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Track:

Properties and Characterization of Surfaces and Interfaces

Photoluminescence of Porous Indium Phosphide: Evolution of Spectra During Air Storage

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***Abstract*— The results of studying the nature of the porous indium phosphide visible photoluminescence are presented in the paper. The nature of PL bands in the spectrum visible portion is described using the quantum-confined approach. The por-InP PL spectra after exposure to air for 3 months were studied. As a result, additional bands appear due to the skulling of pore walls with oxides.**

***Keywords*— porous layers; electrochemical etching; photoluminescence; nanostructures; indium phosphide.**

I. Introduction

Porous semiconductors are an object of study of scientists for several decades [1-5]. Practical application of porous crystals suggests the need for their obtainment with an atomically clean surface [6, 7]. Interest in the study of the surface and interfaces of semiconductors is conditioned by the trend of microelectronics in the miniaturization of devices and elements of integrated circuits [8, 9]. It is obvious that a change of the surface chemical composition is associated with processes causing a modification of its relief [10, 11].

The appearance of visible luminescence in porous semiconductors is explained on the basis of various models [12-14]. The most widely used model is the model based on the size quantization, which explains the appearance of luminescence by transitions to zero and one-dimensional nanocrystallites, and its degradation by the processes arising on the semiconductor surface [15]. As it is known, the operating characteristics of opto-electronic semiconductor devices depend on the crystalline perfection of surface layers [16, 17].

Unlike silicon and germanium the semiconductor compounds of A3B5 type have less hardness and are more chemically active [18, 19]. On the other hand, the surface properties of semiconductor wafers are most often used. This is especially important when creating a nanorelief on the semiconductor surface [20]. Types of treatments, in particular finishing etching and washing, as well as prolonged contact of the semiconductor with air, facilitate the formation of hydroxide layers of thickness from 0.5 to several tens of nanometers [21]. This results in the surface chemical heterogeneity and causes further processes of the semiconductor interaction with surrounding environment. Composition of the residual oxide on the surface of wafers is not uniform in depth. It depends on the nature and ratio of the etchant components [22]. Oxidation of the semiconductor surface is a consequence of air effect after etching. The crystal-oxide interface has a significant defectiveness. At the interface between indium phosphide and oxides the defects of stoichiometric composition are always available, which take part in the formation of surface electronic states [23]. In addition to the states located on the semiconductor surface, surface states appear both inside and on the outer surface of the oxides.

The purpose of this paper is to study the changes of the porous indium phosphide photoluminescence spectra of when stored in air.

II. Samples and Experimental Technique

For the experiment the single-crystal n-InP (100) samples with a carrier concentration of 2.3 × 1018 cm-3 were chosen. Porous layers of InP were prepared by electrochemical etching of monocrystal n-InP in the solution of hydrofluoric acid with platinum electrode at the cathode. Before the experiment, the samples were purified in acetone, isopropanol and methanol, then washed in distilled water and subjected to nitrogen gas. Indium was sprayed onto the InP surface as a contact. Platinum worked as the cathode. After cleaning the samples were placed in an electrolytic bath with working surface area of 0.12 cm2. As the electrolyte we choose a solution of hydrofluoric acid, water and ethanol in a ratio of 1: 1: 2. For the experiment the regime of constant voltage was chosen, current density was chosen in illumination the range 50...100 mA/cm2, etching time – 5-20 min. The surface was uniform over the sample area. Chemical composition of the samples was studied using the EDAX method. The photoluminescence spectra were recorded with the help of the spectrograph VSWU-23 at room temperature. As the excitation source a LGI laser with wavelength of 337 nm was used. Structural studies of porous samples were carried out by X-ray diffraction. To exclude the effect of volume on the X-ray diffraction analysis results the study of porous layer was performed by the method of sliding irradiation.

III. Results and Discussions

The chemical analysis of the porous InP surface (the spectra were taken in 4 points – see Fig. 1) showed a violation of stoichiometry of the initial crystal. On the sample surface the oxygen atoms and an insignificant fraction of fluorine atoms appeared (Table 1). This indicates the creation of so-called native oxides of InP. It is known that formation of the following thermodynamically stable oxides $In(PO_3)_3$, $InPO_4$, $InPO_3$, In_2O_3, P_2O_5 is possible.

