Semiconductor heterosystem InAs-ZnS. Physical and chemical properties

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Abstract. According to the developed methodology based on isothermal diffusion of the initial binary compounds (InAs, ZnS) in the light of their known bulk properties, the InAs-ZnS system solid solutions have been obtained. Pursuant to the results of the X-ray investigation, they have been certified as substitutional solid solutions with the cubic sphalerite structure.
The surface (acid-base) properties of the InAs-ZnS system components corresponding to the weak acidic area have been studied.
Consistent patterns in changes with the composition of the studied properties have been established, which are both statistical (smooth) and extreme. Correlations between the consistent patterns and, respectively, the link between surface and bulk properties, which allow predicting the desired materials for the semiconductor gas analysis have been found.
Key words - solid solutions, bulk and acid-base surface properties, consistent patterns, correlations, semiconductor gas analysis.

1. Introduction

The research target in the present paper is multicomponent diamond-like semiconductors - solid solutions based on binary compounds of the $A^{III}B^{V}$ (InAs) and $A^{II}B^{VI}$ (ZnS) type [1]. Such multicomponent diamond-like semiconductors are of interest due to the unique bulk properties of the initial binary compounds (electrophysical, optical, photo- and piezoelectric), predictability and adjustability of the bulk and surface properties of the developed materials as well as due to the discovery of the unexpected effects [2, 3]. Accordingly, to clarify the prospects for using the developed materials in sophisticated technology, and particularly, sensor technology, the data is required on their physicochemical bulk and surface properties and, first and utmost, surface properties, commonly being the major ones in the semiconductor devices operation and data on the nature of change of these properties with a change in composition, the properties interrelation, the surfaces sensitivity to certain media [4, 5].

2. Problem statement

In precisely this way, taking into account the stated opinions, the submitted paper was written.
When searching for new materials for the sophisticated technology, including sensor technology, multicomponent diamond-like semiconductors – solid solutions – are increasingly attracting attention. At this point, the potential is opened for both regulation and, accordingly, obtaining the expected properties with a change in composition as well as for detecting extreme effects due to the complexity of the unexplored internal processes that occur during the solid solutions formation. Such internal processes include ordering and hardening of the structure, the combined action of constituent components as macro- and microdefects and the potential obtaining of the impurity centers' high concentrations [6].
Extreme effects showing deviations from the rule of additivity (Vegard's law) [7] are of particular interest both scientifically and practically [8].

The system under debate $A^{III}B^{V}$-$A^{II}B^{VI}$ – InAs-ZnS is a representative of such multicomponent diamond-like semiconductors.

3. Theory

When searching for new materials for the sophisticated technology, including sensor technology, multicomponent diamond-like semiconductors — solid solutions — are increasingly attracting attention. At this point, the potential is opened for both regulation and, accordingly, obtaining the expected properties with a change in composition as well as for detecting unexpected, extreme effects due to the complexity of the unexplored internal processes that occur during the solid solutions formation.

Extreme effects caused by deviations from Vegard's law are of particular interest both scientifically and practically.

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4. Experimental part

Solid solutions (InAs)x (ZnS)1-x (x = 0.5; 1.5; 2; 2.7; 78; 81; 87; 93 mol %) were obtained according to the developed methodology (with respect to the chosen system) based on isothermal diffusion of the initial binary compounds (InAs, ZnS), known data on their basic bulk properties according to the previously justified mode and temperature heating program [9, 10]. The formation and structure of the solid solutions were concluded following the results of results of the x-ray studies.

X-ray studies were carried out using Advance D8 Powder X-Ray Diffractometer by BRUKER AXS (CuKα radiation, λ = 0.154056 nm, T = 293 K) involving wide-angle survey technique [11,12] using the position-sensitive detector Lynxeye.

