STRUCTURAL AND MICROSTRUCTURAL PROPERTIES OF ZnO THIN FILMS OBTAINED BY SPRAY PYROLYSIS TECHNIQUE

O.A. Dobrozhan, A.S. Opanasyuk, S.B. Bolshanina. Structural and microstructural properties of ZnO thin films obtained by spray pyrolysis technique. The ZnO thin films obtained by spray pyrolysis method applied at different temperatures of glass substrates have been studied by the methods of X-ray diffraction and scanning electron microscopy. The zinc acetate dihydrate dissolved in distilled water (concentration of 0.3 M)
was used as an initial precursor. The influence of substrate temperature on the grain size, phase structure, films’ texture quality, lattice constants, size of coherent scattering domains has been studied. The research results can be used in the development of functional solar cells layers.

*Keywords*: zinc oxide, thin films, spray pyrolysis, structural and microstructural features.

**Introduction**

The zinc oxide (ZnO) is a semiconductor of n-type conductivity with a high value of direct band gap (3.37 eV at \( T = 300 \) K) and the highest exciton building energy (60 meV) among binary compounds [1, 2]. This material due to its unique physical, electrical and optical properties, chemical and thermal stability of the atmosphere and non-toxicity is very promising to be used in micro- and nanoelectronics [3, 4], optoelectronics [5, 6], sensors [7…10], solar energy engineering [11…13] and others. As zinc oxide does not contain in its composition rare materials and can be obtained using low-cost methods, it is an alternative to traditional materials such as ITO ((In\(_2\)O\(_3\))\(_{0.9}\) — (SnO\(_2\))\(_{0.1}\)) and FTO (SnO\(_2\):F) [14]. In addition, zinc oxide can be used in the construction of solar cells as antireflective coating, window material [15,16].

For zinc oxide thin films synthesis a wide range of techniques that include magnetron sputtering [17, 18], chemical vapor deposition [19], thermal evaporation [20], chemical bath deposition [21, 22], spray pyrolysis [23…26] is used. In comparison with these methods, spray pyrolysis is simple, relatively inexpensive, non-vacuum deposition method for dense, porous thin film coatings and nanostructures of large area on different substrates. When using this method, the properties of thin films depend on the choice of precursors, physical and technological conditions of deposition of films. The analysis of the literature data [23…26] shows that substrate temperature has the greatest influence on the properties of the deposited thin films. Accordingly, the main goal of this work is to study the influence of substrate temperature on the structural and microstructural properties of ZnO thin films deposited by spray pyrolysis.

**Experimental details**

The laboratory setup, the schematic diagram of which is shown in Fig. 1, was used for obtaining zinc oxide thin films. Zn(CH\(_3\)COO\(_2\))·2H\(_2\)O dehydrate zinc acetate solution and distilled water with Zn(Ac)\(_2\) concentration of 0,3 M were taken as a precursor. The laboratory setup consists of a heater, with the help of which the steel plate with fixed substrate is heated; a thermocouple for registering the values of the substrate temperature, a spray gun, comprising: a reservoir for the initial solution, nozzle atomization. The compressor, that provides air flow to transport dispersed precursor particles to the heated substrate, is connected to this gun.

A few drops of HCl were added to the initial solution to increase the degree of precursor solubility. Spraying of the initial solution was carried out on the glass substrate, cleaned before by ethanol, with the size of 2,5×2,5 mm. Substrate temperature range was 473…673 K at intervals of increase of 50 K. The distance between the nozzle and the heated substrate surface was equal to 20 cm. To transport dispersed precursor particles the air flow with a pressure of 0,2 MPa was used. Spraying rate was 2 ml/min at a volume of sprayed solution of 5 ml per sample. It should be noted that spraying was performed in cycles (each spraying in 3 sec) to enable the film formation without saturation of precursor at the surface of the heated substrate.

During spray pyrolysis, dispersed precursor particles, while approaching within the close distance to the surface of the heated substrate, are subjected to thermal decomposition, as the result of which the evaporation of reaction products, followed by the formation of zinc oxide film, occurs.