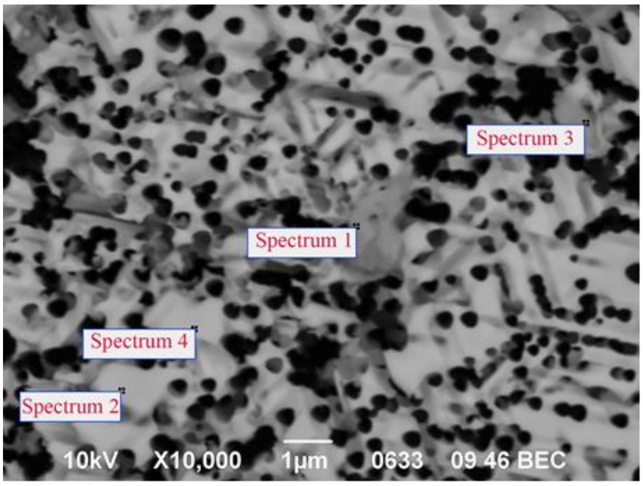

Fig. 1. Surface of porous n-InP(111), $HF:H_2O:C_2H_5OH$, j=80 mA/cm^2, t=10 min

TABLE I. PERCENTAGE COMPOSITION OF ELEMENTS ON THE SURFACE OF POROUS N-INP

Spectrum	O	F	P	In
Spectrum 1	15.33	2.13	22.12	60.41
Spectrum 2	2.12	0.64	22.36	74.89
Spectrum 3	6.76	2.05	21.03	70.15
Spectrum 4	2.73	1.07	22.10	74.10

Analyzing Table 1, we can conclude that a uniform oxide film did not form on the porous crystal surface. The localization of oxides is observed only in some areas. X-ray spectral analysis of the layers did not show the availability of elements present in the electrolyte, except for a small fraction of fluorine (1 – 2%) and oxygen, the appearance of which on the surface of the samples may be associated with interaction of the porous surface with atomic ambient oxygen.

X-ray diffraction analysis of porous InP samples indicates that the porous layer lattice parameter and monocrystal section of the sample coincide (θpor = θmon = 5.8633Å). In addition to the diffractometric peaks from InP, peaks corresponding to the cubic phase of In2O3 were observed. The percentage of other oxides (In_2O, InO, P_2O_5, P_3O_5) is so small that they can be neglected.

The presence of oxygen (2%) on the surface of just prepared samples may be explained by the fact that even during etching it may be embedded in the crystal structure, forming clusters, islands and crystallites consisting of native InP oxides. However, such a small amount of oxygen may not contribute to the processes of radiative recombination of indium phosphide.

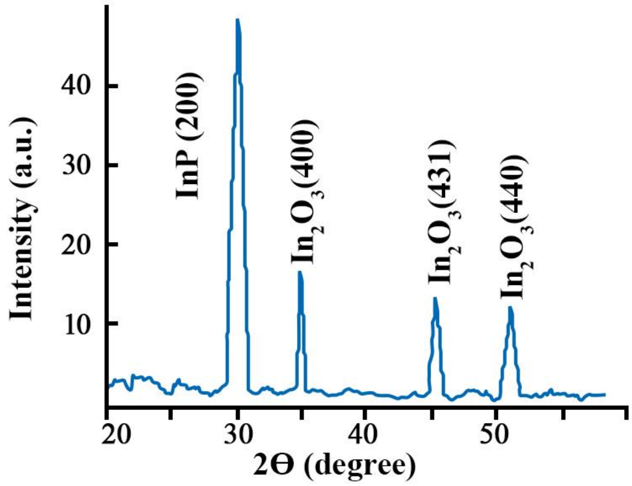

Fig. 2. X-ray diffraction analysis of por-InP (j = 80 mA/cm2, t = 10 min)

Immediately after the purification procedure the samples were placed in the vacuum unit for spectra measurement. In Fig. 3 there are PL spectra of newly prepared samples.

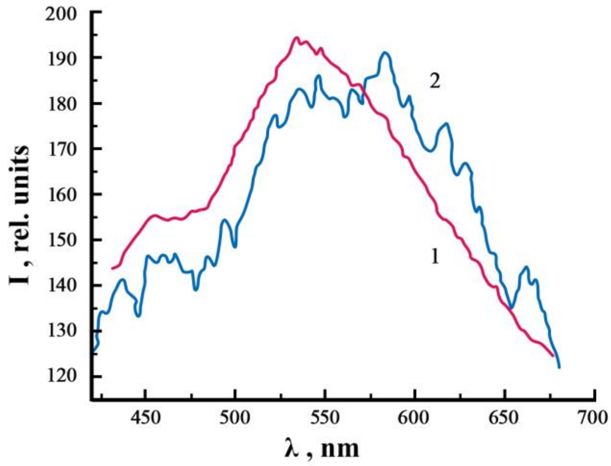

Fig. 3. PL spectra a) sample No. 1 (j = 30 mA/cm2, t = 10 min); sample No. 2 (j = 50mA/cm2, t = 10 min)

The porous indium phosphide PL in the area of 500-800 nm are usually attributed to the inhomogeneously broadened emission of nanocrystallites, which is determined by quantum-size effect [24, 25]. The absence of contact between porous InP and atmospheric oxygen gives grounds for exclusiom from consideration the cause associated with various types of oxides on the pore surfaces and their contribution to the radiative recombination processes.

After the samples stayed in air for 3 months, the oxygen content on the sample surface increased significantly. Depending on the initial porosity the films had a different proportion of oxide. Table 2 shows the oxygen content for samples with various degrees of porosity.