The acid-base properties of the surfaces (pH of the isoelectric state — pHiso) were evaluated using the hydrolytic adsorption method [13]. Within the method, the pH media were found, where ampholyte adsorbents eliminate equal (insignificant) amounts of H + and OH- ions. The binary components (InAs, ZnS) and solid solutions (InAs)x(ZnS)1-x with specific isoelectric points conforming to the minimum solubility acted as ampholyte adsorbents.

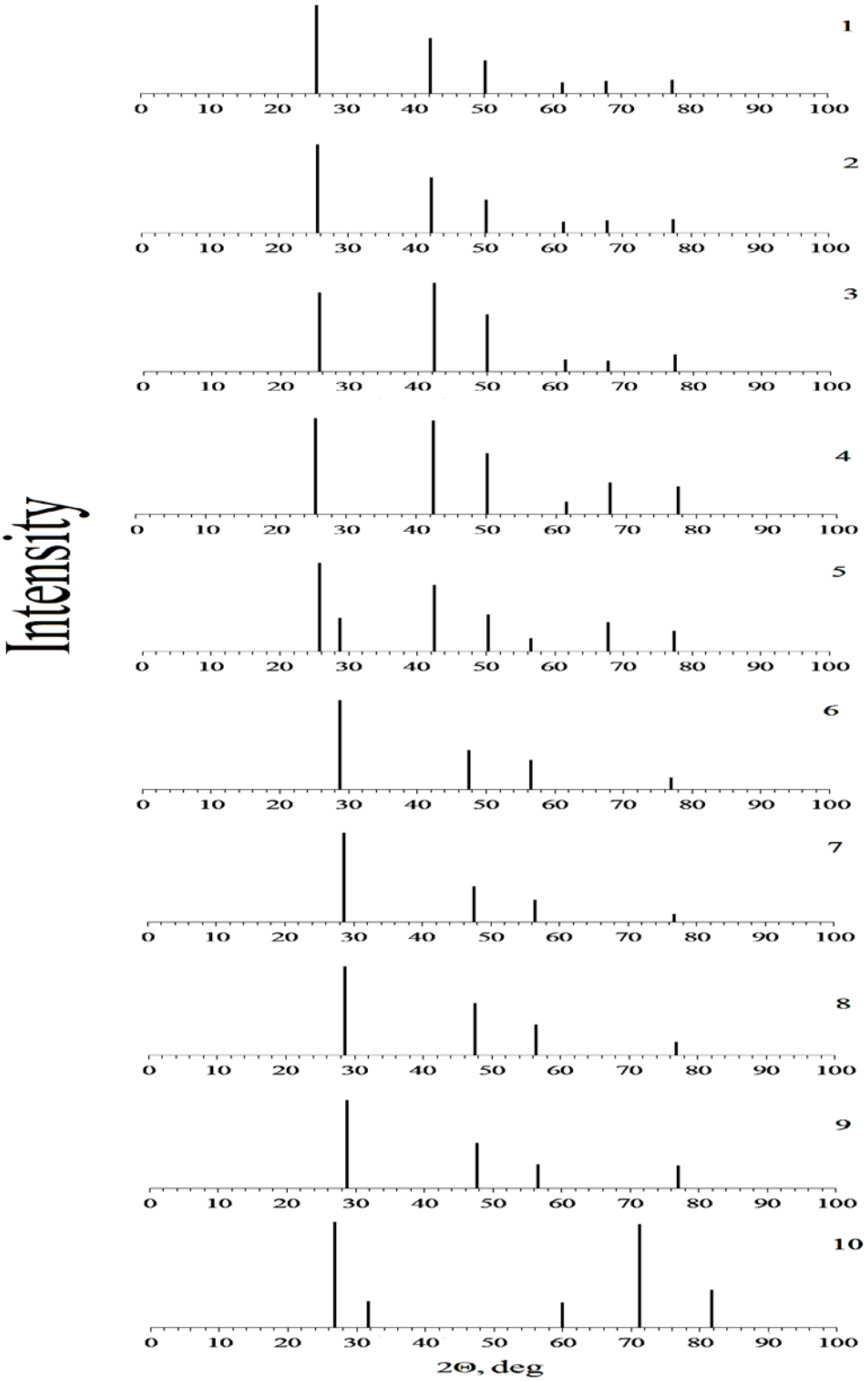
The studied samples were prepared in the form of fine powders (Ssp ≤ 1.35 m2/g).

