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Synthesis and surface physicochemical properties of $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution

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Abstract. The research is centered on $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solutions. The article is aimed at developing innovative primary transducer material for semi-conductor sensors, investigating their surface physicochemical properties and evaluation their applicability in carbon monoxide diagnostics. Powders and nanofilms of $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solutions were obtained by isothermal diffusion and discrete thermal evaporation in vacuum. $(CdTe)_{0.03}(ZnSe)_{0.97}$ applicability in gas analysis was investigated. IR spectroscopy of multiple disturbed complete internal reflections and hydrolytic adsorption were used to study chemical composition and acid-base properties of $(CdTe)_{0.03}(ZnSe)_{0.97}$. Adsorption properties of the given material for carbon oxide (II) and oxygen were studied by the piezoquartz microweighing and volumetrically. The principles of adsorption, depending on the process conditions, were established. Based on the obtained experimental data, CO micro-impurities sensors were developed, the laboratory tests passed successfully

1. Introduction

Sensor systems application is one of the most effective ways for express control of process and surrounding media composition. Special attention is to be given to the sensors with sensitive element represented by A^2B^6 type diamond-like semiconductors polycrystalline films. This allows for toxic gases micro-impurities to be detected at low, even room, temperatures [1].

Substantial improvement of such sensor characteristics can be achieved by using solid solutions of the type A^2B^6–A^2B^6 as well as nanomaterials as gas-sensing materials.

Thus, publications [1, 2] demonstrate that the surface of solid solutions $(ZnSe)_x(CdTe)_{1-x}$ (x=0.05-0.15) exhibit increased adsorptive sensitivity towards CO, O_2 and their mixture as compared to CdTe. Similar principles are registered in case of solid solutions based on ZnSe [3] – the sensitivity of $(CdTe)_{0.05}(ZnSe)_{0.95}$ surface is higher towards CO than that of ZnSe. Whereas the highest CO detection efficiency is characteristic of the sensors with the least thickness of the sorbing nanofilm CdTe [4].

It should be noted, that currently, the binary components of the ZnSe-CdTe system are widely used in optoelectronics and microelectronics, in laser [5], solar cells developments [6], X-ray detectors [7] and γ-ray detectors [8]. The unique surface physicochemical properties of ZnSe and CdTe determine the perspectives of the given materials application in gas analysis [1].

The present article follows the cycle of the investigations devoted to obtaining and studying the surface physicochemical properties for the ZnSe–CdTe system components.

The article is aimed at developing innovative primary transducer materials for semi-conductor sensors, investigating their surface physicochemical properties and evaluation their applicability in carbon monoxide diagnostics.

2. Experimental technique

Powders of solid solutions were obtained by isothermal diffusion method by using a specially developed heating program (Snol 6.7/1300 laboratory oven). To obtain $(CdTe)_{0.03}(ZnSe)_{0.97}$ nanofilms (d=30…100 nm), the method of discrete thermal evaporation in vacuum was used (vacuum universal post VUP-5).
Certification of the solid solutions was performed from results of X-ray analysis (Bruker D8 Advance diffractometer with Cu-Kα radiation, λ=1.5418 Å, using the LynxEye position sensitive detector). Phase identification was carried out using Bruker EVA software paired with the ICDD PDF-2 2006 database.
The chemical composition of the surface of $(CdTe)_{0.03}(ZnSe)_{0.97}$ was determined by IR spectroscopy of multiple disturbed complete internal reflections (Infra LUM FT-02 Fourier spectrometer, PIKE Technologies HATR, crystal type - Ge, spectral range - 830…4000 cm^{-1}). The acid-base properties of surface were studied by hydrolytic adsorption (determination of the isoelectric state pH).
The evaluation of $(CdTe)_{0.03}(ZnSe)_{0.97}$ applicability in carbon monoxide diagnostics was carried out on the basis of adsorption research results. The research having been performed with the piezoquartz microweighing and volumetrically in the temperature range of 243 to 453 K and pressures of 3 to 15 Pa. Adsorbates (CO and O_2) were obtained according to the familiar procedures [2].

3. Results discussion

3.1. Synthesis and identification of the solid solution

As shown in Figure 1 the X-ray diffraction results indicate that the substitutional solid solution with sphalerite cubic structure is formed. The X-ray diffraction lines of the $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution are characteristically shifted relative to the lines of the ZnSe, while their number remains unchanged.

