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Comparison of luminescence properties of ZnO nanorods, obtained by hydrothermal method and pulse electrochemical method

Influence of of the method of synthesis of ZnO rods on their microstructure and spectral-luminescent properties was studied in the work. Pulsed electrochemical and hydrothermal methods were used. The films with a similar value of thickness both methods have been obtained. The diameter of the rods obtained by the hydrothermal method is much smaller than the diameter of rods obtained by the electrochemical method. It is seen from microscopic measurements. X-ray diffraction was measured for ZnO films obtained by pulsed electrochemical method. Crystalline ZnO films with a wurtzite structure are obtained both by hydrothermal and pulsed electrochemical methods. The absorption and fluorescence spectra were measured for the samples. Bandgaps of films are determined from the absorption spectra. Edge luminescence in the ultraviolet region of the spectrum, having an exciton nature and defect luminescence in the visible spectral region is observed in the luminescence spectra of films. Analysis of the absorption and luminescence spectra showed that defectiveness ZnO film make by the electrochemical method is significantly higher film defects make by hydrothermal method.

Keywords: thin film of ZnO, absorption spectrum, luminescence, hydrothermal synthesis, pulse electrochemical synthesis, defectiveness.

Introduction

Despite of long and comprehensive investigations, zinc oxide (ZnO) based materials are in scope of interest of many groups of researchers. This interest connected with its unique optical, electrical and acoustical properties. Distinctive feature is also the number of synthesized nanonstructures on the basis of zinc oxide [1]. There are many investigations, with proposal to use semiconductor properties of zinc oxide in different devices of electronic and optoelectronic techniques [2, 3].

The development of synthesis methods is important for its applied use, which allows receiving materials with specified properties with high economical effectiveness. Methods of precursor precipitation on the water basis, mechanochemical methods are low cost and therefore, potentially high effective. At present time hydrothermal synthesis is intensively developing to produce zinc oxide nanorods [4, 5]. The directed change of properties and morphology of material is possible by selecting the parameters of hydrothermal synthesis.

In the last decade the impulse electrochemical deposition became an important method of receiving nanonstructured ZnO arrays thanks to its technological efficiency, possibility of deposition on big surfaces, cost effective ratio, quality of layer and low temperature of synthesis compared to other methods. As author mentions [6–10] morphology and thickness of arrays in this method, and also its crystal structure and physical-chemical properties can be easily controlled by setting the parameters of deposition, like density of flows and electrode potential, structure and temperature of solution, time of electro-deposition.

Structure, morphology and properties of oxide zinc substantially depend on conditions and technology of its receipt. For applied use of oxide zinc [10] it is relevant to receive rod structure with rod diameter from 50 to 500 nm. Such a structure will be used as a material for excitons and free charge carriers. Method of production will substantially influence on optical and electrophysical properties of received ZnO rods. Therefore in this work investigation of spectral-luminescence properties of ZnO nanorods, received by hydrothermal and impulse electrochemical methods was carried.

Methodology of research

Impulse electrochemical method. The production of oxide zinc nanorods arrays was carried by method of cathode electrochemical deposition in the three electrode electrochemical cell with water electrolyte, that contains 0,1 M NaNO3 and 0,05M Zn(NO3)2, temperature t = 70°C, without mechanical shaking of the solution. As a substrate the glass wafers were used, covered transparent electrically conductive layers alloyed fluorine tin oxide (FTO) by Sigma-Aldrich. Graphite rod was counter electrode, reference electrode — saturated silver-chlorine half-cell electrode Ag/AgCl.

Potentiosat-galvanostat Elins J-30 was used to carry impulse tension. Substrate - cathode was supplied with square wave potential, where the lower limit for samples was Uoff -0.8 and upper limit Uon was -1.4 (the potentials are relate to Ag/AgCl). Pulse duty cycle factor was 2.5. Pulse frequency *f* remained constant and equal to 2 Hz.

Hydrothermal method. Synthesis of ZnO nanorods by hydrothermal method consisted of two stages. The first stage - drawing of the seed layer and the second stage — the synthesis of nanorods on a substrate with the seed layer by hydrothermal deposition. The second stage is the deposition of nanorod arrays.

