*Chemistry, Physics and Technology of Surface. 2015. V. 6. N 2. P. 239-243*

*UDC 546.47+546.62+546.21*

**I.V. Dubrovin, P.P. Gorbyk, G.N. Kashin**

# TEMPLATE SYNTHESIS OF NANOSTRUCTURED ZINC OXIDE

*Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine*
*17 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: dilvua@gmail.com*

*The arrays of nanorods of zinc oxide on the template of anodized aluminum oxide have been fabricated by electrochemical decomposition of molecular oxygen in the presence of $Zn^{2+}$. The template was prepared by anodizing Al foil and Al films deposited in vacuum in oxalic acid. The formation of nanorods was confirmed by scanning electron microscopy. The X-ray phase analysis and Auger electron spectroscopy data have confirmed that the structure and composition of the nanorods correspond with those of zinc oxide.*

***Keywords:*** *zinc oxide, nanostructures, nanorods, template synthesis, electrochemical deposition*

## INTRODUCTION

Nanosized structures of zinc oxide enhance potentialities and efficiency of its applications. In particular, nanorods and nanowhiskers are very promising candidates for development of effective light sources and light-emitting elements radiated in the visible, near-UV and IR ranges, and also effective sensors of various organic or non-organic molecules and substances due to geometrical peculiarities of their shapes (specific surface area, concentration of electric field near tips). Additional advantages may be ensured by arranged arrays and matrices of nanosized structures. One way to fabricate such arrays and matrices is a template synthesis on the basis of anodized alumina (AAO) dielectric material produced by anodization of aluminum in liquid electrolyte by passing through electric current. Anodized alumina has a regular porous structure and high electrophysical, mechanical, thermal and unique optical properties. Using anodized alumina is very advantageous due to well-controlled thickness of its layers and the highly ordered arrangement of pores with homogeneous distribution in diameters. The regular cell-pore structure with submicron (down to nanosized) parameters of these templates allows their application for manufacturing structures with quantum nanosized optical and electrical properties. Also, these properties mean that the anodized alumina templates are almost ideal objects for applications in the processes of electrochemical deposition because they allow someone to control quantity of electrical charge passing through the electrolyte. In addition, the process of electrochemical deposition (ED) allows fabrication of objects consisted of metals, conducting polymers, composites and oxide films [1–4].

Researches in composition materials based on porous matrices (of the bulk or thin-film types) with submicron or nanometer pores filled with semiconductor substances are of great scientific and practical interest taking into account the rapid growth of nanotechnologies and possibility to control and improve significantly the properties of such matrices and widen the scope of their applications.

Semiconducting ZnO is of great interest due to its universality and possible applications in piezolectric transducers, polarized light sources, chemical and gas sensors, catalysis and photoelectric power engineering [5–8].

Many researchers have been succeeded in manufacturing ZnO nanowires by the method of electrochemical deposition. In some cases such nanowires had good photoluminescence characteristics [9–14].

One of the principal challenges in the integral optics and sensor engineering that impedes their further progress is the development of promising light sources and light-emitting elements in the visible and near-IR ranges. Another challenge is fabrication of structures with developed surface to improve their adsorbing properties with respect to various organic and non-organic molecules and substances. A promising solution of this challenge

may be the use of nanoparticles or arrays of nanowhiskers manufactured of $A_2B_6$ or $A_3B_5$ semiconductors or their compositions as light-emitting point sources. In this connection the methods of fabrication of light-emitting, adsorbing and one-electron elements on the basis of the regular arrays of semiconducting materials in the pores of anodized alumina matrix is of particular interest.

The electrochemical method ensures the significant advantages as compared with the others as it is cost-effective and does not require the use of complicated equipment.

In this work we developed the procedures of low-temperature synthesis of nanosized rods of zinc oxide by the electrochemical method and investigated the physical and chemical conditions of their formation with the use of the templates made of porous alumina films.

## EXPERIMENTAL PROCEDURE

Glass or single-crystalline silicon substrates with vacuum-evaporated aluminum films of 0.7–2 μm in thickness or high purity aluminum foil substrates were used as specimens. The porous $Al_2O_3$ films with a system of cylindrical pores have been formed in the process of electrochemical etching of aluminum film surface.