X-ray analysis method using X-ray diffractometer DRON 4-07 in Ni-filtered K\(_\alpha\) radiation of copper anode (\( U = 30 \) kV, \( I = 20 \) mA) was used to determine the structural properties. The measurement was conducted in a range of 20 angles from 20° to 80°, where 20 is Bragg’s angle. Curves were normalized to the peak intensity of the (101) hexagonal phase of the compound. Phase analysis was performed by comparing inter-plane distances and relative intensities of the researched samples and the standard according to JCPDS [27].

Fig. 1. Schematic diagram of experimental laboratory setup for obtaining ZnO thin films by spray-pyrolysis
The texture of the films has been estimated by Harris method, which is convenient for research of flat samples with the axis of the texture that is oriented normally to the surface [28]. Pole density was calculated by the following formula:

\[ P_i = \frac{I_i}{I_0}, \]

where

\[ I_i, I_0 \] — integrated intensities of the \( i \)-th diffraction peak for the film sample and standard;

\[ N \] — the number of lines that are present on the diffraction pattern.

Then \( P_i - (hkl) \) and \( P_i - \phi \) dependences, where \( \phi \) is the angle between the axis of the texture and perpendicular to different crystallographic planes, which correspond to reflections on the diffractograms, \( (hkl) \) — Miller indexes were made. This angle was calculated for the hexagonal lattice, using the expressions given in [28]. Texture axis has those indexes, which correspond to the largest value of \( P_i \). In this case, the orientation factor for the sample can be calculated from the expression

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

Calculation of the constants \( a \) and \( c \) of the hexagonal phase of the material was held by the formulas:

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

\[ c = \frac{\lambda}{2 \sin \theta} \sqrt{\frac{4}{3} (c^2) (h^2 + hk + k^2) + l^2}. \]

The lattice constants were determined using Nelson-Riley extrapolation method [29, 30]. The graphs in the coordinates \( a(c) - \frac{1}{2} \cos^2 \theta \left(\frac{1}{\sin \theta} + \frac{1}{\theta}\right) \) were plotted. Thus a graphical method of successive approximations was used to determine the lattice constants of hexagonal phase. The linear approximation of obtained points was conducted using the method of least squares with the help of OriginPro software package. This method, performed at the intersection of the line with the axis of ordinates, allows finding the lattice constants with an accuracy of 0.001 %.

The average size of coherent scattering domains (CSD) \( L \) was determined by Scherer’s formula [31]:

\[ L = \frac{k \cdot \lambda}{\beta \cdot \cos \theta}, \]

where

\( k \) — coefficient that depends on the shape of the particle (\( k = 1 \));

\( \lambda \) — wavelength of X-rays;

\( \beta \) — broadening of the corresponding X-ray lines;

\( \theta \) — diffraction angles of the analyzed lines.

More detailed methodology for determining the structural and microstructural characteristics of the films are described in [29, 30…32].

**Results and discussions**

Fig. 2 shows the electron microscopy images of the surface of zinc oxide films deposited at different substrate temperatures. It should be noted that at temperatures of 523 K the formation of the polycrystalline film with crystal growth at different angles to the plane of the substrate occurred. By increasing the substrate temperature to 673 K the formation of grains with a hexagonal prism shape with diameters of 0.8...1 μm happened.

Fig. 3 shows the diffraction patterns of ZnO films deposited at different substrate temperatures. Phase analysis of samples was carried out using handbook (JCPDS cards № 36-1451 and 21-1467).
In the diffractograms the line was dominant in the angles of 36.16°…36.32°, which corresponded to the reflection from the plane (101) of the hexagonal phase of ZnO. Also the lines with a sufficiently large intensity at angles of 31.82°, 34.44°, 47.5°, 56.7°, 62.88°, 67.92°, 69.04°, where the intensive reflections from planes (100), (002), (102), (110), (112), (201) at wurtzite phase of ZnO were present on diffractograms. Thus diffraction analysis shows that the samples have a hexagonal structure.

Fig. 2. SEM images of the surface of the ZnO films obtained at non-oriented substrates at substrate temperatures of $T_s$: 523 K (a) and 673 K (b)

To be noted is that $C_4H_6O_4Zn$ phases, which were identified by means of a JCPDS 21-1467 card, are present at substrate temperatures of 473 K, 523 K, 573 K [27]. The analysis diffraction has shown that peaks from zinc acetate phase decreases with increasing substrate temperature. Films obtained at temperatures above 573 K were single phase and contained only hexagonal phase of ZnO.

