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Possibilities of new materials surface sensibility express determination based on ZnSe-CdS system by pH isoelectric state measurements of the surface state

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Abstract. A method for determining the hydrogen index of the surfaces isoelectric state (pH_{iso}) at various gases pressures - possible components of the surrounding and technological media has been developed. With its use, changes in pH of binary and more complex semiconductors-components of the new system-ZnSe-CdS under the influence of nitrogen dioxide-have been found. The limiting sensitivity of surfaces - minimum P_{NO_2} , causing a change in pH has been estimated. The most active components of ZnSe-CdS system, recommended as materials for measuring cells of NO_2 , have been revealed.

The relationship between the changing patterns with the composition of surface (acid-base) and bulk (in particular, theoretical calculated crystal density) properties has been established, allowing to find the most effective materials for sensor technology and for semiconductor analysis.

Keywords: binary and multicomponent semiconductors, a new technique, surface sensitivity to gases, the relationship between surface and bulk properties, measuring cells.

1. Introduction

The solid solutions of ZnSe-CdS system (compared to the initial binary compounds, ZnSe, CdS) studied in the present work represent multicomponent diamond-like semiconductors – promising materials for sophisticated technology, in particular, for sensor technology [1].

When finding out possibilities of using new, often obtained for the first time materials for sensor technology, it is necessary to assess their sensitivity and selectivity to microimpurities of the surrounding and technological media. Direct adsorption measurements are perfect in this case, especially with the use of quartz crystal microbalance, which is widely used in works of the authors [1, 2].

In this case, taking into account the labour coefficient of direct adsorption measurements, an attempt has been made to approach to the rapid determination of sensitivity by measuring the surface isoelectric state pH in the respective gaseous media at different contents of the analyzed gas. Subsequent control adsorption measurements showed the reasonability of using such virtually express



method. As a result, the limiting sensitivity to the selected gas (NO_2) has been established, the pH_{iso} depends on the pressure and composition of the system components.

2. Problem statement

To determine the reasonability of using new materials based on ZnSe-CdS in sensor technology, it is possible to determine the possibility of evaluating their sensitivity to harmful microimpurities by measuring the surface isoelectric state pH (pH_{iso}) in the respective gaseous media. For this purpose, the pH of the ZnSe-CdS-binary semiconductor system components and solid solutions is determined by the method developed, under the influence, in particular, of nitrogen dioxide at different pressures; to estimate the ultimate sensitivity of surfaces; to establish the dependences of $\Delta\text{pH}_{\text{iso}}$ on the pressure and composition of the system components; to identify the most sensitive components of the system to NO_2 microimpurities, which are recommended for the manufacture of suitable measuring cells.

To facilitate the search for effective materials for sensor technology, to establish the relationship between the changing patterns with the composition of surface (pH) and bulk properties.

3. Experimental part

The investigated objects – solid solutions $(\text{ZnSe})_x(\text{CdS})_{1-x}$ ($x = 0.49, 0.55, 0.97$ mol) and the initial binary compounds (ZnSe, CdS) are powders ($S_d \leq 1.4 \text{ m}^2/\text{g}$) and films ($d = 50\text{--}70 \text{ nm}$). Powders of solid solutions were obtained by isothermal diffusion of binary compounds (ZnSe, CdS) in vacuum sealed quartz ampoules at a temperature higher than the melting point of easily melted compound (CdS), according to a special program of temperature heating [1, 2], films of solid solutions and binary compounds – by discrete thermal spraying in vacuum [3, 4] ($T_{\text{cond}} = 298 \text{ K}$, $p = 1.53 \cdot 10^{-4} \text{ Pa}$) mainly on the electrode sites of the piezoquartz resonators of the AT-cut, followed by annealing in the pairs of the objects under study. The thickness of the films was measured by change in the frequency of the piezoquartz resonator, interferometrically and based on spraying conditions [2, 5].

