

Electrochemical Formation and Microstructure of Porous Gallium Phosphide

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Electrochemical formation and microstructure of porous GaP have been investigated. Nanostructured porous GaP layers of thickness up to $\approx 20 \mu\text{m}$ were fabricated on *n*-type (111)-oriented crystalline c-GaP substrates. Studies of microstructure of porous GaP in dependence on electrolyte type and regimes of technological procedure have been carried out by scanning electron microscopy. The samples were characterized by spectroscopic ellipsometry in visible and near UV spectral range. The investigations have shown that the structure and optical response of porous GaP can be efficiently controlled by technological procedure of electrochemical formation. The shape and dimension of pores can be varied from nanometer-scaled cylindrical pores to GaP nanorods.

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1. Introduction

Recently, the low-dimensional structures are widely studied due to large perspectives in various applications. 1D structures like nanowires, nanorods and nanotubes have been shown to possess new physical properties perspective in the development of new-type electronic, optoelectronic and biotechnological devices [1]. Low-dimensional semiconductor structures are formed by various physical and chemical techniques like deposition from colloidal suspensions, metal-organic chemical vapor deposition (MOCVD), hydrothermal methods, etc. However, electrochemical etching technique has been widely used due to low expenses and large possibility to vary the morphology of fabricated structures [2].

A significant progress in understanding the process of electrochemical formation of porous Si [3] has aroused considerable interest in the studies of other porous semiconductors such as GaAs [4], InP [5] and GaP [6]. A particular attention is paid to porous GaP (por-GaP), which is expected to be a perspective material in photonics, optoelectronics and nonlinear optics due to a large refraction index (3.3) and wide forbidden energy gap (2.25 eV).

Anodic etching is the most suitable technique for the preparation of porous semiconductors of III-V group. The advantage of electrochemical formation of porous materials is that there are versatile parameters, e.g., etching current and time, illumination, substrate doping, using of which various morphologies of porous layers can be obtained. Particular features of the etching procedure for III-V semiconductors were determined and compared [2, 7] to those for IV and II-VI compounds. Uniform and

nonuniform nucleation of pores was observed [8] depending on anisotropy of the substances. The pores were classified [9] as “current line oriented” and “crystal oriented”.

Por-GaP has been successfully formed by electrochemical technique using electrolytes based on H_2SO_4 [10–12], HF [13, 14], and HNO_3 [15, 16]. Hence, a selection of various electrolytes presents an opportunity to control the microstructure of porous layers. In this paper, different electrolytes were used in the electrochemical process of the formation of por-GaP under similar conditions. Particular features of microstructure of por-GaP were revealed in the dependence on electrolyte. The optical response of por-GaP was investigated by spectroscopic ellipsometry in order to characterize the structures under investigation.

2. Experimental

Por-GaP samples were prepared by electrochemical anodic etching of 300 μm thick wafer of *n*-GaP with S-donor density $(5.0\text{--}5.3) \times 10^{17} \text{ cm}^{-3}$. The wafers were cleaned in hot isopropyl/ethanol and washed in distilled water. Etching was carried out in dark or moderate room illumination by exposing the (111) face of c-GaP to electrolyte. The aqueous solution of 0.5 M H_2SO_4 , ethanol solution of 3 M HNO_3 and HF: $\text{C}_2\text{H}_5\text{OH}$ (1:1) electrolyte were used. The backside contact was made by means of In-Ga eutectics and graphite electrode. The Pt-electrode was used as cathode in the electrolyte etching cell. The etching area of GaP was 6 mm in diameter.

The galvanostatic etching conditions were realized by using potentiostat Autolab PGSTAT 302 at constant current density j in the range 1–80 mA/cm². The etching time t_{etch} was varied in the range from 10 min to 1 h.

As a result of electrochemical procedure, the structures por-GaP/c-GaP were fabricated. The surface and cross-

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-section morphology of por-GaP was studied by means of scanning electron microscope (SEM) EVO 50 EP (Carl Zeiss SMT). The optical response was investigated in the region 250–800 nm by spectroscopic ellipsometer SOPRA GES 5. The software Winelli (SOPRA) was used for analysis of experimental spectroscopic ellipsometry data.

