Asid-base state of surfaces of binary and multicomponent semiconductors GaB^V-ZnB^VI

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Abstract. Bulk (crystal-chemical, structural, electrophysical) and surface (acid-base) properties of the A^III B^V (GaAs, GaSb), A^II B^VI (ZnSe, ZnTe) type binary compounds, varying in B^V, B^VI elements and substitution solid solutions (GaAs)_x(ZnSe)_{1-x}, (GaSb)_x(ZnTe)_{1-x} formed by them have been studied. The acidic sites’ nature, strength, concentration have been estimated. The consistent patterns have been established in changes in bulk and acid-base properties with changes in the each particular system components composition; general and differential characteristics in the components “behavior” of the two GaAs-ZnSe and GaSb-ZnTe systems have been revealed. Justification has been given. Reasons have been given on the possibility of predicting the surface activity of such systems’ solid solutions. Practical guidelines on the use of their most active representatives in semiconductor gas analysis have been provided.

Keywords – substitution solid solutions, acid-base properties, consistent patterns, general and differential characteristics, forecasting, semiconductor gas analysis.

1. Introduction
The target of the present paper were solid solutions of A^III B^V-A^II B^VI – GaAs-ZnSe, GaSb-ZnTe systems. They belong to representatives of multicomponent diamond-like semiconductors, many of which have already approved themselves in micro- and optoelectronics. The development of new areas of current technology, including nano- and sensor technology urges on the further search for new materials. The most promising appears to be the expansion of the such systems range, the study and use of solid solutions based on them, which include the possibility of not only a smooth control of properties with a change in composition, but also the discovery of extreme, especially interesting effects.

2. Problem statement
To obtain solid solutions of GaAs-ZnSe, GaSb-ZnTe systems according to the developed technique. To study their bulk properties (crystallochemical, structural, electrophysical) used to enrich information on diamond-like semiconductors, first of all, multicomponent ones and certification of the obtained solid solutions.

To perform integrated research of the surface (acid-base) properties.

To establish consistent patterns and correlations in changes of the studied properties within a particular system and when comparing to another systems. To pre-estimate the selective sensitivity of surfaces in relation to gases of a certain electronic nature. To provide appropriate practical guidelines and to justify.

3. Theory
The systems on the basis of which solid solutions $(\text{GaAs})_x(\text{ZnSe})_{1-x}$, $(\text{GaSb})_x(\text{ZnTe})_{1-x}$ were obtained in the present paper, were studied to an extent of their properties (compared to the initial binary compounds) refer to the $A_{\text{III}}B_{\text{V}}-A_{\text{II}}B_{\text{VI}}$ systems - a new type of heterogeneous substitution, where both cationic and anion formers are representatives of different groups of the periodic system.

The first system of this type for which the existence of a continuous series of substitution solid solution was predicted was the GaAs-ZnSe system \[1\].

By the beginning of our research, it had been underinvestigated as evidenced by the inconsistency of the results of its main parameters determining, given in the literature \[2\]. Normally no information was available on the GaSb-ZnTe system.

Paying due consideration due to the unique properties of the initial binary compounds $A_{\text{III}}B_{\text{V}}$, $A_{\text{II}}B_{\text{VI}}$, to the prospects of using solid solutions of such systems as the sought-for materials of the state-of-the-art technology, including the sensor one, it seemed currently important to study their main bulk and especially surface physicochemical properties when expanding the range.

4. Outcomes of experiments

The solid solutions $(\text{GaAs})_x(\text{ZnSe})_{1-x}$ ($x = 25, 50, 75$ mol. %), $(\text{GaSb})_x(\text{ZnTe})_{1-x}$ ($x = 5, 10, 15, 90, 95$ mol. %) were obtained according to the developed technique based on isothermal diffusion of the initial binary compounds (GaAs and ZnSe; GaSb and ZnTe) and essential information on their bulk physical and chemical properties \[2\], in vacuumed, sealed quartz ampoules. The regime for solid solutions obtaining corresponded to a specially designed program of temperature heating.

The formation of solid solutions, their structure, was judged mainly by the results of X-ray studies with the involvement of the results of the specific resistance determination (specific conductivity, accordingly), forbidden bandwidth, and the pH of the surfaces isoelectric state ($\text{pH}_{\text{iso}}$).

