Твердотельная электроника

UDC 539.21

Growing parameters and quality of ZnO seed-layer film (Part 1)

A.Bogdan, **A.Orlov**, Ph. D., **V. Ulianova**
National Technical University of Ukraine 'Kyiv Polytechnic Institute',
pr. Peremogy, 37, Kyiv-56, 03056, Ukraine.

Effects of different growing conditions on the structure and properties of obtained by sol-gel method ZnO seed-layer film are observed. The recent progress in the field of synthesis of ZnO seed-layer film for growing of vertically oriented nanorods is given. The correlation between type, concentration of sol-gel and annealing temperature of ZnO seed-layer film for obtaining of high-quality ZnO nanorods is established. Reference 15, figures 5, tables 1.

Key words: *ZnO seed-layer, sol-gel, zinc nitrate, zinc acetate, annealing temperature.*

Introduction

Nowadays ZnO became a promising component in a wide range of nanoscale devices for future application. It is an attractive material for electronics, photonics and sensing due to having exotic and versatile properties such as mechanical, piezoelectric, optical and electrical properties, biocompatibility, nontoxicity, chemical and photochemical stability, high specific surface area, optical transparency, electrochemical activities and so on [11]. On other hand, ZnO is attracting considerable attention due to its unique ability to form a variety of nanostructures such as nanowires, nanoribbons/nanobels, nanocombs, nanorings, nanocages, nanocastle, nanofibers etc. ZnO nanorods/nanowires have been employed as bio- or gas sensitive element of acoustic wave sensors [15]. ZnO nanorods provide giant effective surface area and strong bonding sites and this way allow more precision managing of their properties and characteristics.

ZnO can be manufactured in a controlled manner to produce nanostructures with a uniform size, distribution and orientation by vapor-phase synthesis, laser ablation, electrochemical method, chemical method, hydrothermal method etc. Hydrothermal method has many advantages when compared to the most common vapor-phase synthesis, such as low-cost, low temperature, scalability and ease handling.

Generally, there are two main steps in ZnO nanostructures growing: (1) preparation of a seed-textured ZnO thin layer and (2) the nanostructures array growth. For the first step atomic layer deposition (ALD) [2], RF sputter deposition [1, 3], sol-gel method [4-10, 12-14] can be applied. Sol-gel technique of the seeds preparation is a low-cost process. Moreover it is attractive due to ability to conveniently synthesize the films with required properties for a given application. The length and diameter of the nanowires are highly dependent on the crystalline properties (i.e., grain size) of the seeding layer films. Typical pre-seeding methods include thermal decomposition of the precursor; spin coating of sol-gel solution and annealing at certain temperature to improve ZnO particles adhesion to the substrate. The type and concentration of precursor, annealing temperature have an obvious influence on the surface structure of ZnO films.

Nowadays there is intensive study of ZnO properties and application in nanotechnology and others fields, but not all problems are solved, such as correlation between growth conditions, geometric parameters and properties of these structures. Solving of these problems allows enhancement of the application in various devices.

In this paper the effects of different conditions of ZnO seed-layer growing by sol-gel method are discussed and critical revive of the recent progress in this field is given.

Effect of the precursor material

It was shown that the morphological features of the sol–gel derived thin films of ZnO depend strongly on the choice of the precursor materials. In general, zinc acetate is the precursor material for preparation of ZnO films using sol–gel process or spray pyrolysis techniques [4, 8]. However, zinc nitrate [13] has also been used for preparation of the seed layer.

The work [6] has shown that the films of ZnO prepared by using zinc nitrate exhibit dendrites while those using zinc acetate are uniform and smooth. As an example, the set of micrographs in

Fig. 1 depict the general character of morphological features as revealed by SEM for the ZnO film grown on a Si substrate by using zinc nitrate as the precursor material. From the micrographs, it appears that the films are patchy and not continuous. There are dendrites with agglomeration in certain areas on the film. This nature of morphology was typical of using zinc nitrate as the starting material.

Figure 2 depicts a typical micrograph obtained for the ZnO film by using zinc acetate as the precursor material. The difference in the morphological features in Fig. 2 may clearly be noticed from those shown in Fig. 1. In the case of use of zinc acetate as the precursor material the morphology of the film is very smooth with no dendrites being formed.