3. Results and discussion

Aqueous solution of H_2SO_4 is most frequently used electrolyte for electrochemical formation of por-GaP [10]. The etching rate increases at increasing the current density. However, the thickness of por-GaP is similar ($\approx 10 \mu\text{m}$) for various j -values (Fig. 1). It is reasonable to assume that Ga–OH compounds limit the thickness of porous layer. At small current densities, the pores were 10–50 nm in size. At increasing current density, the morphology of porous layer significantly changes. New pores arouse from initial pits and the size of pores and hence the porosity increased. At high current densities ($j \approx 80 \text{ mA}/\text{cm}^2$) the frame-type structure is formed (Fig. 2a) with pores 1–2 μm in size and the micropore walls of $\approx 250 \text{ nm}$ in thickness. Similar domains have been observed previously [9, 10, 17] at anodization in aqueous solutions of sulfur acid.

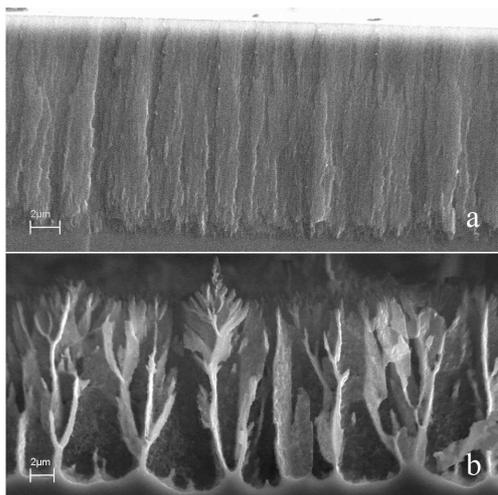


Fig. 1. Cross-sectional SEM images of por-GaP formed in aqueous 0.5 M H_2SO_4 solution in 1 h at $j = 1 \text{ mA}/\text{cm}^2$ (a) and $80 \text{ mA}/\text{cm}^2$ (b).

In aqueous solution of HNO_3 , the size of pores is by $\approx 45\%$ larger than that in H_2SO_4 due to different rate of oxide formation [15]. Nitric acid is a strong oxidizer and oxides, which have been formed in electrochemical processing, are well dissolved [18]. However, large acid concentrations should be used for effective formation of porous layer. A small potential variation leads to a significant change in the morphology of por-GaP [6].

In some cases (e.g., [9, 16]), porous semiconductor layers were formed in organic solutions of acids. In organic media the morphology of porous layers was changed because of decreased surface tension due to better wetting

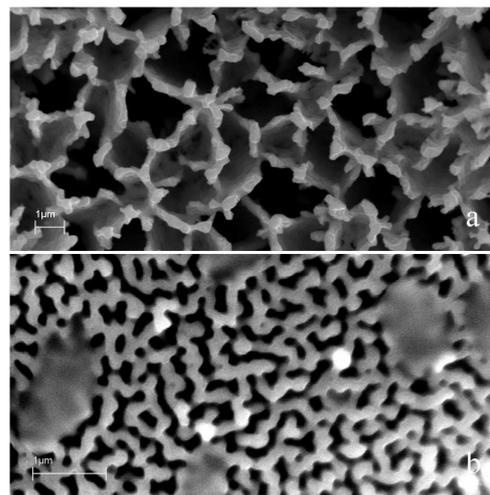


Fig. 2. Frame-structure in por-GaP formed in H_2SO_4 -based (a), HF-based (b) electrolytes at $j = 80 \text{ mA}/\text{cm}^2$ in 1 h.