Application of ZnO seed layer. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, Sigma Aldrich) and monoethanolamine (C_2H_7NO, Sigma Aldrich) were dissolved sequentially in isopropyl alcohol. The concentration of both zinc and monoethanolamine acetate in prepeared solution was 0,5 M. The solution was applied to pre-cleaned glass substrate coated with a conductive layer of tin-doped indium oxide (ITO). The centrifuge method (spin-coating) at a substrate speed of rotation of 2000 r/min was repeated 4 times. Next, the substrate annealed in a muffle furnace at 450 °C for 60 minutes to form a ZnO structure. ZnO nanorod arrays synthesized on ITO substrates precoated ZnO seed layer from an equimolar aqueous solution of zinc nitrate ($Zn(NO_3)$, Sigma Aldrich) and hexamine ($C_6H_{12}N_4$, Sigma Aldrich) for 10 hours. The initial concentration of the solution, and the synthesis temperature was 25 mM and 90 °C. Every 2 hours samples were washed in deionized water and placed in a fresh solution. After completion of the synthesis, ZnO grown arrays were washed repeatedly with deionized water, dried, and annealed at 400 °C for 1 hour.

The crystal structure of the films was analyzed after measurements on the X-ray diffractometer X-Pert MPD PRO (PANalytical) and Drone 2. The morphology of the samples was investigated by the scanning electron microscope with cathode Schottky Mira-3 (Tescan).

Absorption and luminescence spectra of the films are measured to the resulting films. Registration of the absorption spectra of the films was carried out using a spectrophotometer Agilent Cary 300. The fluorescence spectra were measured on a spectrofluorimeter Cary Eclipse.

Results and discussion

Thickness and rod size of the synthesized films was investigated. In the film obtained by the hydrothermal method within 10 hours, thickness was 2.9 microns. The appearance of the rods is shown in Figure 1. The average diameter of the rods was 150 nm. In the case of using a pulse electrochemical method, film thickness was 2.82 micrometers and was achieved by 2 hours synthesis. The average diameter of the rods was 660 nm. In the case of hydrothermal method — the size of the synthesized ZnO rods is less than the electrochemical method. However, the rate of synthesis of the film is higher with use of electrochemical synthesis method.

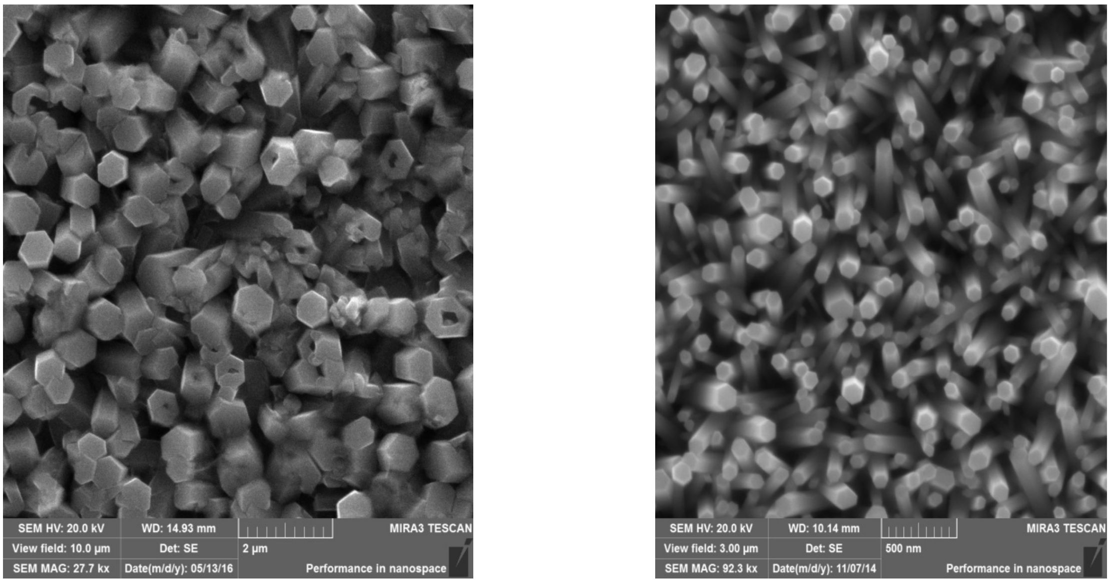

Figure 1. SEM-images samples obtained pulse electrochemical (left) and the hydrothermal method (right)

Investigation of the films synthesized crystalline structure was conducted. The data on the properties of ZnO films prepared by the hydrothermal method described in our previous work [11]. ZnO film deposited on conductive coating of ITO (indium tin oxide) in the case of the electrochemical method. Therefore, in the present diffraction spectra was reflexes associated with indium tin oxide. X-ray diffraction for the sample coated with ITO to exclude those measured from X-ray diffraction data of ZnO films. Analysis of these measurements showed the presence of only the reflexes of tin oxide (SnO_2). Continued consideration of the data showed that the peaks is not related to SnO_2, belong to the hexagonal wurtzite phase of ZnO, with good agreement with the standard values of *d* (JCPDS No. 36-1451) [12].

