Solid solutions of hetero- and homo-substitution of the $\text{A}^\text{III}\text{B}^\text{V}$-CdTe, $\text{A}^\text{II}\text{B}^\text{VI}$-CdTe systems. Physical and chemical properties

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Abstract. In the regions of mutual solubility of the initial binary compounds (InP and CdTe, ZnS and CdTe), according to the specifically developed methods, solid solutions of the InP-CdTe, ZnS-CdTe systems have been obtained, certified based on the results of X-ray, micro-, submicroscopical, UV, infrared studies as substitutional solid solutions with a cubic sphalerite structure. Information on the multicomponent diamond-like semiconductors has been supplemented, including first-ever determined values of the average size ($d_{av}$), the mean number ($n_{av}$) of the predominant particles in the systems components, their forbidden bandwidth values and the surface structure. The acid-base properties of the obtained solid solutions surfaces and binary components of the systems, which are assigned to the weak-acid region ($\text{pH}_{\text{iso}} < 7$), have been studied. Prognosis concerning the increased activity of such surfaces towards the main gases have been established. They possess both smooth and extreme nature. The influence on the dependence type by the degree of difference in the values of the forbidden bandwidth of the initial binary components has been confirmed. The reverse trends in changes with the composition of density ($\rho$) and $\text{pH}_{\text{iso}}$ have been substantiated. The connection between the concentration dependences of bulk and surface properties has been revealed. The possibility of using such connection for a faster, more efficient search for the advanced materials for semiconductor gas analysis and, in particular, for the manufacture of sensors for the main gases trace contamination.

Key words - solid solutions, multicomponent diamond-like semiconductors, crystal-chemical, structural, acid-base properties, consistent patterns, correlations, sensors, semiconductor gas analysis.

1. Introduction
In the present paper, the targets of research are multicomponent diamond-like semiconductors - solid solutions of hetero- and homo-substitution, respectively, of the InP-CdTe and ZnS-CdTe systems. The use of such solid solutions based on binary diamond-like semiconductors (InP, ZnS, CdTe), which have already proven themselves due to their unique properties [1], expands the prospects for the effective materials search for the effective materials of the sophisticated technology, including sensor technology.

Due to a change in the composition, the potential is opened not only for the expected, smooth change in properties, but also for the extreme one. This may be conditioned by the complexity of internal processes accompanying the solid solutions [2] formation, and especially solid solutions of hetero substitution. During their formation, the substituent atoms in the parent lattice act as electrically active impurities, doping the basic substance, and, as they accumulate, change the crystal lattice, physical, physical and chemical properties.

The above considerations constitute grounds for a comparative consideration of the selected objects in a comprehensive study of their bulk and especially surface properties.

2. Problem statement
To develop methods for obtaining solid solutions with respect to the selected systems InP-CdTe, ZnS-CdTe.
To conduct X-ray, micro-, submicroscopical, UV, infrared studies, following the results of which to certify the obtained solid solutions, to get information about their crystal chemical, structural, optical properties and, in general, expand information on multicomponent diamond-like semiconductors.

To study the surface (acid-base) properties of solid solutions and binary components of the InP-CdTe, ZnS-CdTe systems. To evaluate the surfaces activity in relation to gases of a certain electronic nature. To establish the interrelated consistent patterns of changes in the composition of the studied bulk and surface properties.

To determine the possibilities of their use for a less labor-consuming search for the advanced, efficient materials for semiconductor gas analysis.

3. Theory
With the constantly increasing demand for the advanced materials in the sophisticated technology, faster and less expensive search is needed. It depends on the choice and completeness of information on the properties of the promising basic objects.

In the present paper, these are multicomponent diamond-like semiconductors - solid solutions based on binary semiconductors of the AIIIBV, AIIBVI type, which have unique properties (electrophysical, optical, opto-electrical).

