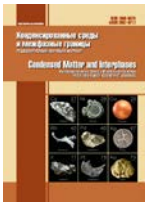

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Creation of thin films on the surface of InP with a controlled gas-sensitive signal under the influence of PbO + Y_2O_3 compositions

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Abstract

Thin-film objects with a reproducible temperature dependence of the resistance, thermally stable, and easy to obtain can be used as the sensitive elements in semiconductor gas sensors. The aim of this study was to create thin films on the InP surface under the influence of an oxide chemostimulator + inert component (PbO + Y_2O_3, respectively) compositions and to determine their gas-sensitive properties and their dependence on the formula of the composition.

Thin films were synthesised on the InP surface by the method of chemically stimulated thermal oxidation under the influence of various PbO + Y_2O_3 compositions. The thickness of the formed films, their elemental and chemical composition were determined (by laser ellipsometry, X-ray phase analysis, and infra-red spectroscopy). A number of experiments were carried out to establish the gas-sensitive properties of the obtained films with respect to ammonia with concentrations of 120, 100, and 80 ppm.

By chemically stimulated thermal oxidation, we obtained thin films with semiconductor properties on the InP surface. It was determined that the samples had n-type conductivity. A gas-sensitive response was detected in the presence of ammonia in the atmosphere. The ability to create thin films with a predetermined value of sensory response was demonstrated.

Keywords: Semiconductors, Indium phosphide, Thin films, Gas sensitivity, Thermal oxidation

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1. Introduction

Currently, the creation of chemical sensors that can detect hazardous, toxic, and harmful gases is a topic of interest. Thus, it is necessary to develop new methods for creating gas-sensitive elements with a simple design, low cost, and high sensitivity and selectivity [1, 2].

The traditional way to increase the selectivity of the material is the search for the optimal microstructure of the material, dopants, and analysis temperature for each gas [3]. Numerous studies on improving the sensory parameters of materials are aimed at optimising the electronic properties or adsorption capacity of the material [4]. The main oxides for gas sensors are SnO_2 and In_2O_3 [5–11]. V_2O_5 [12], Ga_2O_3, and perovskite structures with various impurities [13–15] are also often used. The surface is modified in different ways: by preparing thin films of the In_2O_3 nanocolumn structure [16], by a porous microstructure in multilayer sensor structures SnO_2–CuO [17], through its doping, etc.

The aim of this study was to create thin films on the InP surface under the influence of an oxide chemostimulator + inert component ($PbO + Y_2O_3$, respectively) compositions, to determine their gas-sensitive properties and their dependence on the composition.

2. Experimental

Thin films on an InP surface were created by thermal oxidation under the influence of different compositions of $PbO + Y_2O_3$. The composition changed from one pure component to another with increments of 20 mol%. The samples were oxidised in a horizontal quartz reactor placed in an MTP-2M-50-500 resistance heating furnace at a temperature of 550 °C (± 1 °C). The oxygen flow rate was 30 l/h. Thermal oxidation of the samples was carried out for 60 minutes by postoxidation with a periodisation of 10 minutes. Such a temperature-time regime ensured the thin films formed on the InP surface had a thickness of 100–120 nm. Such values are required for the further study of their electrophysical characteristics (specific surface resistance). Indium phosphide plates (FIEO, orientation (100) with a concentration of major charge carriers of at least $5 \cdot 10^{16}$ cm^{-3} at 300 K and intrinsic n-type conductivity) were used as substrates. The mechanism of the formation of thin films in the processes of chemically stimulated thermal oxidation is considered in more detail in [18, 19].

The thickness of the resulting oxide films was determined using a LEF-754 laser ellipsometer (±2 nm). The elemental and chemical composition of the films was studied using a JEOL-6510LV unit with a Bruker energy dispersive microanalysis system and a Vertex 70 IR Fourier spectrometer, respectively. The specific surface resistance of the obtained thin films was measured by the Van der Pauw method using a TsIUS-4 system. The specific surface resistance of the oxide film samples was measured in air, as well as in the presence of the test gas (ammonia) at concentrations of 120, 100, and 80 ppm. When measuring the resistance, the air humidity was 55 %. The measurements were carried out in a steady-state system. The value of the sensory signal S was determined as the ratio of the resistance of the samples in air (R_a) to the resistance of the samples in the presence of NH_3 in the atmosphere (R_{tg}):

$$S = R_a / R_{tg} \quad (1)$$

3. Results and discussion

In order to determine the inertness of the oxides towards each other, the phase composition of the powders of the mixture after heat treatment was determined by the method of X-ray diffraction analysis (XRD). The heat treatment parameters corresponded to the regime of thermal oxidation of indium phosphide. An example of a diffraction pattern is shown in Fig. 1. The interplanar distances obtained as a result of the data analysis were compared with the reference values [20] of the interplanar distances of yttrium and lead oxides, as well as with the distances of possible mixed compounds of these oxides.