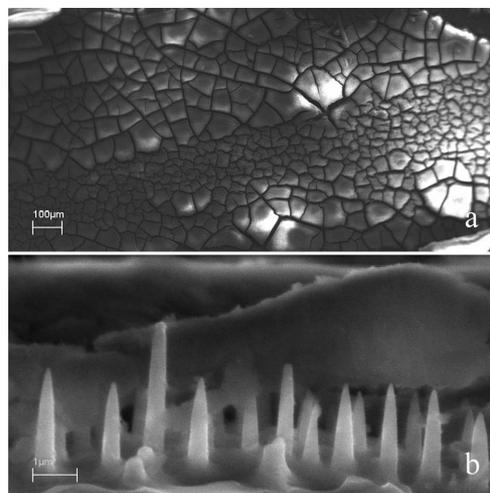


Fig. 3. Surface (a) and cross-sectional (b) SEM images of por-GaP formed in dark in ethanol solution of 3 M HNO_3 in 1 h at $j = 80 \text{ mA}/\text{cm}^2$.

conditions. In ethanol solution of HNO_3 , dissolubility of oxides decreases and the layer of oxides is formed on the top of por-GaP (Fig. 3a). However, due to a high porosity of oxide layer, an intensive etching of GaP continues. As a result, below oxide layer, a structure is formed consisting of nanorods of 200–400 nm in diameter, 2–3 μm in height which are located at a distance of 0.5–1.0 μm (Fig. 3b). It is reasonable to assume that ethanol is acting as stabilizer preventing the occurrence of branched structure.

Anodization in ethanol solution of HF at small current density leads to the formation of domains with irregular pores (Fig. 4a). The observed regularities in pore formation are in agreement with the radial model [10]. The seeds of pores are distributed randomly on surface

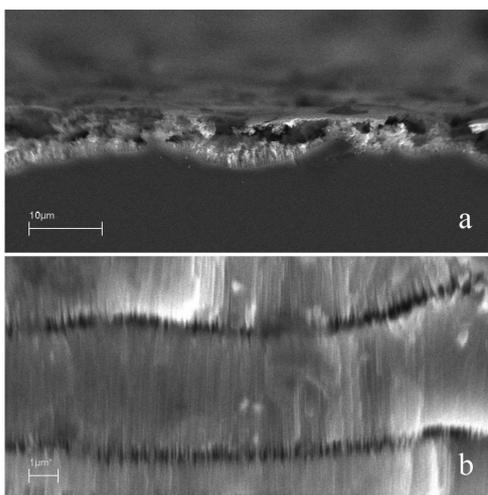


Fig. 4. Cross-sectional view of por-GaP formed in dark in HF:C₂H₅OH (1:1) electrolyte in 1 h at 1 mA/cm² (a) and 80 mA/cm² (b).

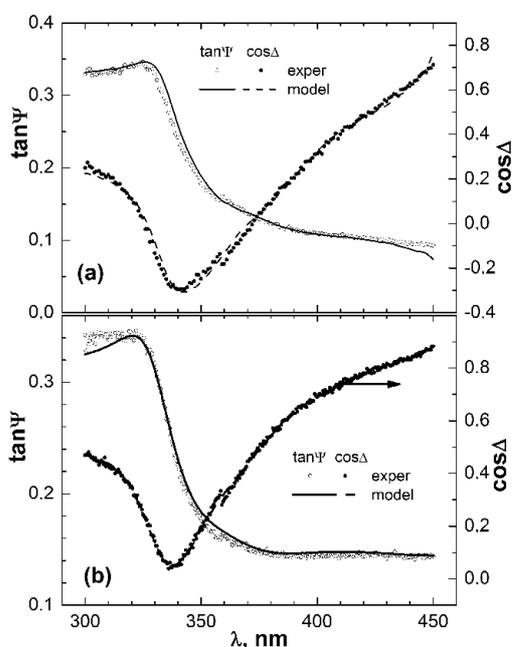


Fig. 5. Experimental (points) and modeled spectra (curves) of ellipsometric parameters for por-GaP formed in H₂SO₄ at $j = 5$ mA/cm² in 20 min (a) and at $j = 10$ mA/cm² in 10 min (b).

defects. As the etching process proceeds, the pits further develop into the petal-like structure and domains form. At high current densities the multilayer structure is formed (Fig. 4b) which consists of several layers of thickness 3–4 µm with pores of ≈ 300 nm in size. On the top of layers, nanorods similar to those formed in HNO₃ electrolyte were formed. The separation of layers is correlated to the burst of etching current at the transition to polishing regime. Inside a separate layer,

