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PHYSICAL CHEMISTRY
OF SURFACE PHENOMENA

Adsorption and Electrophysical Studies of the Sensitivity and Selectivity of the Surface of the InSb–CdTe System with Respect to Toxic Gases

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Abstract—The piezoquartz microweighing and probe compensation methods were used to study the adsorption properties with respect to NO_2 and changes in the electrical conductivity of solid solutions and the binary components of the InSb–CdTe system under the influence of NO_2 and $NO_2 + SO_2$ and $NO_2 + CO$ mixtures at various temperatures and relative gas contents. Solid solutions were prepared by isothermal diffusion and certified using the results of X-ray, thermographic, IR spectroscopic, and electrophysical measurements. The $(InSb)_{0.03}(CdTe)_{0.97}$ component of the system was found to possess high selective sensitivity (adsorption and electronic) already at room temperature. This component was recommended for creating a sensor for NO_2 microimpurities.

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INTRODUCTION

The most important problem of the chemistry of semiconductors is the preparation of new systems on the basis of known binary compounds. These systems should retain the properties of the initial binary compounds and exhibit new, possibly predictable, characteristics. Such systems are semiconducting solid solutions, whose typical representatives are solid solutions based on InSb and CdTe considered in this work. The unique properties of InSb and CdTe (electric, photo- and piezoelectric, and optical) and their capabilities already used in several technologies and semiconducting catalysis allow us to regard $(InSb)_x(CdTe)_{1-x}$ solid solutions as promising adsorbents, catalysts, and materials for modern technology, sensor electronics in the first place. The effectiveness of use in any of these areas depends on the degree to which the physicochemical state of the surface (including chemical composition, structure, and acid–base, adsorption, and electronic properties and their selective changes under the action of various media) has been studied. The present work is concerned with exactly this aspect of studies of the surface of InSb–CdTe system components.

EXPERIMENTAL

The samples studied, InSb, CdTe, and solid solution films, were prepared by discrete thermal deposition in a vacuum ($T_{cond} = 298$ K, $p = 1.33 \times 10^{-3}$ Pa) onto electrode surfaces of piezoquartz resonators followed by annealing in vapor of the initial material [1]. The conditions of annealing were determined on the basis of the physicochemical properties of this material and substrate [2]. Solid solution powders were obtained by isothermal diffusion of the binary components in evacuated sealed quartz ampules at temperatures above the melting point of the low-melting component (InSb) [3]. The composition of solid solutions obtained depended on the mutual solubility of the binary components (up to 6 mol % InSb in CdTe and up to 5 mol % CdTe in InSb).

The thickness of films was determined by interferometry, from changes in piezoquartz resonator frequency [4], and using the equation

$$D = m\sin\beta/(4\pi l^2\rho),$$

where m is the sample weight, ρ is the sample density, l is the distance from the vaporizer to the substrate, and β is the vaporization angle. The D value was 0.25–0.35 μm.

The structure of films was studied by X-ray diffraction. X-ray diffraction along with thermographic analysis and forbidden band width and electrical conductivity measurements was also used to certify the solid solutions obtained [5].

The adsorbates were prepared following standard procedures [2, 6]; that is, carbon(II) oxide, by the decomposition of formic acid in the presence of concentrated sulfuric acid; nitrogen(IV) oxide, by the action of concentrated nitric acid on copper shavings; and sulfur(IV) oxide, by the action of concentrated sulfuric acid on sodium sulfite.

