НАНОТЕХНОЛОГИИ, НАНОСТРУКТУРЫ, КВАНТОВЫЕ ЯВЛЕНИЯ. НАНОЭЛЕКТРОНИКА. ПРИБОРЫ НА КВАНТОВЫХ ЭФФЕКТАХ

IMPACT OF THE ELECTROLYTE AND ELECTROCHEMICAL PARAMETERS UPON THE MORPHOLOGY OF ANODIZED ZINC OXIDE

E. V. Monaico[1], **G. V. Colibaba**[2]

[1] National Center for Materials Study and Testing, Technical University of Moldova,
Bd. Stefan cel Mare 168, MD-2004, Chisinau, Republic of Moldova
[2] Moldova State University, str. A. Mateevici 60, Chisinau MD-2009, Republic of Moldova
Corresponding author: E. V. Monaico (eduard.monaico@cnstm.utm.md)

The influence of the nature of used electrolyte as well as the applied potential in the anodization process of polar ZnO crystals were studied. Micro- and nanostructures obtained by electrochemical etching of O-face ZnO crystals were investigated by scanning electron microscopy. The morphology selectivity depending on the nature of the electrolyte was demonstrated. For the firs time, a columnar ZnO nanostructures obtained be electrochemical etching was reported. The transversal dimensions and their density depend on applied anodization potential. The obtained results will give the possibility for development of semiconductor nanotemplates based on anodized ZnO crystals.

Key words: zinc oxide; anodization; morphology; pyramidal structures, porous, current-voltage curves.

INTRODUCTION

Nowadays, for many concrete applications in electronics, photonics, sensors, the materials and devices at the nano-scale are indispensable. The nanotechnology offers the possibilities to obtain nanomaterials with different morphologies and aspect ratio leading to improved or even completely new material properties due to the high surface aria to volume ratio [1]. Zinc oxide (ZnO) is a direct bandgap semiconductor compound (E_g = 3.37 eV at T = 300 K) and is intensively studied during the last two decades due to its wide band gap, high bond energy (60 meV), high mechanical and thermal stability at room temperatures which make it a perfect candidate for applications in electronics and optoelectronics [2]. A versatile of nanostructures obtained by different deposition approaches was reported [3-6]. The ZnO nanostructures are obtained via bottom-up approaches in which high temperatures, sophisticated electrolytes, activation of the surface leading to the contamination are used.

During the last three decades it was demonstrated that electrochemical etching represents a cost-effective and simple technology for nanostructuring of III-V and II-VI semiconductor compounds in a controlled fashion [7]. Moreover, the environmentally-friendly electrochemical nanostructuring of InP [8], CdSe [9], GaAs [9], and GaN [10] in NaCl-based neutral electrolyte was demonstrated. The electrochemical nanostructuring of ZnO is less studied due to its low chemical stability. Despite this, attempts for nanostructuring of

ZnO on O-face and Zn-face via anodization were reported recently [11]. Accordingly to the reported data, the anodization behavior is different on anodized O-face and Zn-face of polar ZnO. The obtained morphologies are characterized by micro- and nanostructures of pyramidal form on the O-face, and inversed pyramids or tunnels on Zn-face exhibiting a significant enhancement of light emission in the prepared nanostructures. To mention that the form of produced structures corroborates with reported data of wet chemical etching of polar ZnO [12, 13]. The dependence of the morphology from the anodized polar surface also was reported for anodized HVPE grown free-standing GaN substrates [14] and (111) oriented GaAs substrates [9].

The goal of this paper was to investigate the dependence of obtained morphology of anodized ZnO crystals on O-face in different electrolytes and to optimize the applied voltage. A systematic investigation of the morphology and chemical composition were performed by means of scanning electron microscopy.

MATERIALS AND METHODS

ZnO crystals having a hexagonal structure of wurtzite type were grown by chemical vapor transport technique. H_2 (2 atm) + HCl (2 atm) gas mixture was used as a transport agent, growth temperature was 1020 °C, and undercooling was about 50 °C [15]. A post-growth annealing in air at 1000 °C was performed to reduce Zn excess in the grown crystals. This annealing decreases the concentration of intrinsic donor defects (oxygen vacancies and interstitial zinc), and increases the transparency of crystals in a visible spectral range. The concentration of free electrons, estimated from Hall effect measurement, was 3×10^{18} cm^{-3}, as reported in [16]. The grown crystals were cut into plates with 1 mm thickness, which were polished with 1 μm diamond paste. These polished plates were etched in an HCl aqueous solution and annealed in air to decrease a damaged layer generated by polishing. The *c* axis of the hexagonal structure was oriented perpendicularly to the plate surface, hence the investigated surface corresponded to $[000\bar{1}]$ (O-face) planes in all cases. The type of the surface was determined by the shape of etch pits, as presented elsewhere.

