

Preparation of nanoporous n -InP(100) layers by electrochemical etching in HCl solution

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The manufacture procedure of porous InP with 30-40 nm pore size by electrochemical etching of n -type InP single crystals in HCl solution is presented. The X-ray diffraction studies and chemical composition determination using EDAX made it possible to establish the oxide film absence and a surface stoichiometry violation in the porous InP layers.

Представлена методика получения пористого InP с размером пор 30-40 нм методом электрохимического травления монокристаллов n -типа InP в растворе соляной кислоты. Дифрактометрические исследования и исследования химического состава методом энерго-дисперсионной рентгеновской спектроскопии позволили установить отсутствие оксидной пленки и нарушение стехиометрии поверхности пористых слоев InP.

1. Introduction

The porous substrates of A^3B^5 compounds are a material of promise for production of homo- and heteroepitaxial layers of improved structure perfection. So, in [1], unstressed $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers on porous GaAs were obtained; the properties of high-quality cubic GaN films obtained by nitridization on porous GaAs substrates, are presented in our work [2]. In [3], we have studied the photoluminescence of porous GaP films nanostructured by CdSe particles ($d = 2.8$ nm). The porous InP superlattices have been obtained and investigated in [4]. Therefore, the preparation of high-quality porous structures is an important physical and technological problem that became the research object for numerous scientists [5–11]. Nowadays, a special attention given to studying the properties of porous InP, because it is a very important material for producing a light-emission diodes and solar cells. The porous surface area is millions times larger than that of a single crystal.

This amazing feature allows to assess the advantage of porous layers for usage in the manufacture of sensors (because their sensitivity depends on the surface area) and solar cells (the accumulating possibility of a record energy amount). In [10], the electrolytic etching of n -InP (100) in a solution consisting of 1 M HCl (200 ml) and HNO_3 (2.5 ml) is described. Thus an ordered system of pores has been obtained with average pore diameter of 180 nm, the pore spacing (so-called pore walls) of 17 to 20 nm. Similar results were presented also in [12] where a porous n -InP (001) structure has been obtained at etching in electrolyte 1 M HCl (200 ml) + HNO_3 (3 ml). The pore diameter was of the order of 150 nm, the pore spacing, 17 to 26 nm.

The aim of our studies was to obtain porous InP nanostructures with minimum pore size. To that end, we have selected in experiment the threshold voltage of the pore formation onset, the paramount importance of that parameter being emphasized in [5]. The morphology and chemical composi-

tion of the obtained porous layers have been studied, moreover, the X-ray diffraction analysis has been carried out.

2. Experimental

The porous InP films were prepared by electrochemical etching of *n*-type (111) oriented crystalline InP substrate (concentration of carriers $2.3 \cdot 10^{18} \text{ cm}^{-3}$). The InP single crystals were obtained at the Molecular Technology GmbH laboratory (Berlin). As the electrolyte, the 5 % HCl solution was used. As the cathode, a platinum plate was used in the electrochemical cell. All the experiments were carried out at room temperature in dark. Prior to experiment, the samples were cleaned in toluene and isopropanol and then washed in distilled water. In the course of the electrolytical treatment, the voltage was raised at the rate of 1 V/min till the threshold voltage of the pore formation which in this case was 3.5 V ($t = 3 \text{ min}$). That was followed by the fixed voltage mode at which the samples were etched during 2 min. The total etching duration was 5 min. After the experiment, the samples were cleaned in ethanol and dried in a nitrogen flow for 10 min. The morphology of the obtained porous structures was studied by using a JSM-6490 scanning electronic microscope. The chemical composition was studied by EDAX method. The structure of porous InP samples was examined by X-ray diffraction using a DRON-3M diffractometer.

3. Results and discussion

It is emphasized [13] that the pore formation conditions always are limited by a more or less narrow range of polarization voltage. The sharpest, well-defined edge of that range is the minimum (threshold) voltage value necessary for the pore nucleation, so-called the pore formation threshold voltage [5].

The pore formation threshold voltage was determined as follows. The voltage variation rate was 1 V/min (during anodization). The current density (up to the critical voltage value) remained within limits of 20 mA/cm^2 . Starting from $U_c = 3.5 \text{ V}$, the current density increased in time sharply (up to 250 mA/cm^2 within 1 min, Fig. 1). This can be explained by a gradual increase in number of input ports of pores and branching thereof under the sample surface. After 1 min. the current ceased to rise. Thus, the pore formation threshold voltage for *n*-type (100) InP at the impurity concentration

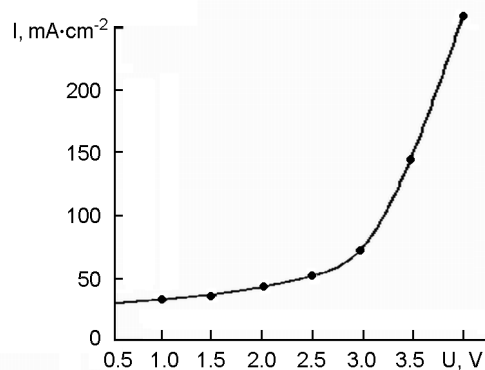


Fig. 1. Current-voltage characteristic of porous InP during anodization.