Changing the composition allows to obtain materials with optimal characteristics for certain areas of technology, in particular for sensor technology, volumetric and especially surface characteristics. The latter often play a crucial role in the semiconductor devices operation due to the miniaturization of their working elements, in various technological processes.

Taking into account the above considerations, solid solutions of the InP-CdTe, ZnS-CdTe systems were obtained, certified and comprehensively studied.

4. Outcomes of experiments
The targets of research were fine powders (S_p = 0.36-1.35 m^2/g) of the initial binary compounds (InP, ZnS, CdTe) and solid solutions (InP)_x(CdTe)_{1-x} (x = 9; 12; 16; 18 mol %), (ZnS)_x(CdTe)_{1-x} (x = 2; 8; 96; 97 mol %). The solid solutions were obtained by the methods developed for the InP-CdTe, ZnS-CdTe systems based on the method of isothermal diffusion of the initial binary compounds (InP, ZnS, CdTe) in the regions of mutual solubility and available information on their bulk physical and physicochemical properties, using preliminarily justified modes and programs of temperature heating. The completion of the synthesis, formation and structure of solid solutions were estimated by the results of X-ray, micro-, submicroscopical, UV, infrared studies.

X-ray studies were performed on the Advance D8 diffractometer (“Bruker”) AXS (CuKα - radiation, λ = 0.154056 nm, T = 293 K) involving remote-angle survey technique [1,2], using a Lynxeye position-sensitive detector, as well as the ICDDPDF-2 database and TOPAS 3.0 software (Bruker), respectively. Microscopical studies were conducted on devices KN 8700 (Xilox, Japan) and Micromed POLAR-3 with a resolution of 7000 [3]. Submicroscopical studies were carried out in a scanning electron microscope JSM-5700, equipped with an attachment for energy dispersive analysis [4,5]. UV spectroscopic studies were performed on spectrophotometers UV-2501 PC “Shimadzu” with a diffuse reflectance attachment ISR-240A and SPECORD-40, in the range 190-900 nm [6]. Infrared studies - on a Fourier-transform spectrophotometer Infra-Lum FT-02 with an attachment of attenuated total internal reflection [7].

The surface properties were studied using the method of hydrolytic adsorption [8], which allows to estimate the pH values of the surfaces isoelectric state (pH_{iso}). At the same time, the pH values of the medium were found, in which the ampholyte adsorbents split off equal (insignificant) amounts of H^+ and OH^- ions. The ampholyte adsorbents were the components of the InP-CdTe, ZnS-CdTe systems with distinctive isoelectric points corresponding to the minimum solubility.

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. Statistical processing of the obtained values, calculation of measurement errors, construction and processing of graphical dependencies were carried out using computer programs Stat-2, Microsoft Excel and Origin.

5. Results and discussion
The results of X-ray studies indicate the formation of substitutional solid solutions with a cubic sphalerite structure in the InP-CdTe, ZnS-CdTe the X-ray diffraction patterns (diffractograms), the shift of lines
corresponding to solid solutions relative to the lines of binary components at their constant number, the corresponding relative position and intensity distribution of the main lines, the absence of additional lines of unreacted binary components, blurring of the main lines (Fig. 1), mainly smooth nature (obeying to Vegard’s law) of concentration dependences of parameter (a), interplanar distances (d_{hkl}) of crystal lattices, and in the ZnS-CdTe system and density (\rho) (Fig. 2). The observed deviation from Vegard’s law in the InP-CdTe system of the concentration dependence \rho = f(X_{\text{CdTe}}) is due to complex internal processes accompanying the formation of solid solutions [9, 10] and, as a consequence, to an uneven distribution of cation-anion complexes. This is also indicated by the results of micro-, submicroscopical studies, demonstrating the polycrystalline structure of the systems components with an inhomogeneous distribution of crystallites (Fig. 2, 3).

