The effect of electrochemical oxidation time on the surface morphology of oxidized indium phosphide

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Abstract. The surface features of oxide layers (< 100nm) grown on single-crystal n-InP (100) samples in acid electrolyte on initial stage were investigated by atomic force and lateral force microscopy. The time of electrochemical oxidation of samples was the variable parameter. There is difference found in the oxide layer phase structure grown in the electrolyte during different time. The initially formed (17 s) islands (a nucleated oxide phase) were divided, then coalescence appeared (26 s), and the occurrence of a second phase was detected. With an increase in the time (40 s) of oxidation, the surface morphology becomes more uniform.

1. Introduction
At present, sensors based on field-effect transistors and metal–insulator–semiconductor (MIS) structures with insulator made of metal oxides and SiO₂, as well as those based on electrochemical and thermochemical detection methods are used as hydrogen sensors. They have obvious disadvantages, such as low performance, high cost, large size and weight. The main problem of most hydrogen sensors is the need to increase the temperature of the sensitive element to 200-400 ºC, which can increase the risk of fire or explosion.

But there is another type of semiconductor hydrogen sensor, in which palladium (Pd) is used as a sensitive layer. In such devices, hydrogen interacts with palladium, so the electrical and photoelectric properties of the structures used in these devices (field effect transistors, MIS structures, structures with a Schottky barrier) change. They possess such qualities as the ability to work at room temperature, selective sensitivity to hydrogen and low energy consumption. [1]. The purpose of a number of works [1-5] is to create and study a photoelectric hydrogen sensor based on Schottky diodes with a palladium contact to indium phosphate (InP).

The study revealed that electrochemical oxidation of the indium phosphide surface can improve the performance of the device based on it: increase the cutoff voltage, reduce reverse currents, reduce noise, etc. Electrochemical oxidation is a technologically simple, flexible and cheap method of creating oxide. However, the advantages of A³B⁵ compounds over silicon are opposed by the fact that they lack a good and technologically compatible dielectric, such as, for example, silicon dioxide SiO₂ in silicon electronics. So several different thermodynamically stable oxide phases can form on its surface, such as: In(PO₃)₃, InPO₄, InPO₃, In₂O₅, P₂O₅, during the anodic oxidation of indium phosphide. As the fraction of In₂O₃ decreases, and the fraction of InPO₄ and In(PO₃)₃ increases, the density of surface states of the interface decreases and the stability increases [1, 4, 5]. The presence of In₂O₃ and its distribution and the thickness and area of the transition layer are the main factors determining the electrophysical
properties of the metal-oxide-semiconductor (MOS) structure [5]. Therefore, the performance of a photodetector with a similar structure varies depending on the structure and composition of this material.

There is currently a discussion on the effect of technological conditions of anodizing on the phase composition of oxide layer on InP.

2. Experiment

AFM methods based on atomic force microscopy (AFM) besides a detailed study of surface morphology allow a qualitative study of various surface properties and characteristics with high lateral resolution. Moreover, by combining several approaches, it becomes possible to detect the phase composition of multicomponent nanostructured materials [6, 7]. Lateral force microscopy in combination with thorough analysis of AFM data (in the forward and backward passages) potentially allows to detect the presence of another phase by detecting changes of friction force between AFM tip and the sample surface [6, 8].

We studied samples representing a plate of single-crystal indium phosphide (InP) of orientation (100). The concentration of the main charge carriers is approximately \( n = 2 \times 10^{16} \text{ cm}^{-3} \). Electrochemical oxidation of the InP surface was performed in acid electrolyte (pH=2) with subsequent heat treatment of the oxide layer at a temperature of 100 °C for 5 hours. The anodization time was the variable parameter. 3 types of samples were obtained, the anodizing time of which was: 17 s, 26 s, 40 s.

Atomic force microscopy was carried out using the Ntegra Terma probe nanolaboratory (NT-MDT) in contact mode. The sizes of scans are 5 by 5 microns, since this size allows you to see both the small features of the surface and its general character. The scanning speed was chosen empirically and equal to 3 \( \mu \text{m/s} \). Too fast scanning speed will lead to incorrect display of the terrain, as the probe, for example, after large irregularities will slip part of the terrain. Too slow speed will greatly delay the measurement process, although it will give a sharper image. Silicon probe sensors of the brand UNISET_ET_EFALON, of the HA_C series were used. The characteristic height of the needle was 9-16 microns, a radius of curvature of 25 nm, an angle of inclination \( \leq 22^\circ \). To the right of the images are bar lines that correspond to depth and lateral strength, respectively, for images on the left and right.

