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Synthesis and microstructure of p-type porous gallium phosphide layers

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Gallium phosphide is a semiconductor material of great interest for new modern LED technologies. Here we report the results of research on obtaining of nanostructured porous gallium phosphide layers by electrochemical etching of the monocrystalline (100) p-type GaP substrate surface. The structure and surface morphology of obtained samples were studied by scanning electron microscopy, atomic force microscopy and Raman spectroscopy. The chemical composition of nanostructured GaP surfaces was studied by energy dispersive X-ray spectroscopy, which showed that the pore formation during electrochemical etching are mostly due to dissolution of phosphorus atoms rather than gallium .It was found that shape and size of structures are strongly depending on electrochemical etching conditions. At constant applied voltage and varied current we observe that the pore size is increasing from 10 μm to 50 μm, and at fixed current, but varying the voltage the pore diameters can be achieved in the range between 100 to 200 nanometers.

Key words: gallium phosphide, porous structure, electrochemical etching, SEM, AFM.
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1 Introduction

Among modern electronic device technologies LED is one of the fast growing in the world [1]. Porous semiconductors are of great interest because of their interesting optical properties different of those for bulk material [2-4]. Gallium phosphide and related nanomaterials are of great interest as a research object for modern LED technologies and other photonic applications [5-7]. Porous gallium phosphide (por-GaP) is a very promising material for various photonic applications [8-10]. The first reports on por-GaP obtaining and characterization are referred since 1990s [11-14]. One of the most effective ways of obtaining porous structure from the $A^{III}B^{V}$ materials is electrochemical etching [15-17]. The advantages of the method are good process controllability and relative cheapness. By changing the parameters of electrochemical etching, such as current density, voltage and duration of etching, one can obtain porous structures of different morphology [18]. However, in most of reports there are description of n-type por-GaP, and the less is for p-type ones [19]. Present paper is devoted for investigation of features of p-type por-GaP layers electrochemical formation, their structure and surface morphology.

2 Experimental details

Porous GaP films were obtained by electrochemical etching of the single crystalline, (100) oriented, p-type GaP substrate surface using electolyte containing the mixture of ethanol (C_2H_5OH) and 40% hydrofluoric acid (HF), taken in a volume ratio of 1:1. Electrochemical etching was carried out in a fluoroplastic etching cell cell. In our experiments applied voltage was varied from 30 to 65 V, current density – from 1 to 10 mA/m^2 and etching time – between 10-40 minutes. Figure 1 shows the schematic representation of experimental electrochemical etching process.

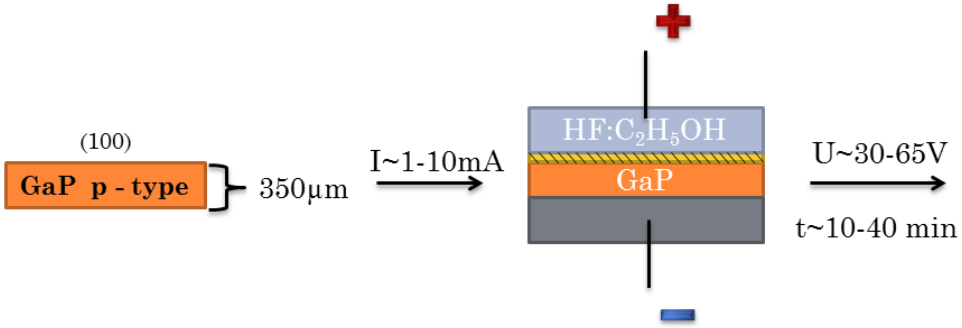

Figure 1 – Schematically representation of electrochemical etching process on the surface of monocrystalline GaP substrate

The microstructure of obtained por-GaP layers has been studied by scanning electron microscopy (SEM) using an ULTRA 55 FE-SEM (Carl Zeiss) microscope, and surface morphology was studied by atomic force microscopy (AFM) which measurements were provided on Integra Spectra (NT-MDT). Raman spectra of samples were measured on Solver Spectrum (NT-MDT) spectrometer in air at room temperature, excitation wavelength was 473 nm, acquisition time 30 s, and diameter of laser spot 2μm. The chemical composition of obtained surfaces was studied by Energy dispersive X-Ray (EDX) spectroscopy. Energy-dispersive X-ray spectra of samples were measured using the Bruker Quantax Flatquad.

