Proceedings of the 2017 IEEE 7th International Conference on Nanomaterials: Applications & Properties, Part 1 NAP-2017

2017 IEEE 7th International Conference on Nanomaterials: Applications & Properties (NAP – 2017)
Zatoka, Ukraine, September 10-15, 2017

Ministry of Education and Science of Ukraine

Proceedings of the 2017 IEEE 7th International Conference on Nanomaterials: Applications & Properties (NAP-2017)

NANomaterials: Applications & Properties

2017, Part 1

ISBN 978-1-5386-2810-2

www.nap.sumdu.edu.ua

Sumy
Sumy State University
2017

Ministry of Education and Science of Ukraine
Sumy State University

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Zatoka, Ukraine
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Founded in 2012

Sumy
Sumy State University
2017

2017 IEEE 7th International Conference on Nanomaterials: Applications & Properties (NAP – 2017)

IEEE Catalog Number: CFP17F65-ART
ISBN: 978-1-5386-2810-2

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40007 Sumy, Ukraine

SUMY STATE UNIVERSITY

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Properties and Characterization of Surfaces and Interfaces

Morphologies and Photoluminescence Properties of Porous n-InP

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***Abstract*— The samples of porous InP were grown up by a method of anode electrochemical etching on a substrate (100) InP n-type. The samples were characterized by scanning electronic microscopy (SEM) and photoluminescence (PL) where a blue shift was observed in PL. To remove surface oxides from the surface of porous InP using the thermal cleaning of the samples in a stream of high purity hydrogen. Chemical composition of surface of porous n-InP after in hydrogen probed treatment the method of Energy dispersive X-ray spectroscopy. Size of walls between pores which makes 3 – 11nm.**

Keywords*— *porous layers; electrochemical etching; photoluminescence; nanostructures; indium phosphide

I. INTRODUCTION

Recently quantum-dimensional structures A3B5 draw attention of many researchers. This is due to the unusual properties of the obtained materials and a fairly simple and inexpensive technology of their manufacture. So, we obtained high-quality films InN on porous InP substrates a method of nitridization [1].

InP is a technologically important material for creation of lasers [2, 3], diodes [4, 5], solar batteries [6]. Therefore, studying of optical properties single crystal and porous InP is rather perspective direction which demands detailed studying and research.

For reception of structures porous InP electrolytes such as HCl [7], HBr [8], HF [9] and KOH [10] are using. Established that the structures formed in solutions of HF, demonstrated visible photoluminescence in the spectral range from yellow to red, whereas in the samples treated in HCl and HBr electrolytes, a significant photoluminescence in the visible range of spectrum were not observed.

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Alongside with type of electrolyte on morphology of pores the light exposure a significant influence [12]. At high illumination level instead of formation of pores electrolytic polishing exists. Most qualitative structures are received in darkness. Research of properties of porous structures of p-InP (100) received with electrochemical etching in solutions of HBr and HF [13] showed, what morphology of received structures and them optical properties it is severe depends from halogen, those present in electrolyte and conditions of etching. Structure, formed in solution HF, was characterized with presence of two strips of: photoluminescence the first stripe-in range of 630-700 nm, probably than in all connected with quantum confinement effect and the second one-in range of 530-590 nm, nature which presence of oxides on surface of porosity material. The spectra photoluminescence samples, processed in HBr, were characterized with presence only of one strip of 520 nm, that is also explained with presence complexes of oxides.

n work [14] it is informed about photoluminescence porous InP, the electrochemical etching received by a method in a solution containing 1M HCl (200ml) and HNO3 (3ml). 103 and 28 nanometers estimated by means of a photoluminescence were as a result formed crystallites.

In work [15] it is underlined possibility of occurrence of quantum-dimensional effect at anode etching monocrystal InP (100). HF (48%), H2O and ethanol in the relation 1:1:2 were used as electrolyte. The current density got out in a range (10-60) mA/cm2, time of etching from 5 till 30 minutes. Maximum photoluminescence thus is in area (735-640) nanometer, and the size of walls between pores makes (6.4 – 8.5) nanometer.

For practical application porous InP the size of nanostructure is critical [16, 17]. Therefore, reception of films with the least size of pores and nanocrystallites is rather actual direction for today [18, 19].

