Porous Nanostructured InP: Preparation and Properties

Y. Suchikova, S. Onishchenko
Dept. of Vocational Education
Berdyansk State Pedagogical University
Berdyansk, Ukraine
yanasuchikova@gmail.com

V. Vambol, O. Kondratenko
Dept. Department of Applied Mechanics
National University of Civil Defence of Ukraine, NUCDU
Kharkiv, Ukraine
violavambol@nuczu.edu.ua

***Abstract*— A general procedure is devised to control the process of formation of porous layers on semiconductor surfaces by the method of electrochemical etching. When controlling the process of pore formation on the surface of crystal, it is necessary to consider: conditions of pore formation, requirements that are put forward to quality of the obtained nanostructures, and mechanisms that underlie the process of pore formation. Main morphological criteria are selected of quality of porous nanostructures. These include diameter and depth of the pore, a degree of porosity of the surface of a nanostructured crystal. Taking into account these criteria, we received porous spaces on the surface of semiconductors InP. We determined the value of boundary voltage of the early pore formation for semiconductors of group A3V5 during etching.**

***Keywords*— porous layers; electrochemical etching; surface of crystal; nanostructures; indium phosphide**

I. Introduction

The last some years' attention of researchers involves porous semiconductors, in particular connections A3B5 [1]-[5]. The scope of porous connections A3B5 constantly extends [6], [7].

Porous substrates on the basis of connections A3B5 are a perspective material for reception homo- and layers of the raised structural perfection. So, in work [8] a new method to transfer the three dimensional (3D) porous layer from InP wafer based on the disturbance, during electrochemical etching of n-InP (100) with chronopotentiometry with current ramp are received. In work [9] the feasibility of liquid-phase sensors based on n-type GaN and n-type InP porous structures was investigated. Properties high-quality of films InN, received by a method nitrodization on porous substrates InP, are presented in work [10]. Porous superlattices on the basis of InP have been received and investigated in work [11].

Therefore, reception of high-quality porous structures is the important physical and technological problem that became an object of research of many scientists [12]–[16].

Similar results were presented also by authors of work [12], which have received porous structure n-InP (001) when etching electrolyte 1M HCl (200 ml) HNO3 (3 ml). Diameter of pores has made the order 150nm, distance between pores 17-26 nm. In work [17], it was demonstrated that fast anodic etching of bulk crystalline substrates of n-InP via photolithographically defined windows leads to the formation of nanomembranes and nanowires being promising for device applications. It was shown that under potentiostatic etching conditions the morphology of etched samples strongly depends on the applied voltage.

Authors of the paper [18] controlled a change in the size and shape of pores using a photolithographic window. Nanomembranes and nanowires formed at the surface of indium phosphide. It was shown that under potentiostatic conditions of etching morphology of the etched samples was highly dependent on the applied voltage. It was discovered that anodizing at 5...7 V leads to the creation of highly porous layers made of mechanically stable skeletons that demonstrate percolations. At the same time, dominant formation of nanowires was observed while increasing the applied voltage to 15 V. Membranes from nanoporous InP were formed for the purpose of growing based on nanowires of Co [19]. The membranes were formed by the method of electrochemical etching in four stages, each of which involved different electrolytes and modes of etching. Grown polycrystalline cobalt nanowires are characterized by a very small size of grain. Studies show a narrow hysteresis loop with dominant orientation in the direction of magnetization along the long axis of a nanowire. Because of this, there occurs anisotropy of cobalt nanowires. Mechanisms that occur at the border "semiconductor–electrolyte" were investigated in articles [20]–[23].

For realization of the task we experimental by selected size of a threshold pressure of the beginning of pores creation about which paramount value it is underlined in work [24]. The morphology and a chemical compound of the received porous layers have been investigated, and also is lead X-ray the microanalysis.

Until now, the obtaining of a regular porous space on the surface of indium phosphide remains a complicated process. The formation of por-InP/InP with a record-small pore size of 40 nm and inter-pore spaces of 5...10 nm has been demonstrated, and the main morphological properties of the obtained structure have been studied in the paper.

II. TECHNICS OF CARRYING OUT OF EXPERIMENT

The porous layers of indium phosphide were formed by electrochemical etching technique. This technique is classical for the synthesis of pores on the surface of semiconductors of the A3B5 group. However, it allows the obtaining of a large variety of low-dimensional structures: textured layers, super gratings, clusters, pores, etc. The type of a formed nanostructure depends on two factors. First, it is the state and properties of an original crystal, and secondly, the conditions of etching.