Adsorption was studied by piezoquartz microweighing (sensitivity 1.23×10^{-11} g/(cm^2 Hz)) over the

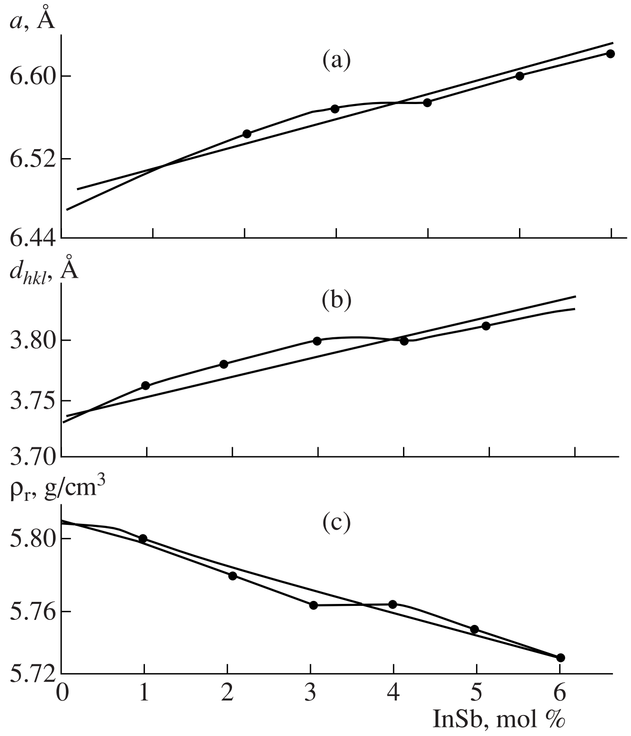

Fig. 1. Concentration dependences of (a) lattice parameter (a), (b) interplanar distance (d_{hkl}), and (c) X-ray density (ρ_r) of InSb–CdTe solid solutions in the region of InSb solubility in CdTe.

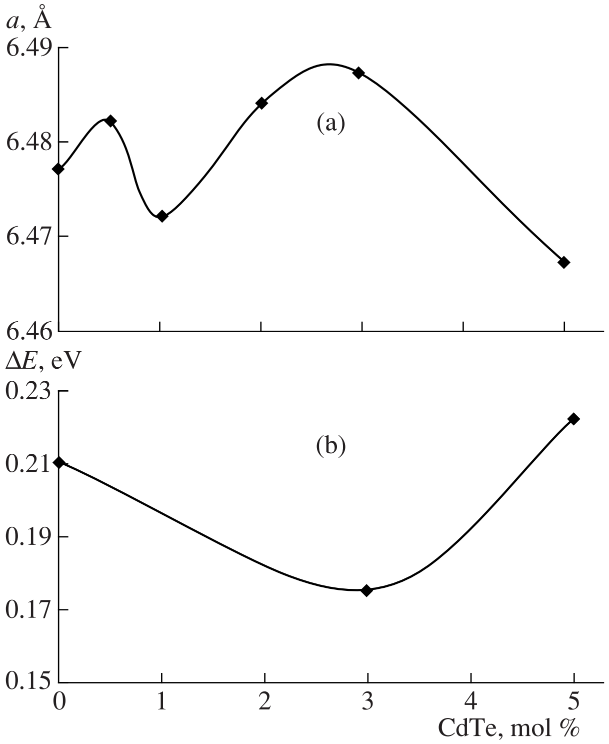

Fig. 2. Dependences of (a) lattice parameter and (b) forbidden band width on the composition of the InSb–CdTe system in the presence of excess InSb in solid solutions.

temperature and pressure ranges 253–358 K and 4–13 Pa. Adsorbent films were deposited onto electrode surfaces of piezoquartz resonators having the shape of an AT cut lens. Resonator intrinsic frequencies were of 7–8 MHz [4].

The same samples were used to simultaneously study changes in electrical conductivity and, accordingly, surface charging under the influence of adsorbed gases with the use of the probe compensation method [4].

RESULTS AND DISCUSSION

The Formation of Substitution Solid Solutions in the InSb–CdTe System

The X-ray diffraction, thermographic, IR spectroscopic, and electrophysical data show that substitution solid solutions are formed in the InSb–CdTe system [7].