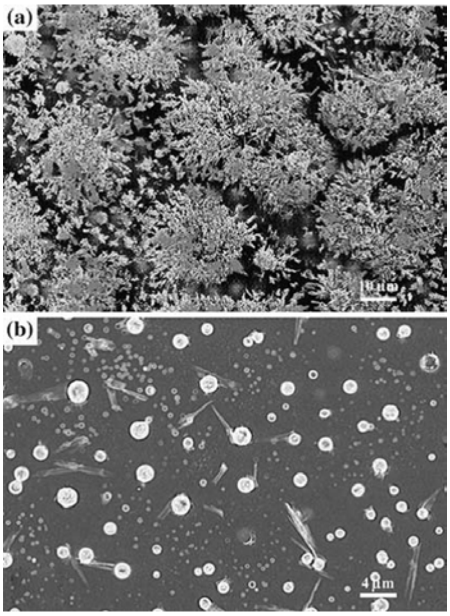

Fig. 1. A set of SEM micrographs showing the dendritic character of morphological features of the ZnO thin film grown on Si substrate by sol–gel spin process using zinc nitrate as the precursor material [9]

Explanations have been offered involving basic chemical processes in the preparation of two types of sols used for growing such films. Zinc nitrate first crystallizes in the form of small crystallites of zinc nitrate followed by decomposition on heating to give small crystallites of zinc oxide. On the other hand, zinc acetate first hydrolyzes followed by the process of condensation, poly-condensation and finally give smooth films of zinc oxide on heating at 450°C.

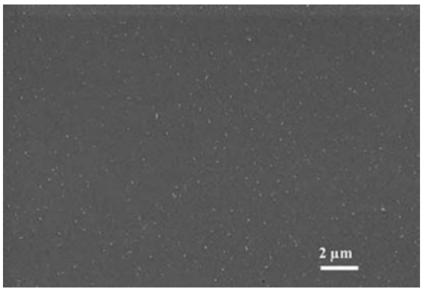

Fig. 2. SEM micrograph showing the smooth character of morphological features of the ZnO thin film grown on Si substrate by sol–gel spin process using zinc acetate as the precursor material [9]

Effect of the sol concentration

Bai et al. [14] presented synthesis of ZnO nanowires by the hydrothermal method, using sol–gel prepared ZnO seed films. Sol concentration was the controlled parameter for the preparation of ZnO seed-layer films.

The textured ZnO seed-layer films were deposited on the Si substrates using the sol–gel method with various sol concentrations ranging from 0.05 to 1.2 M.

It was established that the roughness increased with increasing concentration of precursor until a maximum value of 5.9 nm was obtained. After this point, the roughness decreased as the concentration increased. From the experimental data, it was found that the concentration of precursor affects the surface morphology of the ZnO seedlayer films. The ZnO films with the concentration of precursor of 1.0 M have a larger grain size than those prepared at other concentrations. The larger roughness appears to be due to the larger size of the ZnO grains in the films.

Figure 3 [14] reveals the surface morphologies of ZnO seedlayer films prepared with different concentration of precursor. It is found the grain size increases with increasing of the concentration of precursor. Moreover, from the cross-sectional view of SEM images the SEM data also demonstrate that the thickness of the seed films increases as the concentration of precursor increases. The average thickness of the films with the concentration of precursor of 0.05, 0.1, 0.3, 0.5, 1.0, and 1.2 M are 25, 38, 50, 67, 93, and 136 nm, respectively.

Figure 4 [14] shows the FE-SEM plan and cross-section views of the ZnO nanowires synthesized by the hydrothermal method on Si substrates covered with a ZnO film. The ZnO films were used as the seed layer to assist the growth of the ZnO nanowires. The SEM images illustrate that the length and diameter of the nanowires are highly dependent on the crystalline properties (i.e., grain size) of the seed-layer films. Nanowires with a longer length and wider diameter were grown on seed-layer films with better crystalline characteristics. The SEM images show that the alignment of the nanowires grown on the ZnO film prepared with the concentration of precursor of 1.0 M is significantly better than those prepared on a film with the concentration of precursor of 0.05 M.

