

CHEMICAL THERMODYNAMICS
AND THERMOCHEMISTRY

Surface Properties of Semiconductor Analogs of CdB^{VI} and Their Solid Substitution Solutions

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Abstract—The physicochemical (acidic-basic, adsorption, and electrophysical) surface properties of binary semiconductor analogs of CdB^{VI} (CdTe, CdSe, and CdS), and $(\text{CdTe})_x(\text{CdSe})_{1-x}$, and $(\text{CdTe})_x(\text{CdS})_{1-x}$ solid substitution solutions were studied using modern methods and equipment. The nature of the active centers and the mechanisms of acidic-basic, adsorption (involving CO), and electronic interactions, interrelated tendencies in variation of the surface properties under study, and their correlations with the known bulk physicochemical properties were elucidated; the property–composition diagrams were constructed, which were used to reveal the most active adsorbents suggested for use as materials for CO (carbon monoxide) microimpurity sensors.

Keywords: semiconductors, solid solutions, nanofilms, acidic-basic, adsorption, and electrophysical properties, mechanisms, tendencies, sensors.

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INTRODUCTION

The creation of new materials is one of challenges in modern technology. A promising potential for solving this problem is offered by studies of the physicochemical (bulk and surface) properties of diamond-like semiconductors—analogue series of binary semiconductors and their solid solutions. While retaining many interesting useful properties of the starting binary compounds, the solid solutions can exhibit some distinctions, including predictable ones. The latter are due to the structure ordering and strengthening, combined action of components that play the role of macro and microdefects, and possible formation of impurity centers in high concentrations, which can cause unexpected effects of interest for modern technology (and heterogeneous catalysis) [1].

This paper reports on our studies of the acidic-basic, adsorption (with respect to CO), and electrophysical properties of analogous CdTe, CdSe, and CdS binary semiconductors and $(\text{CdTe})_x(\text{CdSe})_{1-x}$, $(\text{CdTe})_x(\text{CdS})_{1-x}$ solid solutions. The goal of this study was to elucidate the nature of active centers and the mechanisms and tendencies of atomic-molecular (acidic-basic and adsorption) electronic interactions and to examine the applicability of the binary and multicomponent semiconductors under study to creation of gas analyzers for environmental protection purposes.

EXPERIMENTAL

The objects of investigation were the powders ($S_{\text{sp}} = 0.405\text{--}0.91 \text{ m}^2/\text{g}$) and nanosized films ($d = 20\text{--}100 \text{ nm}$) of CdTe, CdSe, and CdS and their solid solutions $(\text{CdTe})_x(\text{CdS})_{1-x}$ ($x = 0.85, 0.75, 0.5, 0.25$, and 0.15 mole fractions) and $(\text{CdTe})_x(\text{CdSe})_{1-x}$ ($x = 0.84, 0.76, 0.5$, and 0.39 mole fractions). The powders of the solid solutions were prepared by isothermal diffusion of binary compounds (CdTe and CdSe, CdTe and CdS) in evacuated sealed quartz ampules in the ranges of their mutual solubility at temperatures close to the melting point of the low-melting CdTe component [1]. The nanofilms of the solid solutions and binary compounds were prepared by discrete thermal spraying in vacuum [2, 3] ($T_{\text{cond}} = 298 \text{ K}$, $P = 1.33 \times 10^{-3} \text{ Pa}$; the substrates were the electrode platforms of piezoelectric resonators of AT-cut with natural vibration frequencies of 7–8 MHz) followed by annealing in the vapors of the compounds under study. The changes in electric conductivity (σ_s) and accordingly the surface charge under the adsorption conditions were simultaneously studied on the same samples (by the probe compensation method [4]).

The film thickness was determined by interferometry from the spraying conditions and the change in the piezoelectric resonator frequency [3, 4]. The structure of the films and powders and the end of synthesis of the solid solutions were determined from the results of X-ray diffraction studies (DRON-3 diffractometer, $\text{CuK}_{\alpha,\beta}$ radiation), which were also used, together with