3 Results and discussion

It us known that the process of porosity formation correlates directly with voltage, current density and etching time [20, 21]. One of the aims of our experimental study was to find up the optimal technological conditions of electrochemical etching for p-type por-GaP structures formation. The top view SEM images of por-GaP samples, obtained under different modes of electrochemical etching are shown in Figure 2a and 2b. One can see that the structural properties of por-GaP layers are directly depend on the parameters of electrochemical etching. It is experimentally shown that the formation of a uniform porosity on the surface is observed when the etching voltage is greater than 50 V. In this case, the surface structure of the samples is uniformly flat, and pore size are almost the same. For sample shown in Figure 2a pores sizes varied from 10 to 100 nm, thus structure could be considered as a nanoporous material. In addition, structure shown in Figure 2b has more loose structure with pore sizes varied from 200 nm to 40 μm. It is clear that the surface structure of samples obtained under low voltage and current intensity is non-uniform. This phenomenon can obviously be explained due to the different rate of dissolution under the influence of electromagnetic fields of different powers, which leads to dissolution of material in one (see Figure 2a) or several directions (see Figure 2b).

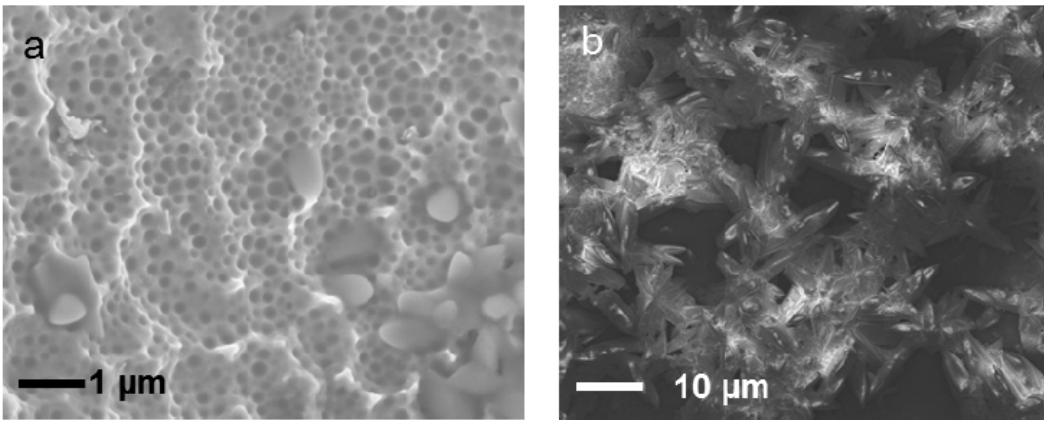

Figure 2 – Planar view SEM images of por-GaP surface obtained by electrochemical etching under: (a) U = 65 V, I = 10 мА, t = 15 min and (b) U = 30 V, I = 7 мА, t = 17 min

The surface morphology was also studied by atomic force microscopy (AFM) which allowed us to observe the pores size distribution on the surface of por-GaP layers. The top view AFM images of the por-GaP obtained under different electrochemical etching parameters are shown in Figure 3a and 3b. It is notable that the surface of porous layers becomes flattened after electrochemical treatment. When the etching time is longer, the surface of the sample is easily polished. The lightly polishing effect can be reached at low anodizing currents densities up to 5 mA/cm^2, voltages up to 40 V and the etching times up to 30 minutes.

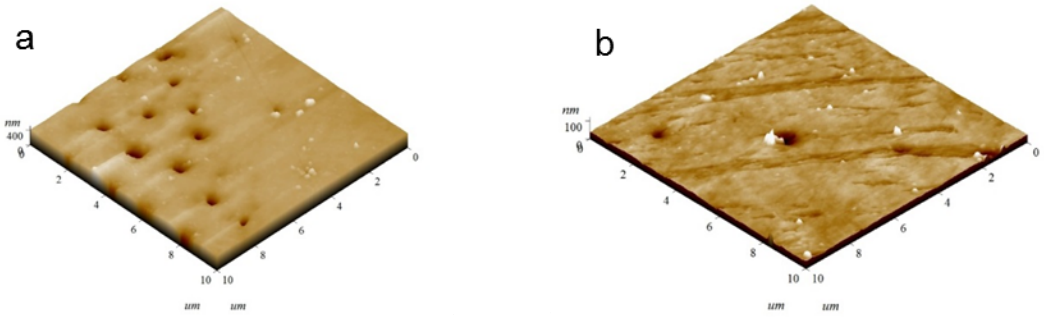

Figure 3 – AFM images of por-GaP surface obtained by electrochemical etching under: (a) U = 30 V, I = 5 мА, t = 25 min and (b) U = 40 V, I = 1 мА, t = 60 min

The method of energy-dispersive X-ray spectroscopy was used in order to identificate the elemental composition of samples. As shown in Figure 4, the basic element on the por-GaP is mainly gallium. The reason of such appearance is in the faster dissolution rate of phosphorus atoms rather the gallium ones. Since the initial substrate of crystalline p-type GaP is doped by Zn, there is also a signal of Zn appeared in EDX spectra. One can see that formation of pores during electrochemical etching process is mainly due to dissolution of phosphorus in electrolyte. Broken bonds of Ga ore passivized by oxygen. Thus por-GaP walls separating the pores are formed by GaO. Therefore, most of the porous skeletons are composed of Ga and GaO. According to data the sample also contains C, F, Zn, and Al, except of Ga, P and O elements in small amounts.

