Solid solutions of the InAs-A\textsuperscript{II}B\textsuperscript{VI} heterosystems. Bulk, surface physical and chemical properties

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Abstract. Using specifically developed methods, solid solutions of the InAs-A\textsuperscript{II}B\textsuperscript{VI} (A\textsuperscript{II}B-ZnS, CdTe) systems have been obtained. In accordance with the results of X-ray studies in combination with the results of micro, submicroscopical studies, they were certified as solid substitution solutions with a cubic sphalerite structure; information on crystal-chemical and structural properties has been obtained; the elemental compositions have been determined, which substantially coincide with the given molar ones. The acid-base properties of the solid solutions surfaces and binary components of the systems revealing a weak-acid character and increased activity towards main gases have been studied. The consistent patterns of changes in bulk and surface properties with a change in composition have been established which obey mainly to a statistical law as applied to the InAs-CdTe system and with extreme manifestations as applied to the InAs-ZnS system, which have been substantiated. The connections between the consistent patterns, the influence of bulk properties (in particular, the forbidden bandwidth, the electronegativity difference) on the surface properties have been revealed. The objectives for the search of the advanced materials for the sensor technology, based on more accessible information on bulk properties, have been set. The practical guidelines have been given on the use of the obtained materials for the manufacture of measuring cells for the main gases trace contamination.

Keywords – multicomponent diamond-like semiconductors, solid solutions, crystal-chemical, structural, acid-base properties, interrelated consistent patterns, advanced materials, measuring cells.

1. Introduction

The present paper was written in terms of searching for the advanced materials of modern technology and, first of all, sensor technology, using multicomponent semiconductors - solid solutions based on the binary semiconductors of the A\textsuperscript{III}B\textsuperscript{V}, A\textsuperscript{II}B\textsuperscript{VI} types, which have already proven themselves due to their unique properties [1].

It would make sense both to expand the range of multicomponent semiconductors with unpredictable possibilities, and to study their bulk and especially surface properties. The latter often play a crucial role in the semiconductor devices operation in a number of technological processes.

For the formation of a scientific base, for a predictable, less expensive search, it is also useful to compare the selected objects, their bulk and surface properties and to establish a connection between them.

All these reasonable aspects are reflected in the present paper, in which the target of research are solid solutions of the A\textsuperscript{III}B\textsuperscript{V}-A\textsuperscript{II}B\textsuperscript{VI} (InAs-ZnS, InAs-CdTe) type systems, which differ in binary components of the A\textsuperscript{II}B\textsuperscript{VI} type (ZnS, CdTe).

2. Problem statement
According to the methodology developed on the basis of the isothermal diffusion method and known information on the bulk physical, physical and chemical properties of the initial binary compounds (InAs, ZnS, CdTe), to obtain solid solutions of the InAs-ZnS, InAs-CdTe systems.

To perform X-ray, micro-, submicroscopical studies, following the results of which the obtained solid solutions are certified, and their crystal chemical and structural properties are determined.

To study the surface (acid-base) properties of the considered systems components.

To establish consistent patterns of changes in bulk and surface properties, connection between consistent patterns, the effect of bulk properties (in particular, the forbidden bandwidth - $\Delta E$, the electronegativity difference - $\Delta \chi$) on the surface properties.

To evaluate the surfaces sensitiveness to gases of a certain electronic nature and, with the predicted response, to give appropriate practical recommendations on the use of the obtained materials in semiconductor gas analysis.

3. Theory

With the ever-increasing demand for the advanced materials of sophisticated technology, including such areas as micro-, optoelectronics, nanooptoelectronics, sensor technology, the search for them remains essential. The multicomponent diamond-like semiconductors - solid solutions based on the already proven themselves binary diamond-like semiconductors, mainly of the AIIIBV, AIIBVI type, are attracting more and more attention. That offers opportunities not only for regulating properties with a change in composition, but also for detecting unexpected (extreme) effects of particular interest. The latter can be conditioned by complex internal processes accompanying the solid solutions formation. These include the structure ordering and strengthening, the combined action of the constituent components acting as macro- and microdefects, and the possible obtaining of high concentrations of impurity sites [1].