The preparation of solid solutions and their structure was judged by the results of X-ray and indirectly by the results of IR and UV spectroscopic studies. The relative position and distribution of the intensities of the main lines on the x-ray diffraction patterns of binary compounds and solid solutions, the relative position and distribution of the intensities of the main bands in the IR and UV spectra, the dependence on the composition of the parameters values of the crystal lattices (a , c), Interplanar distances (d_{hkl}), density (ρ_r). According to the data, solid substitution solutions are formed in the ZnSe-CdS system with the specified compositions, which possess both a cubic sphalerite structure (with insignificant CdS content of ≤ 0.03 mole) and a hexagonal wurtzite structure (at $x_{\text{CdS}} \geq 0.45$ mole). In the first case, solid solutions are related in structure to zinc selenide, in the second – to cadmium sulphide [6].

X-ray diffraction studies were performed on diffractometers Dron-3, in $\text{CuK}\alpha_{\beta}$ -radiation ($\lambda = 0.154178$ and 0.139217 nm) and Advance D8 from Bruker (Germany), in $\text{CuK}\lambda$ -radiation ($\lambda = 0.154056 \text{ nm}$), using the large-angle survey technique [7], using the Lynxeye position-sensitive detector, IR *spectroscopic* - on the Fourier spectrophotometer Infracum FT-02, in the range of $830\text{--}4000 \text{ cm}^{-1}$ [8], UV *spectroscopic* spectrophotometers on the UV-2501 PC spectrophotometer Shimadzu with a diffuse reflection attachment ISR-240 AI and SPECORD-40, in the range $190\text{--}900 \text{ nm}$ [9].

To assess the surfaces sensitivity, the values of the hydrogen index of the isoelectric state of surfaces, pH_{iso} , were determined using the method of hydrolytic adsorption [1, 8].

The pH values of the surfaces allow to judge the average strength, and the pH changes the degree, nature and mechanism of the gases surface interaction. To realize such possibilities, a technique was developed allowing to determine semiconductor adsorbents surfaces pH_{iso} exposed in the air, in argon and then subjected to the action of adsorbate gas (in particular, NO_2) gas in a wide range of pressures, including the achieved minimum.

4. Results and discussion

As table. 1 shows, according to the values of *initial surfaces isoelectric state pH*, components of the ZnSe-CdS system are arranged in the $\text{ZnSe} \rightarrow (\text{ZnSe})_x(\text{CdS})_{1-x} \rightarrow \text{CdS}$ series, indicating predominantly the main nature of zinc selenide and solid solutions surfaces with practically equimolar and excess contents (pH_{iso} varies from 6.4 to 8.2).

Table 1. pH values of surfaces isoelectric conditions of ZnSe-CdS system components exposed in the air.

System component	pH_{iso}
ZnSe	8.20
$(\text{ZnSe})_{0.97}(\text{CdS})_{0.03}$	7.25
$(\text{ZnSe})_{0.55}(\text{CdS})_{0.45}$	7.85
$(\text{ZnSe})_{0.49}(\text{CdS})_{0.51}$	7.95
CdS	6.55

On the basis of this data, one can speak of a predominant contribution to the acid-base state of the system components surfaces with $\text{pH} > 7$ Bronsted centers and their increased activity to acid gases (NO_2 , CO_2 type). The results of direct adsorption studies [1], in particular, $\alpha_{\text{CO}_2} \setminus \alpha_{\text{NH}_3} > 1$, can serve as confirmation. In addition, the adsorption of the main ammonia gas has a reversible (chemical) nature and is therefore accompanied by the formation of weak adsorbent-adsorbate bonds [1].

In accordance with facts mentioned above, it is logical to follow the influence of at least one more acid gas on the acid-base state of the surfaces and to assess their ultimate sensitivity to this gas (i.e., sensitivity at minimum pressure). Finally, studies have been made of the pH_{iso} of the system components, pretreated in argon, at various pressures of nitrogen dioxide (Fig. 1, 2).