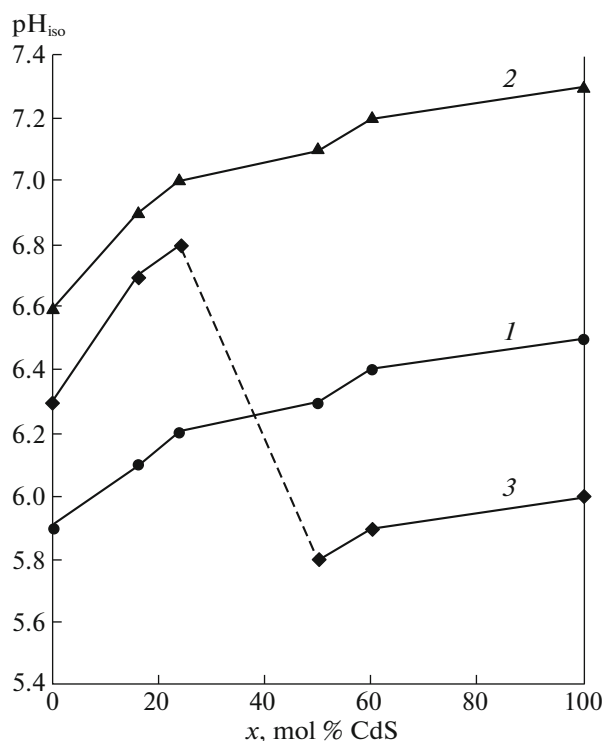


Fig. 1. Concentration dependences of the pH of the isoelectric state of the surface (pH_{iso}) of the components of the CdTe–CdS system exposed to (1) air, (2) NH_3 , and (3) CO.

the results of IR spectroscopic studies (InfraLum FT-02 FTIR spectrometer with an ATR accessory), for certification of the obtained solid solutions.

The acidic-basic properties of the surface were determined by methods for evaluating pH of the isoelectric state (pH_{iso}), mechanochemistry, non-aqueous conductometric titration, and ATR IR spectroscopy.

The pH of the isoelectric state that characterizes the average strength of the acid sites of the surface was evaluated by investigating the hydrolytic adsorption involving the ampholyte adsorbent (amphoteric compound) and estimating the pH of the medium in which the ampholyte adsorbent eliminates different (very small) amounts of H^+ and OH^- ions. In our case, the ampholytes were the semiconductor components of the CdTe–CdSe and CdTe–CdS systems with characteristic isoelectric points corresponding to the solubility minimum.

The use of the mechanochemical method allowed us to handle the freshly treated surface, tracing its behavior in the chosen medium (water) according to the products of the reaction of the latter with the surface atoms of the semiconductor [5, 6] and the change in pH.

Nonaqueous conductometric titration was performed for evaluating the concentration of the acid sites on the surface and determining their nature. The method is

based on measurement of the electric conductivity of the solution after the addition of the titrant. The number of components in the mixture (solutes, ions, etc.) equals the number of inflections on the conductometric titration curve [7]. As a solvent, we used methyl ethyl ketone, which has amphoteric properties. After the equilibrium set in, the system was titrated with a potassium ethylate solution whose concentration was determined by conductometric titration with a 0.1 N acetic acid solution (T_{room} , Ekspert-002-2-6-p conductometer, filling sensor). The differential curves of the dependence of electric conductivity on the titrant volume were constructed according to the results of measurements.

The concentration of acid centers was calculated by the equation

$$C = VN \times 1000/m,$$

where m is the mass of the adsorbent, g; V is the volume of potassium ethylate spent on titration, mL; N is the normal concentration of the potassium ethylate solution, g-equiv/L. The adsorption was studied by several methods: volumetric measurements, piezoelectric microweighing (with a sensitivity of up to 1.23×10^{-11} g/(cm^2 Hz)) at temperatures of 250–477 K and pressures of 2–18 Pa, electric conductivity measurements, and ATR IR spectroscopy [3, 4]. The adsorbate (CO) was prepared by the known procedure [8].

The reproducibility and accuracy of the experimental data were checked by repeating the experiments using the results of parallel measurements and quantitative analysis by mathematical statistics methods. The obtained numerical values were statistically processed (by the least squares method), the measurement error was calculated, and the graphical dependences were constructed and processed using the Stat 2, Microsoft Excel, and Origin programs.

RESULTS AND DISCUSSION

Studies of the acidic-basic properties allowed us to determine the nature, strength, and concentration of acid sites, the character of change in the strength and concentration of acidic centers with change in the composition of semiconductor adsorbents and during treatment with gases (NH_3 , CO).

