Multicomponent semiconductors based on the system GaAs-CdSe. Receiving. Properties

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Abstract. for the first time (for given compositions), solid solutions of the GaAs-CdSe system have been obtained, certified on the basis of X-ray and submicroscopical studies as substitution solid solutions with sphalerite and wurtzite structure. The consistent interrelated patterns in changes with composition changes of the system, crystallochemical and structural properties have been revealed: parameters - a, c; crystal lattices interplanar distances - d_{hkl}; theoretical calculated crystal density - \rho_{c}; the average number of the most displayed particles in the components – n_{av}. The pH values of the system components’ surfaces isoelectric state have been determined, which fit into the faintly-acid range. On the ground of the set of obtained results, revealed patterns, correlations between them, a conclusion has been made about a possible preliminary certification of the obtained solid solutions of systems similar to the studied one and a possible facilitated way of searching for advanced, promising materials for creating measuring cells for main gases micro impurities, in particular ammonia. Key words – substitution solid solutions, properties, consistent patterns, correlation, search for advanced materials, measuring cells.

1. Introduction
Representatives of multicomponent semiconductors, in the first place, diamond-like semiconductors, have already proven themselves as operating elements of numerous micro- and optoelectronics devices. Alternative essential functional areas of such materials are nanotechnology, semiconductor gas analysis using original measuring cells, semiconductor catalysis. Development of new functional areas requires the further search for the advanced materials. The most promising seems the use of solid solutions based on binary semiconductors of the A_{III}B_{V}, A_{II}B_{VI} type, possessing unique properties (optical, electrical, photo-, piezoelectric, etc.). These include solid solutions of the GaAs-CdSe system, which have become the object of research in the present paper.

2. Problem statement
To obtain for the first time (for reasonably predetermined compositions) solid solutions based on semiconductors of the A_{III}B_{V} (GaAs) and A_{II}B_{VI} (CdSe) type. To study the crystal-chemical and structural properties necessary for updating information on diamond-like semiconductors and for certifying the obtained solid solutions.
To define the acid sites strength - pH of the isoelectric state of the surfaces of the GaAs-CdSe system components, their selective sensitivity to gases of certain electronic nature.
To establish consistent patterns and correlations in the changes of the studied properties with a change in the system composition, to use them for implementable forecasts to create a less expensive way of searching for advanced, efficient materials for semiconductor gas analysis.
3. Theory
The research group, representatives of which are the authors of the present work, have been carrying out comprehensive studies of diamond-like semiconductors for decades, starting with Ge and its isoelectronic analogues (GaAs, ZnSe, CuBr) and continuing with their binary and then multicomponent representatives range extension. Specific interest in multicomponent semiconductors (solid solutions), demonstrated by the experts of various profiles is contingent on the predicted possibilities (taking into account the unique properties of the initial binary compounds) to obtain original, efficient materials, not only with tunable properties due to composition changes, but also, due to complex internal processes, accompanying the solid solutions formation of solid solutions, with unexpected, extreme ones.

The relevance of research of the specified, to a large extent unexplored systems, particularly embodied in the GaAs-CdSe system, which is soundly selected in the present work is behind extreme, unexpected, not solved and therefore especially attractive effects.

4. Experimental part
To obtain solid solutions \((\text{GaAs})_x(\text{CdSe})_{1-x}\) \((x = 1.1; 11.5; 97.7; 98.2 \text{ mol%})\) the technique was developed, which is based on the initial binary compounds (GaAs, CdSe)isothermal diffusion and available basic data on their bulk physicochemical properties [1]. The mode for obtaining solid solutions corresponded to a specially designed temperature heating program. The products of the synthesis represented compact polycrystalline ingots on the bottom of the ampoule, from which fine powders were then prepared \((S_{sp} \geq 0.45 \text{ m}^2/\text{g})\). The synthesis completion, the solid solutions formation, their structure were judged by the results of X-ray studies and additionally by the results of submicroscopical studies.

X-ray studies were conducted on the Advance D8 diffractometer by Bruker (Germany) in CuKα radiation \((\lambda = 0.15406 \text{ nm}, T = 293 \text{ K})\) according to wide-angle survey technique [2,3] using the position-sensitive detector Lynxeye.