The absence of mixed phases of the oxides, as well as phases other than Y_2O_3 for yttrium oxide, indicates its inertness both to the second oxide of the composition (PbO) and to its own redox transformations. PbO, on the contrary, exhibits redox transformations at the experimental temperature (550 °C). Since the process takes place in a flow of oxygen, it is accompanied by the partial formation of mixed oxides Pb_2O_3 and Pb_3O_4.

The elemental composition of thin films grown on the InP surface was studied by local

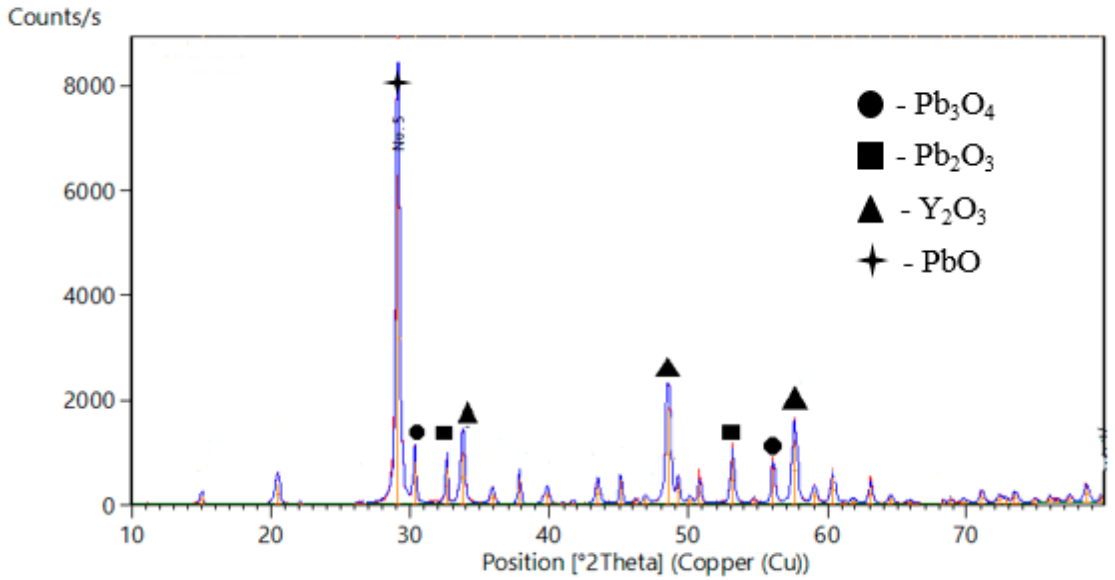

Fig. 1. Diffraction pattern of the $(Y_2O_3)_{0,6}$+$(PbO)_{0,4}$ composition after annealing at 550 °C for 10 min

electron probe microanalysis (EPMA). The obtained results are demonstrated in Table 1.

As follows from the obtained data, the main component of the film is indium. Its content is almost 2 times higher than the content of the second component of the substrate, phosphorus. Such a low phosphorus content in the resulting thin film on the InP surface is obviously due to its partial evaporation in the pentoxide form, which had also been observed in earlier studies [18, 21]. Moreover, for both of these elements, we can see practically no dependence on the various compositions of the oxides, under the influence of which the film on the semiconductor surface was formed. At the same time, the content of lead, which is another component of the film, shows a clear dependence on the composition. This dependence is considered in more detail below and shown in Fig. 2. Another component of the oxide composition, yttrium oxide, was not detected in the film at all. This confirms its inertness not only to the second oxide of the composition, but also to the process of thermal oxidation of InP in general. At the same time the total content of three elements is not 100 at%, which indicates that there is another component in the system. Since the film growth process takes place in a flow of oxygen, it is logical to assume that this is the missing component. Since the presence and amount of oxygen cannot be directly determined by EPMA, its content was calculated as the value lacking from 100 at%. The calculation showed significant oxygen content in the film (about 50 at%). Therefore, all other components of the film are in an oxidised state.