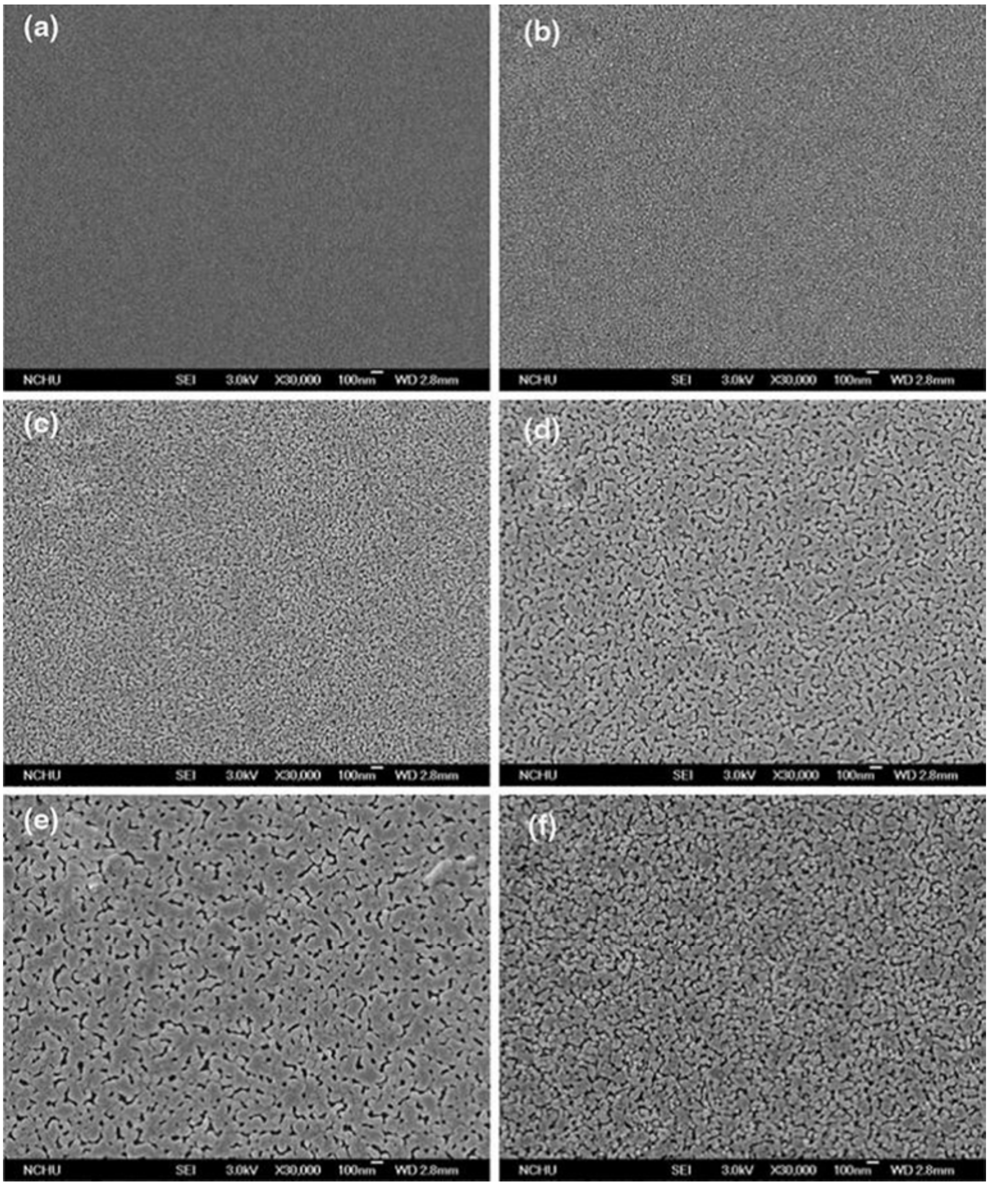

Fig. 3. FE-SEM plan-view images of ZnO seed-layer films prepared with different sol concentrations a 0.05 M, b 0.1 M, c 0.3 M, d 0.5 M, e 1.0 M, f 1.2 M [10]

The estimated length and diameter of the nanowires are 0.8 μm and 78 nm, respectively, for films prepared with the concentration of precursor of 0.05 M; meanwhile, those values are 1.2 μm and 140 nm for films prepared with the concentration of precursor of 1.0 M.