The reproducibility and accuracy of the experimental data were checked subsequent to the results of the parallel measurements involving methods of mathematical statistics and processing the quantitative analysis results. Statistical handling of the obtained values, measurements fault level calculation, plotting and processing of the dependence diagrams were performed using computer programs Stat-2, Microsoft Excel, and Origin.

5. Results and discussion

According to the results of the X-ray studies (Fig. 1, 2, Table 1), substitutional solid solutions are formed in the InAs-ZnS system: lines corresponding to the solid solutions are shifted relative to the lines of the initial binary compounds with their fixed number (Fig. 1); depending on the composition of the parameter values (a) and the crystal lattices interplanar distances (d_{111}) are typically smooth (insignificant peaks appear at 97.3 mol. % ZnS). More noticeable deviations from Vegard's law characterize the dependences ρr = f (x_{ZnS}) and d_{311} = f (x_{ZnS}) (at 22 mol% ZnS). Here, as in the previously described other systems (such as $A^{III}B^{V}$-$A^{II}B^{VI}$ and $A^{II}B^{VI}$-$A^{II}B^{VI}$), the influence of complex internal processes accompanying the solid solutions formation is prominent [8, 9].

The full completion of the synthesis and the solid solutions formation is also evidenced by the absence of the additional lines on the X-ray patterns corresponding to unreacted binary compounds and the smearing of the base lines.



In accordance with the position and distribution of the intensity of the base lines in the X-ray patterns, the solid solutions and binary components of the InAs-ZnS system have a cubic sphalerite structure.

Figure 1. Line X-ray pattern of the InAs- ZnS system components: 1 – InAs,

2 – $(InAs)_{0.93}(ZnS)_{0.07}$, 3 – $(InAs)_{0.87}(ZnS)_{0.13}$, 4 – $(InAs)_{0.81}(ZnS)_{0.19}$, 5 – $(InAs)_{0.78}(ZnS)_{0.22}$,
6 – $(InAs)_{0.027}(ZnS)_{0.973}$, 7 – $(InAs)_{0.02}(ZnS)_{0.98}$, 8 – $(InAs)_{0.015}(ZnS)_{0.985}$, 9 – $(InAs)_{0.005}(ZnS)_{0.995}$,
10 – ZnS

Table 1. Parameter values (*a*), interplanar distances (d_{hkl}) and theoretical calculated crystal density (ρ_r)
of the crystal lattices of the InAs-ZnS system components

X, (mole fraction ZnS)	Crystal lattice type	*a,* Å	$d_{hkl,\ Å}$		ρ_r, g/sm^3
			111	311	
0	cub.	6.05846 ±0,001	3.4911	2.13950	5.681
0.07	cub.	6.0360 ±0,001	3.4849	2.13809	5.5359
0.13	cub.	6.0346 ±0,001	3.4841	2.13673	5.3722
0.19	cub.	6.0337 ±0,001	3.4836	2.13644	5.2071
0.22	cub.	6.0329 ±0,001	3.4831	2.13701	5.2431
0.973	cub.	5.3948 ±0,001	3.1147	1.62973	4.2195
0.98	cub.	5.4001 ±0,001	3.1177	1.62970	4.206
0.985	cub.	5.3910 ±0,001	3.1125	1.62940	4.1867
0.995	cub.	5.3927 ±0,001	3.1135	1.62981	4.1329
1	cub.	5.4101 ±0,001	3.1238	1.6314	4.0882