Using the data obtained by EPMA, we plotted a graph of the dependence of the lead content in the film on the composition (Fig. 2.)

As follows from Fig. 2, the dependence of the lead content in the film is almost linear. Such a dependence of the content of the film on the composition, under the influence of

Table 1. Elemental composition of thin films on the InP surface

Composition of the composition	Elemental composition of the films			
	In, at%	P, at%	Pb, at%	O, at%
$(PbO)_{0,2}(Y_2O_3)_{0,8}$	32.42	17.54	0.33	49.71
$(PbO)_{0.4}(Y_2O_3)_{0.6}$	34.54	16.87	0.88	47.71
$(PbO)_{0.6}(Y_2O_3)_{0.4}$	30.88	17.33	1.31	50.48
$(PbO)_{0.8}(Y_2O_3)_{0.2}$	31.66	17.55	1.61	49.15

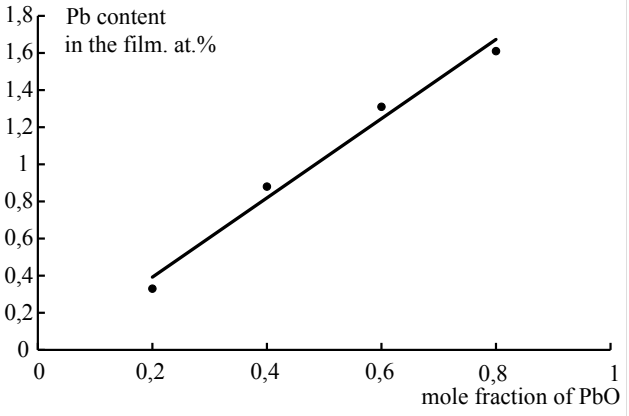

Fig. 2. Dependence of the chemostimulator content in the film on its molar fraction in the composition

which it was formed, makes it possible, using an inert component, to obtain oxide layers with the desired content of chemostimulator. It can help control various properties of the layers, including their electrophysical properties. The obtained result is similar to that achieved earlier [22] and confirms the versatility of using an inert component for the precise doping of thin films with an alloying component.

To confirm the presence of oxygen in the films on the InP surface, as well as the oxidation of the detected elements, the obtained samples were studied by IR spectroscopy. The results are presented in Table 2.

We can distinguish several characteristic absorption lines in the spectra of the samples. According to the literature data [23], frequencies of 565, 541, and 980 cm^{-1} correspond to the formation of In_2O_3 and $InPO_4$. Similar data were obtained during the intrinsic oxidation of indium phosphide. However, the spectra also contain absorption bands characteristic of the used oxide chemostimulator and the film obtained under the influence of the composition with the maximum PbO content, the compound with lead phosphate (538 cm^{-1}). It is necessary to note the absorption bands in the range of 430–440 and 620–630 cm^{-1}, associated with the background of the InP substrate. Thus, infrared spectroscopy was used to confirm the incorporation of lead oxide into the film growing on the InP surface and its interaction with the substrate components. Based on the EPMA data it also confirmed the conclusion that there was oxygen in the film on the InP surface and that all its other components were oxidised.

Table 2. The IR spectroscopic data for the films on the InP surface obtained under the influence of $PbO+Y_2O_3$ compositions

Composition	Absorption band, cm^{-1}	Compound
$(PbO)_{0.2}(Y_2O_3)_{0.8}$	430, 440, 630	InP
	565, 750	In_2O_3
	1025, 1242	$In(PO_3)_3$
	720	PbO
$(PbO)_{0.8}(Y_2O_3)_{0.2}$	430, 440, 620	InP
	500, 541, 980, 1080	$InPO_4$
	565. 750	In_2O_3
	720	PbO
	538	$Pb(PO_3)_2$

This allowed us to expect that the obtained films would have semiconductor properties.

Fig. 3 shows the temperature dependence (within the range of 20–400 °C) of the resistance in air of the samples prepared under the influence of the $PbO + Y_2O_3$ compositions. The dependences demonstrate a clear correlation between the composition of the oxide chemostimulator + inert component and the resistance of the oxide film on the InP surface obtained under its influence. The resistance increases with an increase in the PbO content in the films. The more PbO there is in the composition, the more PbO there is in the film. It results in a high oxide film thickness and, most likely, ensures the formation of films with high resistance parameters. In this case, the films themselves are semiconductors, as evidenced by the nature of the temperature dependence of the resistance.