The main characteristics of a crystal that affect the quality of a nanostructure include: crystallographic parameters of the crystal (surface orientation), the type of conductivity (hole or electron), the presence and number of point defects, the concentration of minor charge carriers, the type of doping impurity, etc. Taking into account these properties of the crystal enables the choosing of the optimal etching modes for formation of porous structures. Morphological properties of nanostructures are determined by: the time of etching; concentration and type of electrolyte; density of current and voltage of pore formation; electrolyte temperature; intensity of illumination of samples during anodizing, etc.

The samples of porous indium phosphide (Table 1) were grown by the technique of electrochemical etching of single-crystal InP of n-type with surface orientation (100), concentration of a doping impurity was $2.3\cdot10^{18}cm^{-3}$). Indium phosphide monocrystals were prepared at the laboratory of the company “Molecular Technology GmbH” (Berlin), cut into ingots and polished on both sides.

TABLE 1. PROPERTIES OF INDIUM PHOSPHIDE

Type of crystal lattice	Sphalerite
Constant of lattice	5.8687A at 300 K
Relative molecular weight	144ю63
Number of atoms in cm^3	3.96X10^{22}
Density in solid state	4.81 g/cm^3
Melting temperature under pressure of phosphorus vapors	1060 ºC
Dielectric permittivity of indium phosphide	Static – 12.5; high frequency – 9.61
Width of forbidden zone	1.35 eV

As electrolyte the solution of 5% HCl was used. As the cathode the plate of platinum served in an electrochemical cell. Experiment was spent at a room temperature in darkness. Before experiment samples were cleared in toluene and then were washed out in the distilled water. The pressure rose in due course with a speed 1V/min before detection of size of a threshold pressure in porous creation which in this case has made 3,5V (t=3min). After that the mode of the fixed pressure at which samples were etching during 2min. General time of etching 5min. After experiment samples were cleared by ethanol and dried in a stream of nitrogen during 10min. The morphology of the received porous structures was investigated by means of raster electronic microscope JSM-6490. The Chemical compound has been studied by means of method EDAX.

III. RESULTS AND THEIR DISCUSSION

Detection of the threshold pressure when creating pores. The conditions for formation of pores on the surface of crystals by the electrochemical etching technique are always limited by a more or less narrow range of polarization voltage. Thus, in paper [25], it is indicated that there always exists a minimum threshold value of voltage necessary for commencement of formation of an etch pit. This value was given the name as the limiting voltage of the initiation of pore formation.

The voltage of the initiation of pore formation in our case was determined as follows. The mode of variable voltage was chosen, the change rate was 1 V/min. The current density before the critical value of voltage was within 20 mA/cm2. Starting from the voltage value $Uc = 3.5V$, the current density quickly accumulate up to 250 mA/cm^2 for 1 minute (Fig. 1) over time. A sharp increase in the current density can be explained by a gradual increase in the number of pore inlet openings.

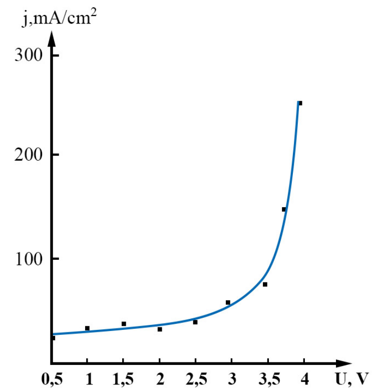

Fig. 1. Dependence of density of a current on a pressure during anodization.

After 1min. the current ceased to accrue (fig.2). Thus, the threshold voltage of the beginning of porous creation for (100) InP n-type with concentration of an impurity $2.3\cdot10^{18}sm^{-3}$ has made 3.5V.

The limiting voltage of the initiation of pore formation can serve as a quantitative characteristic of the process of pore formation, occurring in the specific system “semiconductor/electrolyte”. Up depends on the composition of the electrolyte and the initial state of the crystal surface, so it is individually determined for each case of etching. Under equal conditions, the limiting voltage depends on the type of anion involved in the reaction. Electrolytes are divided into strong and weak by their ability to dissociate into ions at dissolution. Their behavior when dissolved varies. A part of the molecules of weak electrolytes decomposes into ions under the action of a solvent. A dynamic equilibrium between ions and non-dissociated molecules is established in solutions of weak electrolytes. Upon dissolution of strong electrolytes, dissociation occurs almost completely, ionic crystals or molecules decompose with the formation of hydrated ions.