Calculations of pole density $P_i$ made it possible to determine the axial texture of growth in ZnO layers [002], the perfection of which was identified by modes of the obtained films and which increased with increased thickness (Fig. 4, a).

Fig. 3. XRD patterns of ZnO films obtained at different substrate temperatures, $T_s$, K: 473(1), 523 (2), 573 (3), 623 (4), 673 (5)

Appropriate dependences of film’s orientation factor on the substrate temperature at which they were obtained are presented in Fig. 4, b. As can be seen from the figure, with increasing the substrate temperature, the corresponding value of orientation factor also increases. This suggests that with increasing the substrate temperature the quality of obtained films’ textures increases.
The results of calculating the size of coherent scattering domains in ZnO films in directions perpendicular to crystallographic planes (100), (110) and (002) are shown in Fig. 5. It is established that with the change of the substrate temperature the sizes of CSD take the following values: \(L_{(100)}=14...20\), \(L_{(110)}=12...25\), \(L_{(002)}=16...23\) nm. In general, one can trace the growth of the CSD sizes in their corresponding areas with increasing the substrate temperature that shows the growth of the crystalline quality of the films.

The lattice constant of material is a characteristic which is extremely sensitive to changes of its stehiometry, adding impurities, oxidation and others, that’s why precision calculation of these parameters makes it possible to study the relevant processes. We carried X-ray determination of lattice constants of ZnO films, deposited at different modes of condensation. The obtained values of crystal lattice of the material after the 5th iteration are shown in Table.

### The results of calculations of the lattice constants of ZnO films obtained using the Nelson-Riley

<table>
<thead>
<tr>
<th>(T_s, K)</th>
<th>(a)</th>
<th>(c)</th>
<th>(c/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>0.32481</td>
<td>0.51495</td>
<td>1.5854</td>
</tr>
<tr>
<td>523</td>
<td>0.32513</td>
<td>0.51743</td>
<td>1.5916</td>
</tr>
<tr>
<td>573</td>
<td>0.32414</td>
<td>0.52382</td>
<td>1.6160</td>
</tr>
<tr>
<td>623</td>
<td>0.32601</td>
<td>0.51509</td>
<td>1.5800</td>
</tr>
<tr>
<td>673</td>
<td>0.32544</td>
<td>0.52036</td>
<td>1.5994</td>
</tr>
</tbody>
</table>

Reference value: \(a=0.3249\), \(c=0.5206\), \(c/a=1.6023\) [27]

The calculated values of lattice constants \((a = 0.3241...0.3260\) nm and \(c = 0.51495...0.52382\) nm, \(c/a = 1.5800...1.6160\)) correlate with the data given in the JCPDS \((a = 0.3249\) nm, \(c = 0.5206\) nm, \(c/a =1.6023\)) [27].

### Conclusions

In this paper, ZnO films obtained by the X-ray diffraction method and scanning electron microscopy with the help of the spray pyrolysis method using the solution of Zn(CH\(_3\)COO\(_2\))\(_2\)·2H\(_2\)O with the
concentration of 0.3 M as a precursor have been investigated. The influence of substrate temperature on the crystal size, phase composition, texture quality, size of coherent scattering domains films, lattice constants of the material is investigated.

It is shown that the films have polycrystalline structure with a grain size of 0.1…1 μm, which increases with increasing substrate temperature. It was shown by means of X-ray diffraction that the films obtained at temperatures below 573 K are two-phase and contain zinc acetate along with hexagonal phase ZnO. Films obtained at higher temperatures were single phase and had the texture of axial growth [002].

Established is that with the change of the substrate temperature the CSD sizes acquire growing nature and take the following values in the respective planes:
\[ L_{(100)} = 14…20, \quad L_{(110)} = 12…25, \quad L_{(002)} = 16…23 \text{ nm}. \]
\[ a = 0,3241…0,3260 \text{ nm}, \quad c = 0,51495…0,52382 \text{ nm}, \quad c/a = 1,5800…1,6160 \] mostly correlate to reference ones.

Thus, the modes to obtain single-phase zinc oxide films with rather big CSD sizes that states about their high crystalline quality were defined. These obtained layers can be used as windows of thin-film solar cells.

Acknowledgments

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Literature