The solid solutions of the InAs-ZnS, InAs-CdTe system are representatives of multicomponent diamond-like semiconductors discussed in the present paper.

4. Outcomes of experiments

To obtain solid solutions (InAs)$_x$(ZnS)$_{1-x}$ ($x = 0.5; 1.5; 2; 2.7; 78; 87; 93$ mol.%), (InAs)$_x$(CdTe)$_{1-x}$ ($x = 4; 15; 22; 27; 32; 75; 81; 89; 93$ mol.%) the methods were developed (with established modes, temperature heating programs), based on the method of isothermal diffusion and known information about bulk physical, physical and chemical properties of initial binary compounds (InAs, ZnS, CdTe) [1, 2].

The synthesis was carried out in vacuumed, sealed quartz ampoules with respect to the regions of mutual solubility InAs and ZnS, InAs and CdTe.

The completion of the synthesis, formation and structure of solid solutions were estimated by the results of X-ray studies in conjunction with the results of micro-, submicroscopical studies.

The obtained end-products were polycrystalline ingots at the bottom of the ampoules. The test samples of solid solutions and initial binary compounds were prepared in the form of fine powders ($S_{sp} = 0.3–0.48$ m$^2$/g).

Using the results of submicroscopical studies, the correspondence of the given molar compositions to the elemental ones was checked.

X-ray studies were performed on a diffractometer D8 Advance of “Bruker” AXS (Germany) in CuKa radiation ($\lambda = 0.15406$ nm, $T = 298$ K) by wide-angle survey technique [3, 4], using the Lynxeye position-sensitive detector and for decoding the obtained X-ray diffraction patterns (diffractograms), refining the lattice parameters - the powder diffraction database ICDDPDF - 2, TOPAS 3.0 software (“Bruker”), respectively. Submicroscopical studies were performed on a JSM-5700 scanning electron microscope equipped with a JED-2300 attachment for energy dispersive analysis [5]. Microscopic studies were carried out on devices KN 8700 (Xilox, Japan) and Micromed POLAR-3 with a resolution of up to 7000 [6].

Studies of surface (acid-base) properties were conducted using the hydrolytic adsorption [7] method which involves detecting the pH of the medium in which the ampholyte adsorbents split off equal (insignificant) amounts of $H^+$ and $OH^-$ ions. The binary components (InAs, ZnS, CdTe) and
solid solutions \((\text{InAs})_x(\text{ZnS})_{1-x}\), \((\text{InAs})_x(\text{CdTe})_{1-x}\) with distinctive isoelectric points corresponding to the minimum solubility acted as the ampholyte adsorbents. As a result, the hydrogen index values of the surfaces isoelectric state (pH iso) were determined, which were used to evaluate the average strength and the ratio of acid and basic sites on the components surfaces.

The reproducibility and accuracy of the experimental data were checked by the results of parallel measurements using the methods of mathematical statistics and processing the results of quantitative analysis and computer programs Stat-2, Microsoft Excel and Origin.