The pretreated substrates have been electrochemically anodized in 0.1 M solution of oxalic acid at 23±0.5 °C under the galvanostatic mode of polarization with the anode current density 14.0 mA/cm$^2$ in accordance with the procedure presented in the work [15].

After finishing the anodic treatment the specimens have been chemically etched in 5 % orthophosphoric acid ($H_3PO_4$) at 30 °C for the purpose of opening the oxide barrier layer at the lower side of alumina specimen and obtaining the pores that are open at the both sides.

Zinc oxide was deposited in the pores produced during the previous operation in the $Zn(ClO_4)_2$ solution (the concentration 0.1 mol/l) at of 70–90 °C. The electrolyte was saturated with molecular oxygen by its bubbling in the solution. The deposition potential was about –1.0 V. During the electrolysis the open pores in anodized alumina were filling with zinc oxide due to significant difference in the electrical conductance values of these substances. To obtain the standing nanorods of ZnO we have used two solutions for selective etching: the 5 % solution of NaOH and the buffer borate solution with pH = 9. Five cycles of one minute etching in each solution with subsequent rinsing in deionized water after every dipping were sufficient for partial opening the nanorods of ZnO.

The surface morphology of the porous $Al_2O_3$ specimens has been studied by scanning electron microscopy with a field emission cathode, Leo Ultra 55 FEG SEM (Zeiss). The X-ray structure analysis has been performed with the use of DRON-2 X-ray diffractometer with Cu$K\alpha$ radiation ($\lambda$ = 0.15418 nm).

## RESULTS AND DISCUSSION

The rate of oxide layer growth on the surface of aluminum film has been measured and its value equals 0.05–0.2 μm/min at the concentration of oxalic acid of 0.1–0.3 mol/l. By chemical etching of the specimens the oxide films with pores with diameters statistically distributed in the range of 40–300 nm have been produced. The surface density of pores has been evaluated. With the use of simple statistical calculations the value of $1.0\times10^9$ cm$^{-2}$ has been determined. A SEM micrograph (Fig. 1) shows that a significant number of pores remain closed.

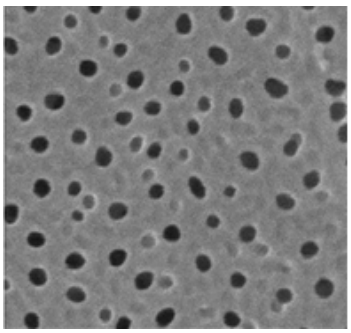

**Fig. 1.** SEM micrograph of the oxide aluminum film on the aluminum foil that was electrochemically polished under the anodizing mode with the current density 14.0 mA/cm$^2$ (the average pore diameter is 70 nm)

A relationship between the deposition rate and the content of zinc perchlorate in the electrolyte has been determined. The electrolysis has been conducted under dc voltage –0.7 V. The rate of zinc oxide deposition changes significantly when the zinc perchlorate content increases. The process rate is at its maximum in 0.1 M solution. After that a decreasing trend for the growth of oxide film has been recorded. Such a trend is due to changes in zinc perchlorate activity when its content increases.

The morphology of specimen surface has been studied by AFM. The recorded micrographs revealed the presence of protuberances of zinc oxide that were randomly distributed along the surface and filled the pores in the anodized alumina matrix (Fig. 2).

The AFM micrographs show that the synthesized nanorods are characterized by a certain spread in sizes. The sizes of projecting crystallites are significantly varied with the process time and the used template configuration.