According to the X-ray data, X-ray pattern lines were shifted with respect to the binary component lines, but the number of lines remained unchanged. The dependences of the lattice parameter (a), interplanar distances (d_{hkl}), and X-ray density (ρ_r) on the composition of solid solutions obtained in the region of InSb solubility in CdTe were close to linear (a small deviation from linearity was only observed for the $(InSb)_{0.03}(CdTe)_{0.97}$ component) (Fig. 1). For solid solutions obtained in the region of CdTe solubility in InSb, these dependences were comparatively complex in character (Fig. 2). It was, however, shown and explained in [3, 8, 9] that the dependences of lattice parameters and other characteristics of semiconducting substitution solid solutions on composition could be nonlinear.

It is also noteworthy that the X-ray patterns do not contain additional lines corresponding to unreacted binary components, and the main lines are not smeared, which is evidence of solid solution synthesis completion. According to the positions and intensity distribution of the main X-ray pattern lines, all system components (InSb, CdTe, and $(InSb)_x(CdTe)_{1-x}$) have sphalerite cubic structures.

The endothermic peaks in the thermograms of InSb, CdTe, and their solid solutions caused by melting and sample oxidation shift predominantly toward higher temperatures in the series InSb $\longrightarrow$ $(InSb)_x(CdTe)_{1-x}$ $\longrightarrow$ CdTe, which is indirect evidence of the formation of substitution solid solutions. The same follows from a smooth increase in electrical conductivity σ as the content of InSb grows (Fig. 3).

The forbidden band widths found from the IR data (from the $h\nu$ intercept of the tangent to the absorption edge [5]) pass a minimum at 3 mol % CdTe as the composition changes (Fig. 2). That is, like $\Delta E = f(c_{A^{II}B^{VI}})$, the $a = f(c_{A^{II}B^{VI}})$ dependence is nonlinear. The appear-

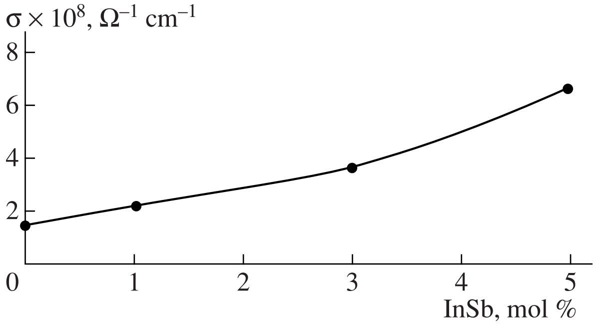

Fig. 3. Dependence of specific conductivity on the composition of the InSb–CdTe system in the presence of excess CdTe in solid solutions.

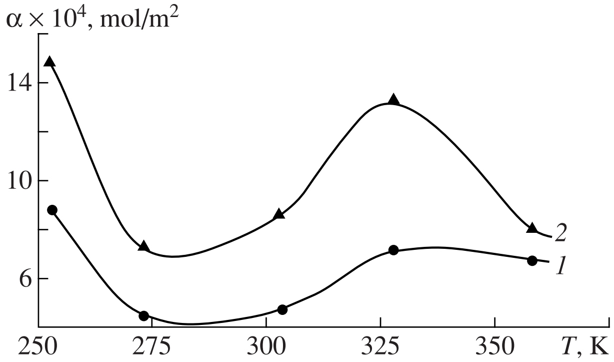

Fig. 4. Isobars of the adsorption of NO_2 on (*1*) CdTe and (*2*) $(InSb)_{0.03}$ $(CdTe)_{0.97}$ solid solution at $p_n = 8$ Pa.

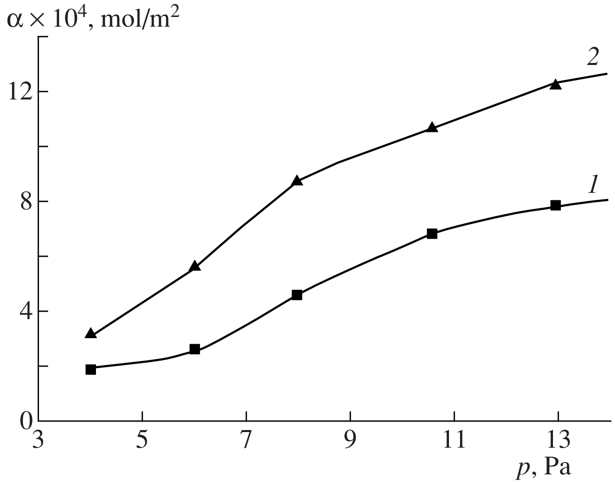

Fig. 5. Equilibrium isotherms of the adsorption of NO_2 on (*1*) CdTe and (*2*) $(InSb)_{0.03}$ $(CdTe)_{0.97}$ solid solution at 303 K.

