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EFFECT OF THE TYPE OF ELECTROLYTE ANION ON THE POROUS InP MORPHOLOGY OBTAINED BY THE ELECTROCHEMICAL ETCHING

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In this work the analysis of the dependence of the porous InP morphology on the type of reacting anion is presented. It is shown that nanoporous InP layers are obtained under certain conditions of electrochemical etching.

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1. INTRODUCTION

At present, various methods for the self-organized formation of nanostructures are actively developing due to their use for the electronic and photon devices, chemical and biochemical sensors [1, 2], etc. In A_3B_5 semiconductors for nanostructure formation a rather expensive method of molecular-beam epitaxy or metal-organic vapor-phase epitaxy (MOVPE) is applied. The possible alternative to these methods is the use of electrochemical processes by analogy with the porous silicon production [3]. Feature of the electrochemical process is the low-temperature process, the slight surface damage, the process simplicity and its low cost. Electrochemical methods allow to obtain the high pore density, which is unattainable if use other methods.

To obtain the porous InP structures, HCl, HBr, HF and KOH electrolytes [4, 5] are used. Established, that the structures formed in HF solutions demonstrate visible photoluminescence (PhL) in the spectral range from yellow color to red color, while in the samples finished in HCl and HBr electrolytes the essential PhL in the visible range was not observed. Illumination [6] together with the electrolyte type has significant influence on the pore morphology. At the high illumination level instead of the pore formation the electrolytic polishing takes place. The most qualitative structures were obtained in the darkness.

The study of the properties of *p*-InP (100) porous structures obtained by the electrochemical etching in HBr and HF solutions [7] showed that their morphology and optical properties strongly depend on the halogen in electrolyte and the etching conditions. The structure formed in HF solution was characterized by the presence of two PhL bands: the first band was in the range of 630-700 nm (most probably it was connected with the dimensional quantification effects), the second band was in the range of 530-590 nm (its

nature was in the presence of oxides on the porous material surface). And the spectrums of PhL samples finished in HBr were characterized by the presence of only one band (520 nm), which is also explained by the presence of oxides.

The same dependence on the electrochemical conditions and the type of halogen (Cl, F) in electrolyte was established in [8] for porous structures grown by the electrochemical etching on *n*-InP (100) in the darkness. The significant influence of the surface state on the pore nucleation was also detected. It was shown that the pore formation potential is lower for the surfaces with defects than for the undamaged ones.

Results of the integrated study of the porous InP structures obtained by the electrochemical etching (HCl, HF and HBr) and published in [9] showed that the features of the PhL spectrums of porous InP are connected with the deformation of the interatomic spacings in quasi-molecules of *p*-InP surface layer and with the change of the electronic structure of clusters in porous InP layers.

2. STATEMENT OF THE PROBLEM

Although the investigation results of the surface morphology and the optical properties of porous InP obtained by the electrochemical etching in different electrolytes are presented by a number of scientific groups, there is a limited amount of publications devoted to the analysis of the dependence of the porous InP structure on the etching regimes. The present paper is dedicated to the study of the effect of the anion type on the porous InP properties that is relevant from the point of view of the control of the pore diameter and the porous surface quality.

3. EXPERIMENTAL TECHNIQUE

Indium phosphide monocrystals were produced in the research laboratory of the "Molecular Technology GmbH" Company (Berlin). Thickness of the samples was 1 mm. Plates were cut out perpendicular to the growth axis and polished on both sides.

InP samples with different surface orientation of the *n*- and *p*-type and with different charge carrier concentrations were chosen for the experiment.

Electrochemical etching was performed using the standard plant in the electrolytic cell with the platinum cathode. The plant scheme is presented in Fig. 1.

Solutions of hydrofluoric and hydrochloric acids with different concentrations were taken as the electrolytes. Etchants based on HF and HCl with added iodides (KOH), ethanol and nitric acid were also used. The experiment was carried out at room temperature.

Samples were thoroughly purified before the experiment. There were the following purification steps:

1. degreasing in hot (75-80 °C) peroxide-ammonia solution;
2. treatment in hot (90-100 °C) concentrated nitric acid (metal ion removal);
3. washing in distilled water;
4. drying of the plates using centrifuge in the purified dry air.

After experiment the samples were purified in acetone and isopropanol, washed in distilled water and dried in extra pure hydrogen, whereupon they were undergone natural aging during three days.

Morphology of the obtained porous structures was investigated using the scanning electron microscope JSM-6490. Chemical composition was studied with the EDAX method, and the diffractometric investigations were carried out using the diffractometer DRON-3M.