According to the results in studies [5, 9, 12, 14], the concentration of precursor of 1.0 M is the optimum condition for the preparation of ZnO seed-layer films. This allows for highly oriented ZnO nanowires to be grown on a Si, 64° YX $LiNbO_3$, and glass substrate coated with the ZnO films by a sol-gel method.

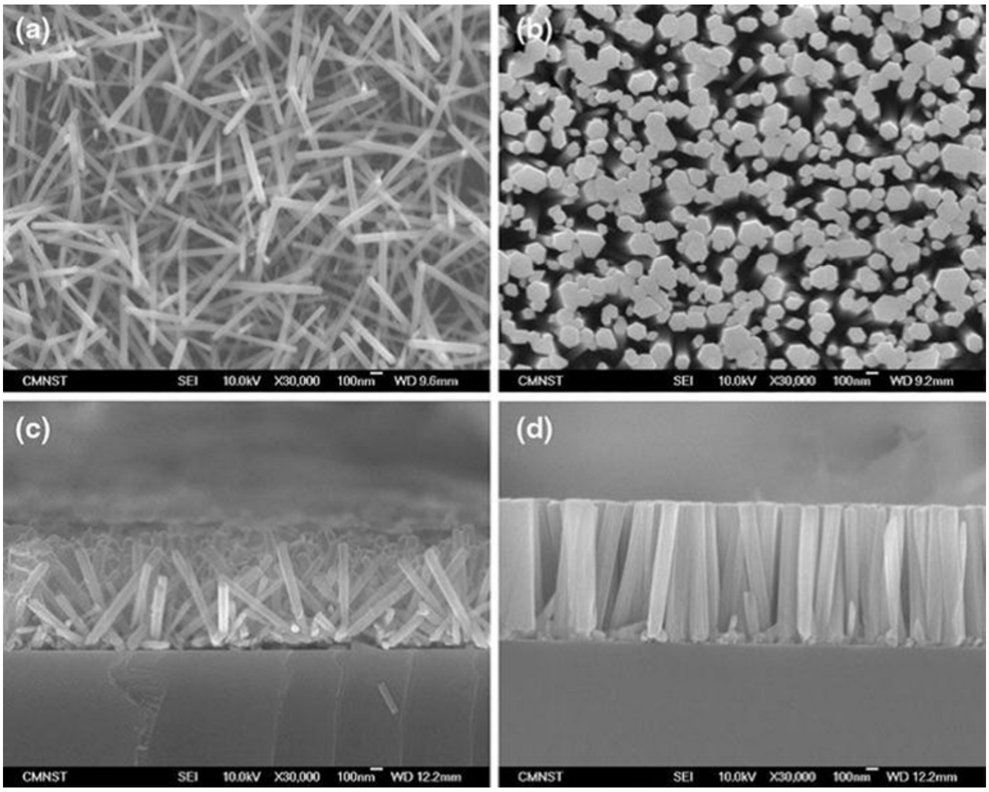

Fig. 4 FE-SEM images of ZnO nanowires synthesized on a Si substrate coated with ZnO seedlayer films. The ZnO films were prepared by the sol–gel method with different sol concentrations a 0.05 M, plan view b 1.0 M, plan view c 0.05 M, crosssection view d 1.0 M, crosssection view [10]

Effect of annealing

The effect of annealing the ZnO thin film at three different temperatures (400°C, 500°C and 600°C) on its structural and optical properties was studied by Nanda Shakti [10]. It was shown that temperature of annealing have effected on properties of the film. Crystallite size of the films was found to be less than 100 nm. The refractive index and extinction coefficient showed some variation with rise in annealing temperature of ZnO film. The Optical energy band gaps gave value of 3.21 eV.