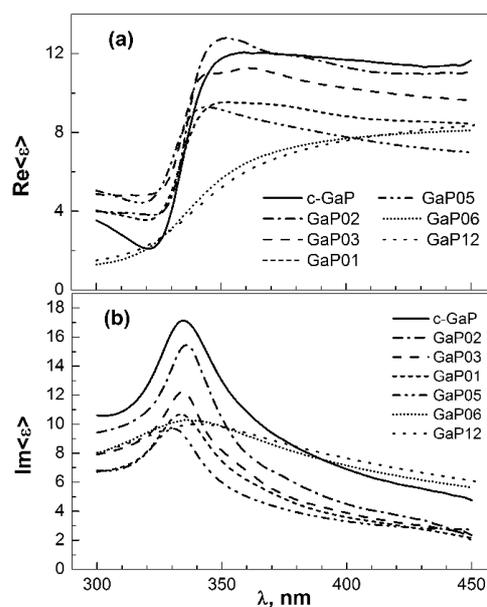


Fig. 6. Spectra of real (a) and imaginary (b) parts of pseudodielectric function for the samples formed at low current densities (1–10 mA/cm²) in H₂SO₄ (GaP1–3,5,6) and HF (GaP12) in short (10–20 min, GaP1–3,5) and long (1 h, GaP6,12) etching times.

a frame-like structure is formed (Fig. 4) with the pore walls of thickness ≈ 100 nm.

The optical response was investigated by spectroscopic ellipsometry to characterize the structures (por-GaP)/(c-GaP). The ellipsometric parameters Ψ and Δ were measured, where Ψ is the change in amplitude ratio and Δ is the change in the phase difference of polarized light upon reflection from a sample surface. Experimental data were analyzed in a pseudodielectric function $\langle \epsilon \rangle$ model [19] in which the optical response was considered in effective media approximation [20] (Fig. 5a) or in the model of a set of Lorentz-type oscillators (Fig. 5b). As parameters for porosity indication, the steepness of dispersion and peak intensity in the spectra of real and imaginary parts of $\langle \epsilon \rangle(\lambda)$, $\text{Re}\langle \epsilon \rangle(\lambda)$ and $\text{Im}\langle \epsilon \rangle(\lambda)$, respectively, at the E_1 peak (Δ -transitions) have been considered (Fig. 6). From the analysis of experimental data it follows that the porosity of GaP in the samples formed at small current densities (Fig. 6) varied in the range 0.05–0.30. The optical response of por-GaP depends critically on the etching time. For a long etching time (≈ 1 h) diffuse scattering of por-GaP has significantly increased.

4. Summary

Present investigations have shown that morphology of porous layers in por-GaP/c-GaP structures is strongly dependent on the electrolyte type. Typical characteristics of the corresponding porous layers were revealed. The electrochemical processing in aqueous solution of H₂SO₄ acid leads to a formation of nano-

sized (10–50 nm) current oriented pores at small current densities (1–10 mA/cm²) and short etching times (10–20 min). A frame structure of large (0.3–2 μm) pores with nanosized (100–250 nm) walls was observed in por-GaP formed in 1 h at large current densities (80 mA/cm²) in aqueous solution of H₂SO₄ and HF–ethanol electrolyte. The frame structure was developed from crystal oriented branched pores. In ethanol solution of HNO₃, a radial growth of pores is typical at low current densities. At high current densities, multilayer structures were fabricated in ethanol solutions of HF and HNO₃. On the top of layers a set of nanorods (100–400 nm) was formed.

The por-GaP/c-GaP structures were characterized by optical response measured by spectroscopic ellipsometry technique. The analysis of experimental spectra has shown that the pseudodielectric function $\langle \epsilon \rangle(\lambda)$ spectra provide characteristic features, the steepness of dispersion in the real part of $\langle \epsilon \rangle(\lambda)$ and peak intensity of imaginary part of $\langle \epsilon \rangle(\lambda)$ at E_1 -transitions, which allow one to estimate the porosity of the structures under investigation.

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