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Influence of current density of anodizing on the geometric characteristics of nanostructures synthesized on the surface of semiconductors of A3B5 group and silicon

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The correlation between the current density of anodizing semiconductors and the morphological characteristics of the formed nanostructures is investigated. The studies were carried out for semiconductors of the A_3B_5 group (InP, GaP, GaAs) and Si. Porous nanostructured layers were obtained by electrochemical etching in a solution of hydrofluoric acid at various current densities. As a result of the study, it was found that the current density affects the pore diameter, surface and bulk porosity and the thickness of the porous layer. The critical points of current density characterizing the beginning and end of active pore formation on the surface of semiconductors are determined.

Keywords: electrochemical etching, current density, nanostructures, porous semiconductors, pore diameter, porosity, thickness of porous layer.

Исследована корреляция между плотностью тока анодирования полупроводников и морфологическими характеристиками сформированных наноструктур. Исследования проводились для полупроводников группы A_3B_5 (InP, GaP, GaAs) и Si. Пористые наноструктурированные слои получены методом электрохимического травления в растворе плавиковой кислоты при различных значениях плотности тока. В результате исследования установлено, что плотность тока влияет на диаметр пор, поверхностную и объемную пористость и толщину пористого слоя. Определены критические точки плотности тока, характеризующие начало и конец активного порообразования на поверхности полупроводников.

Вплив щільності струму анодування на геометричні характеристики наноструктур, синтезованих на поверхні напівпровідників групи A_3B_5 та кремнію. *Я.О.Сичікова, І.Т.Богданов, С.С.Ковачов.*

Досліджено кореляцію між щільністю струму анодування напівпровідників і морфологічними характеристиками сформованих наноструктур. Дослідження проводилися для напівпровідників групи A_3B_5 (InP, GaP, GaAs) і Si. Пористі наноструктуровані шари були отримані методом електрохімічного травлення урозчині плавикової кислоти при різних значеннях щільності струму. У результаті дослідження встановлено, що щільність струму впливає на діаметр пор, поверхневу і об'ємну пористість і товщину пористого шару. Визначено критичні точки щільності струму, що характеризують початок і кінець активного пороутворення на поверхні напівпровідників.

1. Introduction

Porous layers on the surface of semiconductors are formed to provide crystals with new properties that single-crystals do not have [1, 2]. These properties determine the use of semiconductor nanostructures in lasers [3, 4], solar cells [5, 6], sensors [7], etc. Technologies for creating porous layers on the surface of semiconductors are well studied and used for many years. In [8], the porous layers were formed on the surface of gallium phosphide in 5 % of H_2SO_4 solution as an electrolyte. Further, inside the porous layers, two-dimensional metallic semiconductor grids with Pt nanotubes were manufactured by pulsed electrochemical deposition method. The authors have shown that metallic galvanic coatings in porous semiconductor matrices are useful for electronic and photonic applications, in particular for the manufacture of variable capacitive devices with high capacity. The authors of [9] demonstrated the synthesis of porous layers on *p*-GaAs in 49 % HF solution. It was shown that in addition to the porous layer on the surface, As_2O_3 crystallites are also formed. In [10], the authors studied the relationship between the conditions of etching and the configuration of pores on indium phosphide. It was established that the concentration of the electrolyte determines the cross-sectional diameter of the pores. In [11] it is shown that not only the concentration of the electrolyte affects the morphological characteristics of nanostructures, but also the type of anion electrolyte involved in the reaction of the anode dissolution of the semiconductor. The authors of [12] investigated the conditions for the formation of coral-shaped pores on the surface of monocrystalline Si. Such pores were formed by the technology of laser surface melting followed by delving. The proposed hybrid method provides the synthesis of a porous structure that can be used in lithium-ion batteries.

Despite the progress achieved in the technology of synthesis of porous structures, their industrial application is constrained by a number of reasons. First of all, this is due to the variety of methods of synthesis [13, 14] and, as a consequence, the diversity of nanostructures [15, 16]. This complicates the typing and allocation of common approaches to synthesis technologies [17]. Secondly, during the synthesis of nanostructures, their self-organization takes place [18], which is due to the characteristics of the output crystals [19, 20]. This prevents complete control over the synthesis of nanostructures with given parameters [21]. Third, despite the fact that there are many studies of the influence of synthesis conditions on the structural characteristics of nanostructures [22, 23], it has not yet been fully defined what way the synthesis conditions affect the morphological properties of porous layers on semiconductor surfaces [24]. Therefore, it is important to study correlations between the factors of the synthesis of nanostructures and their morphological properties.

