18th INTERNATIONAL MULTIDISCIPLINARY SCIENTIFIC GEOCONFERENCE SGEM 2018

CONFERENCE PROCEEDINGS

VOLUME 18

Nano, Bio, Green and Space - Technologies for a Sustainable Future

Issue: 6.1

MICRO AND NANO TECHNOLOGIES
SPACE TECHNOLOGIES AND PLANETARY SCIENCE

18th INTERNATIONAL MULTIDISCIPLINARY SCIENTIFIC GEOCONFERENCE SGEM2018

CONFERENCE PROCEEDINGS
VOLUME 18

NANO, BIO AND GREEN – TECHNOLOGIES
FOR A SUSTAINABLE FUTURE
ISSUE 6.1

- - - - - - - - - - - - - - - - - -

MICRO AND NANO TECHNOLOGIES,

SPACE TECHNOLOGIES AND PLANETARY SCIENCE

- - - - - - - - - - - - - - - - - -

2 July - 8 July, 2018
Albena, Bulgaria

CONFERENCE PROCEEDINGS CONTENTS

MICRO AND NANO TECHNOLOGIES

ELECTROCHEMICAL ETCHING OF P-TYPE GALLIUM PHOSPHIDE

Dr. Gauhar Mussabek [1,2]

Dana Yermukhamed [1]

Saniya Sarsembek[1]

Kazakhbay Almasuly[1]

Dr. Vladimir Sivakov[3]

[1] al-Farabi Kazakh National University, **Kazakhstan**

[2] National Research Nuclear University "MEPhI", **Russia**

[3] Leibniz Institute of Photonic Technology, **Germany**

ABSTRACT

Gallium phosphide is a semiconductor material of great interest for new LED technologies. Porous $A^{III}B^{V}$ are of great interest because of their interesting optical properties different of those for bulk material. The main goal of this research work is to obtain nanostructured porous gallium phosphide (por-GaP) layers by electrochemical etching of the monocrystalline (100) p-type GaP substrate surface. The structure and surface morphology of obtained samples were studied by scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman spectroscopy. The chemical composition of nanostructured GaP surfaces was studied by Energy Dispersive X-Ray (EDX) spectroscopy. It was found that shape and size of structures is strongly depending on electrochemical etching conditions. At constant applied voltage and varied current we observe that the pore size is increasing from 10 microns to 50 microns, and at fixed current, but varying the voltage the pore diameters can be achieved in the range between 100 to 200 nanometers.

Keywords: gallium phosphide, porous structure, electrochemical etching, SEM, AFM.

INTRODUCTION

Due to their unique physical and chemical properties, semiconductor nanomaterials include a wide range of applications [1-5]. Among modern electronic device technologies LED is one of the fast growing in the world [6]. Gallium phosphide and related nanomaterials are of great interest as a research object for modern LED technologies [7]. Porous gallium phosphide (por-GaP) is a very promising material for various photonic applications [8]. The first reports on por-GaP obtaining and characterization are referred since 1990s [9]. One of the most effective ways of obtaining porous structure from the $A^{III}B^{V}$ materials is electrochemical etching [10]. The advantages of the method are good process controllability and relative cheapness. By changing the parameters of electrochemical etching, such as current density, voltage and duration of etching, one can obtain porous structures of different morphology [11]. However, in most of reports there are description of n-type por-GaP, and the less is for p-type ones [12, 13]. Present paper is devoted for investigation of formation features of p-type por-GaP layers and its structure.

EXPERIMENTAL

Porous GaP films were obtained by electrochemical etching of the single cry... (100) oriented, p-type GaP substrate surface using electolyte containing the m... ethanol (C_2H_5OH) and 40% hydrofluoric acid (HF), taken in a volume ratio ... Electrochemical etching was carried out in a fluoroplastic etching cell cell. ... experiments applied voltage was varied from 30 to 65 V, current - from 1 to 10 mA ... etching time – between 10-40 minutes. *Figure 1* shows the schematic represent... experimental electrochemical etching process.