In the given work the manufacturing techniques are shown and spectra of a photoluminescence porous InP are investigated. Novelty of our researches is processing of samples in especially pure hydrogen for reduction of influence of superficial effects and oxides on processes radiating recombination of porous InP. Besides, a method of electrochemical etching InP of n-type in a solution of 5% HCl we managed to receive structures with the minimum size of pores and nanocrystallites.

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II. Samples and Experimental Technique

Porous samples of InP have been prepared by anodic etching of single crystalline n-type InP (table 1, fig. 1). Single crystalline of InP have been made in the laboratory of the company «Molecular Technology GmbH» (Berlin). The electrolyte used solution of 5% HCl. Cathode in the electrochemical cell served as a plate of platinum (fig. 2). The experiment was conducted at room temperature in the dark. Before the experiment the samples were cleaned in toluene and isopropanol, then washed in distilled water. The voltage was increased with time at a speed 1V/min to detect the threshold voltage pore formation, which in this case amounted to 3.5 V (t = 3min). After that was selected fixed voltage at which the samples were etched more 2min.

TABLE I. Properties of indium phosphide

Type of crystal lattice	Sphalerite
Constant of lattice	5,8687A at 300 K
Relative molecular weight	144,63
Number of atoms in cm3	3,96X1022
Density in solid state	4,81 g/cm^3
Melting temperature under pressure of phosphorus vapors	1060 ^{o}C
Dielectric permittivity of indium phosphide	Static – 12,5; high frequency – 9,61
Width of forbidden zone	1,35 eV
Volatile impurities	for n-type – S, Se, Te, Si, Ge, Sn; for p-type – Zn, Cd
Solubility in water	not soluble
Solvents	hydrochloric acid, acid mixes

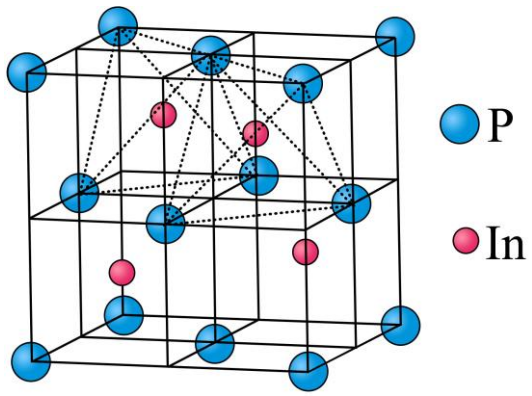

Fig. 1. Crystal lattice of InP

To remove surface oxides from the surface of porous InP using the thermal cleaning of the samples in a stream of high purity hydrogen, the optimal temperature for cleaning oxides In_2O, InO, PO_2, P_2O_3 was 500-600^{o}C, time – 20min. Immediately after purification in the hydrogen flow was measured photoluminescence spectra of porous samples at room temperature without aeration system.

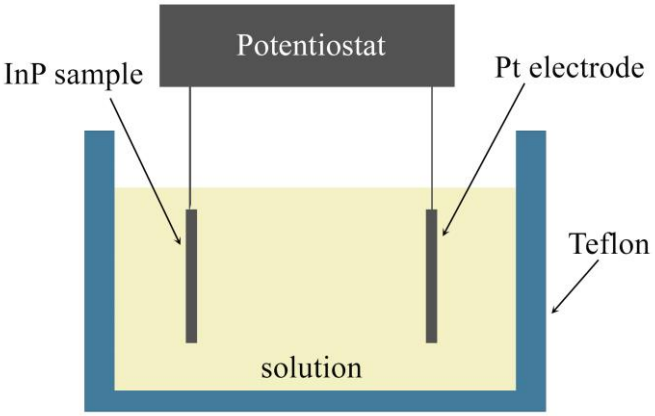

Fig. 2. Device for obtaining porous layers at the surface of monocrystals

As an excitation source using a nitrogen laser (λ = 337nm). The morphology of the obtained porous structures was studied using scanning electronic microscope (SEM) JSM-6490.

III. Results and Discussions

Terms of pore formation is always limited, more or less narrow range of polarization voltages [20, 21]. The sharpest, clearly defines the boundaries of this range is minimal, the threshold voltage required to start pore nucleation, the so-called voltage beginning pore [22]. Voltage beginning pore formation was determined as follows. Rate of change of voltage was 1V/min. The current density (up to the critical value of the voltage) remained in the range of 20 mA/cm^2.