The obtained X-ray patterns (diffractograms) were explained using the powder diffraction database ICDDIPDF-2; the lattice parameters were defined using TOPAS 3.0 (Bruker) by the least squares method.

Submicroscopical studies were carried out with a scanning electronic microscope JCM-5700, equipped with a nitrogen-free x-ray energy-dispersive spectrometer [4].

In accordance with the surface characteristics of the GaAs-CdSe system components, the hydrogen index of the surface isoelectric state \((\text{pH}_{iso})\) was determined using hydrolytic adsorption methods [5] and infrared spectroscopy of repeated frustrated internal reflectance [1].

When determining the \(\text{pH}_{iso}\), the pH media were found where the adsorbent-ampholyte eliminates equal (minor) amounts of \(\text{H}^+\) and \(\text{OH}^-\)ions. Adsorbent ampholytes were semiconductors of the GaAs-CdSe system with characteristic isoelectric points, corresponding to minimum solubility.

Infra-red spectra data was collected using a Fourier spectrometer infrared Infra-LUM FT-2 with a repeated frustrated internal reflectance attachment [1].

Reproducibility and accuracy of the experience-based data was checked by the results of parallel measurements using mathematical statistics and quantitative analysis results processing methods, computer programs Stat-2, Microsoft Excel and Origin.

5. Results and discussion
The results of X-ray studies, given in Fig.1,2 and Table 1 demonstrate the substitution solid solutions formation in the GaAs-CdSe system with the cubic structure of sphalerite (with GaAs excess) and the hexagonal wurtzite structure (with CdSe excess). We point out that on the X-ray patterns, lines accounting for solid solutions are shifted relative to the binary compounds lines at
constant number of them (Fig. 1); dependence on the parameters values composition \((a, c)\), crystal lattices interplanar distances \((d_{hkl})\), density \((\rho_r)\) have smooth nature within the same structure (Table 1, Fig. 2). The main lines relative position and distribution by intensities on X-ray patterns (Fig. 1) indicate the mentioned types of structures.

**Figure 1.** Line X-ray pattern of the GaAs-CdSe system components: 1 – GaAs, 2 – \((\text{GaAs})_{0.982}(\text{CdSe})_{0.018}\), 3 – \((\text{GaAs})_{0.977}(\text{CdSe})_{0.023}\), 4 – \((\text{GaAs})_{0.115}(\text{CdSe})_{0.989}\), 5 – \((\text{GaAs})_{0.011}(\text{CdSe})_{0.989}\), 6 – CdSe
Table 1. Parameter values of crystal lattice (a, c), interplanar distances (d_{hkl}) and theoretical calculated crystal density (\rho_r) of the GaAs-CdSe system components

| Composition (Mole fraction CdSe) | Crystal lattice type | a, Å | c, Å | d_{111}, Å | d_{220}, Å | d_{100}, Å | d_{002}, Å | \rho_r, g/sm^3 |
|--------------------------------|----------------------|------|------|-------------|-------------|-------------|-------------|-------------|
| 0                              | cub.                 | 5.6500 | –   | 3.252       | 1.996       | –           | –           | 5.340       |
| 0.18                           | cub.                 | 5.6557 | –   | 3.269       | 1.999       | –           | –           | 5.341       |
| 0.23                           | cub.                 | 5.6584 | –   | 3.267       | 2.001       | –           | –           | 5.342       |
| 0.885                          | hex.                 | 4.2867 | 7.0048 | –           | –           | 3.712       | 3.502       | 5.541       |
| 0.989                          | hex.                 | 4.2938 | 7.0104 | –           | –           | 3.719       | 3.505       | 5.588       |
| 100                            | hex.                 | 4.3000 | 7.0200 | –           | –           | 3.724       | 3.510       | 5.656       |

Figure 2. Dependence on the parameter composition (a, c), crystal lattices interplanar distances (d_{100}, d_{220}) theoretical calculated crystal density (\rho_r) of the GaAs-CdSe system components