According to the results of pH measurements of the isoelectric state (pH_{iso}), the surfaces of the binary (CdTe, CdSe, CdS) and ternary ((CdTe)_x(CdSe)_{1-x}, (CdTe)_x(CdS)_{1-x}) semiconductors exposed to air are weakly acidic (pH_{iso} changed from 5.84 to 6.81) (Figs. 1 and 2), which indicates that the acid sites prevail on them. Based on the results of our earlier parallel studies of the acidic-basic and adsorption properties of diamond-like semiconductors (see, e.g., [1, 3]), it would be logical to expect increased adsorption activity of the surfaces with respect to the main gases in the given case. Indeed, the surfaces were alkalized after

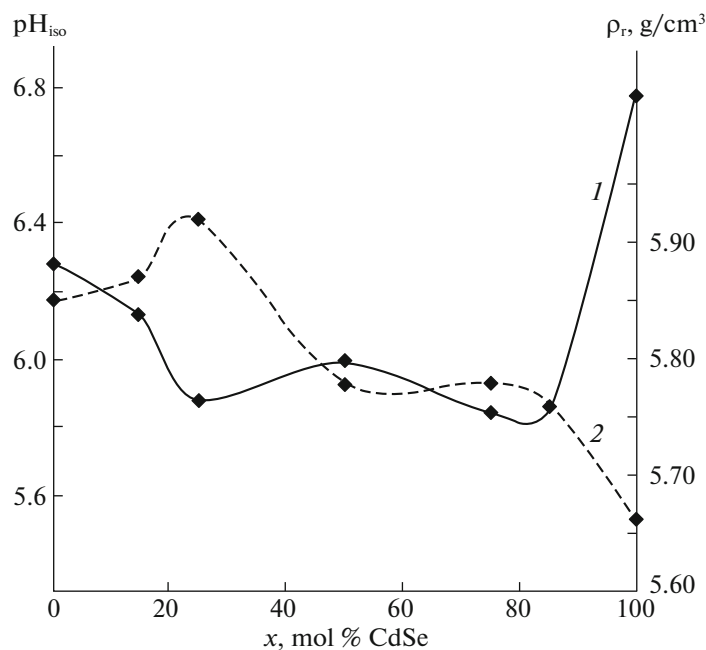


Fig. 2. Dependences of (1) pH of the isoelectric state of the surface and (2) X-ray density of the components of the CdTe–CdSe system on the composition.

treatment with ammonia (pH_{iso} increased). Treatment with carbon oxide, however, led to ambiguous results: the pH_{iso} values shifted depending on the composition of the semiconductor adsorbent to both weakly alkaline and weakly acidic regions (Fig. 1). This behavior of pH_{iso} should be correlated with the electronic structure and the dual function of CO molecules [3]. The character of variation of pH_{iso} during treatment with the indicated gases is consistent with the mechanisms of their adsorption interactions, as reported below.

As shown by the mechanochemical studies, both alkalization and acidification were observed during the dispersion of the semiconductor adsorbents in water when the composition changed (Fig. 3). The results of nonaqueous conductometric titration provided further evidence in addition to the above data. They were used to confirm the nature of acid sites, determine their concentration (C_a), and evaluate its change after treatment with carbon oxide [3, 9].

The presence of three peaks on the differential conductometric titration curves (Fig. 4) of all semiconductor adsorbents under study exposed to air is indicative of the existence of different types of acid sites that differ in the strength on their surface [9]. The coordinatively unsaturated atoms (Lewis sites), adsorbed water molecules, and OH^- groups (Brønsted sites) should be responsible for the acid sites [1, 3, 9]. This is indicated by the presence of the bands in the IR spectra that correspond to the residues of the acids H_2TeO_4 , H_2SeO_4 , H_2SO_3 , and H_2SO_4 , which are the products of the interaction of the medium (water) with

the coordinatively unsaturated atoms of the semiconductor adsorbents during their mechanochemical dispersion [3, 9].

Accordingly, we can assume that the Lewis acid sites are responsible for the first peak, while the Brønsted sites are responsible for the second and third peaks. This is confirmed by the results of pH determination of the isoelectric state of the surface: at increased mole fractions of CdSe and CdS (x_{CdSe} , x_{CdS}), pH_{iso} shifts toward the alkaline region (Figs. 1 and 2).

The dependence of the total concentration of the acid centers (C_a) calculated from the first, second, and third peaks on the composition is extremal (see below). Under the action of carbon oxide C_a decreases, which is explained if we take into account the mechanism of its adsorption suggested earlier [3] and confirmed in the present study.

