*J. Nano- Electron. Phys.*
**2** (2010) No4, P. 142-147

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PACS numbers: 61.43Gt, 78.30Fs, 78.55m

# INFLUENCE OF THE CARRIER CONCENTRATION OF INDIUM PHOSPHIDE ON THE POROUS LAYER FORMATION

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*This paper presents the experimental results demonstrating the influence of the doping level of InP on the porous layer formation on its surface during the electrochemical etching. It is established that the most high-quality porous layers are formed using the crystals with the free carrier concentration of* $2{,}3 \times 10^{18}$ $cm^{-3}$. *The observation results of InP layered heterogeneity are discussed and explained in terms of the features of the growing process of heavily doped crystals.*

***Keywords:*** *POROUS InP, SCANNING ELECTRON MICROSCOPY, ELECTROCHEMICAL ETCHING, NANOSTRUCTURE, SEGREGATION.*

*(Received 06 October 2010, in final form 12 November 2010)*

## 1. INTRODUCTION

Recently, scientific interest is directed to the formation of nanostructures considered as a promising material for the creation of photon devices [1]. The electrochemical process, which is unique due to its simplicity, low process temperature and low cost [2], stands out against different formation techniques of semiconductor nanostructures. The most well-known application of the electrochemical methods is the formation of a porous layer on the surface of semiconductor plate by anode etching. For the first time such structures were obtained on silicon. Lately it was established that porous layers can be also obtained on binary compounds, such as GaAs [3, 4], GaP [5], InP [6].

It is established that different factors, namely, the composition and concentration of electrolyte, current density, etching time [7], influence the formation of porous layer. Behavior of the semiconductor under electrochemical treatment also depends on the type and concentration of majority carriers. Here one should keep in mind that electrochemical process is accompanied by a number of coupled chemical reactions, and final result of the electrochemical treatment of semiconductor depends on the ratio of the reaction rates.

Influence of the doping level on the optical characteristics of porous SiC is studied in [8]. On the substrates, which are heavily doped with nitrogen, porous layers are found to be green and transparent, on the weakly doped substrates – brown and non-transparent layers. The reason of this phenomenon is in the following: pores having the reflection coefficient, which differs from the reflection coefficient of the main material, scatter light. Influence of the doping level on the porous layer characteristics, namely, the pore dia-

meter and porosity, was studied in [9] for 6H-SiC with the *n*-type conductivity. It was established that porous layer with pores of smaller size (diameter and volume), but with larger pore concentration is formed on the heavily doped substrates (in comparison with the weakly doped ones).

In the given work we study the influence of the indium phosphide doping level on the process of pore-formation that is an important problem from the point of view of the control of the pore growth process on semiconductor plate. The need to reveal the dependence of the porous layer configuration on the impurity concentration is conditioned by the high requirements of the techniques made to modern materials.

## 2. SAMPLES AND EXPERIMENTAL TECHNIQUE

Samples of monocrystalline *n*-InP grown by the Chokhralskiy method in the laboratory of "Molecular Technology GmbH" company (Berlin) were chosen for the experiment. The sample thickness is 1 mm. Plates were cut perpendicular to the growth axis and polished from both sides. Crystals were mechanically and chemically polished.

Surface orientation of the chosen plates is (001) and (111). Charge carrier concentration is $3 \times 10^{19}$ cm$^{-3}$, $2{,}3 \times 10^{18}$ cm$^{-3}$, $2 \times 10^{17}$ cm$^{-3}$, $1{,}8 \times 10^{16}$ cm$^{-3}$. Porous surface of InP is obtained by the selective electrochemical etching. Before the experiment, samples were purified in acetone, isopropanol, and methanol, then they were washed in distilled water and underwent the action of gaseous nitrogen. As a contact, indium was sprayed on the InP surface. Platinum was used as a cathode. After purifying samples were placed into electrolytic bath, whose working surface area is 0,12 cm$^2$. As an electrolyte, we have chosen the solution of hydrofluoric acid, water, and ethanol in the ratio 1:1:2. Ethyl alcohol is an organic vehicle of the hydrofluoric acid solution, but together with this it improves the HF penetrability into InP pores. Current density is 100 mA/cm$^2$ and etching time is 5-15 minutes. Experiment was performed at room temperature in the dark. After etching the sample surface was purified by ethyl alcohol and distilled water. Morphology of the obtained porous structures was studied using the scanning electron microscope JSM-6490.

## 3. RESULTS AND DISCUSSION

Additional doping of the monocrystalline InP surface is sufficiently interesting, to our opinion, way to obtain pores of the specified shape and provide the necessary quality of the *por*-InP – monocrystalline InP boundary. This circumstance allows, firstly, to form pores of the required shape, which makes easier further cleaving of the basic plate, and, secondly, to provide the necessary quality of the cleavage surface.