The work is devoted to the establishment of correlations between the current density of anodizing semiconductors and the morphological properties of the porous structures synthesized on the surface of Si, InP, GaAs, GaP by the method of electrochemical etching.

2. Experimental

Sets of InP, GaP, GaAs, and Si *n*-type crystal plates with (111) surface orientation were used for the experiment. All the samples were chemically cleaned to remove surface contaminants before the experiment. The technology of conventional electrochemical etching was chosen as a method of forming a porous surface. The samples were subjected to electrochemical treatment in 50 % HF solution for 15 min. 13 series of experiments were performed at different values of current density for each sample batch from $j = 50$ mA/cm^2 to $j = 300$ mA/cm^2 with a step in $\Delta j = 50$ mA/cm^2 to investigate the correlation between the current density and the basic morphological characteristics of the porous layers on the semiconductor surface.

After the experiment, the samples were washed in deionized water and subjected to annealing in a stream of nitrogen. The morphology of porous layers was investigated using a scanning electron microscope JEOL. The statistical processing of the microphotographs was carried out using ImagePro and Origin software. The investigated morphological characteristics of the porous layers are the following: the thickness of the porous layer, the surface porosity, the volume pore size, and the average diameter of the pores.

The thickness of the porous layer is understood as a length of the channels of pores. As the surface porosity of samples we will understand the ratio of the area occupied by the pores to the total area of the sample:

$$P_{surf} = \frac{S_p}{S}, \qquad (1)$$

where S_p is the total surface area occupied by pores; S is the total area of the sample.

As the pore diameter we will understand the arithmetic average value for all pores in the field of view of the microscope.

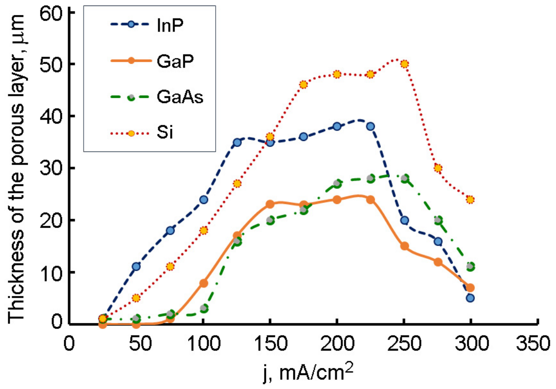

Fig. 1. Dependences of the thickness of the porous layer on the anodizing current density for InP, GaAs, GaP, Si crystals.

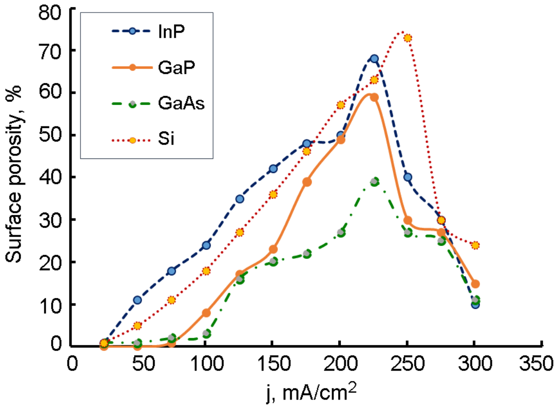

Fig. 2. Dependences of the surface porosity on the current density for InP, GaP, GaAs, Si semiconductors.

Volumetric porosity was determined by a gravimetric method. This method is based on the measurement of sample mass loss after anodizing:

$$P_{vol} = \frac{\rho_{bulk} - \rho_{por}}{\rho_{bulk}}, \tag{2}$$

where ρ_{bulk} is the density of a single-crystalline semiconductor, ρ_{por} is the density of the porous phase.

$$\rho_{por} = \rho_{bulk}\left(1 - \frac{d_{sample}}{d_{por}} \cdot \frac{m_{bulk} - m_{por}}{m_{bulk}}\right), \tag{3}$$

where m_{bulk} is the sample mass prior to the electrochemical treatment, m_{por} is the mass of the sample with the synthesized porous layer, d_{sample} is the thickness of the sample, d_{por} is the thickness of the porous layer synthesized during the anodizing.