5. Results and discussion

According to the results of X-ray studies, substitutional solid solutions with a cubic sphalerite structure are formed in the InAs-ZnS, InAs-CdTe systems (a at predetermined compositions). This is evidenced by the corresponding relative position and intensity distribution of the main lines on the X-ray diffraction patterns (diffractograms) of binary compounds and solid solutions, the shift of lines corresponding to solid solutions relative to the lines of binary compounds with a constant number of them, absence of additional lines of unreacted binary compounds, blurring of the main lines (figure 1), predominantly smooth nature of the dependences on the composition (as applied to the InAs-CdTe system) of a parameter \((a)\), interplanar space \((d_{||})\), theoretical calculated crystal density \((\rho_r)\) of crystal lattices; predominantly smooth variation of parameter \((a)\), interplanar distance \((d_{111})\) as applied to the InAs-ZnS system (figure 2). The deviation from Vegard's law of the dependence \(p_r = f (X_{\text{ZnS}})\) observed in the InAs-ZnS system, as in other previously described systems of the \(\text{A}^{\text{III}}\text{B}^{\text{V}}-\text{A}^{\text{II}}\text{B}^{\text{VI}},\ \text{A}^{\text{II}}\text{B}^{\text{VI}}-\text{A}^{\text{III}}\text{B}^{\text{VI}}\) type is conditioned by the influence of complex internal processes accompanying the solid solutions \([1, 8, 9]\) formation and, accordingly, the uneven distribution of cation-anionic complexes, as indicated by the results of submicroscopical studies. According to these, the structure of the systems components is polycrystalline with an inhomogeneous distribution of crystallites (figure 3).
Figure 1. Bar diffraction patterns of the system components InAs-ZnS (a): 1 – ZnS,
2 – (InAs)_{0.027}(ZnS)_{0.973}, 3 – (InAs)_{0.78}(ZnS)_{0.22}, 4 – (InAs)_{0.81}(ZnS)_{0.19}, 5 – (InAs)_{0.87}(ZnS)_{0.13}, 6 – InAs
InAs-CdTe (b): 1 – CdTe, 2 – (InAs)_{0.04}(CdTe)_{0.96}, 3 – (InAs)_{0.75}(CdTe)_{0.25}, 4 – (InAs)_{0.81}(CdTe)_{0.19},
5 – (InAs)_{0.89}(CdTe)_{0.11}, 6 – InAs
Figure 2. Dependences on the parameter value composition— $a$ (1), of interplanar space — $d_{111}$ (2) and theoretical calculated crystal density — $\rho_r$ (3) of the InAs-ZnS ($a$), InAs-CdTe ($b$) systems components.
The use of the results of submicroscopical studies in combination with the results of microscopic studies (figure 4) also made it possible to determine the average sizes ($d_{av}$), average numbers ($n_{av}$) of dominant particles in the systems components, their elemental compositions, which substantially coincide with the specified molar compositions (table 1).
Table 1. Mole composition and corresponding elemental composition of the InAs-CdTe systems components

| Mole composition | Elemental composition |
|------------------|-----------------------|
| InAs (InAs)$_{0.93}$ (CdTe)$_{0.07}$ | In$_{0.51}$ As$_{0.49}$ |
| (InAs)$_{0.89}$ (CdTe)$_{0.11}$ | In$_{0.46}$ As$_{0.43}$ Cd$_{0.06}$ Te$_{0.05}$ |
| (InAs)$_{0.86}$ (CdTe)$_{0.14}$ | In$_{0.44}$ As$_{0.42}$ Cd$_{0.08}$ Te$_{0.06}$ |
| (InAs)$_{0.75}$ (CdTe)$_{0.25}$ | In$_{0.39}$ As$_{0.36}$ Cd$_{0.11}$ Te$_{0.12}$ |
| (InAs)$_{0.32}$ (CdTe)$_{0.68}$ | In$_{0.17}$ As$_{0.15}$ Cd$_{0.36}$ Te$_{0.32}$ |
| (InAs)$_{0.27}$ (CdTe)$_{0.73}$ | In$_{0.15}$ As$_{0.12}$ Cd$_{0.38}$ Te$_{0.35}$ |
| (InAs)$_{0.22}$ (CdTe)$_{0.78}$ | In$_{0.12}$ As$_{0.10}$ Cd$_{0.41}$ Te$_{0.37}$ |
| (InAs)$_{0.15}$ (CdTe)$_{0.85}$ | In$_{0.08}$ As$_{0.07}$ Cd$_{0.44}$ Te$_{0.41}$ |
| (InAs)$_{0.04}$ (CdTe)$_{0.96}$ | In$_{0.023}$ As$_{0.017}$ Cd$_{0.49}$ Te$_{0.47}$ |
| CdTe | Cd$_{0.505}$ Te$_{0.495}$ |