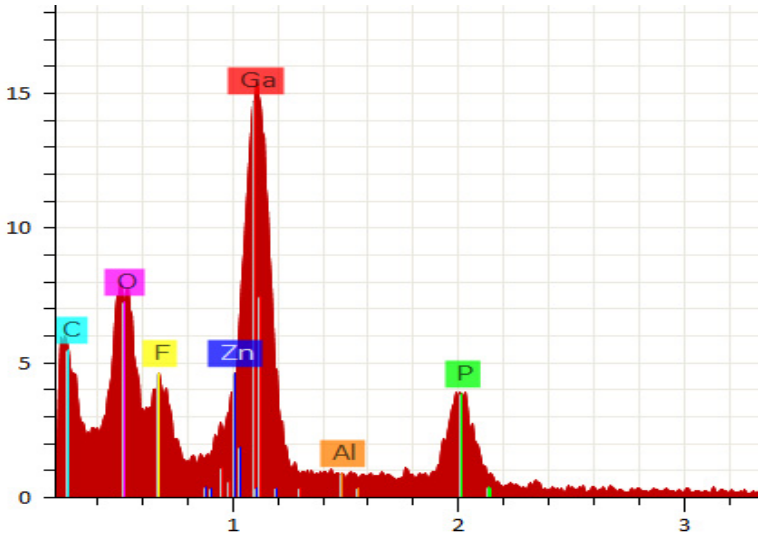

Figure 4 – Energy-dispersive X-ray spectrum of por-GaP sample obtained by electrochemical etching under U=30 V; I=5 мА; t=40 min

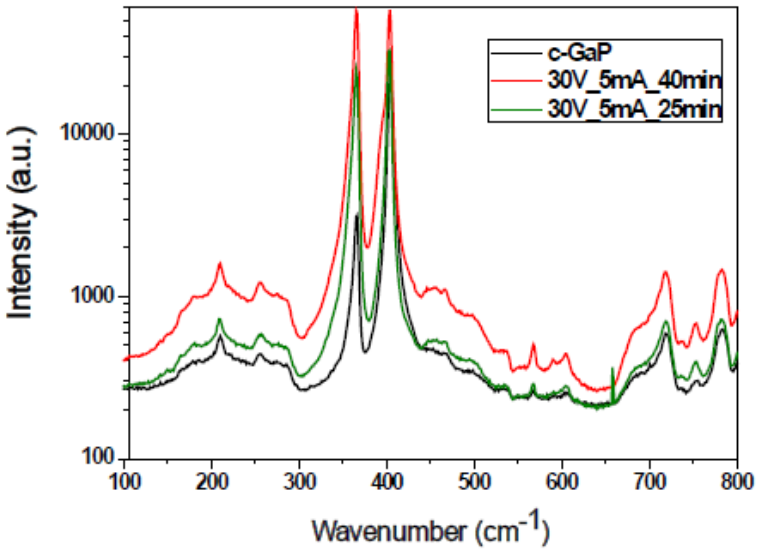

Figure 5 – Raman spectra of por-GaP samples obtained by electrochemical etching under different conditions

One of the linear optical methods for estimating the surface morphology and structure of nanostructures is Raman spectroscopy. In our experiments excitation wavelength was 473 nm, acquisition time was 30 s, diameter of laser spot was 2μm, enhancement factor was 100x, exciting laser power 30W. Figure 5 represents Raman spectra of the crystalline GaP and por-GaP samples obtained by electrochemical etching at different etching times. It should be note that both LO and TO oscillations modes of GaP (at 366 cm^{-1} and 404cm^{-1}) appeared in por-GaP layers spectra. One can see that at long etching times signal has a high intensity, which shows that the structure has changed. Por-GaP sample etched for 40 minutes also has extended shoulders in Raman spectra, which shows the beginning of phase transition from monocrystalline to the amorphous phase.

4 Conclusions

Electrochemical etching method was used to obtain p-type porous gallium phosphide structures, and effective technological conditions were formed. The dependence of the structural properties of the obtained porous gallium phosphide on the electrochemical etching parameters was investigated. The uniform porosity structure formation was observed when the anodizing voltage was higher than 50 V. In such a case, the surface structure of the samples becomes evenly flat. In such modes, the effect of light polishing on surface morphology appears. Energy-dispersive X-ray spectrum of por-GaP samples shows that formation of pores during electrochemical etching process is mainly due to dissolution of phosphorus in electrolyte. Raman spectroscopy showed that the structure of the long etched (40 minutes) samples was close to the amorphous phase. The high concentration of LO- and TO-oscillations shows that the crystalline direction of the first monocrystal GaP is preserved. Obtained results can be useful in further investigations of physical and chemical properties of p-type porous gallium phosphide nanostructures for different applications in photonics and opto-electonics.

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