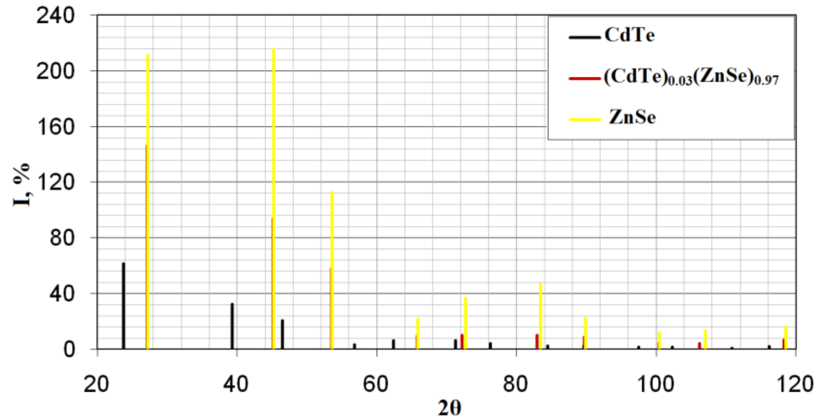

Figure 1. X-ray diffraction diagrams for samples of the ZnSe–CdTe system

As shown in Table 1 the value of unit cell parameter of the $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution occupy an intermediate position between the values of the binary components of the ZnSe-CdTe system.
The values of the X-ray coherent scattering regions (CSR) and X-ray density are minimum in case of solid solution. The absence of extra X-ray diffraction lines from unreacted binary components proves that the synthesis of the $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution is complete.

Table 1. The values of unit cell parameters, a_0, X-ray density, ρ_r, and CSR of the components of the ZnSe-CdTe system

№	Composition	a_0, Å	ρ_r, g/cm^3	CSR$_{(111)}$, Å
1	CdTe	6.4796	5.860	836.4
2	$(CdTe)_{0.03}(ZnSe)_{0.97}$	5.6763	5.242	399.4
3	ZnSe	5.6688	5.263	1328.8

3.2. Chemical composition and acid-base properties of the surface

According to the data obtained with IR spectroscopy of multiple disturbed complete internal reflections (Figure 2), the surface of the solid solution $(CdTe)_{0.03}(ZnSe)_{0.97}$ exposed to air contains mostly adsorbed molecules of water, OH groups, as well as carbon dioxide, this being characteristic of diamond-like semiconductors [9, 10].

After the thermal vacuum treatment till the minimal gas release, the surface of $(CdTe)_{0.03}(ZnSe)_{0.97}$ becomes almost free from the adsorbed impurities and this is reflected in a prominent decrease of all bands intensity.

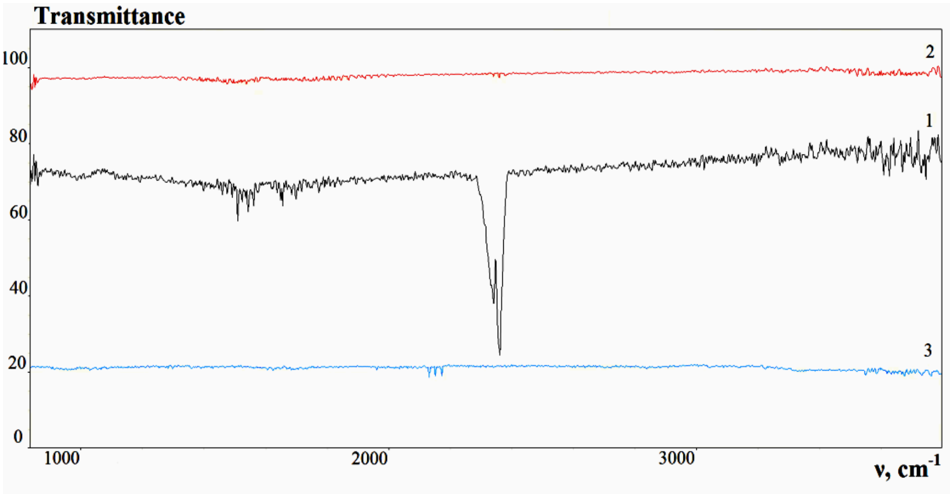

Figure 2. Fourier IR spectra (MDCIR) of the surface of the $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution exposed in air (1), vacuum (2) and CO (3)

It is noteworthy that after the CO adsorption $(CdTe)_{0.03}(ZnSe)_{0.97}$ IR spectra contain bands in the range of 2140…2174 cm^{-1} which can be attributed to linear carbonyls.