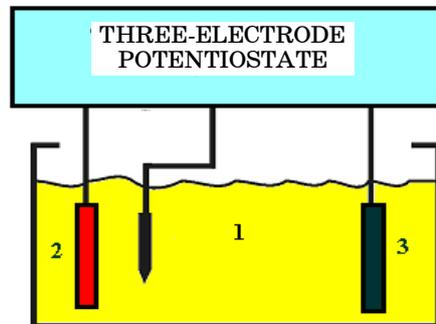


Fig. 1 – Plant for the semiconductor etching

4. RESULTS AND DISCUSSION

Morphology analysis of the tested samples obtained using the scanning electron microscopy (SEM) showed that almost in all cases the active pore-formation was observed. In the conditions when pore-formation is the dominant electrochemical process, which takes place at the given value of the polarizing voltage on the monocrystal semiconductor anode, the steady-state configuration of the porous layer surface is formed by the time of the maximum current density attainment.

Under equal conditions (identical crystals, equal charge and anion concentration in the solution) the electrolytic reaction rate depends on the type of reacting anion. Depending on the degree of dissociation into ions electrolytes can be classified as strong and weak ones. Their behavior on dissolving is different. Some molecules of weak electrolytes dissociate into ions under solvent action. Their dissociation is the reversible process since ions are easily associated in collisions, therefore in solutions of weak electrolytes the dynamic equilibrium between ions and undissociated molecules is attained. When strong electrolytes dissolve the dissociation occurs almost completely, ionic crystals or molecules dissociate with the formation of aquated (solvated) ions. Some of the most important acids, namely, HNO_3 , H_2SO_4 , HClO_4 , HCl , HBr belong to strong electrolytes. Among weak electrolytes are most of inorganic compounds, such as H_2CO_3 , H_2S , HCN , HF .

4.1 HF-based etchants

Small size of F atom substantially influences the fluoride properties. F atom in chemical compounds practically always is negatively charged. F is the most active oxidant among the elementary substances, it reacts with almost all substances. The feature of fluorine chemistry is the presence of stable hydrogen bonds H-F . The average degree of association of HF molecules in a liquid state is closed to 6. Etching acid is considered to be the half-strength acid (the dissociation constant is $6,8 \cdot 10^{-4}$). Electronegativity of F^- atoms in the series F^- , Cl^- , Br^- is the largest and is equal to 4 on the Pauling scale.

In the halogenide-ions series the minimum voltage value of the formation initiation always corresponds to fluorine anion. Morphology of the porous samples obtained using etching acid demonstrates the net of meso- and macropores. Formation of such pores is often connected with the displacement of defects and dislocations on the crystal surface. In this case the substantial overetching of the surface is observed (Fig. 2).

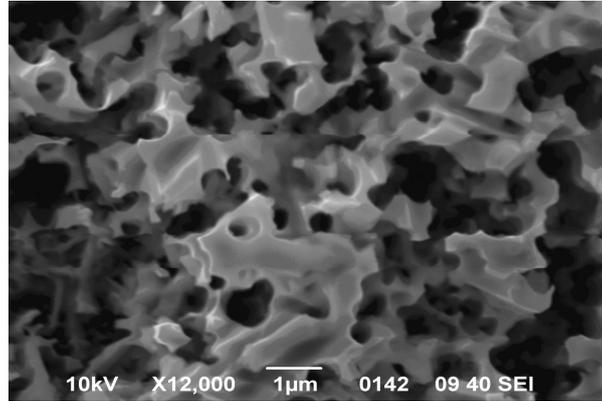


Fig. 2 – Morphology of porous *n*-InP (111); electrolyte HF : H₂O = 1 : 1, $j = 80 \text{ mA/cm}^2$, $t = 10 \text{ min}$

In Fig. 2 it is possible to see clearly the etched regions that imply about very “harsh” etching conditions. Porous surface demonstrates the developed morphology with the formed large etching pits. Such surface has a huge effective area in comparison with the monocrystal one, but it is imperfect enough for use as the substrate for heterostructure production. In this case, in order to decrease the electrolyte effect on the porous structure formation it is reasonable to change the etching regimes (time, current density) for the more soft ones or use more dilute etchant solution.

When adding ethanol to this solution the value of threshold voltage of the pore-formation initiation substantially increases, and here porous layer has more qualitative structure that is appeared in the decrease in the pore size (Fig. 3).