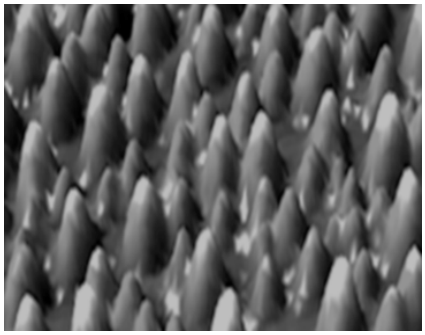

**Fig. 2**. SEM micrograph of ZnO nanorods

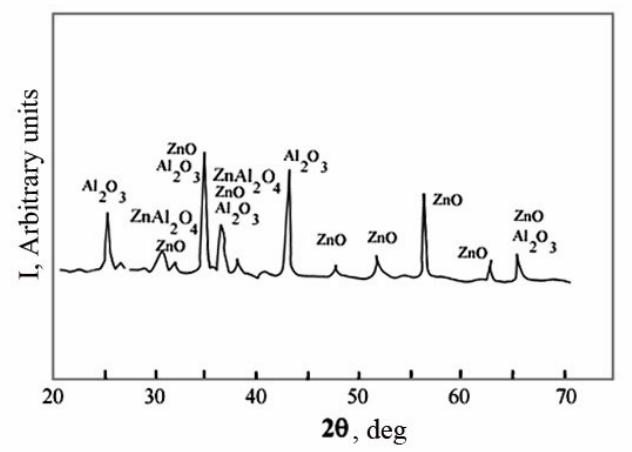


**Fig. 3.** A part of XRD pattern of the surface of the synthesized specimen

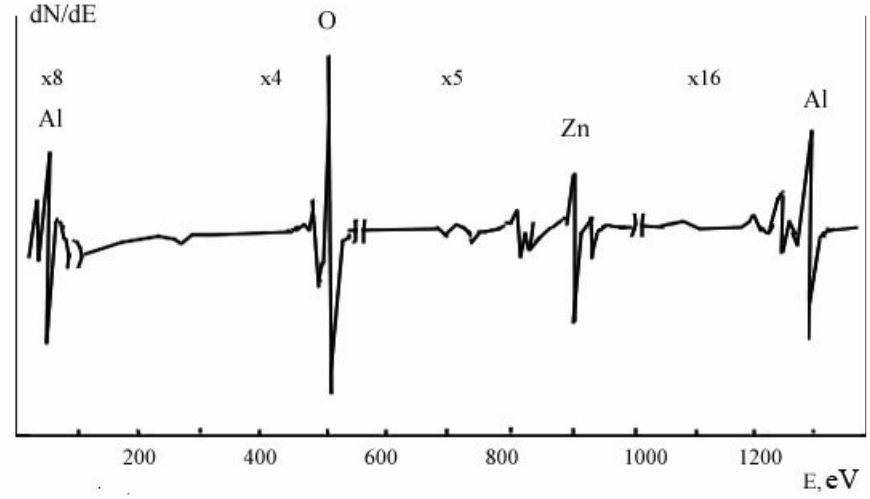


**Fig. 4.** Auger spectrum of the porous alumina film (the matrix) with zinc oxide nanorods grown in the pores

The XRD studies have shown the hexagonal wurtzite structure of synthesized nanorods (Fig. 3) with the unit cell parameters $a = 3.240$ Å, $c = 5.184$ Å which are in accordance with the theoretical values (3.249 and 5.191 Å, respectively). Some discrepancy may be a result of formation of oxygen vacancies and agrees with the XRD data (the reduced unit cell parameters of zinc oxide). The XRD pattern also includes the peaks of aluminum oxide, the matrix component, and a small peak of

the most intensive reflection of zinc aluminate that does not coincide with the peaks of zinc or aluminum oxides.

The presence of all components on the surface of the studied composite material has been confirmed by Auger electron spectroscopy. The film surface and bulk (by $Ar^+$ ion sputtering) compositions have been recorded. The obtained data show correlation between the Al/Zn ratio and the pore density in the anodized alumina matrix.

## CONCLUSION

In summary, we have developed the electrochemical procedure of the template synthesis of zinc oxide nanorods that are randomly distributed in the oxide alumina matrix. The effect of electrolyte concentration on the ZnO crystallization rate has been studied. Also the structure, morphology, phase and element composition of the surface of synthesized composite films as well as their main physical characteristics have been determined.

The composite films of zinc and aluminum oxides manufactured with the use of the proposed procedure are very promising materials for microelectronics, gas sensors, light-emitting diodes and lasers operated in the visible and UV spectral ranges as well as for other optoelectronic devices. Also, the combination of electrical, piezoelectrical, luminescence and adsorbing properties and the possibility of their regulation are of practical interest.