As fig. 1 shows, the changes in pH_{iso} started at $P_{\text{NO}_2} = 0.05$ Pa. The most sensitive to NO_2 were the solid solutions surfaces with practically equimolar and excess content of ZnSe, possessing the base surface ($\text{pH}_{\text{iso}} = 8.2$).

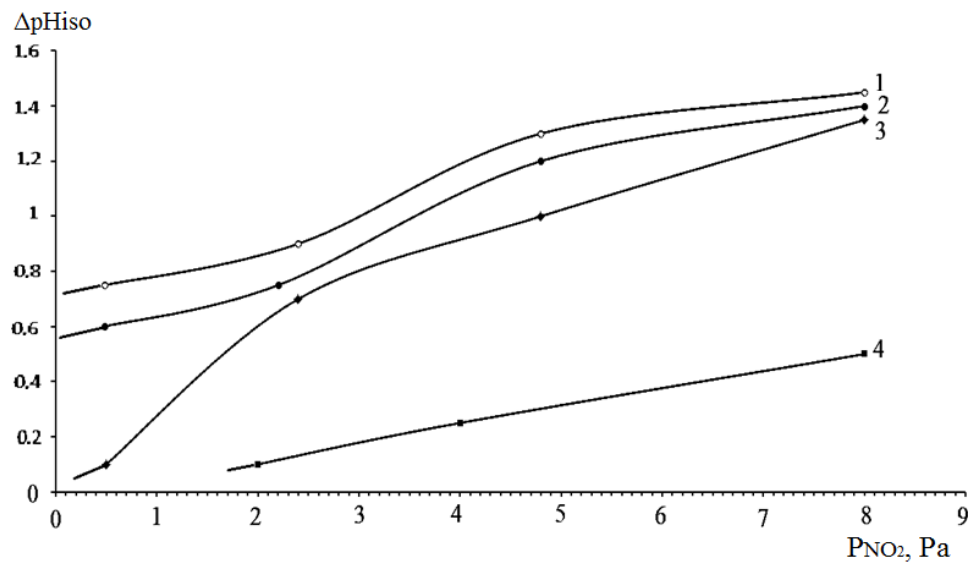


Figure 1. Change dependency of pH isoelectric state of the ZnSe-CdS components system ZnSe-CdS on the partial pressure of NO₂ mixed with argon: 1 – (ZnSe)_{0.49}(CdS)_{0.51}, 2 – (ZnSe)_{0.55}(CdS)_{0.45}, 3 – ZnSe, 4 – CdS.