Note that the above tendencies in variation of the strength of the acid sites (pH_{iso}) of the binary semiconductor analogs of CdB^{VI} are closely interrelated with the tendencies in variation of their main bulk physicochemical properties. Thus, as the forbidden gap (ΔE) increases, the melting point (T_m) and the difference between electronegativities (ΔX) increase, while the lattice parameters (a , c) and the X-ray density (ρ_r) decrease, and pH_{iso} increases with slight deviations (table, Figs. 1 and 2). The deviations from smooth variation of pH_{iso} in the series of CdTe, CdSe, and CdS can be attributed to the difference in the storage time of the semiconductor adsorbents in air. The data

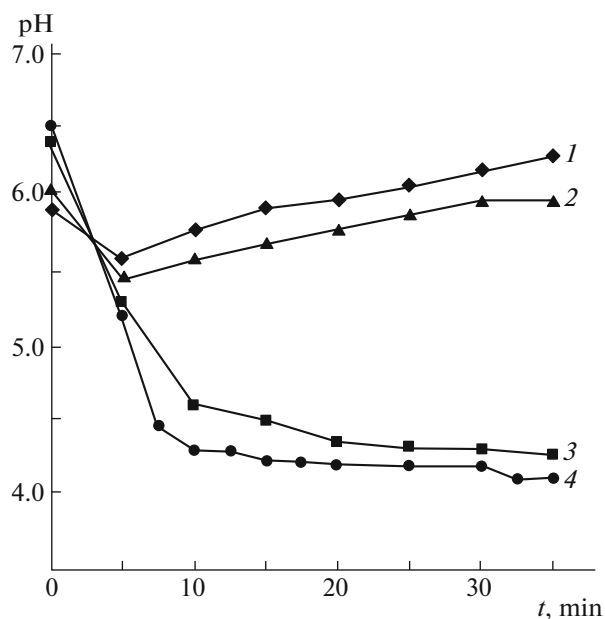
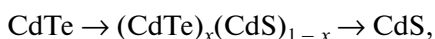
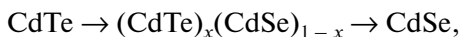


Fig. 3. Kinetic isotherms of the dispersion of coarse powders of the components of CdTe–CdS containing (1) 0, (2) 16, (3) 61, and (4) 100 mol % CdS in water.

of the table in general demonstrate the effect of the chalcogen component (Te, Se, and S) on the indicated properties.

It seems that as the forbidden gap and the difference between electronegativities increase, the fraction of the covalent bond that is responsible for the greatest strength of the crystal lattices decreases; hence the lattice parameters, density, and contribution of coordinatively unsaturated atoms responsible for Lewis sites (i.e., surface acidity) decrease and, accordingly, the degree of surface hydration and, ultimately, pH_{iso} increase.

The influence of the chalcogen component is also pronounced in the series including solid substitution solutions:



as indicated by the phase diagrams shown in Figs. 1 and 2. While noting both smooth and extremal changes in the acidic-basic properties with the com-