Since Us = 3.5 V the current density rapidly increases to 250mA/cm2 for 1 minute (Fig. 2). The sharp increase in current density over time can be explained by a gradual increase in the number of ports and then branched below the surface. After 1min current ceased to grow (Fig. 3). Thus, the threshold voltage for the beginning of pore formation (100) InP n-type impurity concentration of 2.3 x10^{18}cm^{-3} was 3.5 V.

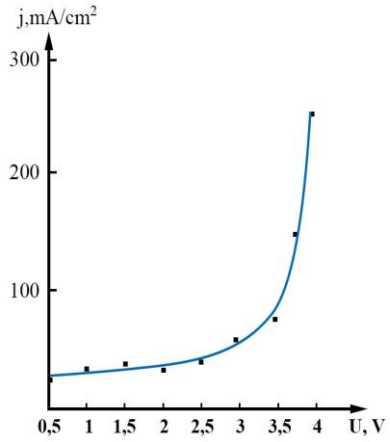

Fig. 3. Dependence of density of a current on a pressure during anodization

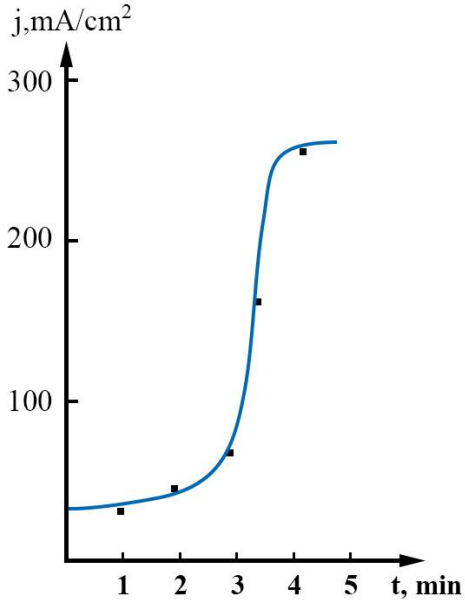

Fig. 4. Change of density of a current in time during electrolytic etchings

It should be noted that the threshold voltage of the beginning of pore formation depends on several factors: the doping level and orientation of the semiconductor composition and temperature of the electrolyte, the concentration of defects on the crystal surface, etc [23, 24]. Therefore, this value has different meanings for each individual case.

Fig. 3, 4 shows the image surface of the morphology of the porous sample InP, obtained by electrolytic etching of n-InP (100) in hydrochloric acid. The figure we can see an ordered ensemble of pores, which was formed on a substrate of single crystal indium phosphide. Pores sprouted across the surface of the ingot. The thickness of a porous layer has made 35 μm and the wall thickness of porous InP is around 3-11 nm.

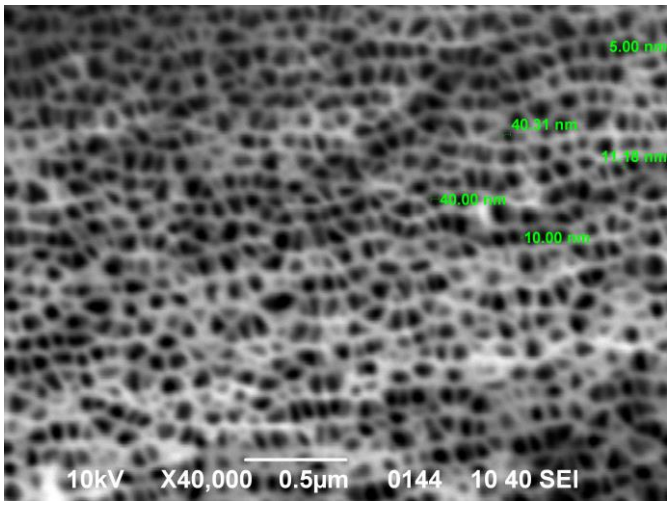

Fig. 5. SEM image of por-InP (surface)

The size of the walls between the pores is in the range 5-11nm. This result is a technologically important as the quality of porous films is determined by the size of nanostructures, the degree of porosity and uniformity of distribution of pores on the surface of the sample.

