i = \frac{(I_i/I_{0i})}{\frac{1}{N}\sum_{i=1}^{N}(I_i/I_{0i})}, \qquad (1)$$

where I_i, I_{0i} – are integral intensities of i-diffraction peak of the sample and etalon; N – is a number of lines in the X-ray diffraction pattern.

Thereafter the dependencies $P_i - \varphi$ (where φ - is an angle between chosen direction and the normal to different crystallographic planes corresponding to the reflexes in the XRD patterns) and $P_i - (hkl)_i$ (where $(hkl)_i$ – Miller indexes) were built on the base of the calculation. The angle φ was calculated for triclinic and hexagonal lattices according to expressions given in [14].

The axis of the texture has values corresponding to the maximum P_i. The orientation factor was calculated as

$$f = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(P_i - 1)^2}. \qquad (2)$$

The interplane distances for wurtzite phases of the ZnO were carried out by position of K_{a1} component of all the most intensive lines registered in XRD-patterns.

Lattice parameters a and c of the hexagonal phase for ZnO were calculated according to the next expressions:

$$a = \frac{\lambda}{2\sin\theta}\sqrt{\frac{4}{3}(h^2 + hk + k^2) + \left(\frac{a}{c}\right)^2 l^2}\,, \qquad (3)$$

$$c = \frac{\lambda}{2\sin\theta}\sqrt{\frac{4}{3}\left(\frac{c}{a}\right)^2 (h^2 + hk + k^2) + l^2}\,, \qquad (4)$$

where λ is X-ray wavelength.

Further we have applied the Nelson–Riley extrapolation method for more precise determination of the parameters a and c for both phases [14-16]. Least-squares method has enabled to linearly approximate the obtained numerical values.

The XRD results were also used for the description of the coherent scattering domain (CSD) size in the films. The values of CSD size (L) in the films can be calculated using the Scherrer's relation [14]:

$$L = \frac{K\lambda}{\beta\cos\theta}, \qquad (5)$$

where K is a coefficient weekly depending on the grain shape (K = 0,94); β is a physical broadening of the X-ray line.

3. INTERPRETATION OF EXPERIMENTAL RESULTS

Chemical composition of solutions, concentration and other process variables that were used for ZnO films deposition are presented in Table 1.

It was noted that in this work two series of samples have been studied. However, the results of X-ray analysis showed that in contrast to the expected results obtaining ZnO thin films, we have obtained $Zn_4SO_4(OH)_6$ films. It was found that obtaining condensates had triclinic structure (Fig. 2 a).

Litreview proves that [18], layers annealing in vacuum leads to decomposition of compound $Zn_4SO_4(OH)_6$ and formation of ZnO or ZnS thin films that depend on the annealing temperature.

Initial layers annealing in air leads to their oxidation and the formation of ZnS_xO_{1-x} solid solution films. Therefore, we have carried out further annealing in vacuum at 500 ^{0}C for 60 min and in the air - at 200 ^{0}C for 20 min. In this case we have obtained low quality ZnO films.

Table 1 – The content of reagents in solution and technological parameters of obtaining films

№	First series of samples					
	$ZnSO_4$ (0,1 mol), ml	$CS(NH_2)_2$ (1 mol), ml	NH_4OH, ml	pH	T_r, ^{0}C	τ, min
1	20	4	2	9-10	85	20
2	10	1	1		20	
3	20	20	2		20	
4	10	1	1		85	
	Second series of samples					
1	50	5	7	10	85	20
2						30
3						60
4						90
5						120

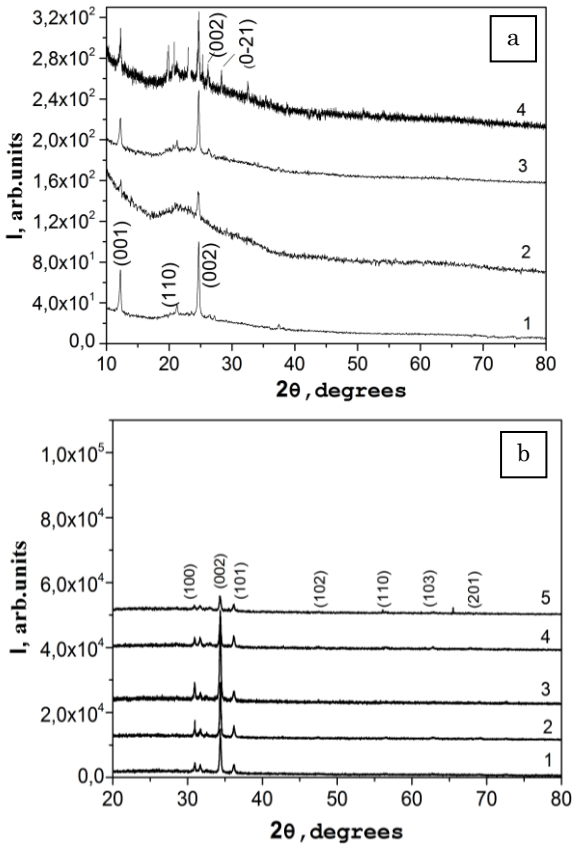

Fig. 2 – X-ray patterns of films: first series (Table 1, 1-4 samples) (a) and second series (Table 1, 1-5 samples) (b) of samples