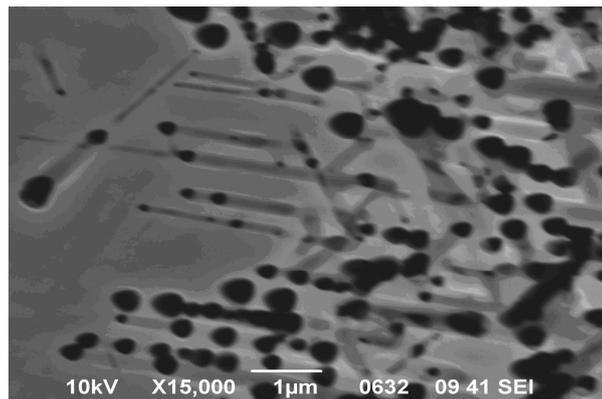


Fig. 3 – Morphology of porous *n*-InP (111); electrolyte HF : H₂O : C₂H₅OH = 1 : 1 : 2, $j = 40 \text{ mA/cm}^2$, $t = 15 \text{ min}$

In general, ethyl alcohol is an organic diluent of electrolyte. When adding it to the aqueous solution of etching acid (the component ratio is HF : H₂O : C₂H₅OH = 1 : 1 : 2) the electrolytic reaction rate slows down, and therefore more time is needed to obtain the porous structures.

The authors of [11] note that ethyl alcohol is used for the improvement of HF penetration into pores. In our case this leads to the formation of the dense net of anisotropically propagating pores along the directions $\langle 111 \rangle_A$ and $\langle 111 \rangle_B$ (Fig. 4). Degree of porosity is about 30% of the total area of the sample.

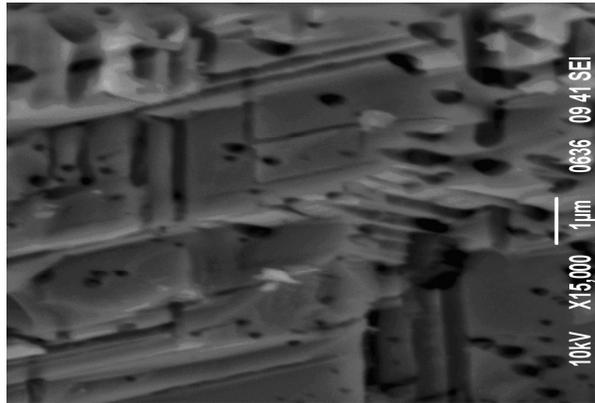


Fig. 4 – Anisotropic pore propagation along the directions $+111, A$ and $+111, B$

In Fig. 5 we present the cleavage of porous n -InP (111) obtained in the HF-based etchant. Irritated area, the appearance of which can be caused by the dislocation displacement, is clearly observed under the crystal surface.

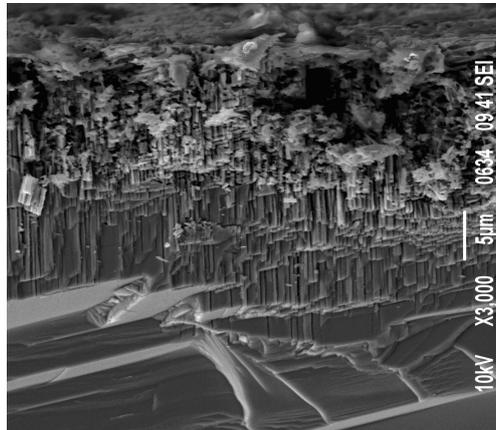


Fig. 5 – Cleavage of porous n -InP (111), electrolyte HF : H₂O : C₂H₅OH = 1 : 1 : 2, $j = 50 \text{ mA/cm}^2$, $t = 10 \text{ min}$

The following fact is found to be interesting: the crystal surface is not so irritated as an area under it. This implies about the pore-formation inside the crystal as well, where pores can be combined due to the thinning of the walls and their accumulation around defects.

4.2 HCl-based etchants

Hydrochloric acid is the aqueous solution of hydrogen chloride, it is strong (monoatomic) acid. The maximum concentration of such solution at 200°C is 38 at% and the density is 1,19 g/cm³. HCl is most often used during the electrochemical etching of the crystals that is explained by the possibility of this acid to easily dissociate into ions.