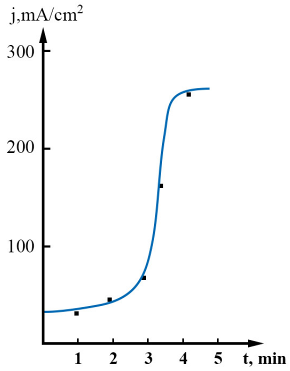

Fig. 2. Change of density of a current in time during electrolytic etchings.

As a result of the anodizing, the thin long channels of a pore are formed parallel to each other, which have a shape close to a regular quadrilateral in the cross section. This shape of the pore is determined by orientation of the surface of a test sample. Fig. 3 shows an ordered porous layer on the surface of monocrystalline indium phosphide. The pores are almost evenly distributed along the surface of the sample. The average pore size is 40 nm. The size of the walls between the pores is within 5-10 nm. The depth of growth of pore channels is about 35 µm. The percentage of porosity is approximately 30% of the total area of the sample. The resulting structures are of high quality, they can be used as supersensitive sensors due to the small diameter of a pore. Moreover, porous semiconductors are considered as substrates of super-capacitors due to an increase in the effective area and volume by hundreds and thousands of times.

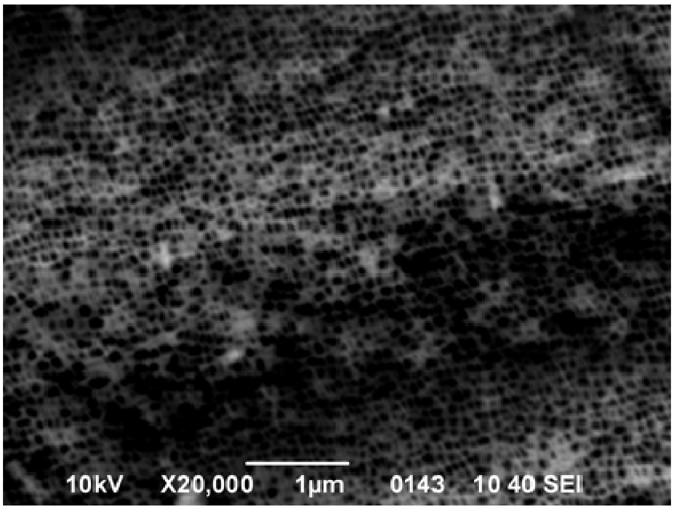

Fig. 3. The REM-image of morphology porous n-InP (100), received by electrochemical etching in 5 % HCl, t=5min

The chemical compound of a surface was investigated by method EDAX. Results of measurements are presented in table 1. Proceeding from results of the chemical analysis n-InP (Fig.4, Table 2), it is possible to approve, that the surface practically does not contain some oxygen so, process of the pores creation occurred without formation film. It proves to be true data researches received by a method X-ray (Fig. 5).

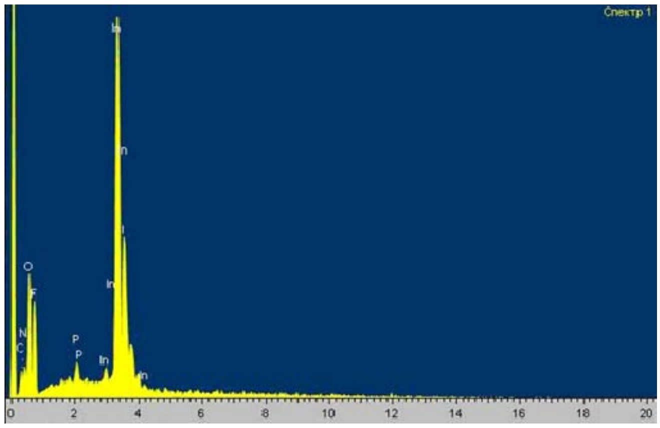

Fig. 4. Change of density of a current in time during electrolytic etchings.