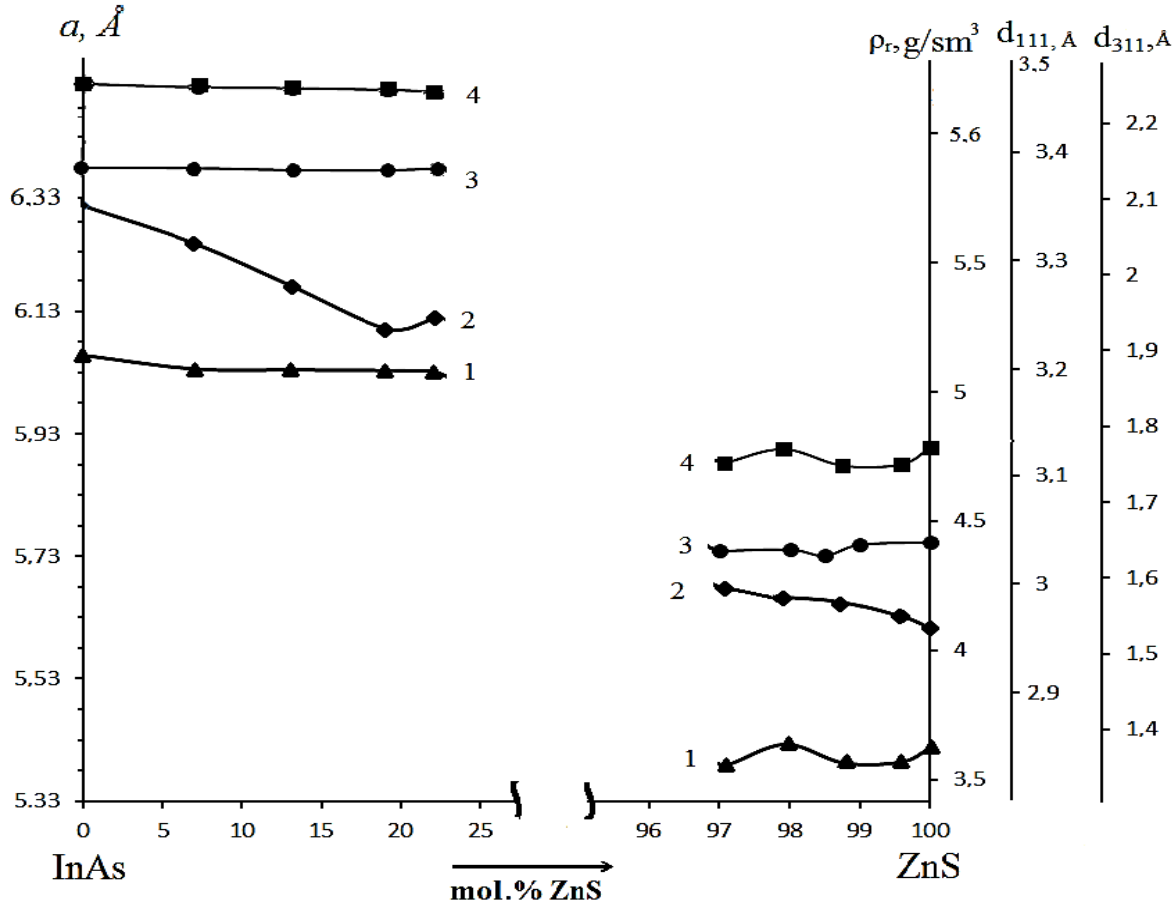


Figure 2. Dependence on the parameter value composition (*a*) – 1; interplanar distances (d_{311}, d_{111}) – 3, 4 and theoretical calculated crystal density (ρ_r) – 2 of the crystal lattices of the InAs-ZnS system components

With respect to the acid-base properties (pH_{iso} values of the air exposed surfaces) (Table 2, Fig. 3) the components of the InAs-ZnS system are arranged in the following sequence:

$$InAs < (InAs)_{0.93}(ZnS)_{0.07} < (InAs)_{0.87}(ZnS)_{0.13} < (InAs)_{0.81}(ZnS)_{0.19} < (InAs)_{0.78}(ZnS)_{0.22} <$$
$$< (InAs)_{0.027}(ZnS)_{0.973} < (InAs)_{0.02}(ZnS)_{0.98} \approx (InAs)_{0.015}(ZnS)_{0.985} > (InAs)_{0.005}(ZnS)_{0.995} < ZnS$$

Table 2. pH values of the surface isoelectric state (pH_{iso}) of the InAs-ZnS system components, air exposed (I) and in the nitrogen dioxide (II).