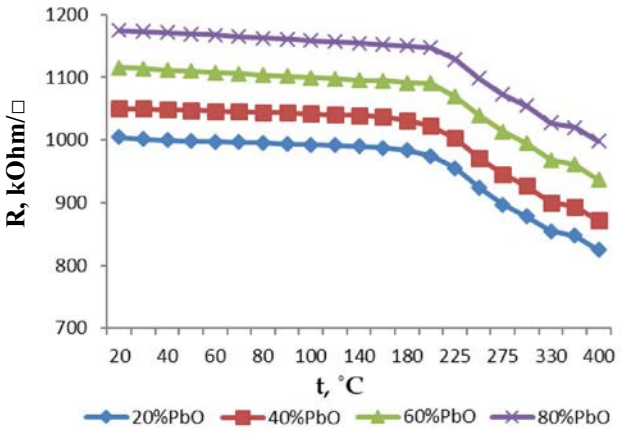

Fig. 3. Specific surface resistance of the samples in air

The gas to be detected in this study was ammonia. We carried out three series of experiments with different concentrations of ammonia: 120, 100, and 80 ppm. A typical temperature dependence of the resistance is shown in Fig. 4 for the lowest concentration studied.

The obtained surface resistance data were used to calculate the sensory signal according to equation (1). The results are shown in Fig. 5. All dependencies have a pronounced extreme character. The extremum corresponding to the maximum sensory signal of the obtained films, for all concentrations, corresponds to the same temperature, 225 °C. With an increase in concentration, the magnitude of the sensory signal increases slightly, but regularly. It is clearly demonstrated in Fig. 6 as an isothermal section at 225 °C.

In this range of gas concentrations, there is a linear dependency. In general, the operating range of the sensor is a logarithmic function. However, in our case it is a straight-line increasing dependence, which indicates that the operating range of the films is wider than the studied interval.

In addition to the dependence of the sensory signal of the film on the concentration of the detected gas, Fig. 5 shows its dependence on the synthesis conditions, namely, on the composition, which influenced the synthesis of this film. This dependence is shown more clearly in Fig. 7.

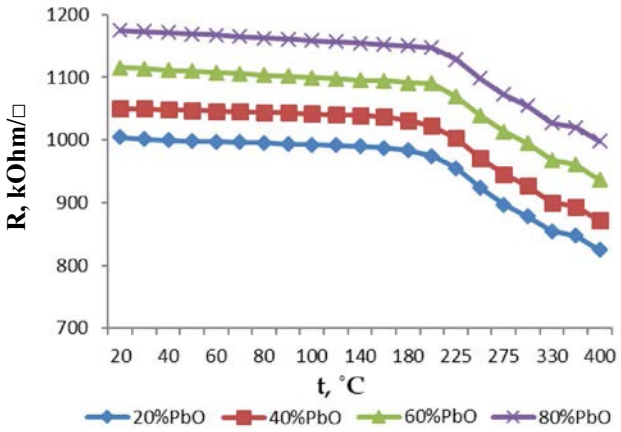

Fig. 4. Specific surface resistance of the samples measured in the presence of ammonia in the atmosphere with a concentration of 80 ppm