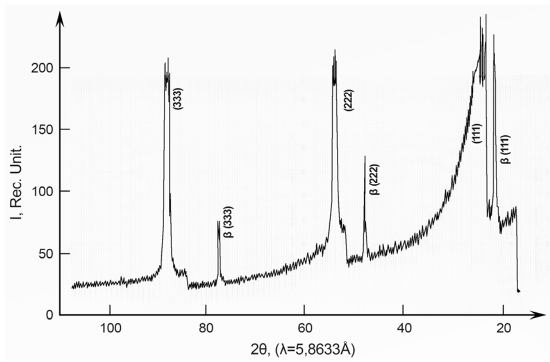

Fig. 5. X-ray spectra porous InP (100)

TABLE 2. PERCENTAGE OF ELEMENTS ON A SURFACE POROUS N-INP

Spectrum	Component		
	O	*P*	*In*
1	2.25	22.82	74.93
2	1.78	23.40	74.82
3	5.82	17.63	76.55
4	3.12	38.69	58.19

X-ray diffraction measurement shows the presence of single-crystal InP of the sfalerite structure only. The stoichiometry of the porous sample is shifted toward an excess of indium. This may be indicative of that the etching is faster than the phosphorus sub-lattice, that is the major role in the process of pores creation is played by the atoms of P. It should be noted that porous structures on the semiconductors surface are inert to the environment, which is also their advantage over organic nanostructures. Photoluminescence of porous layers on the surface of indium phosphide shows a shift in the short-wave region of the spectrum. This causes them to be used as a photonic crystal.

CONCLUSIONS

The paper presents the process of obtaining a regular porous layer on the surface of the n-type monocrystalline indium phosphide. Porous spaces were formed by electrochemical etching in a solution of hydrochloric acid in the mode of gradual increase in voltage. As a result of the experiment, it was found the value of the limiting voltage of the initiation of pore formation of n-InP (100) in a 5% solution of hydrochloric acid. The morphological properties of the obtained nanostructures and the chemical composition of the sample surface were studied. It is shown that under certain conditions, the formation of a regular porous layer with the transverse size of pores of 40 nm and a distance between pores of 5...10 nm is possible on the surface of indium phosphide. The thickness of the porous layer reaches 35 microns. Such structures are of interest for their use in photonics, photovoltaic cells, sensory microelectronics and as electrodes of super-capacitors. Such opportunities are offered due to quantum-dimensional effects, which are manifested in nanostructures. The chemical analysis of the porous layers showed a slight alteration of the stoichiometry of the crystal towards an excess of indium. No oxide films on the surface of the crystal were formed. According to the results of X-ray studies, it is found that the porous layers have a monocrystalline structure and do not form other phase. It is also found that the morphological properties of the porous samples depend on the parameters of an initial crystal and the conditions of pore formation.

ACKNOWLEDGMENT

The work was performed within the framework of the scientific state funded study “Nanostructured semiconductors for energy efficient environmentally safe technologies that increase energy efficiency and environmental safety of urbosystem” (State registration number 0116U006961).

REFERENCES

[1] F. Chen, L. Xu, D. Fang, J. Wang, H. Fan, “Defect related photoluminescence emission from etched GaAs microstructure introduced by electrochemical deposition”, Proc. IEEE 2015 International Conference on Optoelectronics and Microelectronics (ICOM), pp. 383-385, 2015.

[2] M. I. Md Taib, N. Zainal, “Hassan improvement of porous GaAs (100) structure through electrochemical etching based on DMF solution”, Journal of Nanomaterials, 2014.

[3] I. Tiginyanu, E. Monaico, V. Sergentu, A.Tiron, V. Ursaki, “Metallized porous GaP templates for electronic and photonic applications”, ECS Journal of Solid State Science and Technology, 4(3), pp. 57–62, 2015.

[4] Y.A. Suchikova, V.V.Kidalov, G.A. Sukach, “Influence of the carrier concentration of indium phosphide on the porous layer formation”, J. Nano- and Electronic Physics, 2(4), pp. 142–147, 2010.

[5] Y.A. Suchikova, V.V. Kidalov, G.A. Sukach, “Preparation of nanoporous n-InP(100) layers by electrochemical etching in HCI solution”, Functional Materials, 17(1), pp. 131–134, 2010.

[6] T. Sato, Y. Kumazaki, H. Kida, A. Watanabe, Z. Yatabe, “Large photocurrents in GaN porous structures with a redshift of the photoabsorption edge”, Semiconductor Science and Technology, 31(1), 014012, 2015.