X-ray studies were performed on a DRON-3 diffractometer (CuKα, β-radiation, $\lambda = 0.154178$ nm and 0.139217 nm, $T = 293$ K) and Advance D8 powder X-ray Diffractometer manufactured by Bruker AXS (CuKα - radiation, $\lambda = 0.15406$ nm, $T = 293$ K), involving wide-angle survey technique \[3, 4\], using the position-sensitive detector Lynxeye.

For interpretation of the obtained X-ray patterns (X-ray diffraction patterns), the ICDDPDF-2 powder diffraction database was used; the TOPAS 3.0 (Bruker) program and the least-squares method were used to specify the lattice parameters.

The specific resistance of the GaAs-ZnSe, GaSb-ZnTe systems components was determined by the four-probe Van der Pauw method \[5\].

The surface (acid-base) properties were investigated using the methods of hydrolytic adsorption (determination of the isoelectric state $\text{pH} – \text{pH}_{\text{iso}}$) \[6\], mechanochemistry involving qualitative chemical and spectral analyzes, IR spectroscopy \[7\], non-aqueous conductometric titration \[8\].

When identifying $\text{pH}_{\text{iso}}$, the pH media were found where the adsorbent-ampholyte eliminates equal (minor) amounts of $\text{H}^+$ and $\text{OH}^-$ ions. Semiconductors of the GaAs-ZnSe, GaSb-ZnTe systems with characteristic isoelectric points, corresponding to minimum solubility, acted as adsorbents-ampholytes.

The method of non-aqueous conductometric titration, used to estimate the acid sites concentration on the surfaces and to reveal their nature is based on measuring the conductivity of the solution when adding titrant. As a solvent, methyl-ethyl ketone was used, having ampholyptic properties, as a titrant – the potassium ethylate solution, the concentration of which was evaluated by conductometric titration with 0.1n of acetic acid solution ($T_{\text{room}}$, conductometer Expert-002-2-6-P, pouring sensor). Based on the measurement results, differential influence curves of the specific electric conductivity on the titrant volume were plotted and the acid sites concentration (for individual peaks and the general one) was calculated by formula:

$$C = \frac{N \cdot V \cdot 1000}{m}$$
(m – adsorbent weight, g; V – potassium ethylate volume used for titration, ml; N – normal concentration of the potassium ethylate solution, e.p.m.).

The mechanochemical method allowed to work with newly formed surfaces and monitor their behavior in the chosen reaction medium (water) through the products of interaction of the latter with the surface atoms of the semiconductors detected by qualitative chemical and spectral analyzes of the “medium-dispersible semiconductor” systems suspension as well as through IR spectra and accordingly by the change in the medium pH.

IR spectra were collected on a Srecord IR-75 spectrometer and a Fourier spectrometer infrared Infra-LUM FT-2 with a repeated frustrated internal reflectance attachment in the wave numbers area 400 – 4000 cm⁻¹.

Studies of the behavior of newly formed surfaces in the chosen reaction medium, carried out in accordance with a specifically developed method [2, 7], were aimed at a clearer identification of the active sites nature as well as the possibilities of mechanochemical activation of the surfaces.

While studying the surface (acid-base) properties, methods of adsorption of bases and acids from the gas phase, thermal desorption with mass spectrometric and chromatographic analyzes, and potentiometric titration with potassium ethylate in methyl-ethyl ketone were additionally involved [9].

Reproducibility and accuracy of the empirical data were checked in accordance with the parallel measurements findings using mathematical statistics and quantitative analysis results processing. Statistical processing of the obtained numerical values, calculation of measurement errors, plotting and processing of graphical dependencies were carried out using computer programs Stat-2, Microsoft Excel and Origin.

5. Results and discussion

According to the results of X-ray studies [10], substitution solid solutions with mainly cubic sphalerite structure are formed in GaAs–ZnSe, GaSb–ZnTe systems (with given binary components balance). This is proved by the relative shift, position and distribution by intensities of the main lines on the X-ray patterns corresponding to the binary components and solid solutions, smooth changes with the composition of the parameter’s calculated values (a), crystal lattices interplanar distances (dhkl), theoretical calculated crystal density (ρᵣ) (Fig. 1 I). Indirectly, the conclusion is confirmed by smooth changes with the composition of the specific conductivity (σ) and the forbidden bandwidth (ΔE) (Fig. 1 I, 1 II).