Other phases, Zn or other oxides besides ZnO phase weren't recorded on X-ray diffraction data. This confirms that crystalline films of ZnO obtained by electrochemical deposition method (Table).

Table

Data of x-ray analysis of ZnO films obtained by pulse electrochemical method

2θ (degrees)	hkl	Calculated values dhkl (Å)	Values dhkl (Å) on the basis of JCPDS
18,60	100	2,816	2,8179
20,10	002	2,602	2,6049
21,20	101	2,476	2,4786
27,90	102	1,911	1,9128
33,50	110	1,626	1,6269
37,25	103	1,477	1,4784
40,50	112	1,379	1,3799

Absorption and luminescence spectra were measured for the obtained films. The absorption spectra of the films are shown in Figure 2. The optical density films (D) produced by different methods and measured at 380 and 800 nm has similar values. The optical density of films differs significantly in the blue-green part of the spectrum. The size of the band gap (Eg) ZnO is calculated for the obtained films. A smaller value of E_g calculated for ZnO films obtained by an electrochemical method, compared with the published data [13]. This can be explained by the high defectiveness of the films. Indirect evidence of this is the shape of the absorption curve 2 shown in Figure 2. The technique given in [14] was used for the calculations. The value of E_g was 3.3 eV for the film obtained by the hydrothermal method, and 3.175 eV for the film obtained pulse electrochemical method.

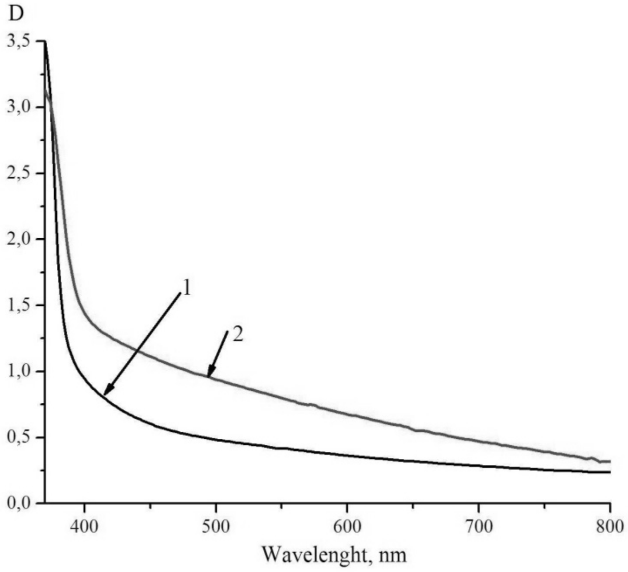

Figure 2. Absorption spectra of the nanorods obtained by electrochemical pulse method (1) and the hydrothermal method (2)

Also luminescence spectra of ZnO films have measured. Comparative analysis of the luminescence spectra of the nanorods (Figure 3) obtained by the hydrothermal method and electrochemical methods carried out. The ratio between values of the maximum amplitude of the luminescence intensity band in the visible area of light-spectrum (I_{VA}) and the of the maximum value of edge luminescence amplitude in the shortwave area of light-spectrum I_{UV} has often been compared to determine the crystallinity of the ZnO nanostructures.

Defectiveness films obtained by pulsed electrochemical method is more than the film obtained by the hydrothermal method. It follows from the luminescence spectra of ZnO films. Ratio between I_{VA}/I_{UV} was 0.55 for the electrochemical films and 0.13 for hydrothermal films.

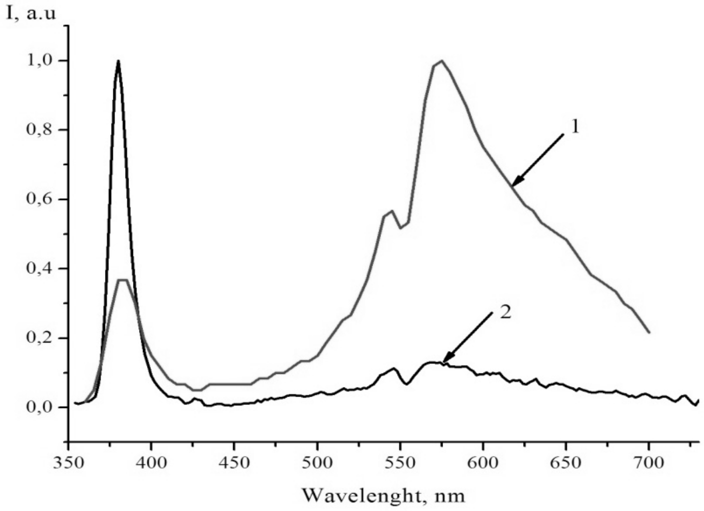

Figure 3. Luminescence spectra of nanorods obtained pulse electrochemical (a)
and hydrothermal method (b)