HCl-based etchants allow to obtain the layer composed of the nanopores mainly. Fig. 6 demonstrates the ordered assembly of pores formed on the monocrystal InP substrate during the etching in 5% hydrochloric acid solution. Pores appeared all over the sample surface. The average pore size is 40 nm that implies about the nanodimensionality of the given structure. The wall size between pores is in the range 5-10 nm. Such a result is important technologically, since the quality of porous films is determined by the nanostructure sizes, degree of porosity and uniformity of the pore distribution over the sample surface. The smaller pore size and the larger porosity percent, the more qualitative porous structure is. Degree of porosity is about 60% of the total area of the sample.

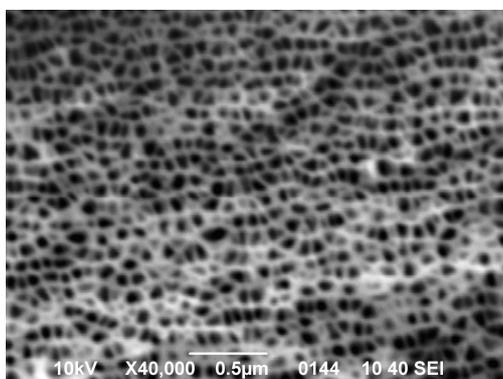


Fig. 6 – Morphology of porous *n*-InP (100) obtained by the electrochemical etching in 5% HCl solution, $t = 5$ min

In Fig. 7 we present the cleavage of the porous sample obtained in 5% hydrochloric acid solution. This figure demonstrates the long parallel pore channels placed strictly perpendicular to the crystal surface. Such pores are directed along the lines of flow and reach the depth of 60 μm inside the sample.

4.3 Salts and acids addition to the electrolyte solution

Iodide addition to the fluoride solution essentially influences the pore-formation process. When adding KI (potassium iodide) to 50% etching acid solution, the pore-formation process slows down somewhat, what the current-voltage characteristics taken during anodization imply about. Morphology of the samples obtained in such solution demonstrates the decrease of the pore inlets (degree of porosity is about 15%). However, the branching of the pore channels under the crystal surface increases. Here the irregular layer preceding the long mutually parallel pores widens up to 2 μm (in comparison with the irregular pore layer formed in the aqueous-fluoride solution, which in this case is 0,5-1 μm).

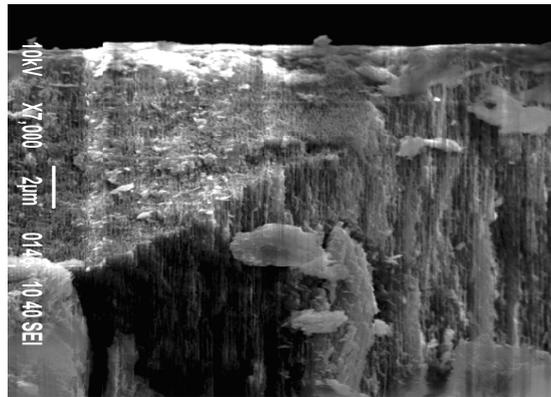


Fig. 7 – Cleavage of porous *n*-InP (100) obtained by the electrochemical etching in 5% HCl solution, $t = 5$ min

Nitric acid addition to the chloride solutions accelerates the electrolytic reaction rate and allows to obtain the porous surfaces with the more densely packed pores (degree of porosity is 60-70%). However, as in the case of iodides, nitric acid influences the thickness of irregular porous layer. In this case the given value is about 1,8 μm (in the absence of nitric acid it is 0,4-0,7 μm).

5. CONCLUSIONS

In this paper we present the analysis of the dependence of the porous InP morphology on the type of reacting anion. The main conclusions of the work are reproduced below.

Under equal conditions (identical crystals, equal charge and anion concentration in the solution) the electrolytic reaction rate depends on the type of reacting anion.

In the halogenide-ions series the minimum voltage value of the formation initiation always corresponds to fluorine anion. Morphology of the porous samples obtained using etching acid demonstrates the net of meso- and macropores. Formation of such pores is often connected with the displacement of defects and dislocations on the crystal surface.

HCl-based etchants allow to obtain the layer composed of the nanopores mainly. And therefore this etchant can be considered as the most appropriate for the porous InP nanostructure production.

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Morphology of the samples obtained in such solution demonstrates the decrease of the pore inlets (degree of porosity is about 15%). However, the branching of the pore channels under the crystal surface increases.

Nitric acid addition to the chloride solutions accelerates the electrolytic reaction rate and allows to obtain the porous surfaces with the more densely packed pores (degree of porosity is 60-70%).

The factors stated above enable to produce the porous structures with specified parameters that corresponds to the modern electronics and techniques requirements.

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