TABLE II. OXYGEN CONTENT FOR POR-INP SAMPLES WITH VARIOUS DEGREES OF POROSITY

Porosity, %	Oxygen content, %
20	15
26	17
42	20
64	27

Such behavior of the samples is conditioned by various factors. First, as a result of electrochemical etching the semiconductor surface contains a significant amount of defects, such as etched areas, dislocations exposing the crystal surface. Secondly, such a surface is characterized by increased concentration of broken bonds, which occurs as a result of uneven etching of phosphorus and indium sublattices. All this result in the formation on the crystal surface of oxide "islands" and films.

As the porous indium phosphide is aged in air, the maximum of the main band shifts to the short-wave side. The PL brightness in por-InP aging increases. The spectra of PL samples stayed in the air for 3 months are characterized by the availability of two luminescence bands in the visible spectral range – in the range of 535-560 nm and 440-460 nm (Fig. 4). The band localized in the interval 440-460 nm may be explained by the appearance of oxides on the crystal surface. It should be noted that the study of the porous indium phosphide PL spectra evolution over the time is a critical moment for the further use of these structures, since the material oxidation with time significantly changes its optical properties.

The shift of photoluminescence maximum to the spectrum short-wave area may be explained by the skulling of nanocrystallites by oxide layers, the interporous spaces become much thinner (Fig. 5). The skulling of porous nanomaterial by a layer of oxide occurs for certain reasons.

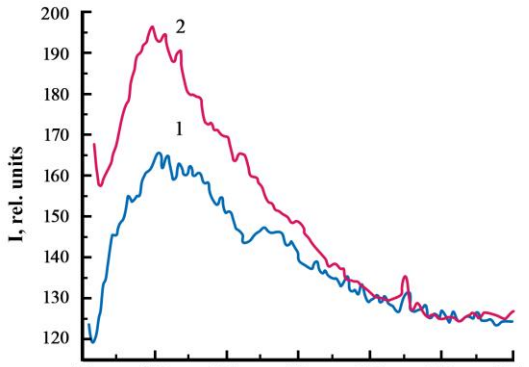

Fig. 4. The PL spectra of porous InP samples that stayed in the air for 3 months

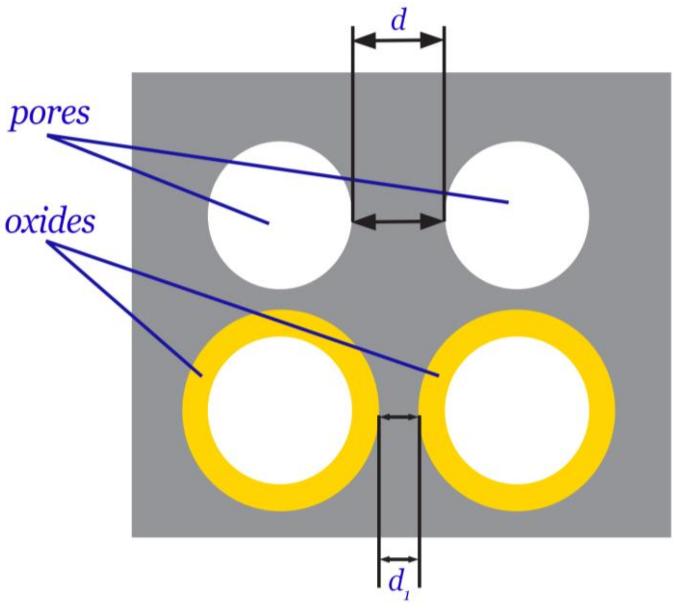

Fig. 5. Diagram showing the skulling of walls between pores by oxides

Porous surfaces are characterized by high density of surface states in the forbidden band, which results in the fixation of Fermi level, the position of which on the surface slightly depend on the nature of the adsorbed atoms. This circumstance negatively affects the operation of many micro- and optoelectronic devices, preventing to fully reveal the high potential of these semiconductors. To eliminate the undesirable surface effects on the properties of devices, the direction, called "passivation", is actively developing in the technology within the framework of which various methods of surface treatment associated with the application of coatings are developed [26].

IV. CONCLUSIONS

The results of studying the effect of electrochemical pore formation regimes on the surface of indium phosphide demonstrated the dependence of the optical properties of porous structures on etching conditions. A study of newly prepared porous samples using diffractometry and EDAX method showed that the oxygen content on the surface of these structures does not exceed 2%. PL spectra taken immediately after the InP electrolytic anodization process demonstrate the shift of the PL base band as compared to the monocrystal indium phosphide to the short-wavelength area of the spectrum. In this case the photoluminescence maximum is localized in the area of (520 - 570) nm. The absence of contact with atmospheric oxygen from newly prepared porous structures allows for the conclusion that in this case it is the low-dimensional effects that are responsible for the visible photoluminescence in the InP porous layers.

The repeated studies of the samples after their presence in air for 3 months demonstrate an increase in the oxygen proportion on the crystal surfaces up to 27%. This effect is conditioned by the oxidation of porous structures, which is the more intense the higher the porosity degree of the samples to be studied. This behavior may be described from the point of view of the effect of defects, dislocations and dangling bonds on the process of the surface population by oxides. In this case, spectra of the PL samples demonstrate the appearance of additional emission band located in the range of 440-460 nm, the nature of which is the presence of native oxides on the porous InP surface.

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