Rate of a chemical reaction essentially depends on the doping level of the semiconductor. Threshold voltage of the pore-formation decreases with the increase in the volume concentration of free electrons. Moreover, increase in the doping level leads to the reduction of the dislocation density, but simultaneously is accompanied by the generation of microdefects (stacking faults, small prism dislocation loops, disperse second-phase release). As known, the pore growth occurs along preferential directions, which the given defects of the crystal surface are. Fig. 1 illustrates the morphology of the InP porous surface with different charge carrier concentration.

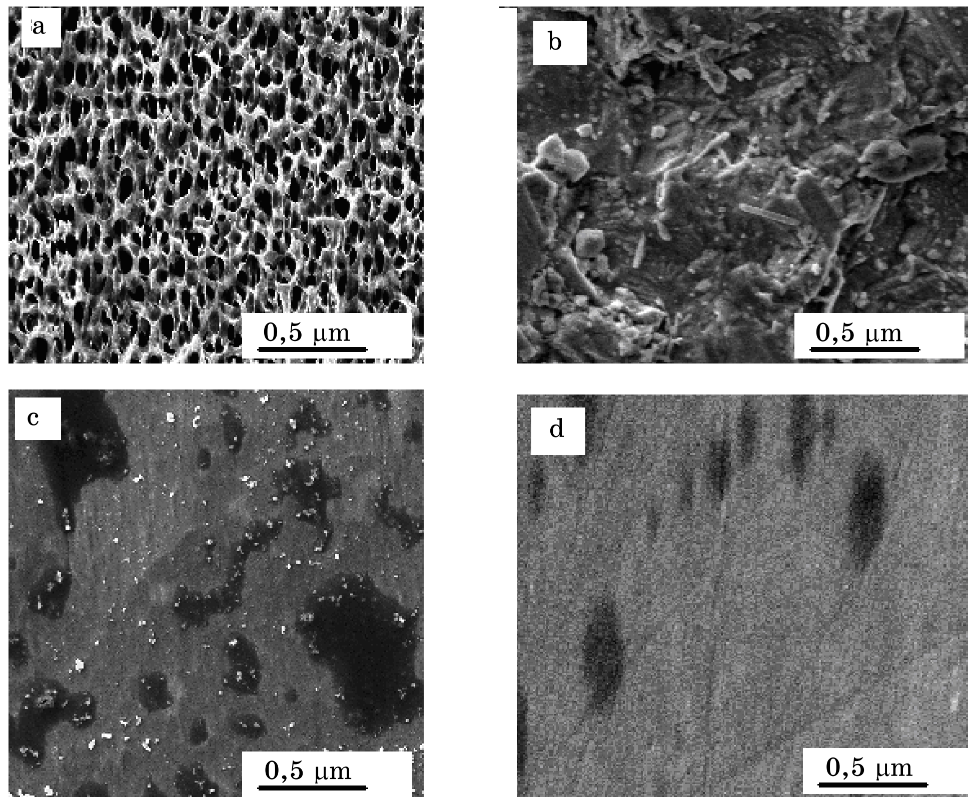


***Fig. 1*** – *SEM-image of the (001) InP porous surface,* $j = 100$ *mA/cm*$^2$*,* $t = 10$ *min. Concentration of impurity charge carriers:* $2{,}3 \times 10^{18}$ *cm*$^{-3}$ *(a),* $3 \times 10^{19}$ *cm*$^{-3}$ *(b),* $2 \times 10^{17}$ *cm*$^{-3}$ *(c),* $1{,}8 \times 10^{16}$ *cm*$^{-3}$ *(d)*

A porous layer with low pore density is formed during the etching of the semiconductor with the concentration of impurity charge carriers of the order of $1{,}8 \times 10^{16}$ cm$^{-3}$. However, in this case the obtained pores are sufficiently small (20-50 nm) and demonstrate a certain order and uniform distribution over the ingot surface. Moreover, the coarse etched areas, which appear due to the dislocation outcrop, can be observed on the sample surface. With the increase in the number of charge carriers, one can observe a completely different scenario for the pore distribution over the sample surface. Pores with different diameters (from 100 nm to 3 μm) appear under electrochemical treatment of the samples, which are doped with sulphur up to the concentration $2 \times 10^{17}$ cm$^{-3}$. Appearance of crystallites, which can indicate the formation of oxide islands on the upper porous semiconductor layer, is possible in this case. Another situation takes place during electrochemical treatment of the heavily doped InP crystals (about $2{,}3 \times 10^{18}$ cm$^{-3}$). Such concentration of impurity charge carriers is the most favorable for the formation of a qualitative porous layer on the surface of monocrystalline InP that is expressed in a high pore density and their uniform distribution over the plate surface. Pores, which are formed in this case, have a size of the order of tens nanometers, the degree of porosity is 60%. Varying other etching

conditions (current density, etching time), it is possible to obtain porous structures with different parameters (pore diameter, porosity, depth of the porous layer). However, while using materials for crystal etching with higher impurity concentration ($3 \times 10^{19}$ cm$^{-3}$), the surface etching without pore-formation is observed, that is the upper crystal layers just break off along certain planes. Such structures cannot be used as effectively as porous ones due to the fact that the surface layer is strongly disturbed. Thus, the given experiment demonstrates the role of the charge carrier concentration for the pore-formation on the semiconductor surface.