## Темплатний синтез наноструктур оксиду цинку

**І.В. Дубровін, П.П. Горбик, Г.М. Кашин**

*Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України*
*вул. Генерала Наумова, 17, Київ, 03164, Україна, dilvua@gmail.com*

*Електрохімічним розкладанням молекулярного кисню в присутності $Zn^{2+}$ отримані масиви наностержнів оксиду цинку на темплаті з анодного оксиду алюмінію, попередньо отриманого анодуванням в щавлевій кислоті напилених у вакуумі плівок і фольги алюмінію. Утворення наностержнів оксиду цинку доведено методом електронної мікроскопії. Дані рентгенофазового аналізу та Оже- спектроскопії підтвердили, що наностержні мають структуру і елементний склад оксиду цинку.*

***Ключові слова:*** *оксид цинку, наноструктури, наностержні, темплатний синтез, електрохімічне осадження*

## Темплатный синтез наноструктур оксида цинка

**И.В. Дубровин, П.П. Горбик, Г.Н. Кашин**

*Институт химии поверхности им. А.А. Чуйко Национальной академии наук Украины*
*ул. Генерала Наумова, 17, Киев, 03164, Украина, dilvua@gmail.com*

*Электрохимическим разложением молекулярного кислорода в присутствии $Zn^{2+}$ получены массивы наностержней оксида цинка на темплате из анодного оксида алюминия, предварительно полученного анодированием в щавелевой кислоте напыленных в вакууме пленок и фольги алюминия. Образование наностержней оксида цинка доказано методом электронной микроскопии. Данные рентгенофазового анализа и Оже- спектроскопии подтвердили, что наностержни имеют структуру и элементный состав оксида цинка.*

***Ключевые слова:*** *оксид цинка, наноструктуры, наностержни, темплатный синтез, электрохимическое осаждение*

REFERENCES


1. *Possin G., Possin G.E.* Forming very small diameter wires, Rev. Sci. Instrum., 41 (1970) 772.
2. *Granström M., Carlberg J., Inganäs O.* I. Electrically conducting fibers with mesoscopic diameters: Studies of electrical properties and structure, Polymer, 36 (1995) 2867.
3. *Huber C., Huber T., Sadoqi M. et al.* Nanowire array composites, Science, 263 (1994) 800.
4. *Oh J., Tak Y., Lee J.* Electrodeposition of $Cu_2O$ nanowires using nanoporous alumina template, Electrochem. Solid-State Lett., 7 (2004) C27.
5. *Könenkamp R., Word R.C., Schlegel C.* Vertical nanowire light-emitting diode, Appl. Phys. Lett., 85 (2004) 6004.
6. *Nanto H., Minami T.,Takata S.* Zinc oxide thin film ammonia gas sensors with high sensitivity and excellent selectivity, J. Appl. Phys., 60 (1986) 482.
7. *Sarvari M.H., Sharghi H.* Zinc oxide (ZnO) as a new, highly efficient, and reusable catalyst for acylation of alcohols, phenols and amines under solvent free conditions, Tetrahedron, 61 (2005) 10903.
8. *Yoshida T., Minoura H.* Electrochemical self-assembly of dye-modified zinc oxide thin films, Adv. Mater., 12 (2000) 1219.
9. *Wang Q., Wanga G., Xua B. et al.* Non-aqueous cathodic electrodeposition of large-scale uniform ZnO nanowire arrays embedded in anodic alumina membrane, Mater. Lett., 1059 (2005) 1378.
10. *Zheng M.J., Zhang L.D., Li G.H., Shen W.Z.* Fabrication and optical properties of large-scale uniform zinc oxide nanowire arrays by one-step electrochemical deposition technique, Chem. Phys. Lett., 363 (2002) 123.
11. *Lai Min, Jason Riley D.* Mechanism of ZnO nanotube growth by hydrothermal methods on ZnO film-coated Si substrates, Chem. Mater., 18 (2006) 2233.
12. *Leprince–Wang B.Y., Yacoubi-Ouslim A., Wang G.Y.* Structure study of electrodeposited ZnO nanowires, Microelectron. J., 36 (2005) 625.
13. *Yuldashev Sh.U., Woo Choi S., Won Kang T., Nosova L.A.* Growth of ZnO nanowires by electrochemical deposition into porous alumina on silicon substrates, J. Korean Phys. Soc., 42 (2003) S216.
14. *Leprince–Wang Y., Wang G.Y., Zhang X.Z., Yu D.P.* Persistent *n*-type photoconductivity in *p*-type ZnO, J. Cryst. Growth, 287 (2006) 89.
15. *Green S., Badan J. A., Gilles M. et al.* Optical properties of nanoporous $Al_2O_3$ obtained by aluminium anodization, Phys. Stat. Sol. (c), 4 (2007) 618.


*Received 16.09.2014, accepted 23.04.2015*