Anodization of the O-face was carried out in 5% HCl, 1M HNO_3, and $K_2Cr_2O_7$ (1g $K_2Cr_2O_7$:10 ml H_2SO_4:100 ml H_2O) aqueous solutions for 2 min, in a potentiostatic mode, under different applied voltages selected based on I-V curves. The anodization of ZnO crystals was carried out in a common two-electrode cell, where the sample served as working electrode as described elsewhere [17]. Briefly, an electrical contact with a conductive silver paste was made on the backside of the samples. From the top side, the sample was pressed by an O-ring to leave a surface with an area of 0.15 cm^2 exposed to the electrolyte. A mesh with the surface of 6 cm^2 from platinum wire with 0.5 mm diameter was used as counter electrode. All experiments were performed inside a fume hood at room temperature. A Keithley's Series 2400 Source Measure Unit was used as potentiostat.

A Vega Tescan 5130 MM Scanning Electron Microscope (SEM) equipped with an Oxford Instruments INCA Energy EDX system operated at 20 kV was used to investigate the morphology of anodized ZnO crystals.

RESULTS AND DISCUSSION

Figure 1*a* shows the current-voltage (I–V) curves of the electrochemical dissolution behaviors of O-face ZnO crystals in HCl, HNO_3 and $K_2Cr_2O_7$ electrolytes. The behavior of polarization curves in HCl and HNO_3 electrolytes is practically the same. At the beginning of anodization, a very low anodic current level flow through the sample till the potential

4 V is reached. In this interval the applied potentials are slower than pore formation potential. With further increase of the applied voltages an exponential increase of the current can be observed reaching a plateau at 8 V in the case of HNO_3 electrolyte.

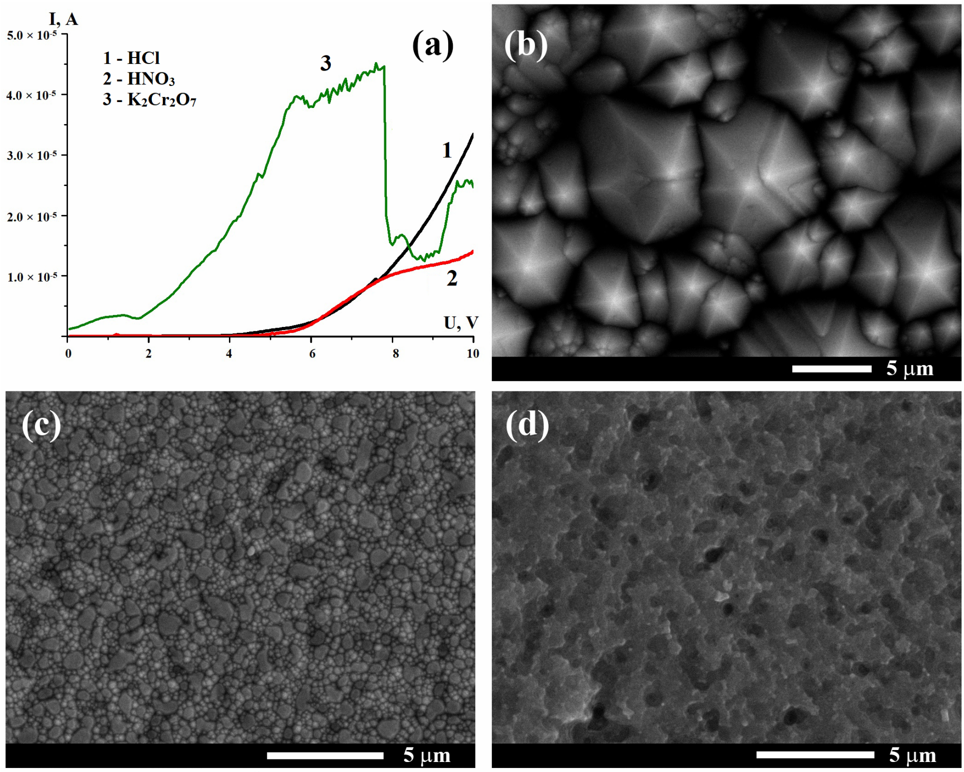
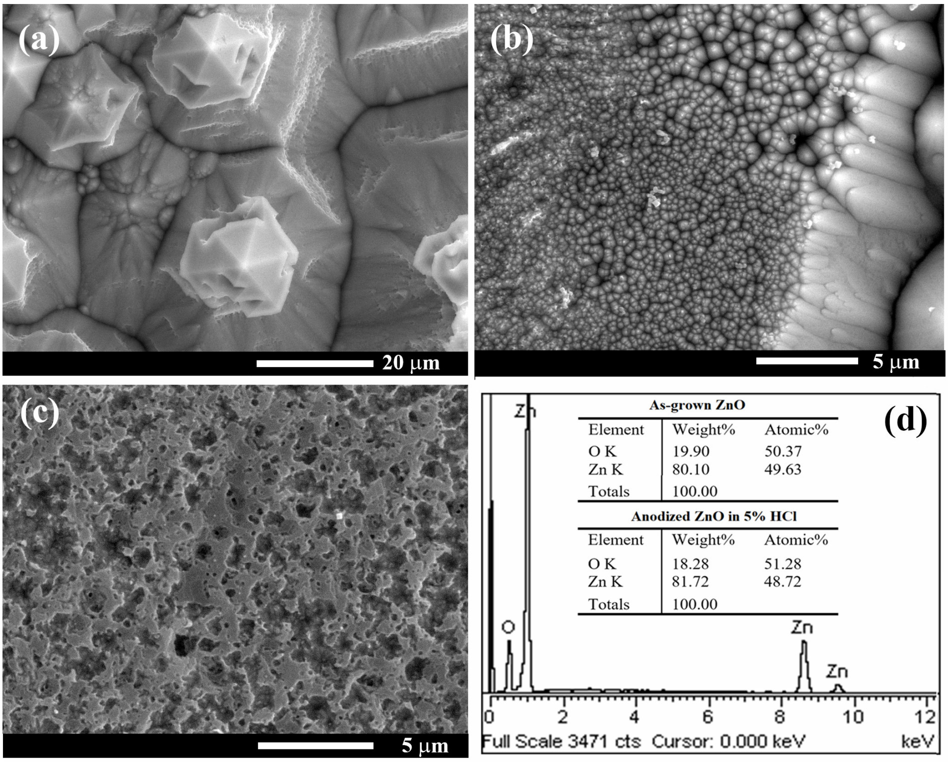