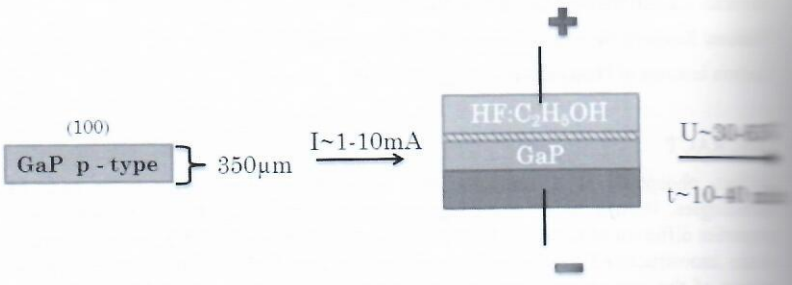


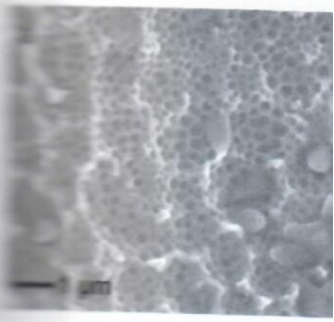
Figure 1. Schematically representation of electrochemical etching process of the surface of GaP substrate.

The structure and morphology of obtained samples were studied by SEM ... ULTRA 55 FE-SEM (Carl Zeiss) microscope, AFM measurements were provided ... Integra Spectra (NT-MDT). Raman spectra of samples were measured on ... Spectrum (NT-MDT), excitation wavelength 473 nm, acquisition time was 3... diameter of laser spot was 2μm. The chemical composition of obtained surfaces was ... studied by Energy Dispersive X-Ray (EDX) spectroscopy. Energy-dispersive X-ray ... spectra of samples were measured using the Bruker Quantax Flatquad. Raman ... spectroscopy measurements were carried out in air at room temperature.

RESULTS AND DISSCUSSION

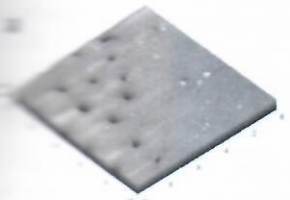
The process of porosity correlates directly with voltage, current density and etching ... time. One of the aims of our experimental study was to find up the optimal ... technological conditions of electrochemical etching for porous structures formation. The ... top view SEM images of por-GaP samples, obtained under different modes of ... electrochemical etching are shown in *Figure 2a and 2b*. One can see that the structural ... properties of por-GaP layers are directly depend on the parameters of electrochemical ... etching. It is experimentally shown that the formation of a uniform porosity on the ... surface is observed when the etching voltage is greater than 50 V. In this case, the ... surface structure of the samples is uniformly flat, and pore size are almost the same. The ... sample shown in *Fig. 2a* pores sizes varied from 10 to 100 nm, thus structure could be ... considered as a nanoporous material. In addition, structure shown in *Fig. 2b* has mac...

... structure with pore sizes varied ... structure of samples obtained under l... This phenomenon can obviously be e... under the influence of electromagne... dissolution of material in one (see *Fig.*



... 2. A top view SEM images of ... etching under: (a) U = 65 V, I = 10 mA

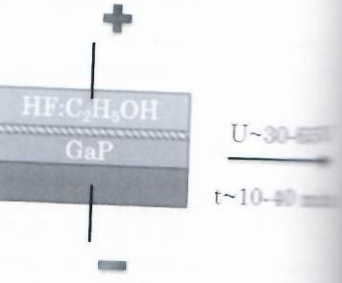
... surface morphology was also studi... allowed us to observe the pores size dis... top view AFM images of the por-GaP o... measurements are shown in *Figure 3a and ...* ... were flattened after electrochemical ... surface of the sample is easily polished. ... the oxidizing currents densities up to 5... time up to 30 minutes.



... 3. AFM images of por-GaP surfac... at U = 30 V, I = 5 mA, t = 25 min

... doi.org/10.5593/sgem2018/6.1

nical etching of the single crystalline
ng electolyte containing the mixture of
(HF), taken in a volume ratio of 1:1
fluoroplastic etching cell cell. In our
to 65 V, current - from 1 to 10 mA and
shows the schematic representation of



rochemical etching process of the
strate.

les were studied by SEM using an
FM measurements were provided on
samples were measured on Solver
3 nm, acquisition time was 30 s.
mposition of obtained surfaces was
ctroscopy. Energy-dispersive X-ray
Bruker Quantax Flatquad. Raman
t room temperature.