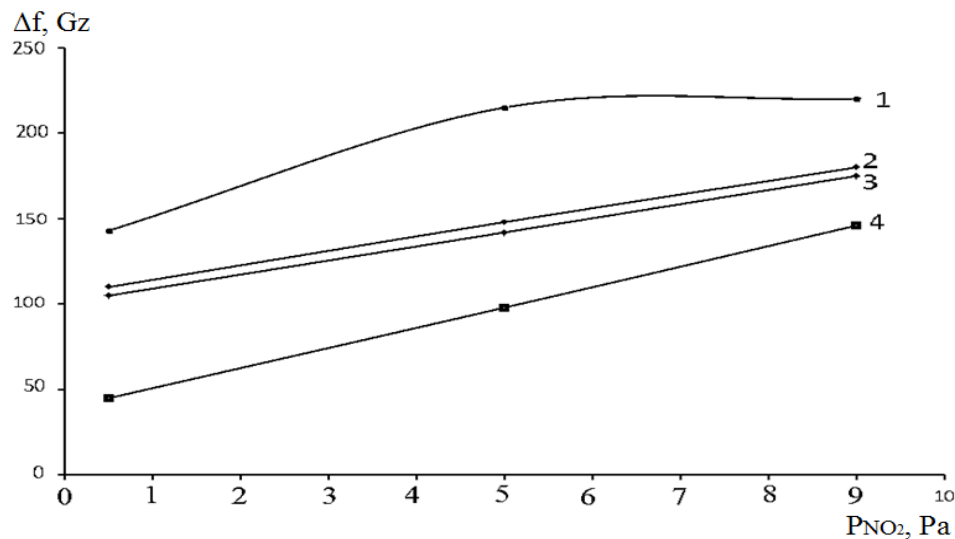


Figure 2. Dependence of piezoquartz resonator frequency variations with the films of the ZnSe-CdS-system components on the partial pressure of NO₂ mixed with argon: 1 – (ZnSe)_{0.49}(CdS)_{0.51}, 2 – (ZnSe)_{0.55}(CdS)_{0.45}, 3 – ZnSe, 4 – CdS.

Fig. 1 correlates with fig. 2, reflecting the results of the most delicate measurements-piezoquartz resonator frequency variations with the supported nanofilms of the ZnSe-CdS system components, proportional to the adsorption values, from the NO₂ pressure.

Fig. 3 clearly demonstrates *comparative surfaces sensitivity* of the system under study to NO₂ with the dependences of ΔpH_{iso} and Δf on the composition at the same pressure.

On the ground of fig. 1-3 analysis, one can make a conclusion of such possibilities as the evaluation of new materials sensitivity to gases of a certain electronic nature with respect to the values and changes in pH_{iso}, without conducting direct adsorption studies, in this particular case the use of solid solutions

of $(\text{ZnSe})_x(\text{CdS})_{1-x}$ with practically equimolar and excessive content of ZnSe for the manufacture of measuring cells for NO_2 microimpurities.

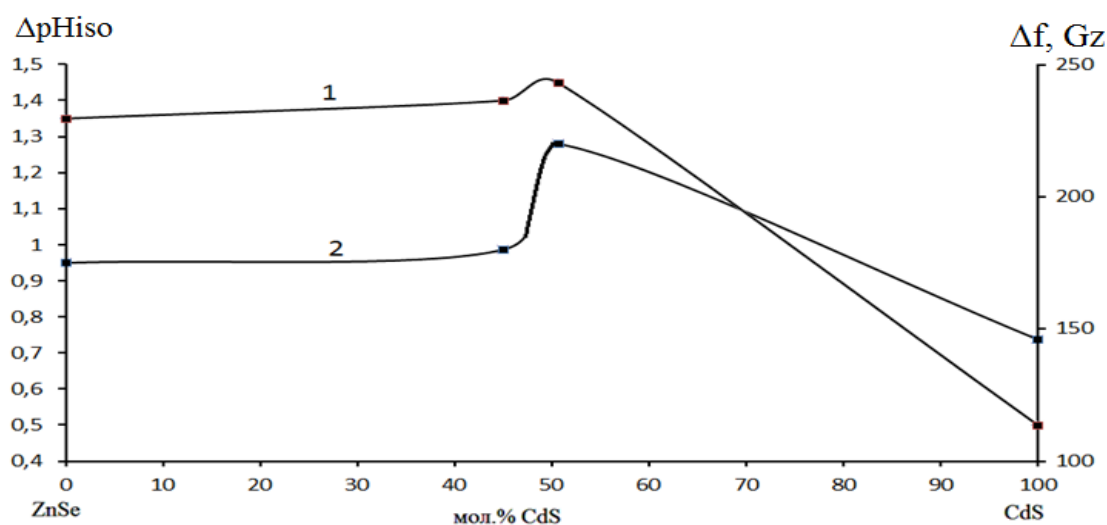


Figure 3. Dependences on the composition of oscillations frequency changes (Δf) (1) and pH index of the surfaces isoelectric state ($\Delta \text{pH}_{\text{iso}}$) (2) of the ZnSe-CdS system components

A definite relationship between the changing patterns of the surface and bulk properties of the ZnSe-CdS system components with a change in composition is of some interest.