Figure 1. (*a*) The polarization curves measured with a slope 10 mV·s^{-1} at the beginning of the electrochemical anodization of ZnO substrates on O-faces in different electrolytes. SEM images of anodized O-face ZnO crystals in HCl (*b*), HNO_3 (*c*) and $K_2Cr_2O_7$ (*d*) electrolytes at applied potential of 5 V

The situation is quite different for $K_2Cr_2O_7$ electrolyte, where a small current is registered at the beginning of the I-V curve. One can see that with applied low voltages current increase reaching a maximum value at nearly 8 V, the further decrease of the current after the peak is usually explained by the oxide formation making difficult the current flow. At a certain threshold voltage, a reduction of oxide occurs leading to an increase of current. This behavior is characteristic for another III-V and II-VI semiconductor compounds, e.g. InP [8], GaAs [9], CdSe [18]. It is proposed that the anodization of ZnO in a strong oxidizing media can occurs via the following chemical reaction $K_2Cr_2O_7 + ZnO = Zn(Cr_2O_7) + K_2O$. At higher anodization potentials an isotropic electrochemical polishing of ZnO substrates was observed.

For anodization the potentials of 5 V and 8 V was chosen based on the results from the I–V curves and to compare the obtained results with early reported data of anodization in HCl electrolyte [11]. As can see from the Figure 1*b*, the anodization at 5 V in HCl electrolyte results in formation of microstructures consisting from hexagonal pyramids with a base of 1–5 µm. Anodization in HNO_3 electrolyte results in morphology with submicrometric islands as can be seen from Figure 1, *c*, while a sponge like morphology is obtained at anodization in $K_2Cr_2O_7$ electrolyte (Figure 1, *d*).

To mention that applied voltage 5 V is close to the pore formation potential estimated at about 3.3 V. In order to investigate the evolution of the morphology at higher applied voltage, the anodization was performed at 8 V. One can see from Figure 2, *a* that the large hexagonal pyramids with a base 10–20 μm are formed for anodization in HCl electrolyte. The obtained results corroborate with previously published results [11]. It is well known that the nature of electrolyte attacks the semiconductor crystals surface in a different way. In our case, the anodization in HNO_3 electrolyte substantially change the obtained morphology. As can be seen from Figure 2, *b*, a columnar morphology is observed rather than hexagonal pyramids, and is reported for the first time for electrochemical etching of ZnO. The ZnO columns possess a diameter from 400 nm up to 1–2 μm and a length about 5 μm as was estimated from the SEM images. At the same time, no essential changes in the morphology occurs during the anodization in $K_2Cr_2O_7$ electrolyte. An increase of etching pits and density of pores at anodization potential 8 V can be observed in Figure 2, *c*. The elemental chemical composition analysis performed before and after electrochemical etching demonstrated stoichiometric composition of the nanostructured ZnO crystals (see Figure 2, *d*).