The pH values of the initial surfaces of the GaAs–ZnSe, GaSb–ZnTe systems components (air exposed) stay within 6.4–8.3 and 6.2–7.7, growing with increase in ZnSe content in the GaAs–ZnSe and ZnTe system in the GaSb–ZnTe system. That is, in both systems, with the composition changes, a transition from a faintly-acid area to a weakly alkaline one is observed. Basically smooth character of the transition is an additional confirmation of the substitution solid solutions formation in these systems.

Characteristics of the cations’ acceptor properties - ionization potential (I_Ga/I_Zn) and the charge-to-radius ratio (e/r = 4.8 for Ga and 2.4 for Zn) also confirm the decrease in the strength of acid sites (pHₐ) upon transition in the systems under review from A³B⁵ (GaAs, GaSb) semiconductors to A²B⁶ (ZnSe, ZnTe) semiconductors.

Analogous series in the acid sites strength are also produced the heats of ammonia adsorption [11], calculated by Clausius–Clapeyron relation and proposed in [12]. Their drop with occupation of the surfaces indicates the energy inhomogeneity of such, presence of various acid sites on them, and formation of cationic - anionic complexes in solid solutions, which are distributed unevenly [2].
Figure 1. Dependence of the parameter values $a$ (1), interplanar distances $d_{311}$ (2) of crystal lattices, theoretical calculated crystal density $\rho_r$ (3), specific conductivity $\sigma$ (4) on the components composition of the GaSb-ZnTe system (I) and forbidden bandwidth $\Delta E$ on the components composition of the GaAs-ZnSe system (II).

This fact is justified by the results of non-aqueous conductometric titration, as well as by the results of potentiometric titration and thermal desorption (see, for example, Fig. 2, 3). Actually, we note that the differential curves of the non-aqueous conductometric titration of the studied air-exposed components and the chromatograms of the thermal desorption of ammonia adsorbed on them contain three peaks each, confirming the existence of different types of acid sites on the surfaces and the cationic - anionic complexes formation distributed unevenly[2].

Based on the background of experience in studying the surface properties of diamond-like semiconductors [7, 11, 13, 14], it is logical to assume that the Lewis acid sites (coordinatively unsaturated atoms) are responsible for the first peaks on the graphic images (Figs 2, 3) and Bronsted acid sites (adsorbed water molecules, OH- groups) are responsible for the second and third ones (adsorbed water molecules, OH- groups). It is confirmed by the noted displacement of the $\mathrm{pH}_{\text{iso}}$ values into the alkaline area with increasing content in the ZnSe and ZnTe systems.

$$\Delta \sigma/\Delta V, \text{Om}^{-1}\cdot\text{ml}^{-1}$$

Figure 2. Differential curves of non-aqueous conductometric titration of the system GaSb-ZnTe components, air-exposed: 1 – GaSb, 2 – (GaSb)$_{0.95}$(ZnTe)$_{0.05}$, 3 – (GaSb)$_{0.90}$(ZnTe)$_{0.10}$.
Consequently, it is possible to talk about the manifestation of three forms of adsorbed ammonia, varying in the desorption activation energy, which correspond to different in strength acid sites on the surfaces.

At least three forms of adsorbed ammonia revealed mass spectra of ammonia thermal desorption products [11].

The total concentration of acid sites (C_{tot}), calculated for all differential curves peaks of non-aqueous conductometric and potentiometric titration (Fig. 2), with changes in the composition of the GaAs–ZnSe, GaSb–ZnTe systems components varies extremely: C_{tot} maxima accrue to solid solutions of the (GaAs)_{0.5}(ZnSe)_{0.5} и (GaSb)_{0.95}(ZnTe)_{0.05} compositions. They can conceivably be considered as the most active adsorbents with respect to the main gases. On the whole, according to the results obtained, it is possible to expect an increased adsorption activity of the systems components with weakly acidic surfaces (pH_{iso} < 7) to the main gases, with slightly alkaline (pH_{iso} > 7) – to acid gases and to speak about the possibility of using them as materials for the corresponding measuring cells [7, 13, 14].

When identifying the nature of the active centers responsible for the surfaces acidity, the mechanism of acid-base interactions, mechanochemical studies proved to be beneficial, allowing to work with newly formed surfaces and discover those functional groups that do not manifest themselves on samples with their “life history” (although thermo vacuum treated) [7, 11].