System InAs-ZnS components	pH_{iso} values	
	I	II
InAs	5.7	5.05
$InAs_{(0.93)}ZnS_{(0.07)}$	5.95	5.0
$InAs_{(0.87)}ZnS_{(0.13)}$	6.0	4.7
$InAs_{(0.81)}ZnS_{(0.19)}$	6.05	5.1
$InAs_{(0.78)}ZnS_{(0.22)}$	6.1	4.85
$InAs_{(0.027)}ZnS_{(0.973)}$	6.3	5.65

$InAs_{(0.002)}ZnS_{(0.98)}$	6.7	5.75
$InAs_{(0.015)}ZnS_{(0.985)}$	6.8	5.7
$InAs_{(0.005)}ZnS_{(0.995)}$	6.2	5.8
ZnS	6.4	5.9

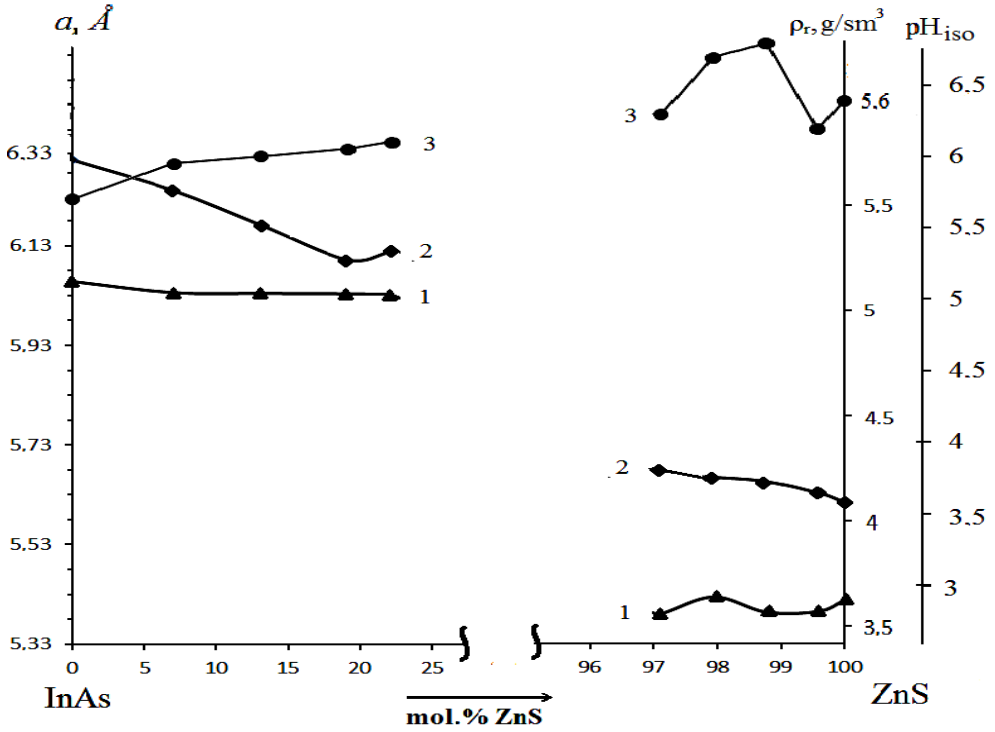


Figure 3. Dependence of the surfaces isoelectric state (pH_{iso}) – 3; parameter value composition (*a*) – 1 and theoretical calculated crystal density (ρ_r) – 2 InAs-ZnS system components

This data allows to state the weak acid surfaces nature (pH_{iso} <7), some prevalence of Lewis acid sites as well as predominantly smooth change in the surfaces acidity with a change in composition (Fig. 2). Small deviations are observed in compositions close to the second binary component composition - ZnS (x_{ZnS} = 98.5…99.5 mol. %). That is, surface properties are affected, although in a minor way, by the internal processes that accompany the solid solutions formation.