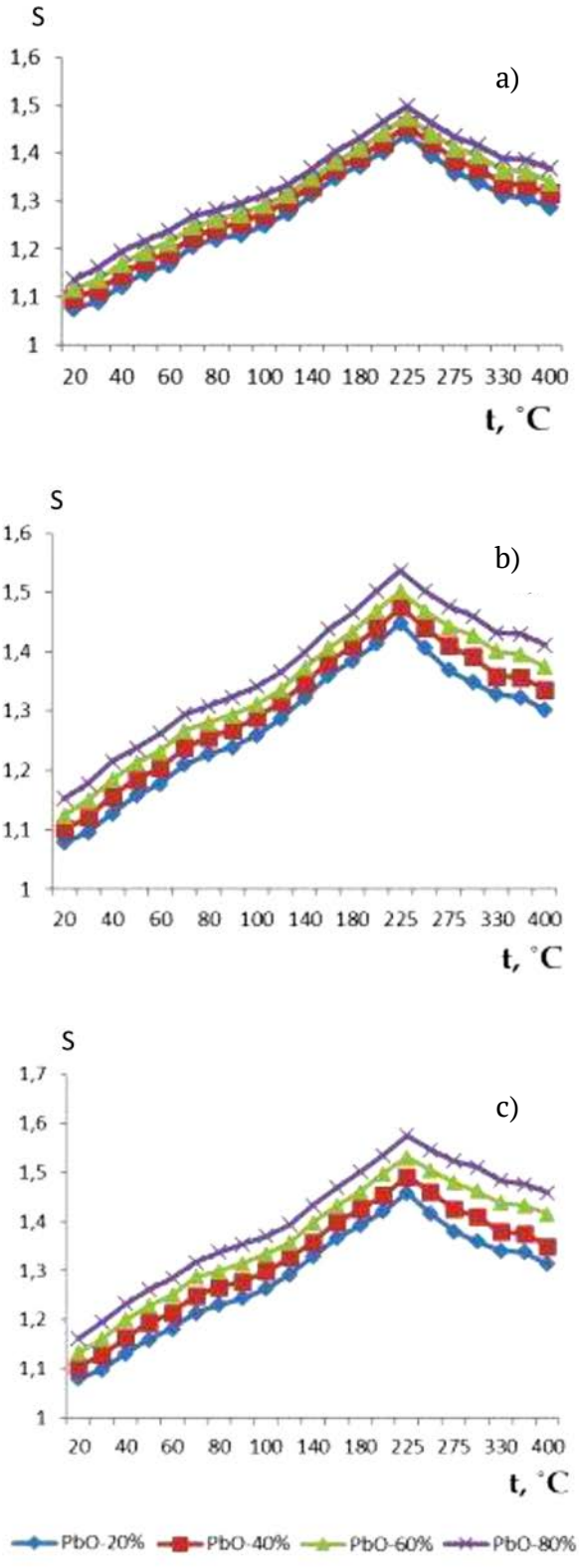

Fig. 5. Temperature dependence of the sensory signal of oxide films on the InP surface in the presence of ammonia in the atmosphere with a concentration of: a) 80 ppm; b) 100 ppm; c) 120 ppm

We chose a concentration of 120 ppm and a temperature of 225 °C, at which the magnitude of the sensory signal is maximum.

If we examine Figures 2 and 7 jointly, we can conclude that the use of oxide compositions, one of which is an inert component, as chemostimulators of the InP thermal oxidation process, makes it possible to obtain films with the desired content of the alloying component (in this case it was lead). This allows controlling the magnitude of the sensory signal formed on the surface of a thin film semiconductor.

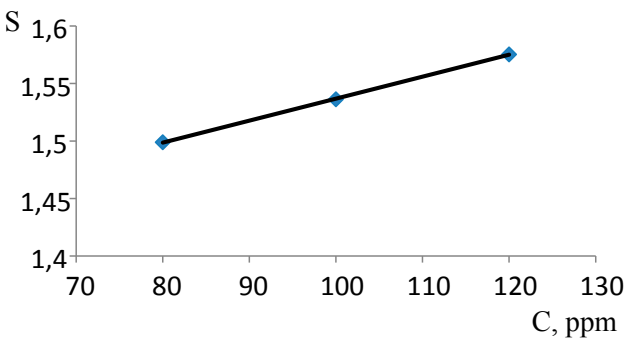

Fig. 6. Dependence of the sensory signal on the ammonia concentration

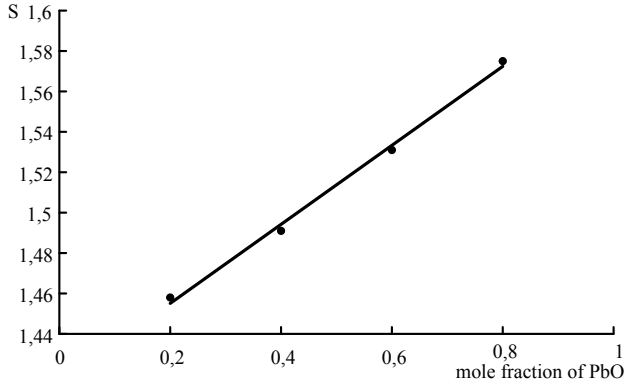

Fig. 7. Dependence of the sensory signal on the PbO content in the $PbO+Y_2O_3$ composition

4. Conclusions

Thin films were synthesized on the InP surface under the action of $PbO + Y_2O_3$ composites. The formed films predominantly consist of lead-containing substrate components in an oxidised state. Using the Van der Pauw method, we determined that the thin films were gas-sensitive and detected the presence of ammonia in the atmosphere. We revealed the possibility of precision doping of a thin film growing on the InP surface with a chemostimulator. It makes it possible to obtain films with a desired value of sensory signal.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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