The values of pH_{iso} for $(CdTe)_{0.03}(ZnSe)_{0.97}$, exposed to air for a long time, are less than 7, signifying the prevalence of acid sites on the surface.

The value of pH_{iso} $(CdTe)_{0.03}(ZnSe)_{0.97}$ (6.51) takes an intermediate position between those of pH_{iso} ZnSe (6.67) and CdTe (5.99), and this is another evidence of the solid substitution solutions formation in ZnSe–CdTe system.

3.3. Adsorption investigation

The research of the $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution adsorptive properties has demonstrated high selective sensitivity of the material to the chosen adsorbates (Figure 3, 4). The observed order of CO and O_2 adsorption values (10^{-7} mol./m2) is typical for adsorption processes on powders of diamond-like semiconductors. The adsorption value temperature dependence curves allow us to claim that physical adsorption takes place in the range of 257…298 K, while chemical activated adsorption began at 298 K. It should be noted that activated adsorption seems to be realized in one form, as indicated by the presence of one ascending sector on isobars.

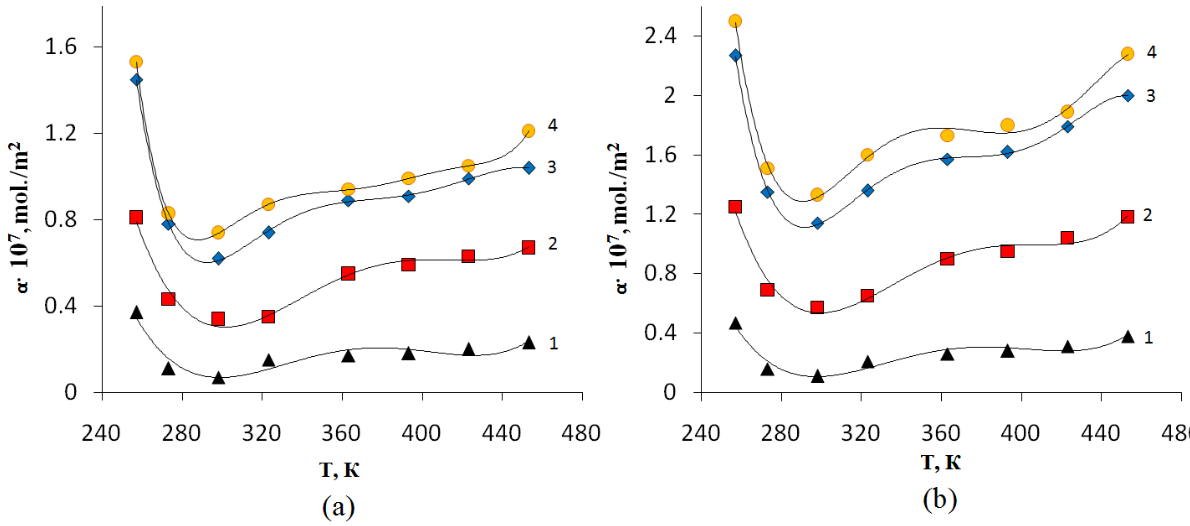

Figure 3. Temperature dependencies of CO (a) and O_2 (b) adsorption values on $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution at P_n: 3 (1), 6,5 (2), 12 (3) and 15 (4) Pa

The calculated values of differential heat (q) of CO and O_2 adsorption, amounted to 4.5 and 5.1 kJ /mol. respectively, and changes in the entropy (-ΔS) amounted to 63,0…80,1 J/(mol.·K), are typical for the chemical nature of the adsorption processes on diamond-like semiconductors [1].