Thus, as the zinc selenide content increases in it, the interplanar distances decrease (d_{hkl}), crystal lattice parameters (a , c), theoretical calculated crystal density (ρ_r), pH_{iso} (fig. 1, 4) change extremely (with an excess of ZnSe). Attention is drawn to the presence of both direct and opposite relationship between ρ_r and pH_{iso} .

Direct relationship is a consequence of decrease incoordination unsaturation of atoms both in the volume and on the surface with increasing ρ_r , respectively, with an increase in their packing density per unit of the crystal lattice volume. That is bound to cause a decrease in the contribution of the Lewis acid sites, an increase in the contribution of the Brönsted acid sites, and therefore an increase in the pH_{iso} in the series $\text{ZnSe} \rightarrow (\text{ZnSe})_x(\text{CdS})_{1-x} \rightarrow \text{CdS}$.

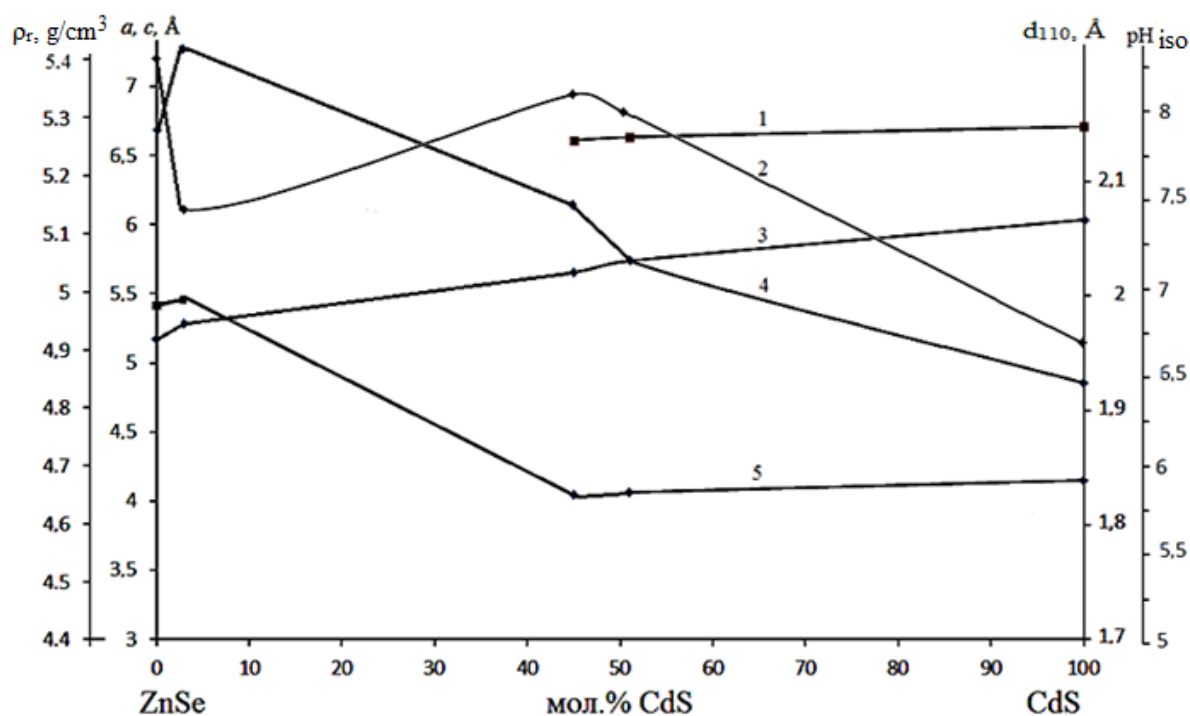


Figure 4. Dependence on the composition of crystal lattices parameters values a (5), c (1), the interplanar distance d_{111} (3), theoretical calculated crystal density ρ_r (4), and the isoelectric state pH of the pH_{iso} (2) surfaces of the ZnSe-CdS system components.