oltage, current density and etching
udy was to find up the optimal
for porous structures formation. The
tained under different modes of
2b. One can see that the structure
the parameters of electrochemical
tion of a uniform porosity on the
eater than 50 V. In this case, the
pore size are almost the same. For
to 100 nm, thus structure could be
ucture shown in *Fig. 2b* has more

lose structure with pore sizes varied from 200 nm to 40 μm. It is clear that the surface structure of samples obtained under low voltage and current intensity is non-uniform. This phenomenon can obviously be explained due to the different rate of dissolution under the influence of electromagnetic fields of different powers, which leads to dissolution of material in one (see *Fig. 2a*) or several directions (see *Fig. 2b*).

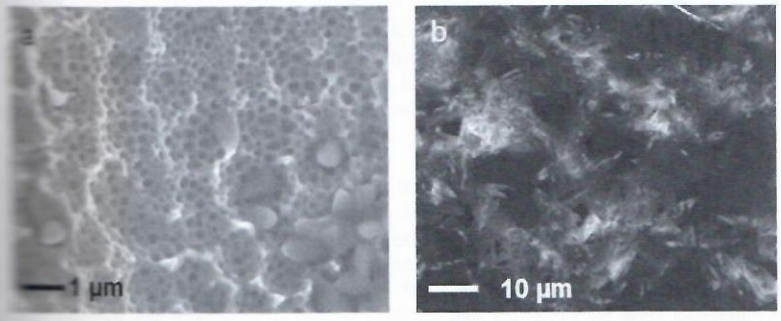


Figure 2. A top view SEM images of por-GaP surface obtained by electrochemical etching under: (a) U = 65 V, I = 10 mA, t = 15 min and (b) U = 30 V, I = 7 mA, t = 17 min.

The surface morphology was also studied by atomic force microscopy (AFM) which allowed us to observe the pores size distribution on the surface of por-GaP layers. The top view AFM images of the por-GaP obtained under different electrochemical etching parameters are shown in *Figure 3a and 3b*. It is notable that the surface of porous layers becomes flattened after electrochemical treatment. When the etching time is longer, the surface of the sample is easily polished. The lightly polishing effect can be reached at low anodizing currents densities up to 5 mA/cm^2, voltages up to 40 V and the etching time up to 30 minutes.

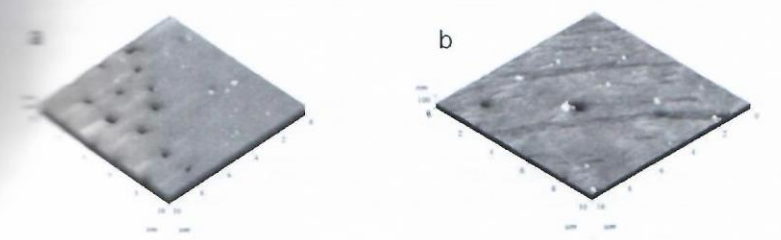


Figure 3. AFM images of por-GaP surface obtained by electrochemical etching under: a. U = 30 V, I = 5 mA, t = 25 min and (b) U = 40 V, I = 1 mA, t = 60 min.

The method of energy-dispersive X-ray spectroscopy was used in order to identify the elemental composition of samples. As shown in *Figure 4*, the basic element of the por-GaP is mainly gallium. The reason of such appearance is in the faster dissolution rate of phosphorus atoms rather the gallium ones. Since the initial substrate of crystalline p-type GaP is doped by Zn, there is also a signal of Zn appeared in EDX spectra. One can see that formation of pores during electrochemical etching process is mainly due to dissolution of phosphorus in electrolyte. Broken bonds of Ga are passivized by oxygen. Thus por-GaP walls separating the pores are formed by GaO. Therefore, most of the porous skeletons are composed of Ga and GaO. According to data the sample also contains C, F, Zn, and Al, except of Ga, P and O elements in small amounts.