Due to the weak acid surfaces nature, it is logical to expect their increased activity towards the main gases: an increase in pH_{iso} upon contact with alike and a decrease in pH_{iso} when in contact with acid gases.

According to the Table 2, pH_{iso} actually decreases notably when exposed to acid gas (NO_2). In this case, NO_2 molecules interact, along with coordinately - unsaturated atoms with formation of $NO_2^{+\delta} \cdots A^{-\delta}$ $(_{ads})$ bonds, with OH groups with formation of –OH ⋯ $NO_2(_{ads})$ bonds, which is accompanied by a content reduction of Bronsted centers on the surfaces.

When analyzing the results of the studies performed, certain correlations between bulk, surface and bulk properties are traced. The point at issue is the similarity in the consistent patterns $\rho_r = f(X_{ZnS})$ and $d_{111} = f(X_{ZnS})$ (maximums at 22 mol% ZnS); $a = f(X_{ZnS})$ and $d_{111} = f(X_{ZnS})$ (maximums at 98 mol% ZnS) as well as $pH_{iso} = f(X_{ZnS})$ and $\alpha = f(X_{ZnS})$ (maximums at 97.3 and 98 mol% ZnS) (Fig. 2). Naturally, the noted correlations are of a certain scientific and practical interest. They may be used

in the search for the advanced materials for semiconductor gas analysis, without resorting to more laborious studies of surface properties.

In this regard reverse trends in the composition of the pH isoelectric state of the surfaces (pH_{iso}) of the InAs-ZnS system components and their theoretical calculated crystal density (ρ_r) come under notice: with the ZnS accumulations, the pH_{iso} increases and ρ_r decreases. Here, the significant difference in the bulk properties values of the initial binary compounds (InAs, ZnS) as the forbidden bandwidth (ΔE_{InAs} = 0.36, ΔE_{ZnS} = 3.67 eV), electronegativity difference (ΔX_{InAs} = 0.30, ΔX_{ZnS} = 0.9) , which caused with the ZnS accumulation the increase in the fraction of ionic bonds and, accordingly, the degree of the surfaces hydration (content of OH– groups) are of essence. Therefore, despite the increase in the coordination unsaturation of atoms surface atoms and the contribution of Lewis sites with a decrease in ρ_r, Bronsted centers exerted a predominant relative influence.

The reasonableness of such considerations is indicated by the "behavior" of pH_{iso} and ρ_r in the InP-ZnS system, which differs from the studied one by the first binary component (InP) [14]. It is emphasized that with a smaller difference in the forbidden bandwidth and a smaller electronegativity difference of the initial binary components (ΔE_{InP} = 1.35 eV, ΔE_{ZnS} = 3.67 eV; ΔX_{InP} = 0.40, ΔX_{ZnS} = 0.90), with a decrease in ρ_r and, accordingly, with an increase in coordination unsaturation of the surface atoms, the relative contribution of Lewis sites becomes principal (pH iso decreases simultaneously with a decrease in ρ_r) (Fig. 4).