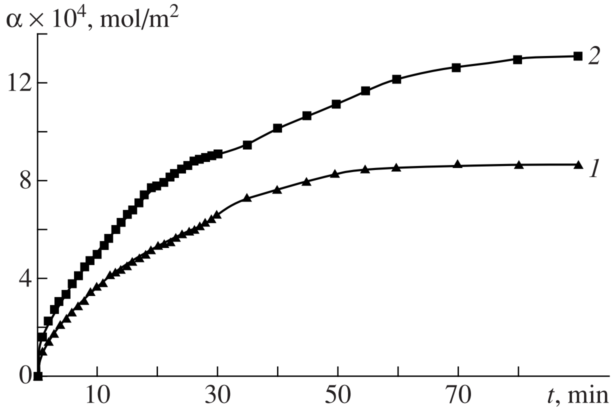

Fig. 6. Kinetic isotherms of the adsorption of NO_2 on $(InSb)_{0.03}$ $(CdTe)_{0.97}$ solid solution at $p_n = 8$ Pa and (*1*) 303 and (*2*) 328 K.

ance of the minimum is in all probability related to the accumulation of defects during the interaction of the binary components accompanied by the formation of donor-acceptor complexes [3, 10].

Such a behavior of σ is in conformity with the scheme of the component conductivity mechanism suggested in [3] for $A^{III}B^{V}$–$A^{II}B^{VI}$ systems.

The Adsorption Properties of the InSb–CdTe System Components

The adsorption properties of the InSb–CdTe system components were studied most thoroughly with respect to nitrogen dioxide because of its highest activity among the gases selected.

The adsorption values of NO_2 on all the system components vary from $\alpha \times 10^{-4}$ to $\alpha \times 10^{-3}$ mol/m^2. The typical experimental dependences of adsorption shown in Figs. 4–6 are similar for all the components. They are evidence of physical adsorption below 273 K and chemical activation adsorption at higher temperatures. This is substantiated by the results of thermodynamic and kinetic analyses. The heats of adsorption calculated by the Clausius–Clapeyron equation for descending isobar portions $\alpha_p = f(T)$ and the semiempirical equation suggested by one of these authors [4] at various T and α over the whole temperature range studied are of 6.1–13.4 kJ/mol, which corresponds to chemical adsorption on diamond-like semiconductors [2]. The mean activation energy values calculated by the Roginskii equation [4] valid for our systems are 43–86 kJ/mol at various surface coverages (adsorption values α).

The observed decrease in the heat and increase in the activation energy of adsorption as surface coverage grows and linear kinetic isotherms in the logarithmic coordinates are indicative of surface inhomogeneity and the presence of active centers of different strengths in different energy states. The same follows from the acid–base properties of our adsorbents determined using IR spectroscopy, isoelectric state pH measurements, and mechanochemical and conductometric titra-

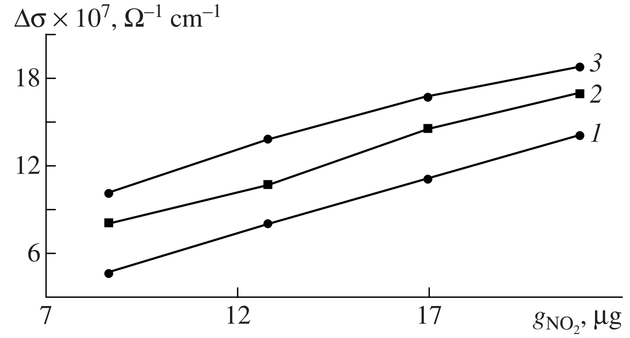

Fig. 7. Dependences of changes in the specific conductivity of a thin $(InSb)_{0.95}$ $(CdTe)_{0.05}$ solid solution film on the content of NO_2 in the sample (g_{NO_2}) at the carrier gas volume flow rate 8 ml/min and temperatures of (*1*) 20, (*2*) 50, and (*3*) 80°C.