Hiroyo Segawa et al. [7] reported about Low-temperature crystallization of oriented ZnO film using seed layers prepared by sol–gel method.

Table 1. Crystallite size along prominent diffraction planes for ZnO films annealed at 400°C, 500°C and 600°C [14]

Annealing Temperature (°C)	Crystallite Size (in nm) along diffraction planes		
	(100)	(002)	(101)
400	46	38	34
500	46	67	45
600	53	38	54

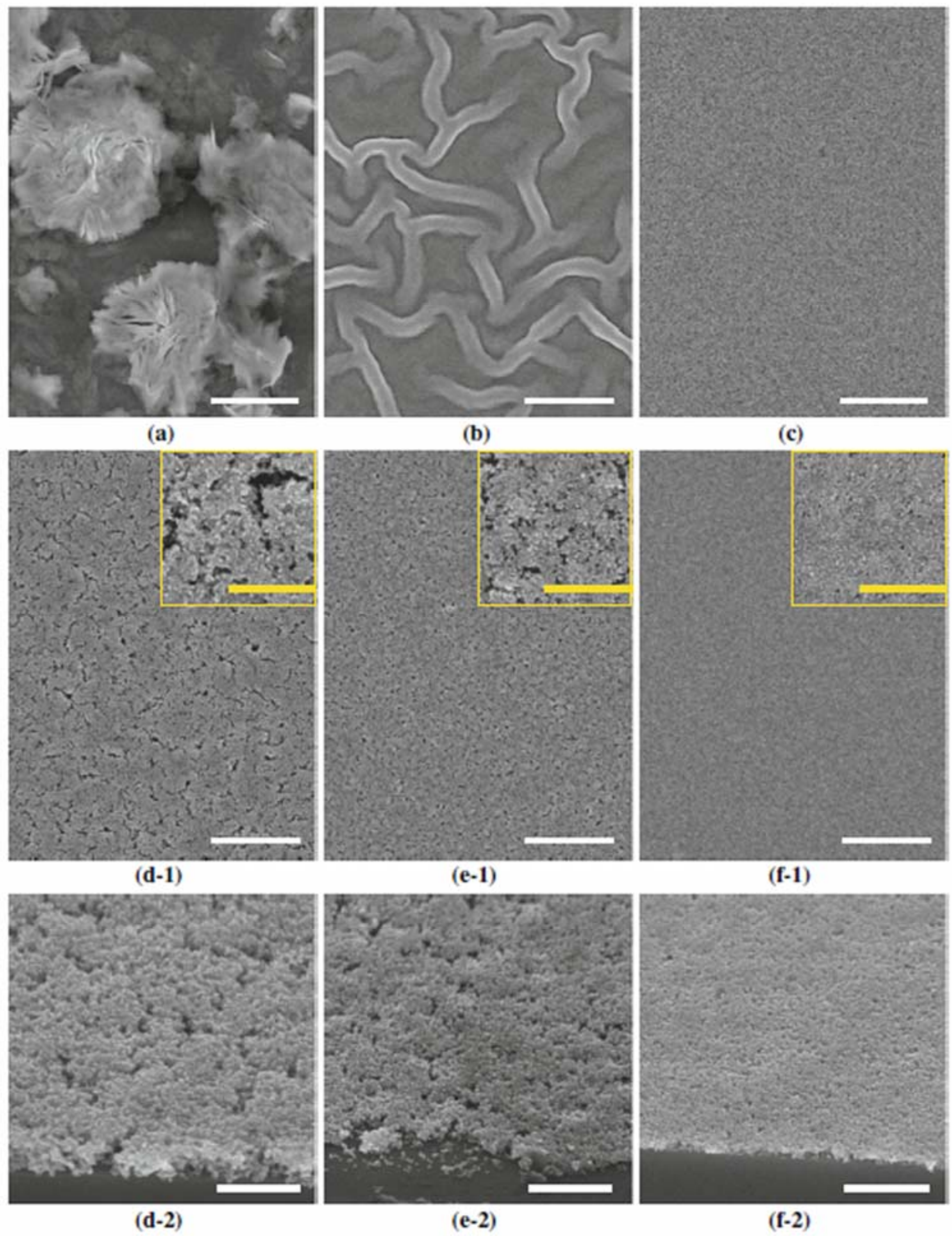

Fig.5. SEM images of seed layers prepared on the hot plate at a 100°C, b 150°C, c 250°C, and those prepared at 100°C in a petri dish from precursors d 1.2 M ZnAc, e 0.5 M ZnAc, and f 0.5 M ZnAcH. The bars are 2 μm, and the bars in the expanded image are 400 nm. d-2, e-2, and f-2 show the 40° images from upper side [15]