3. Results and discussion

Samples of oxide layers (< 100nm) grown on n-InP (100) plates with different oxidation times were studied. The surface relief and lateral forces for samples differing in anodization time of 40 s, 26 s and 17 s, obtained using AFM, are shown in Figures 1, 2, and 3, respectively. All images are shown with the same scan size of 5 \( \mu \text{m} \times 5 \mu \text{m} \).

It can be concluded that the uniformity of the oxide film distribution depends on the time of anodization. So, on the surface, which was anodized for 17 seconds, fairly large structures (≈ 30 nm) in height and diameter (≈ 250-1000 nm) are visible that are separated by a distance (≈ 100-200 nm) from each other, which are nucleated oxide phases. Further, for time = 26 seconds, they began merging with each other, and for 40 seconds the surface is become quite uniform. This suggests that with an increase in the time of anodic oxidation, the oxide layer is better distributed over the surface of the material. The statistical parameters of the surfaces are shown in table 1.

| Table 1. Statistical parameters of surfaces |
|-------------------------------------------|
| Roughness parameter | 40 seconds | 26 seconds | 17 seconds |
| Height swing, nm  | 39.1       | 39.9       | 26.3       |
| Standard deviation, nm  | 3.6        | 5.3        | 3.3        |
| Average roughness, nm  | 2.8        | 4.3        | 2.7        |
| Average height, nm  | 17.2       | 22.5       | 13.4       |

The observed growth pattern — the island structure of the oxide layer with smooth and rounded island boundaries — is in good agreement with studies in this field [9]. They had observed for longer procedure (10 min.) an appearance of islands with smooth borders for all studied conditions of oxide growth, and a coalescence process of islands were observed as well.
Figure 1. Relief (a), lateral forces (b) and surface profile (c), anodizing time – 40 seconds

Figure 2. Relief (a), lateral forces (b) and surface profile (c), anodizing time – 26 seconds
On the maps of the lateral forces distribution, regions that are different from each other are visible, while they do not repeat the surface relief. Apparently, these regions correspond to different phases. So, for 17 seconds we see a certain phase, and at 26 a new one. At 40 seconds, the various phases are practically indistinguishable, since perhaps one of them is already under the other. One can assume the lateral force microscopy (LFM) results associated with the detection of regions differing in lateral friction forces can be explained by the formation of two oxide phases with different compositions. As is known from previous studies, with electrochemical anodic oxidation, the formation of a mixture of oxides \( \text{In}_2\text{O}_3, \text{P}_2\text{O}_5, \text{In(PO}_3\text{)}_3, \text{InPO}_4, \text{InPO}_3 \) is possible \([1, 4, 5, 9]\). The obtained LFM results provide information on the sizes, interrelation, and relative positions of the detected phases, which provides essential information for further study of the composition of the oxide layer (choice of method, scale of the study area, etc.).

4. Conclusion

Samples of indium phosphide with anodic oxide layer electrochemically grown on them were studied using atomic force microscopy. Samples differed in anodic oxidation times: 17, 26 and 40 seconds. So, increasing the anodizing time, the following changes were observed on the relief: initially appeared island structure of the oxide layer, representing a nucleated oxide phase. Then islands begun coalescing due to oxide growth in the regions between the touching islands. With a further increase in the oxidation time, the surface becomes more uniform, presumably due to the coalescence of growing oxide islands.

When measuring lateral forces at a certain moment (26 seconds), the occurrence of a second phase was detected, which disappears when anodizing is continued. The detected second phase shows a lower value of the lateral force signal (lower value of the friction force of the AFM probe on the surface). The sizes of the second phase regions are in order of units of micrometers (2-5 µm) with elongated extended

Figure 3. Relief (a), lateral forces (b) and surface profile (c), anodizing time – 17 seconds
regions with a width of about 100-200 nm. The obtained LFM results allow to specify the conditions for studying the complex composition of the oxide layers of indium phosphide in the further study.

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