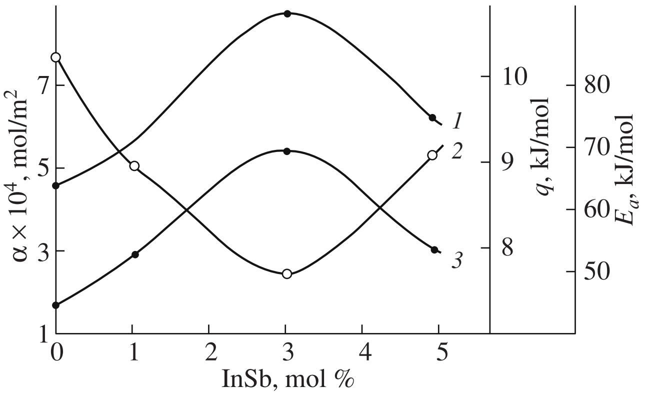

Fig. 8. Dependences of (*1*) adsorption value, (*2*) activation energy of adsorption, and (*3*) heat of adsorption on the composition of the InSb–CdTe system at $p_n = 8$ Pa and T = (*1*, *3*) 300 and (*2*) 300–358 K.

tion data [11]. These studies allowed us to identify at least four types of acid centers. As on the other diamond-like semiconductors, coordination unsaturated atoms with vacancy defects around them (Lewis centers) and adsorbed H_2O molecules and OH^- groups (Broensted centers) can be responsible for them.

The acid–base properties of the surface of the adsorbents and the electronic structure of NO_2 molecules led us to suggest a donor–acceptor mechanism of the adsorption of NO_2 (by analogy with the adsorption of CO_2 [12]), predominantly with the participation of surface A atoms (with more pronounced metallic properties) and B atom vacancies, adsorbate molecules (NO_2) playing the role of donors.

The electron donor function of NO_2 molecules is substantiated by an increase in electrical conductivity (σ) under the conditions of the adsorption of NO_2 (Fig. 7).

A comparison of binary and quaternary (solid solution) components of the InSb–CdTe system and adsorbents with respect to NO_2 shows them to be similar. Solid solutions, however, exhibit special features. *Similarity* follows from similar shapes of the $\alpha_p = f(T)$, $\alpha_T = f(p)$, and $\alpha_T = f(t)$ experimental dependences, similar adsorption values and thermodynamic and kinetic characteristics, the same nature of active centers and mechanisms and adsorption interaction characteristics. The *special feature* of quaternary adsorbents is the presence of extrema in adsorption characteristic–composition dependences (Fig. 8).

According to these dependences, the $(InSb)_{0.03}(CdTe)_{0.97}$ solid solution has the highest adsorption activity. For the same solution, the dependence of the lattice constant on system composition deviates from the linear Vegard law (Fig. 1), which, according to [3], can be related to the largest number of defects and coordination unsaturation of surface atoms.

The $(InSb)_{0.03}$ $(CdTe)_{0.97}$ solid solution as the component of the system most active with respect to NO_2 found with the use of adsorption characteristic–composition diagrams can be suggested as a material for a sensor for NO_2 microimpurities. We studied changes in the electrical conductivity of this solid solution and the other system components under the action of NO_2 and, to determine selectivity, mixtures of NO_2 with the other gases.