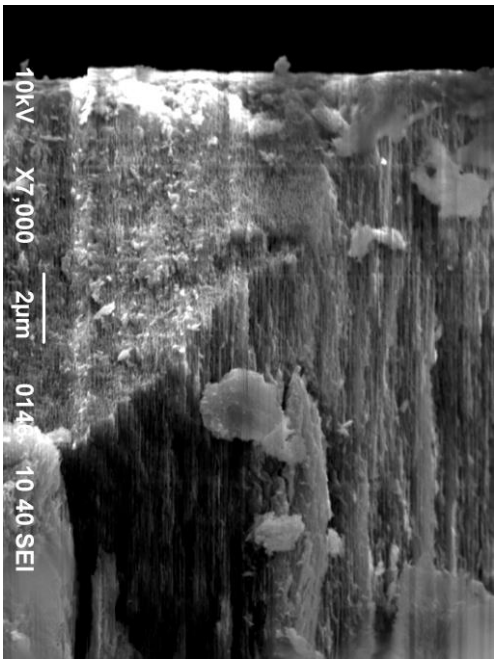

Fig. 6. SEM image of por-InP (cleavage)

The smaller the pore size and the larger percentage of porosity, the better the quality is a porous structure. For example, photoluminescence in the visible spectrum is observed only for the structures, the size of nanocrystallites in which the order of nanometers.

The depth of germination of channels has approximately 35 μm. It should be noted that the depth of the porous layer is also an important characteristic. The percentage of porosity is approximately 50% of the total area of the sample.

Chemical composition of surface of porous n-InP after in hydrogen probed treatment the methods of Energy Dispersive X-ray spectroscopy (fig. 7) and EDAX (fig. 8).

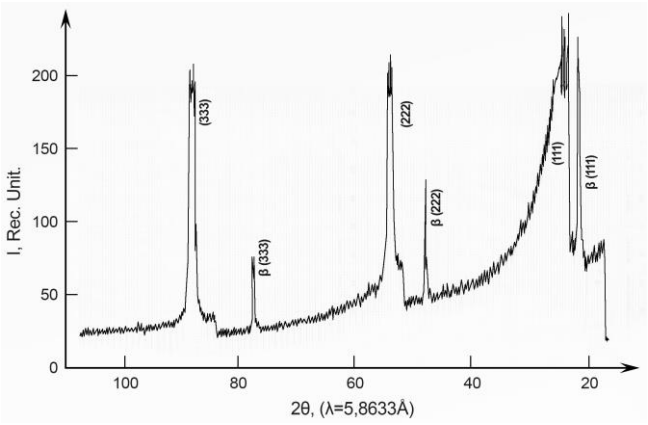

Fig. 7. X-ray spectra porous InP (100)

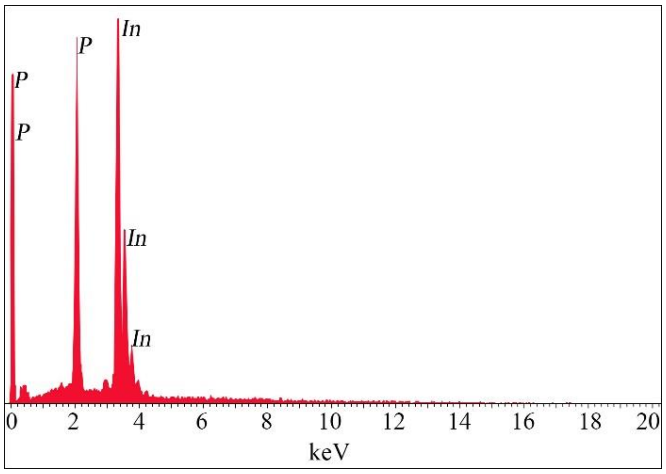

Fig. 8. Change of density of a current in time during electrolytic etchings

Based on the results of chemical analysis of n-InP it can be argued that the surface of the samples after the hydrogen thermal treatment practically does not contain oxygen, which means that the crystals are free of oxide film.

X-ray diffraction measurement shows are present only single-crystal InP of structure of sfalerite. The stoichiometry of the porous sample is shifted toward an excess of indium. This may indicative of that during the etching is etched faster than the phosphorus sublattice, the major role in the process of pores creation is played by the atoms of P [25, 26].

PL spectra of porous InP (fig. 9) shows that the spectrum significantly expanded, its maximum emission band localized near the energy 2.4 eV (520 nm).