These results represented that the transparent and high oriented ZnO films could be coated at temperatures below 100°C, at which ZnO were coated even on plastic substrate such as a poly-propylene, under controlling the morphology and the crystallinity of seed layer.

Conclusion

Almost any substrate can be used for the growth of vertical ZnO nanorods by using ZnO seed-layer film. ZnO nanostructures can be successfully growth on Si, sapphire, glass, paper, LiNbO3. The fabrication procedure for the growth of the nanorods consists generally of two steps: (1) preparation of a seed-textured ZnO thin layer and (2) the nanorod array growth. Sol–gel technique of seed preparation is a lowcost process and is attractive as the film properties can be tailored conveniently for a given application. In general, zinc acetate is the precursor material for preparation of ZnO seeds using sol–gel process. The length and diameter of the nanowires are highly dependent on the crystalline properties (i.e., grain size) of the seed-layer films. The concentration of precursor and annealing temperature have a significant influence on the surface structure of ZnO films. The most appropriate concentration of precursor is 1.0 M and annealing temperature is 300-450°C for seed-layer film ZnO to obtain vertically oriented nanorods ZnO.

References

1. *Ashley D*. Mason, Investigation of Growth Parameter Influence on Hydrothermally Grown ZnO Nanowires Using a Research Grade Microwave / Ashley D. Mason, Tyler F. Roberts, John F. Conley Jr., David T. Price, Derryl D. J. Allman, Michael S. McGuire // Semiconductor Device Research Symposium. – 2009.
2. *Francisco Solis-Pomar*, Growth of vertically aligned ZnO nanorods using textured ZnO films / Francisco Solis-Pomar, Eduardo Martinez, Manuel F Melendrez, Eduardo Perez-Tijerina // Nanoscale Research Letters. – 2011. – 6. – P. 524.
3. *Giri P.K.,* Effect of ZnO seed layer on the catalytic growth of vertically aligned ZnO nanorod arrays / P.K. Giri, Soumen Dhar, Ritun Chakraborty // Materials Chemistry and Physics. – 2010. – 122. – P.18–22.
4. *Guozhi Jia*, Growth mechnism of ZnO nanostructure using chemical bath deposition / Guozhi Jia, Yunfeng Wang, Jianghong Yao // Journal of Ovonic Research. – 2010. – Vol. 6, No. 6. – P. 303-307.
5. *Guozhi Jia*, Fabrication and optical properties of well-aligned zno nanorods on sapphire prepared by chemical bath deposition / Guozhi Jia, Yunfeng Wanga, Jianghong Yao // Digest Journal of Nanomaterials and Biostructures. – 2012. – Vol. 7, No. 1. – P. 261 – 267.
6. *Harish Bahadur*, Morphologies of Sol–Gel Derived Thin Films of ZnO Using Different Precursor Materials and their Nanostructures / Harish Bahadur. A. K. Srivastava .R. K. Sharma. Sudhir Chandra // Nanoscale Res Lett. – 2007. – 2. – P. 469–475.
7. *Hiroyo Segawa*, Low-temperature crystallization of oriented ZnO film using seed layers prepared by sol–gel method / Hiroyo Segawa, Hideaki Sakurai, Reiko Izumi, Toshiharu Hayashi, Tetsuji Yano, Shuichi Shibata // J Mater Sci. – 2011. – P. 46:3537–3543.
8. *Ilican S.,* Preparation and characterization of ZnO thin filmsdeposited by sol-gel spin coating method / S. Ilican, Y. Caglar, M. Caglar // Journal of optoelectronics and advanced materials. – 2008. – Vol. 10, No. 10. – P. 2578 – 2583.
9. *Min-Yeol Choi*, Mechanically Powered Transparent Flexible Charge-Generating Nanodevices with Piezoelectric ZnO Nanorods / Min-Yeol Choi, Dukhyun Choi, Mi-Jin Jin, Insoo Kim, Sang-Hyeob Kim, Jae-Young Choi, Sang Yoon Lee, Jong Min Kim, and Sang-Woo Kim // Adv. Mater. – 2009. – 21. – P. 2185–2189.
10. *Nanda Shakti*, Structural and Optical Properties of Sol-gel Prepared ZnO Thin Film / Nanda Shakti // Applied Physics Research. – 2010. – Vol. 2, No. 1. – P. 19-28.
11. *Ozgur Umit*, ZnO devices and applications: a review of current status and future prospects / Umit Ozgur, Hadis Morkoc // Proceedings of the IEEE 98. – 2010. – 7. – P. 1255-1268.
12. *Sadek Z.*, A ZnO Nanorod Based Layered ZnO/64° YX LiNbO3 SAW Hydrogen Gas Sensor / Z. Sadek, W. Wlodarski, Y. X. Li, W. Yu, X. Li, X. Yu, K. Kalantar-zadeh // Thin solid film. – 2007. – vol. 515. –P. 8705-8708.
13. *Shih-Fong Lee*, A Nanostructural Zinc Oxide Electrode Prepared by a Hydrothermal Method for Dye-Sensitized Solar-Cell Application / Shih-Fong Lee, Li-Ying Lee, Yung-Ping Chang // Journal of Science and Engineering Technology. – 2009. – Vol. 5, No. 3. – P. 13-20.
14. *Shr-Nan Bai*, Synthesis of ZnO nanowires by the hydrothermal method,using sol–gel prepared ZnO seed films / Shr-Nan Bai, Shich-Chuan Wu // J Mater Sci: Mater Electron. – 2011. – 22. – P. 339–344.
15. *Yicheng Lu*, Multifunctional Biosensor Based on Zno Nanostructures / Yicheng Lu // The Journal of the Acoustical Society of America. – American Institute of Physics. – 2012. – V. 131, issue 2. – P. 1667-1667.