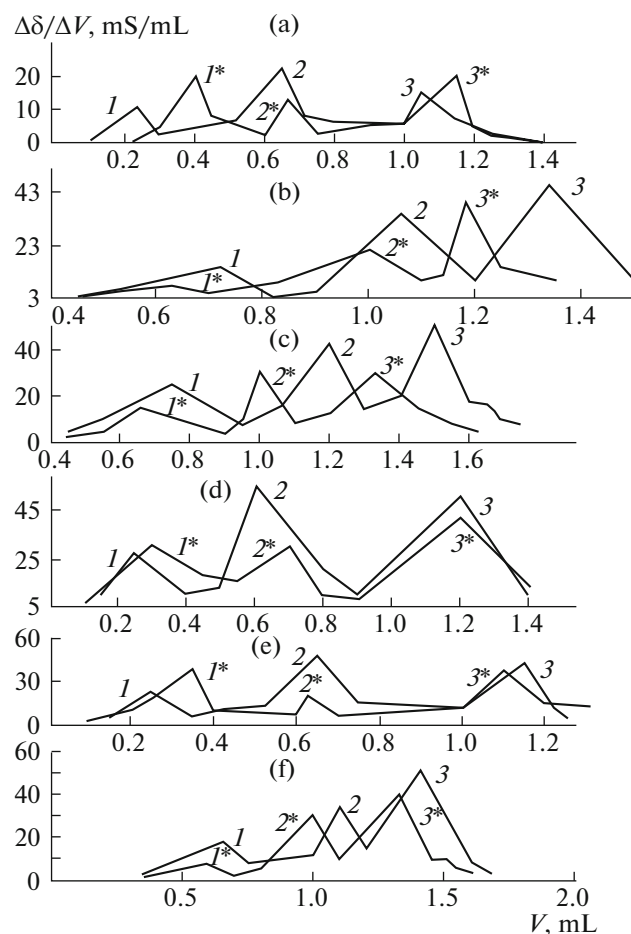


Fig. 4. Differential conductometric titration curves of the components of the CdS–CdTe system: (a) CdS, (b) $(\text{CdS})_{0.16}(\text{CdTe})_{0.84}$, (c) $(\text{CdS})_{0.24}(\text{CdTe})_{0.76}$, (d) $(\text{CdS})_{0.5}(\text{CdTe})_{0.5}$, (e) $(\text{CdS})_{0.6}(\text{CdTe})_{0.4}$, and (f) CdTe exposed to (1–3) air and (1*–3*) CO.

position of the CdTe–CdSe and CdTe–CdS systems, we should also take into account the influence of other factors indicated above that accompany the formation of solid solutions [1].

Adsorption and electrophysical studies. The main experimental dependences of CO adsorption, namely, the isobars and the equilibrium and kinetic isotherms ($\alpha_p = f(T)$, $\alpha_T = f(p)$, $\alpha_T = f(t)$) are similar for binary compounds (CdTe, CdSe, CdS) and solid solutions

Selected bulk physicochemical properties and pH of the isoelectric state of the surface of the CdB^{VI} semiconductors (S)

S	$T_m, ^\circ\text{C}$	$\Delta E, \text{eV}$	ΔX	a, c, nm	$\rho_r, \text{g/cm}^3$	pH_{iso}
CdTe	1092	1.51	0.4	0.581	5.86	5.9
CdSe	1258	1.74; 1.88	0.9	0.43; 0.703	5.81	6.81
CdS	1750 (1475)	2.42	0.8	0.413; 0.671	4.82	6.5

T_m is the melting point, ΔE is the forbidden gap, ΔX is the difference between electronegativities, a and c are the lattice constants, and ρ_r is the X-ray density.

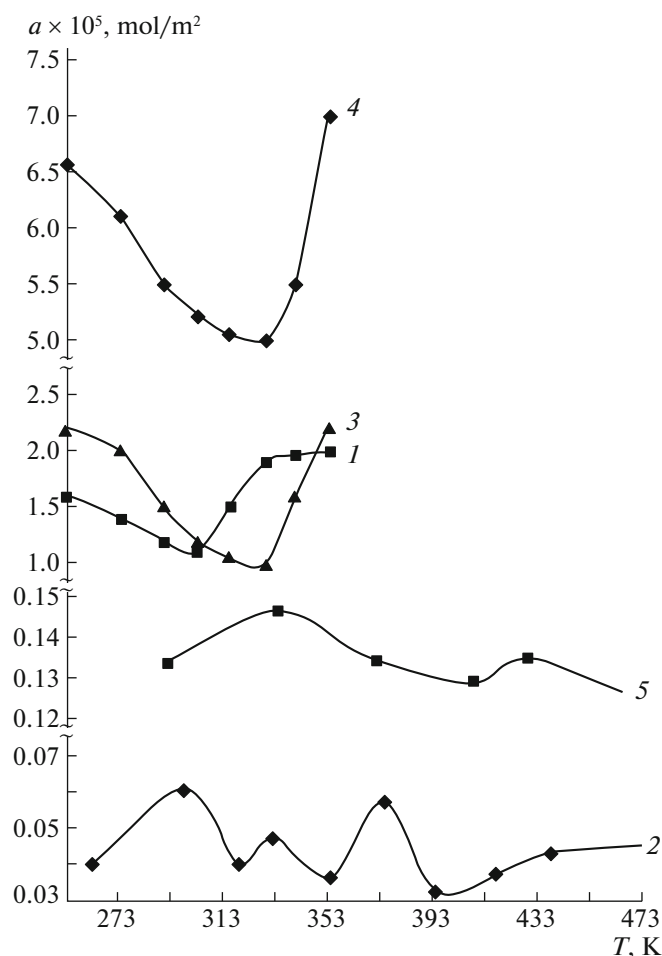


Fig. 5. CO adsorption isobars for (1) CdTe, (2) CdSe, (3) CdS, (4) $(\text{CdTe})_{0.84}(\text{CdS})_{0.16}$, and (5) $(\text{CdTe})_{0.85}(\text{CdS})_{0.15}$ at $P_{\text{st}} = 13\text{--}18$ Pa.