The Influence of the Adsorption of Nitrogen Dioxide on the Electrical Conductivity of InSb–CdTe System Components

Our studies showed that indium antimonide was virtually insensitive to NO_2 at room temperature. An increase in the content of cadmium telluride in the InSb–CdTe system increases sensitivity to NO_2, which reaches a maximum for the $(InSb)_{0.95}$ $(CdTe)_{0.05}$ solid solution (Fig. 9). Heating increases the sensitivity to NO_2 of all the system components, most noticeably that of $(InSb)_{0.95}$ $(CdTe)_{0.05}$ (Fig. 7). The volume flow rate (V_{vol}) of the carrier gas (argon) also influences sensitivity (NO_2 signal value).

A more optimal value for the $(InSb)_{0.95}(CdTe)_{0.05}$ solid solution was $V_{vol} = 8$ ml/min (Fig. 9).

Since the $(InSb)_{0.95}$ $(CdTe)_{0.05}$ solid solution was recommended as a material for a sensor for NO_2 microimpurities, it was important to estimate the time of the restoration of the initial value of its specific conductivity (relaxation time) after contact with the gas to be determined (NO_2) and its selectivity with respect to this gas in the presence of the other gases (CO and SO_2). The relaxation time in argon was 2–7 min depending on the concentration of NO_2 and temperature and noticeably decreased as the temperature increased.

The $(InSb)_{0.95}$ $(CdTe)_{0.05}$ solid solution exhibits the highest selectivity with respect to NO_2 at room temperature. The presence of CO and SO_2 (in an amount four times larger than that of NO_2) virtually did not influence the signal of NO_2. The signal of NO_2 insignificantly

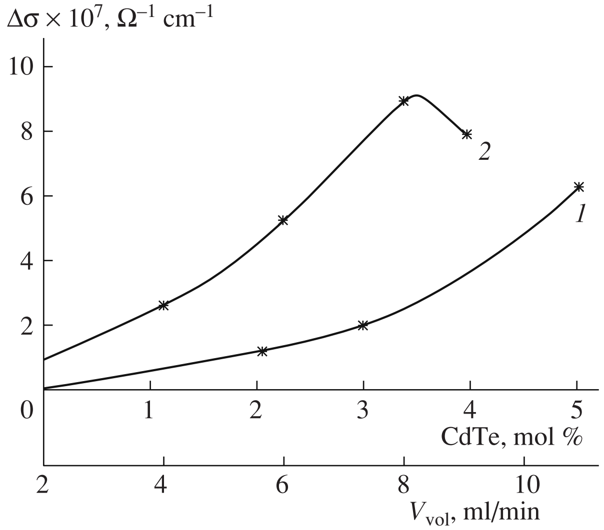

Fig. 9. Dependences of changes in the specific conductivity of (*1*) thin InSb–CdTe films on composition at an NO_2 content of 10 μg in the sample, 20°C, and carrier gas volume flow rate 8 ml/min and (*2*) a thin $(InSb)_{0.95}(CdTe)_{0.05}$ solid solution film on carrier gas volume flow rate.

decreased as the temperature increased to 80°C, and the material became slightly sensitive toward CO and SO_2.

To summarize, the InSb–CdTe solid solutions obtained in the form of powders and films were certified using the X-ray diffraction, thermographic, IR spectroscopic, and electrophysical methods. The adsorption and electronic (specific conductivity changes) properties of the solid solutions and binary components (InSb and CdTe) brought in contact with NO_2, $NO_2 + SO_2$, and NO_2 + CO were studied. The adsorbent ($(InSb)_{0.95}(CdTe)_{0.05}$ solid solution) with the highest surface (adsorption and electronic) sensitivity and selectivity with respect to NO_2 already at room temperature was found. This allowed us to recommend it as a material for the corresponding sensor.

A similar study was performed for the InSb–CdS and InP–CdS systems in comparison with the InSb–CdTe system described above [13, 14]. This allowed us to study the influence of not only binary ($A^{III}B^{V}$ and $A^{II}B^{VI}$) but also elemental (A and B) constituents on adsorption and electronic properties. These results should be considered separately.

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