УДК 539.21

Параметри росту та якість плівки зародкового шару ZnO (частина 1)

О. В. Богдан, **А.Т. Орлов**, канд. техн. наук, **В.О. Ульянова**

Національний технічний університет України “Київський політехнічний інститут”,

пр. Перемоги, 37, Київ-56, 03056, Україна.

Розглянуто вплив різноманітних умов синтезу на структуру та властивості отриманого за допомогою золь-гель методу зародкового шару ZnO. Показано основні досягнення у галузі синтезу зародкового шару ZnO для створення вертикальних нанострижнів. Встановлено зв’язок між складом, концентрацією золь-гелю і температурою відпалу зародкової плівки та характеристиками зародкового шару для формування високоякісних стрижневих структур ZnO. Бібл. 15, рис. 5, табл.1.

Ключові слова: *зародковий шар ZnO, золь-гель, гексагідрат нітрату цинку, ацетат цинку, температура відпалу.*

УДК 539.21

Параметры роста и качество пленки зародышевого слоя ZnO (часть 1)

А.В. Богдан, **А.Т. Орлов**, канд. техн. наук, **В.А. Ульянова**

Национальный технический университет Украины “Киевский политехнический институт”,

пр. Победы, 37, Киев-56, 03056, Украина.

Рассмотрено влияние различных условий синтеза на структуру и свойства полученного с помощью золь-гель метода зародышевого слоя ZnO. Показаны основные достижения в области синтеза зародышевого слоя ZnO для создания вертикальных наностержней. Установлена связь между составом, концентрацией золь-геля и температурой отжига зародышевой пленки и характеристиками зародышевого слоя для формирования высококачественных стержневых структур ZnO. Библ. 15, рис. 5, табл. .1.

Ключевые слова: *зародышевый слой ZnO, золь-гель, гексагидрат нитрата цинка, ацетат цинка, температура отжига.*

Поступила в редакцию 26 ноября 2012 г.