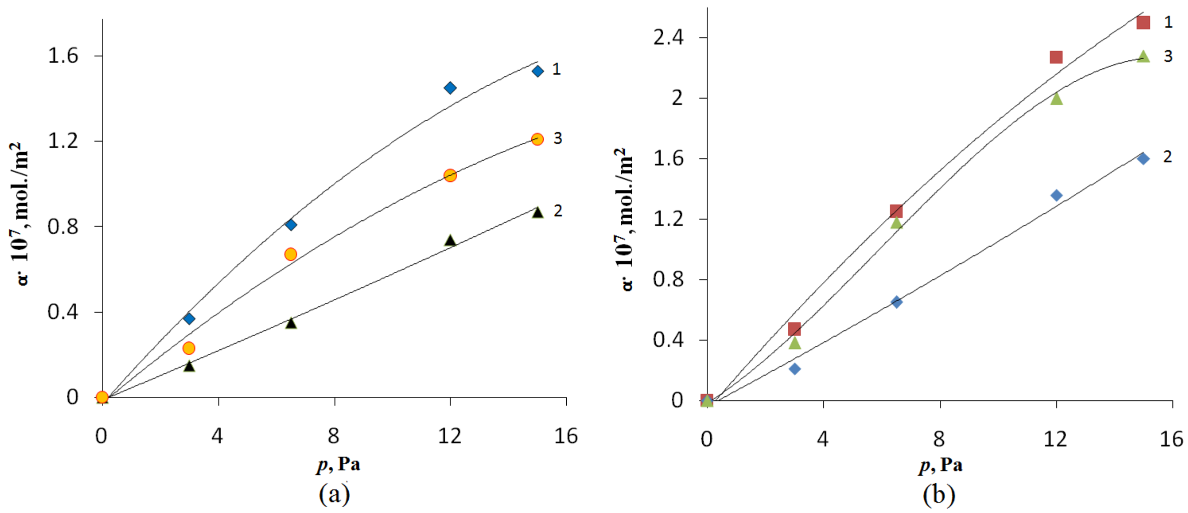

Figure 4. CO (a) and O_2 (b) equilibrium adsorption isotherms on $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution at T: 257 (1), 323 (2), 453 (3) K

The analysis of $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution adsorptive properties leads to the conclusion that this adsorbent surface is highly sensitive to O_2 in contrast to CO in all investigated temperature and pressure ranges (Figure 5). It should be noted that similar ratios of CO and O_2 adsorption values are also typical for ZnSe [1].

The heat of adsorption declines upon an increase in the degree of occupation (Figure 6), indicating the heterogeneous character of the surface, the presence active sites that differ in strength, and the energetic state.

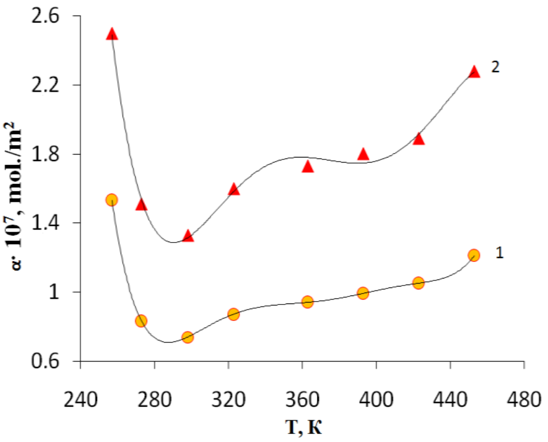

Figure 5. Temperature dependencies of CO (1) and O_2 (2) adsorption values on $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution at Pn=15 Pa

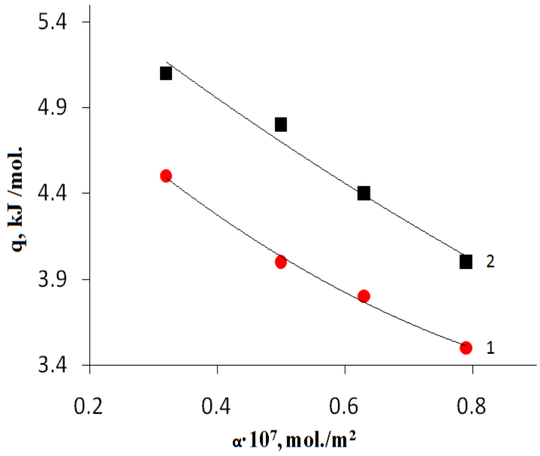

Figure 6. Dependencies of the heat of CO (1) and O_2 (2) adsorption on degree of occupation of $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution

Coordination-unsaturated atoms of Zn and Cd are largely responsible for the CO actives sites of the investigated $(CdTe)_{0.03}(ZnSe)_{0.97}$ surface, at the same time F centers are largely responsible for the O_2 actives sites, as well as other components of the ZnSe-CdTe system [1,2].

Comparing the characteristics of $(CdTe)_{0.03}(ZnSe)_{0.97}$ and the previously studied components of ZnSe–CdTe system [1-3] makes us conclude that the surface of the solid solutions $(CdTe)_x(ZnSe)_{1-x}$ possesses an increased sensitivity towards CO as compared to ZnSe. Thus, we notice: in the row ZnSe→$(CdTe)_{0.03}(ZnSe)_{0.97}$→$(CdTe)_{0.05}(ZnSe)_{0.95}$ the adsorption values increase and, consequently, CO adsorption heat does as well. The given principle correlated with the data of X-ray investigations as well as with those of acid-base properties studies (Figure 7).