The second series of samples was obtained from a solution of zinc sulfate, thiourea and ammonia in order to control pH value. pH was raised at 10. On X-Ray diffraction patterns of this series of samples we have registered reflexes with dominant intensity on degrees 34.41^0-34.42^0. Experimentally revealed diffraction peaks may be interpreted as reflexes from the plane (002) of the hexagonal phase ZnO (Fig. 2 b). Along with the peaks mentioned above we have registered reflexes on degrees 31.75^0-31.76^0 and 36.24^0-36.25^0 which can be interpreted as reflexes from the planes (100) and (101) respectively. Consequently there took place formation ZnO thin films with hexagonal structure.

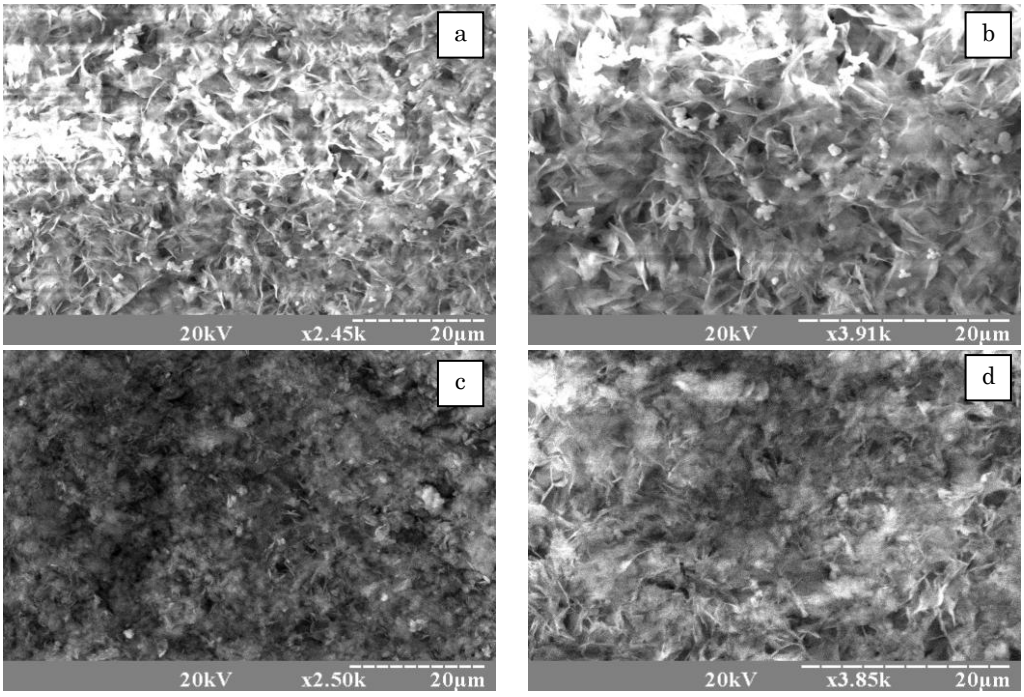

Fig. 3 – SEM images of ZnO films obtained under deposition time: 90 min (a, b); 120 min (c, d)

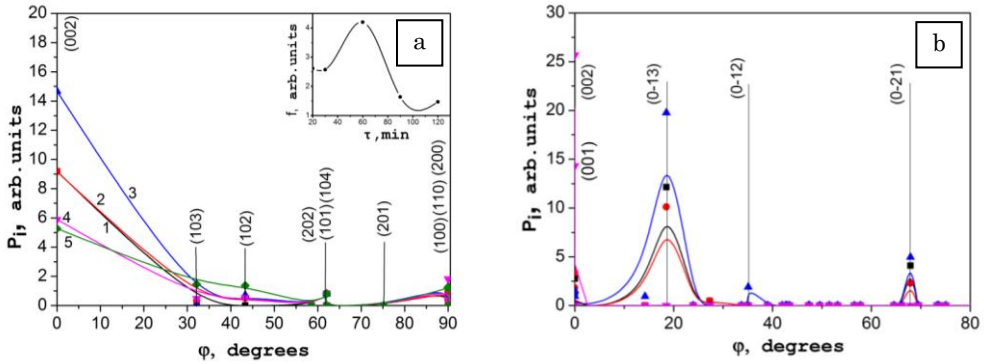

Fig. 4 – Pole density P_i and orientation factor f as a function of the incidence angle φ between the direction and the normal to the reflection plane for films: first series (Table 1, 1-4 samples) (a) and second series (Table 1, 1-5 samples) (b)

Fig. 3 displays images of the surface for ZnO. It is found that density of crystallites increases with the increase of time deposition. Accordingly there took place formation of the continuous film at a thickness more than 1 μm.