With an excess of zinc selenide ($x = 0.97$ mol), the packing density of ZnSe atoms per unit volume increases so much and their bond with surface atoms decreases so weakly that a burst in the coordination unsaturation of the latter is revealed, and as a result, the pH_{iso} is reduced (fig.4). Besides, with the other compositions of the ZnSe-CdS system, a predominant effect on the acid-base state of zinc selenide surfaces is observed, which, compared with CdS, has a larger bandgap ($\Delta E_{\text{ZnSe}} = 2.7\text{--}2.9$ eV, $\Delta E_{\text{CdS}} = 2.42$ eV).

Thus, the correlation between the density (ρ_r), the relative contribution of the coordinatively unsaturated atoms (Lewis sites) and the acidity of the surface is clearly traced.

The discovered connections between surface and bulk physicochemical properties (fig. 3, 4), with indisputable scientific significance, offer additional possibilities in the search for effective materials (in this case for measuring cells) on the basis of information on bulk physicochemical properties (in particular, on theoretical calculated crystal density), without carrying out not only labor-intensive adsorption studies, but also determination of acid-base properties.

Specific practical recommendations on the use of obtained materials for the manufacture of measuring cells for the NO_2 microimpurities on the basis of the results of the performed studies of the acid-base surfaces properties is mentioned above.

5. Conclusions

Changes in the surface isoelectric state pH ($\Delta\text{pH}_{\text{iso}}$) of the system of ZnSe-CdS components – binary semiconductors and their solid solutions under the influence of nitrogen dioxide at various pressures have been determined according to the developed method. The limiting sensitivity of surfaces has been estimated. The dependences of $\Delta\text{pH}_{\text{iso}}$ on the pressure and composition of the system components have been established. The most sensitive components of the system, recommended for the manufacture of appropriate measuring cells have been identified.

Relationships between the changing patterns with the composition of surface (pH_{iso}) and bulk properties making the search for effective materials for the sensor technology easier have been revealed.

References

- [1] Kirovskaya I A 2010 *Solid solutions of binary and multicomponent semiconductor systems* (Omsk: Omsk State Technical University) p 400
- [2] Kirovskaya I A 1995 *Adsorption processes* (Irkutsk: ISU) p 300
- [3] *State diagrams of systems based on semiconductor compounds $A^{II}B^{VI}$* 1982 (Kiev: Naukova Dumka) p 162
- [4] Williamson, W J 1989 Thin films of indium antimonide. Preparation, properties, applications edited by V A Kasian, (Chisinau: Shtiintsa) p 162 <https://catalogue.nla.gov.au/Record/2809644>
- [5] Kirovskaya I A 2006 The development of new materials for analyzers, environmental *Modern problems of science and education* № 3 p 70
- [6] Kirovskaya I A, Mironova E V, Ushakov O V, Deeva A A and Yurieva A V 2016 Obtaining Hetero- substituted Semiconductor Materials $(\text{ZnSe})_x(\text{CdS})_{1-x}$ and their Crystallochemical and Structural Properties *Procedia Engineering* V **152** pp 681–688
- [7] Parkhomenko Y N, Shlenskii A A, Pavlov V F, Shepekina G V and Yugova T G 2010 X-ray diffraction determination of the composition of in x ga1-x sb solid solution *Inorganic Materials* V **46** № 14 pp 1526–1528
- [8] Kirovskaya I A 2015 *Physico-chemical properties of binary and multicomponent diamond-like semiconductors* (Novosibirsk: SB RAS) p 367
- [9] Sobolev V V, Sobolev V Val and Shushkov S V 2011 Optical spectra of six silicon phases *Semiconductors* Vol **45** pp 1247–1250