However, one should take into account that additional doping leads to the impurity segregation, which appears during the crystal growth. Elastic long-range stresses can impede the formation of continuous splicing surface. The regions of compositional and structural inhomogeneities, namely, the bands of impurity segregation and crystalline defect clusters [10] are the sources of these stresses. Microfluctuations of the growth rate on the boundary of the solid and liquid phases lead to the formation of the sulphur segregation bands (growth bands). Denser pore clusters in the central segregation lines with respect to the peripheral ones indicate the increase in the sulphur concentration along the direction from the centre to the InP crystal periphery. Moreover, sulphur distribution in InP crystals can be non-uniform not only along but also across the growth axis. In this case, change in the lattice parameter of the solid solution excites elastic stresses [10, 11].

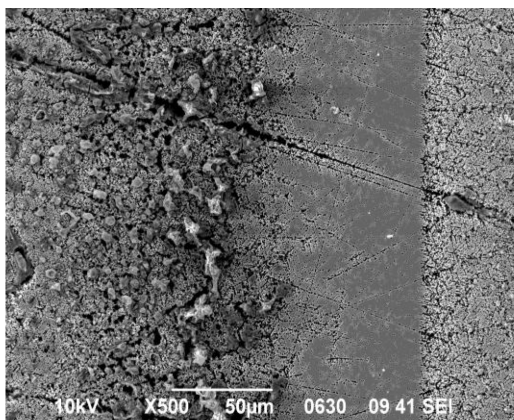


***Fig. 2** – SEM-image, which demonstrates the selective pore-formation on the heavily doped (111) n-InP; the impurity concentration is* $2,3 \times 10^{18}$ *cm*$^{-3}$

Moreover, significant etching of the crystal surface is observed in the areas of dense pore clusters. This can be connected with the outcrop of the secondary pores, as well as with the coalescence of small pores into bulk holes.

Generation of the bulk etching holes can be explained from the point of view of the impurity influence on the defect formation in the crystal. Doping with donor impurities up to the high concentrations is accompanied by the appearance of microdefects, but leads to the decrease in the dislocation density. Intrinsic point defects play the main role in the microdefect formation. At high doping levels, decomposition of supersaturated solid solution of the doping impurity influences the formation of microdefects. The main production problems during InP crystal growth are the following: tendency to twin-

ning, formation of dislocation clusters, and segregation phenomena conditioned by high impurity content in semi-insulating crystals. Impurity concentration, which is the function of the crystal growth rate, has periodicity and excites the so-called "doping streakiness". This is partly explained by the fact that the crystal growth rate on the microscopic level is not the same, but cyclic.

Appearance of nanoregions with different element concentration can lead to the qualitative change in the InP properties. Imperfection of the crystals connected with the striate growth structure influences the semiconductor properties of the crystals. Presence of the domain (the twin) structure is an undesirable factor from the point of view of using the given materials in optical devices and sensors. Therefore, investigation of the mentioned phenomenon is of a great importance from the point of view of both the crystal production technique and research of the properties connected with non-uniformity of the element distribution, which enter into the composition of the grown crystals.

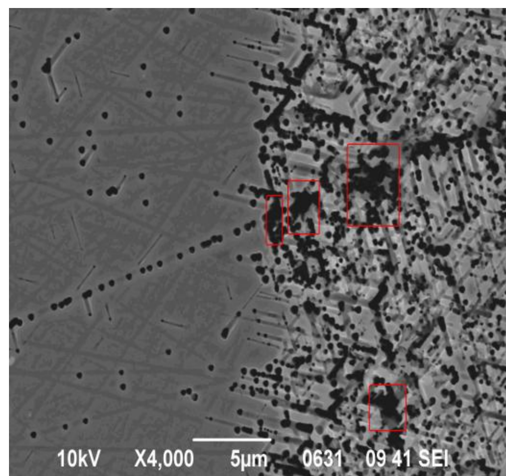


***Fig. 3*** *– Etched areas on the InP surface appeared due to the selective electrochemical etching*

## 4. CONCLUSIONS

Results of the performed study confirm the assumption that the concentration of impurity charge carriers of the semiconductor plays fundamental role for the porous layer formation on the surface. It is shown that in order the electrochemical process of InP etching is accompanied by the active pore-formation, it is necessary to use crystals with sufficiently high doping level. The best results are obtained if use $n$-InP with the charge carrier concentration $2,3 \times 10^{18}$ cm$^{-3}$. In this case it is possible to obtain a net of nanopores with high percentage of porosity. However, during the strong crystal doping the foliation of impurity distribution over the volume occurs that is undesirable phenomenon. Therefore, the quality improvement of the grown plates is the problem of modern physical engineering. Electrochemical etching can be a good performance criterion of monocrystals, since it allows to demonstrate the plate imperfection.

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