As the content of A$^{II}$B$^{VI}$ (ZnS and CdTe) components increases in InAs-ZnS, InAs-CdTe systems, the reverse tendencies are observed in change in density $\rho_r$ found on the basis of X-ray studies: decrease in the first and increase in the second cases (figure 5). The consequence of increase in $\rho_r$ should be saturation of free bonds, a decrease in the number of coordination unsaturated atoms, which are mainly responsible for the Lewis acid sites, and, as a result, an increase in the relative contribution of Bronsted sites. With decreasing $\rho_r$, the decrease in the saturation of free bonds, the increase in the number of coordination unsaturated atoms, and the increase in the relative contribution of Lewis sites should be expected.

![Figure 5](image_url)

**Figure 5.** Dependences on the particles average number composition prevailing in the range of 2-6 μm – $n_{av}$ (1), theoretical calculated crystal density $\rho_r$ – (2), pH of the isoelectric state of surfaces – $pH_{iso}$ (3) systems InAs-ZnS (a) и InAs-CdTe (b) components
The results of direct studies of the acid-base properties confirmed the predictions made in relation to the InAs-CdTe system and showed the opposite in relation to the InAs-ZnS system (figure 5).

The $pH_{iso}$ values of the components of the InAs-CdTe system are 5.75 – 6.27, increasing in the sequence:

\[
\text{InAs} \rightarrow (\text{InAs})_{x} (\text{CdTe})_{1-x} \rightarrow \text{CdTe}.
\]

In the same sequence, the density ($\rho_r$) and the average number of particles ($n_{av}$) run parallel (figure 5). That is, there is a close connection between the bulk ($\rho_r$, $n_{av}$) and surface ($pH_{iso}$) properties of the components of the InAs-CdTe system, the reason for which is in the nature of active (acid) sites.

The connection between the bulk and surface properties of the InAs-CdTe system components can be traced not only by comparison the dependences $n_{av} = f(X_{\text{CdTe}})$, $\rho_r = f(X_{\text{CdTe}})$, and $pH_{iso} = f(X_{\text{CdTe}})$, but also by comparison the absolute values of the indicated properties. Thus, the density values of solid solutions of the InAs-CdTe system change in 5.81-6.05 range, the $pH_{iso}$ values – in 5.75–6.27 range, confirming the increase in the relative contribution of Bronsted sites ($pH_{iso}$ growth) with an increase in $n_{av}$, $\rho_r$ and a decrease in the coordination unsaturation of the surface atoms.

In the reverse tendencies noted for the InAs-ZnS system for changes in the pH of the isoelectric state of the solid solutions ($pH_{iso}$) surfaces and their theoretical calculated crystal density ($\rho_r$) with the accumulation of ZnS (increase in $pH_{iso}$ and decrease in $\rho_r$), a crucial role was played by significant difference in the values of such initial binary compounds (InAs, ZnS) bulk properties as the forbidden bandwidth ($\Delta E_{\text{InAs}} = 0.36$ eV, $\Delta E_{\text{ZnS}} = 3.67$ eV), the electronegativity difference ($\Delta X_{\text{InAs}} = 0.30$; $\Delta X_{\text{ZnS}} = 0.90$). This led to an increase in the fraction of ionic bonds with the accumulation of ZnS and, accordingly, in the degree of surface hydration (content of OH groups). Despite the increase in the coordination unsaturation of surface atoms and Lewis sites contribution with $\rho_r$ decreasing, the Bronsted sites exerted a predominant relative influence.