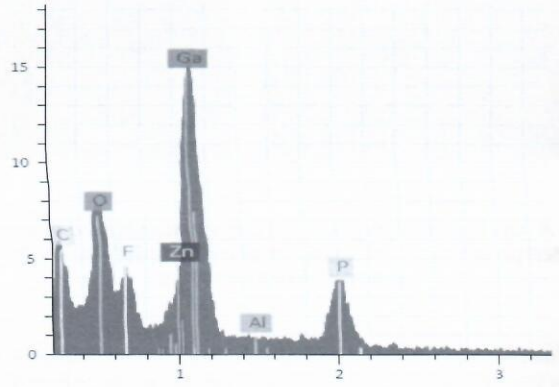


Figure 4. Energy-dispersive X-ray spectrum of por-GaP sample obtained by electrochemical etching under U=30 V; I=5 мА; t=40 min.

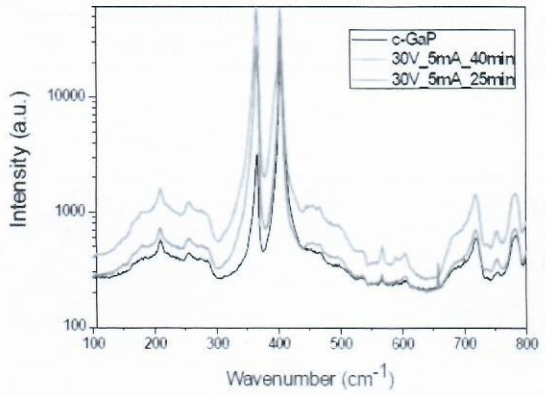
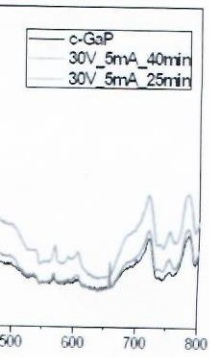


Figure 5. Raman spectra of por-GaP samples obtained by electrochemical etching under different conditions.

troscopy was used in order to identify
own in *Figure 4*, the basic element on the
uch appearance is in the faster dissolution
um ones. Since the initial substrate of
e is also a signal of Zn appeared in EDX
during electrochemical etching process
in electrolyte. Broken bonds of Ga on
separating the pores are formed by GaO
composed of Ga and GaO. According to
l, except of Ga, P and O elements in small

trum of por-GaP sample obtained by
J=30 V; I=5 мА; t=40 min.



btained by electrochemical etching under
ditions.

One of the linear optical methods for estimating the surface morphology and structure of nanostructures is Raman spectroscopy. In our experiments excitation wavelength was 473 nm, acquisition time was 30 s, diameter of laser spot was 2μm, enhancement factor was 100x, exciting laser power 30W. *Figure 5* represents Raman spectra of the crystalline GaP and por-GaP samples obtained by electrochemical etching at different etching times. It should be note that both LO and TO oscillations modes of GaP (at 366 cm^{-1} and 404cm^{-1}) appeared in por-GaP layers spectra. One can see that at long etching time signal has a high intensity, which shows that the structure has changed. Por-GaP sample etched for 40 minutes also has extended shoulders in Raman spectra, which shows the beginning of phase transition from monocrystalline to the amorphous phase.

CONCLUSIONS

Electrochemical etching method was used to obtain porous gallium phosphide, and effective technological conditions were formed. The dependence of the structural properties of the obtained porous gallium phosphide on the electrochemical etching parameters was investigated. The uniform porosity structure formation was observed when the anodizing voltage was higher than 50 V. In such a case, the surface structure of the samples becomes evenly flat. In such modes, the effect of light polishing on surface morphology appears. Energy-dispersive X-ray spectrum of por-GaP samples shows that formation of pores during electrochemical etching process is mainly due to dissolution of phosphorus in electrolyte. Raman spectroscopy showed that the structure of the long etched (40 minutes) samples was close to the amorphous phase. The high concentration of LO- and TO-oscillations shows that the crystalline direction of the first monocrystal GaP is preserved. Obtained results can be useful in further investigations of physical and chemical properties of p-type porous gallium phosphide nanostructures for different applications in photonics and opto-electonics.

ACKNOWLEDGEMENTS

This work was supported by the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan (Grant AP05130069).

REFERENCES

[1] Tao-Mukhamedova G.Sh., Belyaev, V., Mussabek G., Sagyndykov A., Modern trend of composite coatings formation problem, SGEM 2017, Albena Bulgaria, 2017, pp 229-236.

[2] Tao-Mukhamedova G.Sh., Muradov A., Mukashev K., Mathematical model of composite materials formation, SGEM 2017, Albena Bulgaria, 2017, pp 201-208.