(e.g., Figs. 5 and 6). The form of the adsorption isobars allows us to draw the preliminary conclusion that physical adsorption occurs below 303–323 K and chemical activated adsorption takes place at higher temperatures. This is confirmed by the results of the analysis of the equilibrium and kinetic isotherms, calculated activation energies and adsorption heats, and experimental electric conductivities. Thus, in the range of hypothetical chemical adsorption, the kinetic isotherms $\alpha_T = f(t)$ are described by the Roginskii–Zel’dovich–Elovich equation (linearization in the coordinates $a - RT \log t$), which is valid for surfaces with evenly nonuniform distribution [4, 10]. The mean activation energies of adsorption were calculated for different surface coverages (α) (27.3–81 kJ/mol) by the controlling band method created by Roginskii [10].

The growth of the activation energy and decrease in the adsorption heat with an increase of surface coverage confirm that the surface is nonuniform and contains active sites that differ in strength and energy state. This is also supported by the results of the studies

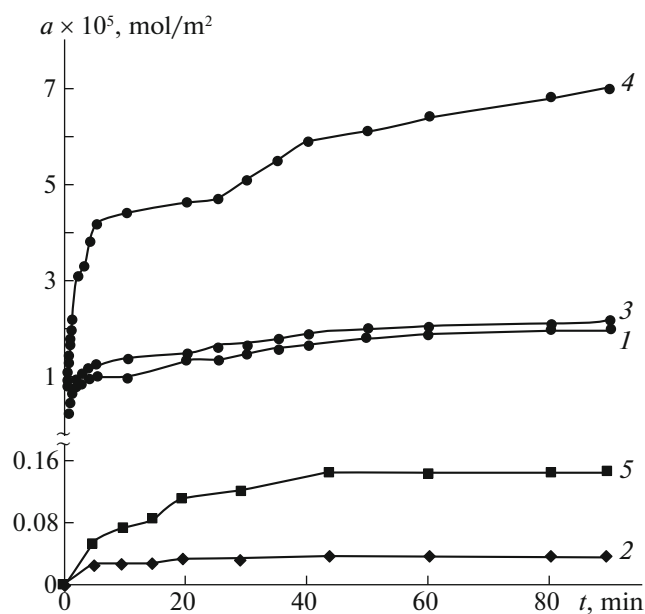
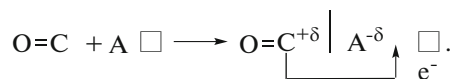


Fig. 6. Kinetic CO adsorption isotherms at $P_{\text{st}} = 13$ Pa, $T = 353$ K; for (1–5), see Fig. 5.

of the acidic-basic properties of the adsorbent surface described above. They indicate that the surface contains at least three types of acid sites. As in the case of other diamond-like semiconductors [1, 3], the coordinatively unsaturated atoms, adsorbed water molecules, and OH^- groups are most likely to be responsible for the acid sites.

An analysis of the results of the adsorption studies including the acidic-basic properties of the adsorbent surface, the electronic structure of adsorbate molecules, and their behavior on other diamond-like semiconductors [1, 3] showed that CO adsorption occurs by the donor-acceptor mechanism involving predominantly the surface atoms A (with vacant d and p orbitals and with more pronounced metallic properties) as acceptors and adsorbate molecules as donors:



The formation of donor-acceptor bonds is indicated by the presence of the appropriate bands in the IR spectra after CO adsorption (Fig. 7, [11]). The possible role of CO molecules as electron donors was also suggested by the results of conductivity measurements (σ_s) under the adsorption conditions (Fig. 8). At the same time, the dual effect of CO on pH of the isoelectric state of the surface (pH_{iso}) depending on the CdS and CdSe content in the systems [9] and on electric conductivity depending on the film thickness of the adsorbent and adsorbate pressure (P_{co}) [3] makes it possible to draw the conclusion about the possible for-