[7] Y.A. Suchikova, V.V. Kidalov, G.A. Sukach, “Influence of type anion of electrolit on morphology porous inp obtained by electrochemical etching”, Journal of Nano- and Electronic Physics, 1(4), pp. 111–118, 2009.

[8] Zhang, Yang, et al. “Transferring porous layer from InP wafer based on the disturbance”, Proc. 2016 IEEE International Conference on Manipulation, Manufacturing and Measurement on the Nanoscale (3M-NANO), 2016.

[9] Sato, Taketomo, et al., “Electrochemical formation of N-type GaN and N-type InP porous structures for chemical sensor applications”, 2016 IEEE SENSORS, 2016.

[10] Suchikova, J. A., “Synthesis of indium nitride epitaxial layers on a substrate of porous indium phosphide” J. Nano-and Electronic Physics, 7, 3, 2015, pp. 3017-1.

[11] Faria Junior, P. E., T. Campos, and Guilherme Matos Sipahi, “Interband polarized absorption in InP polytypic superlattices”, J. Appl. Phys., 11, 619, 193501, 2014.

[12] Heidari, Mehdi, and Jiwang Yan, “Ultraprecision surface flattening of porous silicon by diamond turning”, Precision Engineering, 49, 2017, pp. 262–277.

[13] F. Chen, et al., “Defect related photoluminescence emission from etched GaAs microstructure introduced by electrochemical deposition”, Proc. IEEE 2015 Internl Conf. Optoelectronics and Microelectronics (ICOM), 2015, pp. 383-385.

[14] Suchikova, Y. O., “Sulfide Passivation of Indium Phosphide Porous Surfaces”, J. Nano-and Electronic Physics, 9, 1, 2017, pp. 1006-1.

[15] Vambol, Sergij, et al. “Analysis of the ways to provide ecological safety for the products of nanotechnologies throughout their life cycle”, Eastern-European J. Enterprise Technologies, 1, vol. 10, 2017, pp. 27-36.

[16] Chai, Xiangyu, et al. “Tunable oscillatory phenomenon during anodic of n-InP (100) by the CPCR model”, Proc. IEEE International Conf. Manipulation, Manufacturing and Measurement on the Nanoscale (3M-NANO), Taipei, 2014.

[17] Monaico, Eduard, et al. “ZnSe-based conductive nanotemplates for nanofabrication”, Physica status solidi (RRL)-Rapid Research Letters 3.4, pp. 97–99, 2009.

[18] Monaico, Eduard, et al. “Formation of InP nanomembranes and nanowires under fast anodic etching of bulk substrates”, Electrochemistry Communications, vol. 47, pp. 29–32, 2014.

[19] Gerngross, Mark-Daniel, Jürgen Carstensen, and Helmut Föll. “Electrochemical growth of Co nanowires in ultra-high aspect ratio InP membranes: FFT-impedance spectroscopy of the growth process and magnetic properties”, Nanoscale Research Letters, 9.1, 2014: 316.

[20] Zhu, Changqing, et al. “Electrochemically etched triangular pore arrays on GaP and their photoelectrochemical properties from water oxidation”, Internl J. Hydrogen Energy, 39.21, pp. 10861–10869, 2014.

[21] Janovská M., “Elastic constants of nanoporous III-V semiconductors”, J. Phys. D: Appl. Phys. vol. 48, No 24, pp. 245102, 2015.

[22] J.A. Suchikova, “Synthesis of indium nitride epitaxial layers on a substrate of porous indium phosphide”, J. Nano-and Electronic Physics, 7.3, pp. 3017-1, 2015.

[23] Suchikova, Y. A., V. V. Kidalov, and G. A. Sukach, “Influence of dislocations on the process of pore formation in n-InP (111) single crystals”, Semiconductors, 45.1, pp. 121–124, 2011.

[24] Sychikova, Ya A., V. V. Kidalov, and G. A. Sukach, “Dependence of the threshold voltage in indium-phosphide pore formation on the electrolyte composition”, J. Surface Investigation. X-ray, Synchrotron and Neutron Techniques, 7.4, pp. 626–630, 2013.

[25] Ulin, V. P., and S. G. Konnikov, “Nature of Electrochemical Pore Formation Processes in A III B V Crystals (Part I)”, Fizika Tekh. Poluprovodnikov, 41.7, pp. 854–866, 2007 (in Russian).