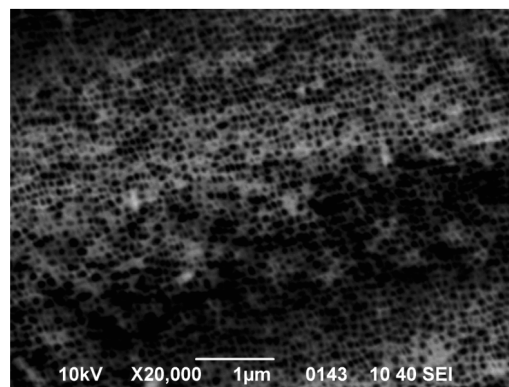


Fig. 2. SEM image *n*-InP (100) of surface after pore formation in 5 % HCl.

$2.3 \cdot 10^{18} \text{ cm}^{-3}$ is 3.5 V. It is to note that the pore formation threshold voltage depends on several factors: the semiconductor doping level and its orientation, the electrolyte composition and temperature, concentration of defects at the crystal surface, etc. Therefore, this quantity has different values for each individual case.

Fig. 2 images the morphology of a porous InP sample obtained by electrolytic etching of *n*-InP (100) in a hydrochloric acid solution. An ordered ensemble of pores is seen that was formed on a InP single crystal substrate. The pores penetrated the whole ingot surface. The pore size averages 40 nm, thus evidencing that the structure is nanosized [7, 10, 12]. The pore spacing is within limits of 5 to 10 nm. That result is of a technological importance, since the quality of porous films is defined by the nanostructure sizes, the porosity range and distribution uniformity of pores over the sample surface. The smaller is the pore size and the higher is the porosity range, the higher is the porous structure quality. So, for example, the photoluminescence in vis-

Table 1. Composition of porous InP surface by energy dispersive X-ray analysis

Element	O	P	In	Total
Atomic %	2.25	22.82	74.93	100.00

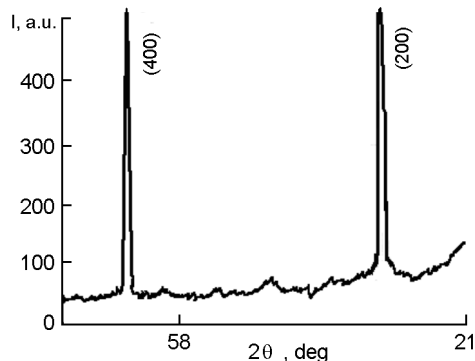


Fig. 3. X-ray diffraction pattern of porous InP (100).

ible spectral region is observed only for structures where the nanocrystallite size makes the order of nanometers [10, 12]. The penetration depth of pore channels is approximately 35 μm . It is to note that the porous layer depth is also an important characteristic. Numerous researchers are working in this direction [6, 7, 14-16]. The porosity range is approximately 30 % of the sample total surface.

The surface chemical composition was examined by EDAX method. Results of measurements are presented in Table 1. Proceeding from the chemical analysis results of *n*-InP (Table 1), it is possible to assert that the surface is practically oxygen-free, thus, the pore formation process occurred without oxide film formation. This is confirmed by the data of X-ray diffractometry using DRON-3M (Fig. 3). In Fig. 3, there are reflexes from InP single crystal structure (sphalerite) only. That is, during etching, no reorganization in the crystal lattice of indium phosphide occurred. The stoichiometry of the porous sample is shifted towards indium excess. This may be an evidence that it is just the phosphorus sublattice that is etched at a higher rate, i.e. that it is just *P* atoms that play the main part in the pore formation.

4. Conclusions

Thus, we managed to obtain nanoporous InP layers by the electrolytic etching of *n*-InP (100) crystals in a hydrochloric acid solution. The layers show the pore size of 40 nm and the pore spacing of 5–10 nm. The porous layer thickness amounted 35 μm . This testifies that the anodization results in formation of thin long pore channels parallel to each other having a shape close to a regular quadrangle in cross-section. Such a pore shape is defined by the surface orientation of the sample being studied.

No oxides have been formed during the electrolytic process at the sample surface, however, the initial crystal stoichiometry was distorted due to a faster etching of phosphorus sublattice. The porous samples obtained have the single crystal structure of sphalerite type.

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Отримання нанопористого *n*-InP (100), методом електролітичного травлення у розчині HCl

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Представлено методику отримання поруватого InP з розміром пор 30-40 нм методом електрохімічного травлення монокристалів *n*-типу InP в розчині соляної кислоти. Дифрактометричні дослідження й дослідження хімічного складу методом енерго-дисперсійної рентгенівської спектроскопії дозволили встановити відсутність оксидної плівки та порушення стехіометрії поверхні поруватих шарів InP.