The purpose of the experiment was to establish correlations between the morphological properties of the porous layers and the current density of anodizing, as well as to establish the peculiarities of the synthesis of the porous layer on the surface of different semiconductors under the same conditions of processing.

3. Results and discussion

3.1. Correlation between the thickness of the porous layer and the current density

Obviously, the thickness of the porous layer synthesized on the semiconductor surface depends on the technological modes of sample processing. Although the crucial role in this belongs to the parameters of the semiconductor crystal, which cause the appearance of synergistic phenomena, it is necessary to take the influence of processing modes into account for understanding the possibility of controlling the properties of nanostructures in the synthesis process. Fig. 1 shows the diagrams of the thickness of the porous layer on InP, GaAs, GaP and Si semiconductors depending on the current density of anodizing.

Analysis of Fig. 1 shows that InP and Si exhibit greater pore formation ability than GaP and GaAs. The activation of the process of pore growth into the depth of InP and Si crystals is already observed at a current density of $j = 50$ mA/cm^2. Whereas for GaP and GaAs, the minimum current density is 75 and 100 mA/cm^2, respectively.

The thickest porous layer was obtained on the silicon surface using the current density $j = 250$ mA/cm^2. Under these conditions, the thickness of the por-Si (porous-Si) layer reaches 50 µm. For por-InP, the greatest thickness of the porous layer is 40 µm at $j = 225$ mA/cm^2. The largest values of the thickness of the porous layer for por-GaP and por-GaAs are 24 and 28 µm, respectively.

In the range of current density of (125–200) mA/cm^2, an almost linear correlation is observed. That is, the higher the value of current density, the deeper the pores moving into the depth of the crystal. When the saturation value is reached, the current density ceases to cause the growth of pores in depth. The diagram shows a plateau. The optimal current density to obtain a thick porous layer on the surface of semiconductors can be considered as the first critical point of the current density $j_{crit1por}$. Under these conditions, a regular porous layer forms that does not collapse. A decrease in the thickness of the porous layer is observed when the second critical value of the current density $j_{crit2por}$ is reached. This is

Table 1. Values of the critical points of current density for InP, GaP, GaAs, Si semiconductors (etching conditions: $HF:H_2O = 1:1$, $t = 15$ min)

Semiconductor	$J_{crit1por}$, mA/cm^2	$J_{crit2por}$, mA/cm^2
InP	125	225
GaP	150	225
GaAs	200	250
Si	175	250

due to the fact that, at very high values of current density, an alternative electrochemical process — polishing the surface of the semiconductor — occurs. It is interesting that with a sharp increase in current density, the porous layer is separated from the single-crystal substrate and crumbles into the electrolyte. The values of the critical points of current density are presented in Table 1.

The analysis of the Table data shows that in the given conditions of etching (electrolyte $HF:H_2O = 1:1$, etching time $t = 10$ min), indium phosphide has the widest current density range of formation of a porous layer in the sample depth ($\Delta j = 100$ mA/cm^2), the least range is for gallium arsenide ($\Delta j = 50$ mA/cm^2). For silicon and indium phosphide, the range of current density suitable for the formation of porous space is $\Delta j = 75$ mA/cm^2.

3.2. The dependence of surface and volume porosity on the current density of anodizing

Fig. 2 and 3 show the correlation dependences of surface and volume porosity on the current density of anodizing. Analysis of these dependences allows us to see that intensive pore formation begins with the value of current density specified for each individual case. Silicon is the most active in the ability to pore formation. Gallium arsenide shows the lowest porosity indexes. Correlation dependences follow the power law. However, starting with some value of the anodization current, both volumetric and surface porosity shows a sharp decrease in its value. These results correlate well with the above-discussed dependences of the porous layer thickness on the current density. That is, the hypothesis is confirmed that excessively high values of current density lead to electrochemical polishing of the crystal surface.

Analysis of the dependences also shows that the growth rate of the surface porosity is higher than the rate of volume one. This result is logical, since the process of pore growth begins with the formation of etching pits on the crystal surface (Fig. 4). The higher the value of current density, the faster the etching pit grows in width. This leads to the growth of surface porosity. The greatest value of the surface porosity is registered for silicon: at the value of the applied current density of 250 mA/cm^2, $p_{surface} = 73$ %. This correlates well with the value of the second critical point $j_{crit2por} = 250$ mA/cm^2.