Conclusions

Rods of ZnO synthesized by hydrothermal methods and pulse electrochemical synthesis as a result of the work done. The crystal structure and morphology of ZnO films was investigated. The resulting films have good crystallinity and all the peaks correspond to the hexagonal lattice ZnO, wurtzite structure. The absorption and fluorescence spectra were measured for ZnO films. Bandgaps of films are determined from the absorption spectra. The edge luminescence in the ultraviolet region of the spectrum, which has an exciton nature and defect luminescence in the visible spectral region are observed in the luminescence spectra of the produced films.

The value of the maximum intensity of the luminescence band in the visible region to the value of the peak amplitude of the edge luminescence band (CRL) in the short-wave region were compared. The comparison showed that the nanorods obtained by the pulsed electrochemical method have a more defective structure than the rods obtained by the hydrothermal method. These data are confirmed by the analysis of the absorption spectra and fluorescence spectra. The results of the work show that using different methods of synthesis it is possible to obtain ZnO films with different geometrical properties and defectiveness.

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Гидротермалдық және импульсті электрохимиялық әдіспен алынған ZnO наноөзекшенің люминесценттік қасиеттерін салыстыру

Мақалада ZnO наноөзекшесін синтездеу әдісінің ZnO микроқұрылымдары мен спектрлік-люминесценттік қасиеттеріне әсері зерттелді. Синтездеудің гидротермиялық және импульстік электрохимиялық әдістері жүргізілді. Осы аталған синтездеу әдістері арқылы жұқа қалыңдықтағы қабыршақтар алынды. Микроскопиялық өлшеулер нәтижесінде гидротермиялық синтездеу әдісі арқылы алынған наноөзекшелердің диаметрлері, электрохимиялық әдістер арқылы алынған наноөзекшелерінің диаметрлеріне қарағанда, айтарлықтай кіші екендігі анықталды. Импульстік электрохимиялық әдіс арқылы алынған ZnO қабыршағының рентгендік дифракциясы өлшенді. Гидротермиялық және импульстік электрохимиялық әдістер арқылы алынған гексагоналды торға ие ZnO кристалдық қабыршағы вюрциттік құрылымда болатыны көрсетілді. Алынған үлгілердің жұтылу және флуоресценция спектрлері өлшенді. Жұтылу спектрін өлшеу барысында ZnO қабыршағының рұқсат етілмеген зонасының ені анықталды. Алынған қабыршақтың люминесценция спектрінде экситондық табиғатқа ие шектік люминесценция спектрдің ультракүлгін облысында, ал ақаулы люминесценция спектрдің көрінетін облысында байқалды. Жұтылу спектрі мен люминесценцияға талдау жасау барысында электрохимиялық әдісі арқылы алынған ZnO қабыршағының ақаулары, гидротермиялық синтез арқылы алынған ZnO қабыршағына қарағанда, айтарлықтай жоғары мәнге ие екендігі анықталды.

Кілт сөздер: жұқа қабыршақ, ZnO, жұтылу спектрі, люминесценция, гидротермалды синтез, импульсті электрохимиялық синтез, ақаулар.

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Сравнение люминесцентных свойств наностержней ZnO, полученных гидротермальным и импульсным электрохимическим методами

В работе изучено влияние метода синтеза стержней ZnO на их микроструктурные и спектрально-люминесцентные свойства. Использованы гидротермальный и импульсный электрохимический методы синтеза. Данными методами получены пленки с близким значением толщины. Микроскопическими измерениями показано, что диаметр стержней, полученных гидротермальным методом, значительно меньше диаметра стержней, полученных электрохимическим методом. Измерена рентгеновская дифракция пленок ZnO, полученных импульсным электрохимическим методом. Показано, что как гидротермальным, так и импульсным электрохимическим методами получены кристаллические пленки ZnO со структурой вюрцита. Были измерены спектры поглощения и флуоресценции образцов. Из спектров поглощения определена ширина запрещенной зоны пленок ZnO. В спектрах люминесценции полученных пленок наблюдается краевая люминесценция в ультрафиолетовой области спектра, имеющая экситонную природу, и дефектная люминесценция в видимой области спектра. Анализ спектров поглощения и люминесценции показал, что дефектность пленки ZnO, полученной электрохимическим методом, значительно выше дефектности пленки, полученной гидротермальным методом синтеза.

Ключевые слова: тонкие пленки ZnO, спектр поглощения, люминесценция, гидротермальный синтез, импульсный электрохимический синтез, дефектность.

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