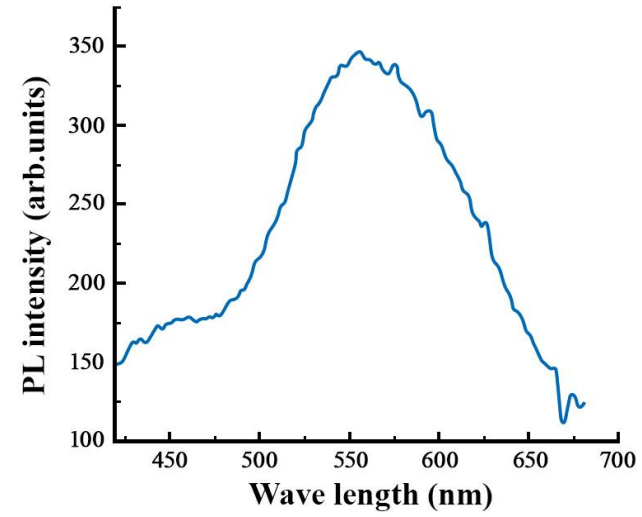

Fig. 9. Change of density of a current in time during electrolytic etchings

The bandgap of bulk indium phosphide is 1.34 eV at 300 K. Thus, for layers of porous InP there is a significant shift of the main PL band at shorter wavelengths [27, 28].

Lack of contact with the porous InP by atmospheric oxygen gives a basis to exclude from the consideration of causes associated with different kinds of oxides at the surface of pores and their contribution to the processes of radiative recombination. This fact is confirmed by diffractometric studies and the results obtained using the method of EDAX. The sharp increase of the PL band of porous InP due to the size quantization energy of charge carriers due to the formation of nanoobjects with approximately the same, but several different sizes of columns of porous material. Thus, in this study confirmed the fact that the shift of the maximum of the PL band of porous InP is due to quantum size effects in a string of received material.

Photoluminescence showed that the size of nanocrystallites is approximately 3–10 nm in diameter. This result is consistent with the data obtained with the help of this and that, according to which the size of the walls between the pores is 3–10nm.

IV. Conclusions

We have developed a technology for production of porous layers on the surface of single crystalline n-InP (n = 2.3x1018 cm-3), by electrochemical etching in a solution of hydrochloric acid. The thickness of a porous layer has made 35 μm and the wall thickness of porous InP is around 3-10 nm. This suggests that as a result of anodization formed long thin parallel to each other channels now, which in cross section have a shape close to a regular quadrangle. This form has determined the orientation of the surface of the sample.

For the chosen experimental conditions was determined value of the threshold voltage pore (Us = 3.5 V), which must be individually determined for each case of etching. This is due to the fact that the voltage of the polarization depends on several factors including: the composition and temperature of the electrolyte, the orientation of the crystal surface, the carrier concentration, the level of defects in the sample, etc.

In addition, were investigated PL spectra of these samples, which showed a shift of photoluminescence peak energy in the shorter wavelengths compared with single-crystal InP. To reduce the influence of oxides and surface effects on the processes of radiative recombination, we carried out treatment of the samples in particularly pure hydrogen.

The method was established EDAX chemical composition of the obtained porous layers of indium phosphide after treatment in particularly pure hydrogen. Analysis of these results showed that the sample surface is free of oxides.

X-ray measurements of porous InP films showed the absence of oxides on the surface. Given the marked characteristics of the PL and based on the results obtained with SEM, we have concluded that it is low-dimensional effects are responsible for visible photoluminescence in porous layers of InP. In this analysis of the results of these methods showed good agreement between the figures on the amount of walls between the pores, which is 3 - 11nm.

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).

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Scientific Edition

Proceedings of the 2017 IEEE 7th International Conference on Nanomaterials: Applications & Properties (NAP-2017)

2017, Part 1

Zatoka, Ukraine
September 10–15, 2017

Managing Editor Yurii Shabelnyk

Computer design Yurii Shabelnyk
Kateryna Smyrnova
Kateryna Belovol
Margarita Lisovenko

Підписано до друку 31.08.2017. Формат 70 × 100/16.
Папір офс. Друк офс.
Ум. друк. арк. 20,57. Обл.-вид. арк. 19,80.
Наклад 100 пр. Замовлення № ____.
Сумський державний університет. вул. Р.-Корсакова, 2, 40007, м. Суми.
Свідоцтво про внесення суб'єкта видавничої справи до Державного реєстру
ДК № 3062 від 17.12.2007.

Надруковано у друкарні СумДУ, вул. Р.-Корсакова, 2, 40007, м. Суми.