[3] Tao-Mukhamedova G., Darisheva A., Kasimzhanov K., Physicochemical investigations of scheelite concentrate decomposition, Eurasian Chemico-Technological Journal, 2015, No 17, p. 209–212.

[4] Yar-Mukhamedova G.Sh., Sakhnenko N.D., Ved M.V. Ternary cobalt-molybdenum-zirconium coatings for alternative energies, Applied Surface Science, 2017, 421 (1), pp. 68-76.

[5] Yar-Mukhamedova G.Sh., Ved M.V., Karakurkchi A.V., Sakhnenko N.D., Mixed alumina and cobalt containing plasma electrolytic oxide coatings, IOP Conference Series: Materials Science and Engineering, 2017, 213(1), pp. 012020.

[6] Yazdan Mehr M., Toroghinejad M.R., Karimzadeh F., van Driel W.D., Zhang G.Q., A review on discoloration and high accelerated testing of optical materials in LED based-products, Microelectronics Reliability, 2018, Vol. 81, pp. 136-142.

[7] Martin A., Combrié S., de Rossi A., Beaudoin G., Sagnes I., Raineri F., Nonlinear gallium phosphide nanoscale photonics, Photonics Research, 2018, Vol. 6, Issue 5, pp. B43-B49.

[8] Kuyanov P., McNamee S. A., LaPierre R.R., GaAs quantum dots in a GaP nanowire photodetector. Nanotechnology, 2018, Vol. 29, No 12, pp. 124003.

[9] Anedda A., Serpi A., Time resolved blue and ultraviolet photoluminescence in porous GaP. Appl. Phys. Lett. 1995, Vol. 67, pp. 3316.

[10] Tjerkstra R. W., Gómez Rivas J., Vanmaekelbergh D., Kelly J. J., Porous GaP multilayers formed by electrochemical etching, Electrochem. Solid-State Lett., 2002, Vol. 5, No.5, pp. G32-G35.

[11] Shen Y.C., Hon M.H., Leu I.C., Teoh L.G. Morphological characterization of porous GaP prepared by electrochemical etching, Applied Physics., 2010, Vol. 98, No.2, P. 429-434.

[12] Treideris M., Simkiene I., Selskis A., Balevicius Z., Babonas G. J., Electrochemical formation and microstructure of porous gallium phosphide, Acta Physica Polonica, 2011, Vol. 119, No. 2, pp. 131-134.

[13] Mel'nikov V. A., Golovan L. A., Konorov S. O., Muzychenko D. A., Fedotov A. B., Zheltikov A. M., Timoshenko V. Yu., Kashkarov P. K., Second-harmonic generation in strongly scattering porous gallium phosphide, Appl. Phys. B., 2004, Vol. 79, No.2, pp. 225 - 228.

ELECTROCHEMICAL METH
NANOSTRUCTURATION AND FU
AND BIO

Prof. univ. dr. Lidia BENEA[1]

Research (Competences) Centre: Interfac
(ITIS), Dunarea de Jos University of Galati, R

ABSTRACT

Electrochemical method for the preparati
functionalization through active biomolec
work. There are two applied electrochem
nanocomposite structured layers or advan
electrochemical oxidation or anodizati
nanostructured oxide films and (ii) d
codeposition process of nanocomposite la
make a summary of results obtaine
modification techniques in obtaining adva
characterization in terms of surface r
roughness and layers thicknesses, corrosi
properties as nanohardness or wear resistan
electrodeposition with other electrochemi
modification can lead to a large class of nan
and composite coatings (films) on differen
for a future based on nanotechnology a
properties of materials face of aggressiv
improving surface properties of materials
systems in specific environments give
applications by increasing the efficiency and

Keywords: electrochemical methods, nano
anodic oxidation, electrodeposition.

INTRODUCTION

In recent years, the development of nanotec
an explosion of new functional coatings a
coming years. Functional and intelligent coa
enormous technological interest [1-12]. Out
surface modification and protection, this
advantages of electrochemical methods appli
to improve their properties. Electrochemic
within the author's field of expertise [1-12].

Two electrochemical methods are applied an
with specific applications, but both with
resistance to degradation of surfaces in specif

DOI: doi.org/10.5593/sgem2018/6.1