The substitution solid solution formation in the GaAs-CdSe system is confirmed by the smooth dependence on the composition (within the same structure, within 1-4-μm range) of the average number of the most displayed in the components particles (n_{av}), calculated in accordance with the results of submicroscopical studies (according to SEM-images) (Fig.3-5, Table 2).
Figure 3. SEM – images of GaAs (a), (GaAs)$_{0.982}$(CdSe)$_{0.018}$ (b), (GaAs)$_{0.977}$(CdSe)$_{0.023}$ (c), (GaAs)$_{0.115}$(CdSe)$_{0.989}$ (d) (GaAs)$_{0.011}$(CdSe)$_{0.989}$ (e) and CdSe (e) powders in phase contrast mode
Table 2. The dispersion analysis results of the GaAs-CdSe system components

| Composition           | Average number of particles ($n_{av}$) | Size ($d_{av}$), µm |
|-----------------------|----------------------------------------|---------------------|
|                       | <1          | 1…2      | 2…4      | 4…6      | 6…10     |
| GaAs                  | –          | 5        | 15       | 30       | 9        |
| GaAs$_{0.982}$CdSe$_{0.018}$ | –     | 7        | 12       | 25       | 5        |
| GaAs$_{0.977}$CdSe$_{0.023}$ | –     | 6        | 10       | 20       | 6        |
| CdSe$_{0.885}$GaAs$_{0.115}$ | 11     | 12       | 20       | 6        | –        |
| CdSe$_{0.989}$ GaAs$_{0.011}$ | 10     | 13       | 25       | 8        | 1        |
| CdSe                  | 30         | 18       | 16       | 7        | –        |

Figure 4. Dependence of the GaAs-CdSe system components on the composition of the average number of particles ($n_{av}$)
The following facts come under notice. With the addition of cadmium selenide to gallium arsenide and gallium arsenide to cadmium selenide, the average number of particles \( n_{av} \) decreases (the particle size increases accordingly). Theoretical calculated crystal density \( \rho_r \) changes in the same way (Fig. 2, 4).

The results of \( n_{av} \) calculations according to SEM images virtually coincide with the results of calculations in accordance with images obtained with optical microscopes KH 8700 (HiLox, Japan) and Micromed POLAR 3 [8]. It means that on the basis of these, without carrying out X-ray and submicroscopical studies on expensive equipment, it is possible to identify (certify) preliminary the obtained solid solutions of at least diamond-like semiconductors

In other words, it gives access to a more facilitated way of searching for advanced prospective materials. This conclusion is confirmed by the results of acid-base properties studies of the GaAs-CdSe system components surfaces. According to the values of the isoelectric state \( \text{pH}_{\text{iso}} \) hydrogen index which fall within the range 6.2-6.8, they are slightly acidic, therefore they should be active with respect to the main gases (NH\(_3\) type) and suitable for manufacturing the corresponding measuring cells [1,6, 7].

6. Conclusions

For the first time (for given compositions) solid solutions of the GaAs-CdSe system have been obtained.

On the basis of X-ray studies the obtained solid solutions have been certified as substitution solid solutions with cubic sphalerite structure (with GaAs excess) and hexagonal wurtzite structure (with CdSe excess).

The results of X-ray studies have been supplemented by the results of submicroscopical studies: SEM images have been taken, the sizes \( d_{av} \) and average numbers \( n_{av} \) of the most displayed particles of the system components have been calculated.

The smooth nature of the dependence \( n_{av} = f(X_{\text{GaAs}}) \) confirms the substitution solid solutions \((\text{GaAs})_x(\text{CdSe})_{1-x}\) formation and correlates with the dependence \( \rho_r = f(X_{\text{GaAs}}) \).

The isoelectric state pH values of the GaAs-CdSe system components surfaces corresponding to the faintly-acid areas have been determined.

Based on the correlations between the dependence \( n_{av} = f(X_{\text{GaAs}}), \rho_r = f(X_{\text{GaAs}}) \), the agreement of calculation \( n_{av} \) results according to SEM - and common micro images, the \( \text{pH}_{\text{iso}} \) values found, a conclusion has been made on a possible easier, preliminary certification of the obtained solid solutions of systems similar to the studied one and easier ways to find advanced, promising materials for measuring cells for main gases traces.

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