Figure 1. X-ray patterns of the InP-CdTe (I) system components: 1 – InP, 2 – (InP)_{0.18}(CdTe)_{0.82}, 3 – (InP)_{0.16}(CdTe)_{0.84}, 4 – (InP)_{0.12}(CdTe)_{0.88}, 5 – (InP)_{0.09}(CdTe)_{0.91}, 6 – CdTe and ZnS-CdTe (II): 1 – ZnS, 2 – (ZnS)_{0.97}(CdTe)_{0.03}, 3 – (ZnS)_{0.96}(CdTe)_{0.04}, 4 – (ZnS)_{0.03}(CdTe)_{0.97}, 5 – (ZnS)_{0.02}(CdTe)_{0.98}, 6 – CdTe
As well as the results of submicroscopical studies, the results of UV and infrared studies additionally confirm the substitutional solid solutions formation in the InP-CdTe, ZnS-CdTe systems. With an increase in
the CdTe content in systems, there is a shift in the relative position of the main peak in the UV spectra and a change in its intensity (Fig. 3), a shift in the IR bands corresponding to the valence vibrations of molecularly adsorbed CO$_2$ and structural hydroxyl groups (Fig. 4), regular change in the forbidden bandwidth ($\Delta E$) ([6], Fig. 3.5), the average number of dominant particles ($n_{av}$), determined from microscopic and SEM images (Fig. 6).

The elemental compositions of solid solutions determined in the same way substantially coincide with the given molar ones.

**According to the results of studies of the surface (acid-base) properties** of the InP-CdTe, ZnS-CdTe systems components surfaces exposed in air, it should be classified as weakly acidic: the pH values of the isoelectric state ($pH_{iso}$) are within 5.58-6.3 and 6.29-6.68, respectively, growing with an increase in the CdTe content in the InP-CdTe system and ZnS in the ZnS-CdTe system.

At such pH$_{iso}$ values of the system components ($pH_{iso} < 7$), it is logical to expect their increased activity with respect to the main gases. The test showed that exposure of the system components in ammonia leads to a shift of pH$_{iso}$ to the alkaline region ($pH_{iso}$ increases, within the limit by 0.9, unlike exposure in acid gas - NO$_2$ ($pH_{iso}$ decreases, within the limit by 0.6)). In this case, the very fact of changes in pH$_{iso}$ in the specified gases indicates their adsorption interactions.

**With a change in the composition, the properties of the systems solid solutions change differently.** With an increase in the common component CdTe content, the bulk (crystal chemical, structural) and surface (pH$_{iso}$) properties of solid solutions of the ZnS-CdTe system change mainly smoothly. There is an increase in parameter ($a$), interplanar distances ($d_{hkl}$), theoretical calculated crystal density ($\rho_r$) of crystal lattices and a decrease in pH$_{iso}$ (Fig. 6.7).

With an increase in the CdTe content in solid solutions of the InP-CdTe system parameter ($a$), interplanar distances ($d_{hkl}$) of crystal lattices change (decrease) smoothly, but theoretical calculated crystal density ($\rho_r$) and pH$_{iso}$ (through min) change extremely, that is, with a deviation from Vegard's law (Fig. 6.7). There was a noticeable effect of the first binary components of the systems (InP, ZnS), which differ significantly in the values of the forbidden bandwidth ($\Delta E_{InP} = 1.35$, $\Delta E_{ZnS} = 3.67$ eV). The repeatedly noted facts of influence of the degree of difference in the forbidden bandwidth values of the initial binary compounds on the nature of the dependences on the composition of the properties of the solid solutions formed by them were confirmed (for example [11, 12]). In the case under study, the difference between the values of the forbidden bandwidth of the binary components of the InP-CdTe and ZnS-CdTe systems is 0.16 and 2.16 eV, respectively. Thus, with a decrease in the difference between the $\Delta E$ of binary components of systems, the
tendency to an extreme character of the dependences of the properties of solid solutions on composition increases (Fig. 7).