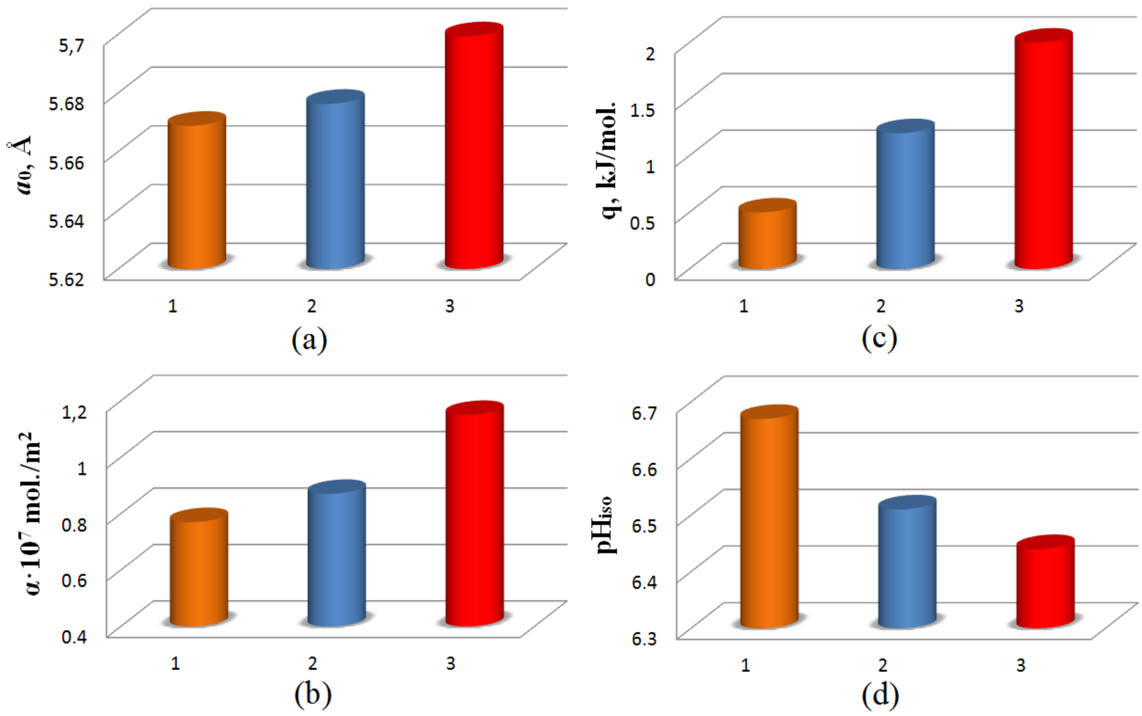

Figure 7. The values of unit cell parameters (a), CO adsorption value (b), CO adsorption heat (c) and pH_{iso} (d) for ZnSe (1), $(CdTe)_{0.03}(ZnSe)_{0.97}$ (2) and $(CdTe)_{0.05}(ZnSe)_{0.95}$ (3)

3.4. Carbon monoxide micro-impurities sensor

The detected high selective sensitivity of $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution surface towards CO, particularly at room temperatures, demonstrates the viability of the studied material application in semiconductor gas analysis.

CO micro-impurities sensor was developed based on the obtained data. The sensor primary transducer represents an AT-cut piezoquartz resonator with applied nanoscale (d=30 nm) sorbing $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solution film.

The sensor response is the changes in piezoquartz resonator oscillation frequency due to the analyte adsorption (desorption) on $(CdTe)_{0.03}(ZnSe)_{0.97}$ nanofilm. The designed sensor passed the laboratory tests successfully, enhanced detection efficiency compared with sensors based on ZnSe [11] is noted.

4. Conclusions

Powders and nanofilms of $(CdTe)_{0.03}(ZnSe)_{0.97}$ solid solutions were obtained. The chemical composition and acid-base properties of $(CdTe)_{0.03}(ZnSe)_{0.97}$ were studied by IR spectroscopy MDCIR and hydrolytic adsorption.

Adsorption properties of the given material for CO and O_2 were investigated by the piezoquartz microweighing and volumetrically. Carbon monoxide micro-impurities sensor was developed. The laboratory tests passed successfully.

5. References

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