When you create heterojunctions based on ZnO thin films it is important that layers coupling occurred in the same crystallographic plane in different crystallites [17]. This is due to the fact that the density of interfacial defects depends on the plane contact type of hetero pair materials. Consequently condition interfacial area determines the transport mechanism of charge carriers through heterojunction. Therefore it determines the efficiency of its use in such devices as solar cells and photodetectors. This caused the urgency of determining of the effect on the time deposition on texture quality.

Reverse pole figures from ZnO are shown in Fig.4 a. As it seen, the samples are well textured. Along with this, the dominated orientations of crystallites is [002]. The quality of texture depends on technological conditions. In the obtained ZnO films increasing deposition time τ from 20 to 60 minutes leads to improvement, and then (from 90 to 120 min) to a significant deterioration of the texture quality (inset in Fig. 4 a). This is associated with growth features of obtained layer.

It is found that condensates deposited for τ = 20 min have nanorods form as hexagonal prisms. These structures grew with dimension: d = (0.25-1.00) μm in diameter and l = (2.50-3.00) μm on length.

It should be noted that nanorods grew at different angles (in most cases - perpendicular) to the substrate and oriented perpendicular to the substrate by crystallographic axis c, which coincides with the texture axis. And this makes high quality of texture at the early stages of the film growth. With the increasing condensation time due to the secondary nucleation there took place growth of plate crystallites between nanorods intervals. Finally this fact leads to the formation of a continuous film and decrease texture quality.

Along with this, $Zn_4SO_4(OH)_6$ thin films had texture on plane [0-13]. These kinds of exotic textures quite often take place in films obtained by chemical bath deposition [18].

The result of lattice constants estimation are presented in Table 2.

Table 2 – Lattice parameters of ZnO with hexagonal structure

τ, (min)	Lattice parameters, (nm)			CSD size, L (nm)	
				hkl	
	a	c	c/a	(100)	(002)
20	0.37645	0.57117	1.517	40.1	45.0
30	0.33407	0.50727	1.518	35.9	46.4
60	0.33895	0.51446	1.517	92.9	43.1
90	0.32168	0.48838	1.518	49.1	54.3
120	0.33425	0.50696	1.516	35.5	40.8
Ref. [13]	0.34298	0.52066	1.520		

From Table 2, lattice parameters of films with low thickness (τ = 20 min) are a = 0.37602 nm, c = 0.57081 nm. These values are more than reference ones (a = 0.34298 nm, c = 0.52066 nm) [13]. This effect may be due to a small size of crystallites in condensates, which has nanorods form as already mentioned. With the increase of time deposition and film thickness corresponding lattice constants value is approaching to the reference one.

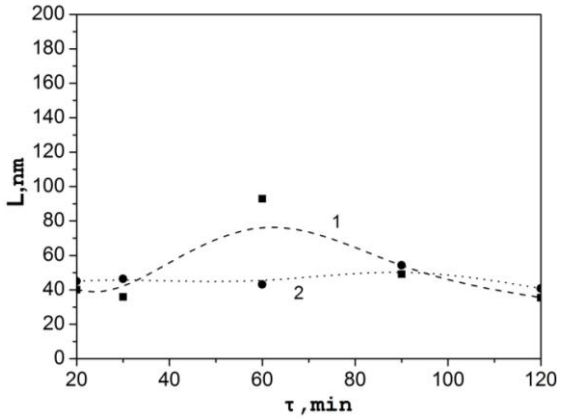

Fig. 5 – Effect of the time deposition on the CSD size in ZnO thin films. The CSD sizes in directions normal to the crystallographic planes (100) (1) and (002) (2) are determined

Fig. 5 depicts the effect of the time deposition on the CSD in directions normal to the crystallographic planes (100) and (002) in ZnO thin films. These values correspond to the size of CSD in perpendicular directions to a and c axes of ZnO lattice.

The values of CSD were equal to $L_{(100)}$ = (35-93) nm, $L_{(002)}$ = (40-54) nm. These data are much smaller than electron-defined (d = (0.25-1.00) μm, l = (2.50-3.00) μm). This indicates that crystallites consist of several CSD.

4. CONCLUSIONS

ZnO thin films with different thickness have been obtained from zinc sulfate, ammonia and thiourea aqueous solution with the help of chemical bath deposition technique. It is found that growth of thin layers took place by the formation of nanorods as hexagonal prisms and grew perpendicular to the substrate with further growth of plate crystallites between nanorods intervals. It is shown that the films have a hexagonal structure with lattice constant, varying with increasing thickness from a = 0.37601 nm, c = 0.57079 to a = 0.33408 nm and c = 0.50714 nm.

In addition it was studied the effect of the time deposition on texture quality of ZnO thin films. Furthermore it is shown that the quality of texture was worsened with increasing deposition time. CSD estimating allowed us to evaluate that crystallites which formed at the initial stage of film growth consist of several subgrain.

AKNOWLEDGEMENTS

This work is supported by the Ukraine State Agency for the Science, Innovation and Informatization and by the NRF grant funded by the MEST of Korea (2011-0019204) within the project «Advanced materials for low-cost high-efficiency polycrystalline heterojunction thin films solar cells» and by the Ministry of Education and Science, Youth and Sport of Ukraine (Grant №. № 0112U000772).

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