**Figure 6.** Dependences on the systems InP-CdTe (I), ZnS-CdTe (II) composition of the parameter \(a\) – 1, interplanar space \(d_{111}\) – 2 and theoretical calculated crystal density \(\rho_r\) – 3 crystal lattices

The extreme change in the composition of pHiso indicates competition between the relative contributions of the Lewis and Bronsted sites, which is natural against complex internal processes accompanying the solid solutions formation [1, 9].

**Figure 7.** Dependences on the systems InP-CdTe (I), ZnS-CdTe (II) composition of the forbidden bandwidth \(\Delta E\) (1), theoretical calculated crystal density \(\rho_r\) (2), average number of the most presented particles \(n_{av}\) (4), pH-isolectric state of surfaces pHiso (3)

The fact that, with respect to solid solutions of the InP-CdTe system, the minimum theoretical calculated crystal density corresponds to the minimum of pHiso, indicates the crucial role of Lewis sites, mainly surface atoms, the coordination unsaturation of which increases with decreasing density, as well as the presence of a
correlation between structural \( (\rho_\text{r}) \) and surface \( (\text{pH}_{\text{iso}}) \) properties. Such presence allows to preliminary estimate the surface activity by \( \rho_\text{r} \).

With respect to solid solutions of the ZnS-CdTe system, the reverse trends in changes with the composition of density and acidity of surfaces come under notice: increase in \( \rho_\text{r} \) and decrease in \( \text{pH}_{\text{iso}} \). Here, on the one hand, as \( \rho_\text{r} \) increases, the coordination unsaturation of the surface atoms responsible for the Lewis sites decreases. On the other hand, with an increase in the CdTe content in solid solutions, possessing in comparison with ZnS, a small difference in electronegativities \( (\Delta X_{\text{CdTe}} = 0.4, \Delta X_{\text{ZnS}} = 0.9) \) and, accordingly, a low degree of surface hydration (a small concentration of OH –– groups), the contribution of Bronsted sites decreases. The final relationship between such manifestations was responsible for the marked increase in the acidity of the surfaces (decrease in \( \text{pH}_{\text{iso}} \)).

6. Summary and conclusions

Solid solutions of the InP-CdTe, ZnS-CdTe systems were obtained by specifically developed methods in justified modes.

X-ray, micro-, submicroscopical, UV, infrared studies were performed, following the cumulative results of which the obtained solid solutions were certified as substitutional solid solutions with a cubic sphalerite structure; for the first time, the average sizes (\( d_\text{av} \)), the mean numbers (\( n_\text{av} \)) of the predominant particles in the components of the systems, the values of the forbidden bandwidth, the surfaces structure were determined, and in general, the information on multicomponent diamond-like semiconductors was expanded. The surface (acid-base) properties of solid solutions and binary components of systems were investigated. According to the average strength of acid sites \( (\text{pH}_{\text{iso}}) \), they should be classified as weakly acidic \( (\text{pH}_{\text{iso}} < 7) \) with a relatively increased acidity of the surfaces of solid solutions of the InP-CdTe system. The interrelated consistent patterns of changes in the composition of bulk and surface properties, which are both smooth (following Vegard’s law) and extreme, were established. The influence on the regularities nature of the degree of difference in the values of the forbidden bandwidth and, accordingly, in the values of the electronegativity difference, the degree of hydration of the surfaces of the initial binary components of the (InP and CdTe, ZnS and CdTe) systems was shown. The explanation of the reverse trends in changes in the composition of \( \rho_\text{r} \) and \( \text{pH}_{\text{iso}} \) in the ZnS-CdTe system was given. The relative roles of the common binary component (CdTe) and the first binary components (InP, ZnS) were revealed.

On the basis of the correlations between the established consistent patterns, the relationship between surface and bulk properties, the possibility of a less labour-consuming search for the advanced materials for the manufacture of sensors for trace contamination of gases of a certain electronic nature, in particular, for trace contamination of main gases of NH3 type was substantiated.

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