As-grown ZnO

Element	Weight%	Atomic%
O K	19.90	50.37
Zn K	80.10	49.63
Totals	100.00	

Anodized ZnO in 5% HCl

Element	Weight%	Atomic%
O K	18.28	51.28
Zn K	81.72	48.72
Totals	100.00	

Figure 2. SEM images of anodized O-face ZnO crystals in HCl (*a*), HNO_3 (*b*) and $K_2Cr_2O_7$ (*c*) electrolytes at applied potential of 8 V. (*d*) EDX spectrum and elemental analysis for the as-grown and anodized in HCl electrolyte O-face ZnO crystal

In contrast to O-face, our preliminary results of anodization on Zn-face demonstrated no to strong influence of the nature of electrolyte upon the obtained morphology demonstrating porous structure like in Figure 2, *c*. Beside this, the formation of hexagonal tunnels, their growth and dissolution at the same time was observed. A further optimization of the electrolyte concentration will be performed for the porous morphology optimization.

CONCLUSIONS

The micro- and nanostructures with controlled morphology of anodized O-face ZnO is demonstrated in a controlled fashion via cost effective and simple technology. As was demonstrated, the nature of electrolyte strongly influences the shape of obtained ZnO nanostructures, while the applied anodization voltage influences their geometrical dimensions and nucleation density. For the fist time, a columnar morphology obtained by electrochemical etching in HNO_3 electrolyte was reported. The preliminary results of anodization on Zn-face ZnO showed not so strong influence of the electrolyte upon morphology. In all three electrolytes the hexagonal tunnels were obtained with their subsequentially dissolution. The further optimization of the electrolyte concentration will be performed. The chemical composition analysis demonstrated stochiometric composition of the nanostructured ZnO. An enlargement of the surface after anodization of the ZnO crystals will give the possibilities to increase the area of their application in gas sensors, optoelectronic and photovoltaic.

FUNDING

The authors acknowledge financial support from the Ministry of Education, Culture and Research of Moldova under the Grants #20.80009.5007.16 “Photosensitizers for applications in pharmaceutical medicine and photovoltaics” and #22.80013.5007.4BL “Nano- and hetero-structures based on zinc oxide and A3B5 compounds for optoelectronics, photonics and biosensorics”. E.M. acknowledge financial support for his postdoctoral grant #21.00208.5007.15/PD “Micro- and nano-engineering of semiconductor compounds based on electrochemical technologies for electronic and photonic applications”.

REFERENCES

1. Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations / J. Jeevanandam [et al.] // Beilstein journal of nanotechnology.— 2018.— V. 9. P. 1050–1074. Doi: https://doi.org/10.3762/bjnano.9.98.
2. A review on ZnO: Fundamental properties and applications / D.K. Sharma [et al.] // Materials Today: Proceedings. —2022.— V. 49.— P. 3028–3035. Doi: https://doi.org/10.1016/j.matpr.2020.10.238.
3. The effect of zinc nitrate, zinc acetate and zinc chloride precursors on investigation of structural and optical properties of ZnO thin films / E. Bacaksiz [et al.] // Alloy. Compd.— 2008.— V. 466.— P. 447–450. Doi: https://doi.org/10.1016/j.jallcom.2007.11.061.
4. Synthesis and characterization of multipod, flower-like, and shuttle-like ZnO frameworks in ionic liquids / J. Wang [et al.] // Mater. Lett. 2005. — Vol. 59. — P. 1405–1408. Doi: https://doi.org/10.1016/j.matlet.2004.11.062.
5. Splendid one-dimensional nanostructures of zinc oxide: A new nanomaterial family for nanotechnology / Wang Z.L. // ACS Nano.– 2008.– V. 2.– P. 1987–1992. Doi: https://doi.org/10.1021/nn800631r.
6. Zinc Oxide-From Synthesis to Application: A Review / A. Kołodziejczak-Radzimska, T. Jesionowski // Materials. — 2014. — V. 7. — P. 2833–2881. doi: https://doi.org/10.3390/ma7042833.
7. Porous semiconductor compounds / E. Monaico, I. Tiginyanu, V. Ursaki // Semicond. Sci. Technol. — 2020. — 35. — 103001 (63 pp.). Doi: https://doi.org/10.1088/1361-6641/ab9477.
8. Ordered arrays of metal nanotubes in semiconductor envelope / I. Tiginyanu, El. Monaico, Ed. Monaico // Electrochem. Comm. — 2008. — V.10. — P. 731–734. Doi: https://doi.org/10.1016/j.elecom.2008.02.02.