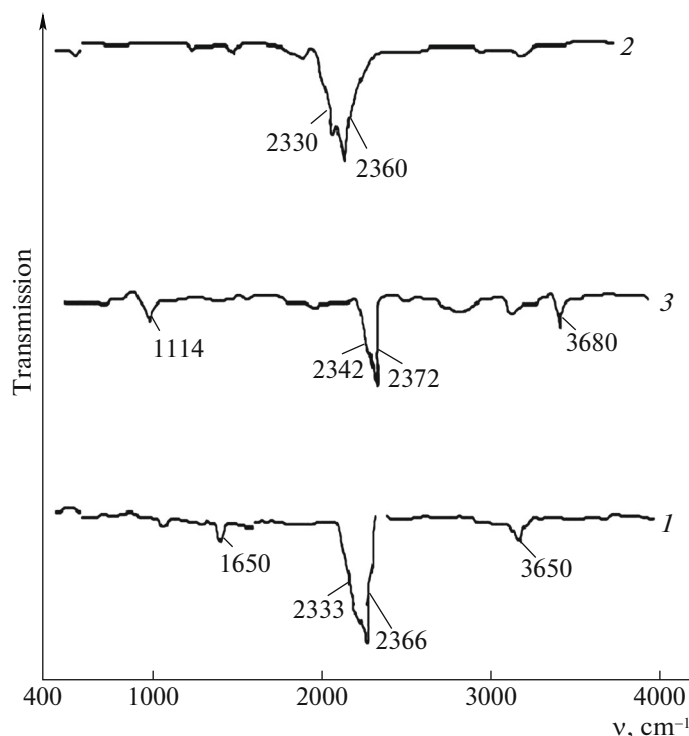
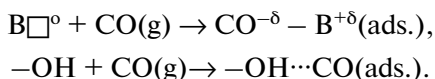


Fig. 7. IR spectra of the surface of (1) CdTe, (2) CdS, and (3) $(\text{CdTe})_{0.84}(\text{CdS})_{0.16}$ exposed to CO.

mation and definite contribution of the dative and hydrogen bonds.



The formation of several bonds that differ in stability and degree of electron delocalization is also favored by the above-mentioned difference in the coordina-

tion unsaturation of the surface atoms (especially in multicomponent systems—solid solutions), which was also indicated by the differential conductometric titration curves (Fig. 4). A discussion of the adsorption mechanism should also take into account the role of the collective (electronic) properties of the surface of semiconductor adsorbents.

The observed change in the electric conductivity in the course of CO adsorption (Fig. 8) and, accordingly, the charging of the surface suggest that the adsorption ability of CO molecules depend not only on the local factor (the chemical properties of molecules and the active center), but also on the collective (electronic) factor, which is determined by the position of the Fermi level and the character of the energy spectrum of the surface [3, 4]. These peculiarities of the $\text{CO}^{+\delta}-\text{A}^{-\delta}$ donor-acceptor bond suggest the participation of free carriers in the elementary adsorption act. The selectivity of gas adsorption depends on the local properties of the surface [3, 12].

Noting the participation of the free carriers (the collective factor) in the elementary adsorption (and, accordingly, catalytic) act, it is necessary to remind that the concentration of free carriers (electrons (n) and holes (p)) in crystals is related to the forbidden gap and the position of the Fermi level in it:

$$\begin{aligned} n &= c \exp(-(E_2 - E_F)/kT); \\ p &= c \exp(-(E_1 - E_F)/kT), \end{aligned}$$

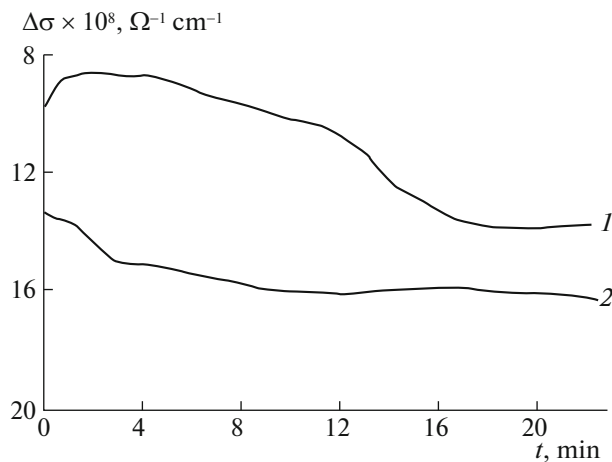


Fig. 8. Kinetic isotherms of variation of the electric conductivity of the p -CdTe single crystal under the adsorption conditions of (1) CO and (2) CO : O₂ = 1 : 2 mixture at $P_{\text{st}} = 10$ Pa and $T = 360$ K.