In the course of dispersion of the coarse-dispersed powders of binary components and solid solutions of the GaAs-ZnSe, GaSb-ZnTe systems, medium acidifying is observed (see, for example, Fig. 4). In accordance with the considerations made in [7, 11, etc.], in the present case, in the course of dispersion in water of the said components, the formation with coordinatively saturated atoms (As, Sb, Se, Te) on the newly created surfaces acids of surface origin H_{3}AsO_{4}, H_{3}SbO_{4}, H_{2}SeO_{4}, H_{2}TeO_{4} is possible. Under the mechanochemical influences they transform into the volume with the elimination of their AsO_{4}^{3-}, SbO_{4}^{3-}, SeO_{4}^{2-}, TeO_{4}^{2-} residues. Availability of such “dispersible semiconductor - medium (water)” in suspensions is proved by qualitative chemical, spectral analysis, according to IR spectra [7, 11].

![Figure 3. Chromatogramm of ammonia thermal desorption from GaAs (a) and ZnSe (b) surfaces](image-url)
Figure 4. Kinetic isotherms of coarse powders GaSb (1), (GaSb)$_{0.90}$ (ZnTe)$_{0.10}$ (2), (GaSb)$_{0.95}$ (ZnTe)$_{0.05}$ (3), (GaSb)$_{0.15}$ (ZnTe)$_{0.85}$ (4), (GaSb)$_{0.10}$ (ZnTe)$_{0.90}$ (5), (GaSb)$_{0.05}$ (ZnTe)$_{0.95}$ (6), ZnTe (7) dispersion in water

6. Summary and conclusions

When summarizing the obtained results, analyzing the changes in properties within each studied system and comparing them in different systems, common and differential characteristic come under notice.

**Common characteristics include:**
- substitution solid solutions formation with cubic sphalerite structure in the GaAs-ZnSe, GaSb-ZnTe systems;
- smooth changes with parameter values composition ($a$), crystal lattices interplanar distances (d$_{hkl}$), theoretical calculated crystal density ($\rho_r$), specific conductivity ($\sigma$), forbidden bandwidth ($\Delta E$);
- smooth $pH_{iso}$ change with a transition from faintly-acid areas to weakly alkaline areas, but an extreme change in the total acid sites concentration ($C_{tot}$).

It is worth mentioning that the predominantly smooth changes in these properties with the composition (i.e., the predominance of the statistical factor role) are observed with noticeable differences in the properties of the initial binary components of the systems characterizing the crystal lattices strength, such as melting temperature ($T_m$), electronegativity difference ($\Delta x$), forbidden bandwidth ($\Delta E$). The latter, respectively, are:

for GaAs and ZnSe  1237$^\circ$C and 1515$^\circ$C;  0.38 and 0.8;  1.43 and 2.7 – 29 eV;
for GaSb and ZnTe  710$^\circ$C and 1295$^\circ$C;  0.20 and 0.5;  0.72 and 2.12 – 2.27 eV.

**As for the differential characteristic,** they include not identical contents in the binary component A$^{II}$B$^{VI}$ (ZnSe, ZnTe) systems at which the transition of the solid solutions surfaces into weakly alkaline areas begins: for the system GaAs–ZnSe – at 50 mol. % ZnSe, for the system GaSb–ZnTe – at 95 mol. % ZnTe. This corresponds to a larger electronegativity difference of ZnSe ($\Delta x = 0.8$), compared to ZnTe ($\Delta x = 0.5$), correspondingly to a greater ionic link proportion, a greater degree of hydration and its surface basicity.

It is logical to relate the manifestations of $C_{tot}$ maxima in the systems with such characteristics of ZnSe: with a higher ZnSe content (50 mol. %) in the GaAs-ZnSe system, compared to the ZnTe content (5 mol. %) in the GaSb-ZnTe system. It's most likely that the most significant contribution to $C_{tot}$ is made in the first case by Bronsted centers, in the second case, by Lewis centers.

In order to reveal the fundamental difference in the “behavior” of the A$^{III}B^{V}$–A$^{II}B^{VI}$ and A$^{III}B^{VI}$–A$^{II}B^{VI}$, the basic properties of both in comparison should be analyzed. The representatives of the A$^{III}B^{VI}$–
A\textsuperscript{II}\textsuperscript{VI} systems can be the CdTe–CdSe, CdTe–CdS \cite{15} systems CdTe–CdSe, CdTe–CdS \cite{15}, which will be discussed in the next paper.

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