Table 2. Average diameter of pores on the surface of InP, GaP, GaAs, Si semiconductors at different values of the anodizing current

j, mA/cm^2	d, nm			
	InP	GaP	GaAs	Si
25	18	0	14	5
50	41	0	21	17
75	54	51	72	25
100	55	58	130	48
125	58	73	169	71
150	75	104	198	83
175	79	167	209	145
200	139	209	278	257
225	168	293	305	263
250	61	130	381	333
275	31	23	78	130
300	11	0	0	27

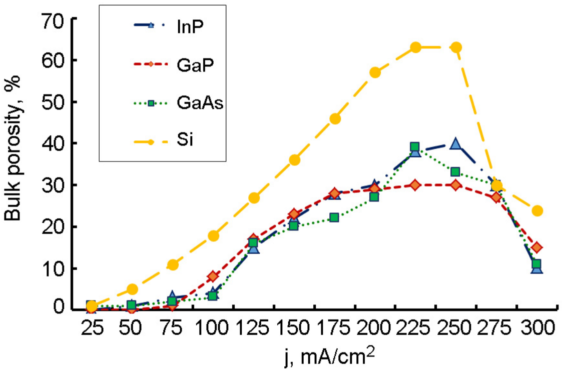

Fig. 3. Dependences of the volume porosity on the current density for InP, GaP, GaAs, Si semiconductors.

3.3. Influence of current density on the pore average diameter

Table 2 shows the values of average diameter of pores on the surface of InP, GaP, GaAs, Si semiconductors at different values of the anodizing current. From the analysis of the data it follows that under given etching conditions, the smallest pores are formed on the surface of indium phosphide (the maximum average diameter d = 168 nm at j = 225 mA/cm^2. The largest pores formed on the surface of gallium arsenide (d = 381 nm) at j = 300 mA/cm^2.

It can be seen from Table 2 that the pore diameter increases with increasing anodizing current density. This dependence is observed for a wide range of current density. The etching of crystals at values of $j >> j_{crit2por}$ leads to the formation of single meso- and macropores, the appearance of which can be explained by etching of surface defects.

Increasing the pore diameter at high current densities ($j \to j_{crit2por}$) compared with low current modes indicates that the porosity of the samples increases not by increasing the number of pores. The number of formed pores at different values of current density remains almost the same. Growth of porosity (both volumetric and surface) occurs as a result of an increase in the effective diameter of pores. This behavior is characteristic of all investigated semiconductors. Reducing volumetric porosity (and hence the surface of the pores) when $j > j_{crit2por}$ occurs due to the etching of the upper porous layers, that is, due to the decrease in the thickness of the porous layer.

4. Conclusions

Thus, the study of correlations between the current density and the morphological characteristics of porous layers synthesized on the surface of InP, GaP, GaAs, Si semiconductors made it possible to understand some general patterns of nanospace formation during anodic treatment of crystals:

For given etching conditions ($HF:H_2O$ = 1:1, t = 15 min), there is a more or less narrow range of current density $j_{crit1por} \le j \le j_{crit2por}$, where the formation of a porous layer on the surface of semiconductors becomes possible. These ranges are: (125–225) mA/cm^2 for InP, (150–225) mA/cm^2 for GaP, (200–250) mA/cm^2 for GaAs, and (175–250) mA/cm^2 for Si. Electrochemical etching in this range leads to the formation of porous space on the surface of semiconductors. For other etching conditions (electrolyte composition and processing time), another range of critical values of current density will be characteristic. However, the general patterns of pore formation will be maintained.

The anodizing current density determines the micromorphology of the porous layers, in particular, it determines the morphological characteristics such as: surface and volume porosity, the thickness of the porous layer and the diameter of the pores. As the anodizing current increases, these characteristics of the porous surface grow. This occurs for current values lower than the second critical current density $j_{crit2por}$. When applying the $j > j_{crit2por}$ modes, the anodizing occurs by alternative electrochemical mechanisms, namely, the polishing of the surface of the samples takes place.

Increase of porosity with increase of anodizing current is caused not by increase in the number of pores, but by the growth of pore transverse diameter. The number of pores at different values of current density remains almost the same.

Different semiconductors under the same conditions of electrochemical treatment demonstrate a different ability to pore formation. For the selected etching conditions ($HF:H_2O$ = 1:1, t = 15 min) and the parameters of the output crystals (orientation of the <111> surface, n-type of conductivity), indium phosphide is the most active in the pore formation, gallium arsenide is the least active.

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