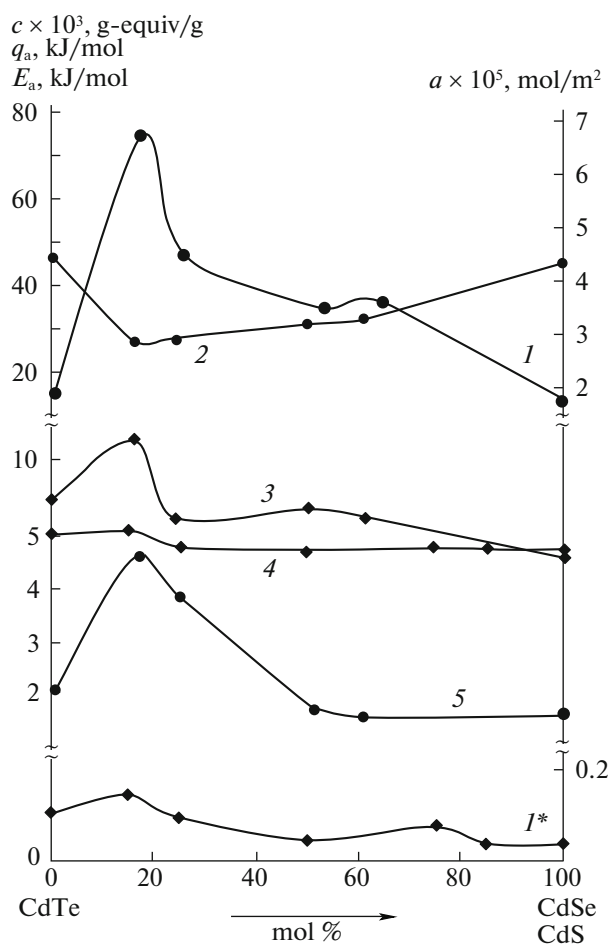


Fig. 9. Dependences of (1, 1*) adsorption; (2) activation energy; (3, 4) heat of CO adsorption; and (5) total concentration of acid sites on the starting surface on the composition of the (1*, 4) CdTe–CdSe and (1–3, 5) CdTe–CdS systems.

where E_1 and E_2 are the energies corresponding to the top of the valence band and the bottom of the conduction band, E_F is the Fermi energy, k is Boltzmann's constant, and c is the constant that depends on the effective mass of carriers and temperature. Hence Vol'kenshtein's thesis of the electronic theory of adsorption and catalysis is understandable: the Fermi level is a regulator of the chemical adsorption and catalytic activity [12].

When considering the results of our studies, we found the following facts and tendencies, which are interesting from both scientific and practical viewpoints. The most active semiconductors with respect to CO under the chemical adsorption conditions were cadmium telluride among binary semiconductors and the $(\text{CdTe})_{0.85}(\text{CdSe})_{0.15}$ and $(\text{CdTe})_{0.84}(\text{CdS})_{0.16}$ solid solutions among multicomponent ones. Note that in the indicated most active solid solutions, the cadmium telluride contents (0.85 and 0.84 mole fractions) and pH_{iso} values (6.13 and 6.1) are almost the same. Also

identical are the sequences of pH_{iso} for binary semiconductors ($\text{pH}_{\text{isoCdTe}} < \text{pH}_{\text{isoCdS}} < \text{pH}_{\text{isoCdSe}}$), amount of CO adsorption on them ($\alpha_{\text{CO/CdTe}} > \alpha_{\text{CO/CdS}} > \alpha_{\text{CO/CdSe}}$ under comparable conditions), and relative position of adsorption isobars (Fig. 5).

According to the diagrams in Fig. 9, there is satisfactory agreement between the adsorption data and also between the adsorption data and the composition dependence of the acid site concentration, which is important for confirming our conclusions about the nature of active sites and adsorption mechanism and for predicting the adsorption and catalytic properties based on acidic-basic ones [1, 3]. The most active (with respect to CO) adsorbents were predicted from the “acidic-basic characteristic–composition” dependences and found from the “adsorption characteristic–composition” dependences; these were the solid solutions of the “extremal compositions” of the CdTe–CdSe and CdTe–CdS systems. They served as materials for creating the corresponding sensors.

CONCLUSIONS

Thus, the results of our comprehensive study of the acidic-basic, adsorption (with respect to CO), and electrophysical properties of analogous binary semiconductors (CdTe, CdSe, CdS) and their solid solutions, taking into account the known bulk physicochemical properties, were as follows:

1. The nature of the active centers and the mechanisms of acidic-basic, adsorption, and electronic interactions was elucidated.
2. The role of the local and collective factors was revealed.
3. The substantiated interrelated tendencies of variation in the surface properties under study in series of CdB^{VI} analogs and $(\text{CdTe})_x\text{B}_{1-x}^{\text{VI}}$ substitution solid solutions, correlating with the tendencies of variation in the bulk physicochemical properties, were found.
4. The “property–composition” diagrams were constructed.
5. The most active adsorbents were revealed and suggested as materials for carbon(II) oxide gas analyzers (sensors).

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