The nature of the changes in $pH_{iso}$ and $\rho_r$ in the A$^{III}$B$^{V}$-A$^{II}$B$^{VI}$ (InP-ZnS) type system, which differs from that studied by the first binary component (InP), as well as $pH_{iso}$ and $n_{av}$ in the A$^{II}$B$^{VI}$-A$^{II}$B$^{VI}$ (CdTe-CdSe) type system, support the above considerations. With smaller differences in the values of the forbidden bandwidth and electronegativities of the initial binary compounds ($\Delta E_{\text{InP}} = 1.35$ eV, $\Delta E_{\text{ZnS}} = 3.67$ eV; $\Delta X_{\text{InP}} = 0.40$; $\Delta X_{\text{ZnS}} = 0.90$ and $\Delta E_{\text{CdTe}} = 1.51$ eV, $\Delta E_{\text{CdSe}} = 1.88$ eV; $\Delta X_{\text{CdTe}} = 0.40$; $\Delta X_{\text{CdSe}} = 0.80$) with a decrease in $\rho_r$ and $n_{av}$, respectively, with an increase in the coordination unsaturation of the surface atoms, the relative contribution of Lewis sites becomes significative ($pH_{iso}$ decreases in parallel with a decrease in $\rho_r$ and $n_{av}$) (figure 6, 7).

**Figure 6.** Dependences on the composition of pH values of the isoelectric state of surfaces ($pH_{iso}$) – 1 and theoretical calculated crystal density ($\rho_r$) – 2 of the InP-ZnS system components.
Figure 7. Dependences on the composition of the components of the CdSe-CdTe system of the values of the dominant particles average number – $n_{av}$ (1), the pH value of the isoelectric state of surfaces – $\text{pH}_{iso}$ (2).

Special attention should be paid to the correlations between the dependences “bulk property – composition”, “surface property – composition”, that is, the connection between the bulk and surface properties of the obtained solid solutions. The presence of such connections makes it possible to predict surface (in particular, acid-base) properties by bulk properties that are already known or more available (compared to surface ones) for determination (for example, by $p_r$, $n_{av}$).

The possibility of a preliminary evaluation of the activity with respect to gases of different electronic nature of the selected objects follows herefrom. As a result, the search for the requested materials for sensor technology (semiconductor gas analysis) is facilitated.

The forecasts made were confirmed: the new materials obtained in the work – solid solutions of the InAs-ZnS, InAs-CdTe systems (mainly with the lowest $\text{pH}_{iso}$) were recommended for the manufacture of measuring cells for the main gases trace contamination (in particular, NH$_3$), which successfully passed laboratory studies.

6. Summary and conclusions
The methods were developed for the obtaining of multicomponent diamond-like semiconductors – solid solutions of the InAs-ZnS, InAs-CdTe systems, based on the method of isothermal diffusion and known information on the main bulk physical, physical and chemical properties of the initial binary compounds (InAs, ZnS, CdTe).

In comparison with the initial binary compounds, X-ray, micro-, submicroscopical studies of the obtained solid solutions were carried out, according to the results of which they were certified as substitutional solid solutions with a cubic sphalerite structure and, in general, information on multicomponent diamond-like semiconductors was expanded.

The elemental compositions determined on the basis of submicroscopical studies substantially coincide with the specified molar ones.

The established consistent patterns of changes in the composition of bulk and surface properties are predominantly of a statistical (smooth) nature for solid solutions of the InAs-CdTe system and include extrema for solid solutions of the InAs-ZnS system, that is permissible taking into account the complexity of internal processes accompanying the solid solutions formation.
The reverse trends in changes in the composition of the theoretical calculated crystal density \( (p_r) \) and pH of the isoelectric state of the InAs-ZnS system components surfaces were substantiated. The possibility of using the revealed correlations between the regularities of changes in bulk and surface properties for a less labor-consuming search for the advanced materials for sensor technology was demonstrated. The specific practical recommendations for the search were given, indicating the bulk properties (in particular, \( p_r, n_{iv} \)) of the objects under consideration as reference points.

7. References

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