9. Electrochemical nanostructuring of (111) oriented GaAs crystals: from porous structures to nanowires / E.I. Monaico [et al.] // Beilstein J. Nanotechnol. — 2020. — V. 11. — P. 966–975. Doi: https://doi.org/10.3762/bjnano.11.81.
10. Towards uniform electrochemical porosification of bulk HVPE-grown GaN / Ed. Monaico [et al.] // Journal of the Electrochem, Soc.— 2019.— V. 166, № 5. — P. H1–H8. Doi: https://doi.org/10.1149/2.0251905jes.
11. Enhanced emission properties of anodized polar ZnO crystals / V. Zalamai [et al.] // Journal of Surface Engineering and Applied Electrochemistry.— 2021.— V. 57, № 1.— P. 117–123. Doi: https://doi.org/10.3103/S1068375521010166.
12. Formation of Hexagonal Pyramids and Pits on V-/VI-Polar and III-/II-Polar GaN/ZnO Surfaces by Wet Etching / S.-Ch. Han [et al.] // J. Electrochem. Soc.— 2010.— V. 157.— P. D60–D64. Doi: https://doi.org/10.1149/1.3253564.
13. Controlled Etching Behavior of O-Polar and Zn-Polar ZnO Single Crystals / M. Mehta, C. Meier // J. Electrochem. Soc. — 2011. —V. 158.— P. H119–H123. Doi: https://doi.org/10.1149/1.3519999.
14. Self-organized three-dimensional nanostructured architectures in bulk GaN generated by spatial modulation of doping. I. Tiginyanu [et al.] // ECS Journal of Solid State Science and Technology. — 2016. — V. 5, № 5. — P. 218-227. Doi: https://doi.org/10.1149/2.0091605jss.
15. Halide-hydrogen vapor transport for growth of ZnO single crystals with controllable electrical parameters / G.V. Colibaba // Mater. Sci. Semicond. Process. — 2016. — V. 43. — P. 75–81. Doi: http://dx.doi.org/10.1016/j.mssp.2015.12.005.
16. Effects of impurity band in heavily doped ZnO:HCl / G.V. Colibaba [et al.] // Physica B: Condens. Matt. — 2019. — V. 553. — P. 174–181. Doi: https://doi.org/10.1016/j.physb.2018.10.031.
17. Evolution of pore growth in GaAs in transitory anodization regime from one applied voltage to another one / E.I. Monaico [et al.] // Journal of Surface Engineering and Applied Electrochemistry.— 2021.— V. 57, № 2. — P. 165–172. Doi: https://doi.org/10.3103/S106837552102006X.
18. Pore Etching in III-V and II-VI Semiconductor Compounds in Neutral Electrolyte / I.M. Tiginyanu [et al.] // Electrochem. Solid-State Lett. — 2007. — V. 10, № 11. — P. D127–D129. Doi: https://doi.org/10.1149/1.2771076.

FABRICATION OF DIAMETER MODULATED GALLIUM ARSENIDE NANOWIRES VIA ANODIZATION

E. I. Monaico

National Center for Materials Study and Testing, Technical University of Moldova,
Bd. Stefan cel Mare 168, MD-2004, Chisinau, Republic of Moldova
Corresponding author: E. I. Monaico (elena.monaico@cnstm.utm.md)

In this paper, the technological approach for diameter modulated GaAs nanowires fabrication via electrochemical etching representing simple and cost-effective technology is demonstrated. At optimized applied potential, in the same technological process, the growth of GaAs nanowires oriented perpendicular to the crystal surface occurs. At the same time, simultaneously growing tilted pores penetrate the nanowires resulting in modulation of nanowires along the whole length. In 40 min of anodization the as long as 200 μm nanowires were obtained. A selective modulation of nanowires via anodization at two different applied potentials is demonstrated. The tree-dimensional modulation of diameter will give the possibility to increase the area of their applications.

Key words: gallium arsenide; porous GaAs; electrochemical etching; morphology; current line oriented pores; perforated nanowires.