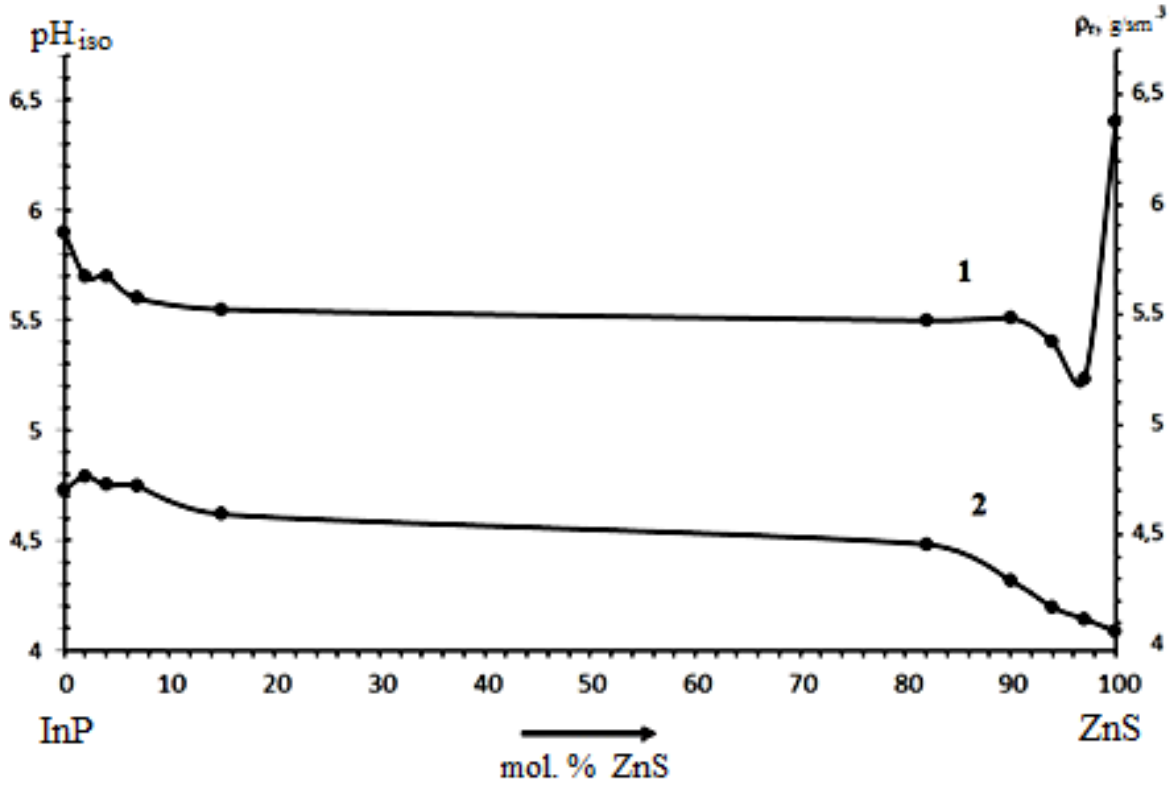


Figure 4. Dependence of the surfaces isoelectric state (pH_{iso}) – 1 and theoretical calculated crystal density (ρ_r) – 2 InP-ZnS system components on the pH values composition

Taking into account the influence of n_{av} on the coordinative unsaturation of the surface atoms responsible for Lewis acid sites, respectively, for the surface activity with respect to gases of a certain

electronic nature, one can speak of a possible, easier estimation of the obtained materials suitability for manufacturing measuring cells using more available common microscopic images.

6. Conclusions

According to the methodology developed using the isothermal diffusion method of the initial binary compounds (InAs, ZnS) and basic data on their bulk properties, solid solutions of the InAs-ZnS system were obtained. Based on the results of x-ray studies, they are certified as substitutional solid solutions with the cubic structure of sphalerite.

The surface (acid-base) properties of the obtained solid solutions and binary components of the InAs-ZnS system corresponding to the weak acid area (pH_{iso} <7) were studied, which suggests their increased activity to the main gases.

Consistent patterns in changes with the composition of the bulk and surface properties were established, in which both statistical and extreme factors appeared.

Correlations between regularities were revealed and therefore relations between the bulk, surface and bulk properties, which can be used for a less expensive search for the advanced materials for semiconductor gas analysis.

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