THE COMPOSITE GAS SENSITIVITY ON THE BASIS OF POLYMERS AND Cu₂S AND CdS NANPARTICLES

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The gas sensitivity of the samples gelatin/ Cu_2S and gelatin/CdS at the influence of the steams of different solvents and ethyl alcohol is investigated. It is shown, that the composites on polymer base with Cu_2S and CdS nano-particles are sensitive on the steams of different solvents. The gas sensitivity of nano-composites depends on the population of matrix and chemical data of tested gas. These materials can be applied in the capacity of sensitive element of different gas sensors and sensing elements.

The demand of environment and ecology control always stimulates investigations on the working of gas sensors. These sensors are necessary at technological control of chemical-metallurgical and gas-, oil-producing industry. There are different gas-sensitive sensors, differing on industry action and technology. The solid-body sensors, which differ by the construction and portability simplenesses, are the one from the sensor varieties. The electric signals, manufactured by such portative sensors allow obtaining the information about substance content and its physical parameters. The workings in this region lead to the formation of multi-functional devices [1] on their base. The different semiconductor devices are sensitive elements in gas sensors [2].

The nano-composites are the one of materials, presenting the big interest at formation of gas sensors. In these materials the nano-composite interaction processes with molecules of gas phase are determinant ones. Nowadays, the sensors of resistive type [3, 4] on the polymer base with metallic filler have wide distribution. The polymer composites with semiconductor particles present the essential interest. The nano-heterogeneous polymer composites consist of polymer matrix with ultra-disperse particles by dimensions 20-100 nm and distances between them of the same order [5]. Such systems have the unusual photo and gas sensitive properties, which are defined by the charge redistribution process because of external interactions. The electoconductivity of these systems changes very strongly even at room temperature in the result of adsorption of different steams and gases [6]. The electroconductivity change of nano-composites at sorption of different gases depends on many factors: population of polymer matrix with semiconductor particles, inter-particle space, and interphase interaction between matrix and semiconductor particles [7]. In this connection the nano-particle formation technology of chalcogenide semiconductors in the volume of polymer matrix with the help of ion sandwich chemical absorption allows goalseeking changing the particle concentration and inter-particle distance in nano-composites [8].

The aim of presented work is the study of composite gas sensitivity on the basis of gelatin polymer matrix and cuprum sulfide particles (gelatin/Cu₂S) and cadmium sulfide (gelatin/CdS) at the influence of steams of different solvents and ethyl alcohol.

Experimental part

The sample, on the surface of which the electrodes are situated parallel, is put in measured cell for gas sensitivity testing. The resistance change with time at the definite pressure in the different gaseous mediums is registered by automatic recorder through teraohmmeter E6-13A. The measurements are carried out by two methods: 1) the volume is evacuated up to vacuum 10^{-1} atm (76 torr) and the sample sensitivity to given gas is defined after lap of tested gas or steams on the change of resistance value the gas sensitivity of samples on the steams of ethyl alcohol and acetone; 2) the vessel with tested substance (alcohol or solvent) is put in the duar and previously cooled with the help of liquid nitrogen. After freezing the vacuum system with measured cell and vessel are evacuated up to vacuum 10^{-2} atm. Further the vessel with tested substance is heated in different modes. The pressure in the measured cell increases up to pressure of saturated steams of given liquid at given temperature and registration of resistance change with pressure change is carried out. The gas sensitivity is defined on the following formula:

$$\gamma = \left(R_1 - R_0\right) / \left(P_1 - P_0\right) = \Delta R / \Delta P \quad , \qquad (1)$$

where P_0 and R_0 are initial values of pressure and resistance;

 P_1 and R_1 are final values of pressure and resistance;

 ΔP and ΔR are changes of pressure and resistance.

Result discussion.

The resistance change with time for samples gelatin/Cu₂S 15 cycles (a) and 30 cycles (b) of formation after lap of ethyl alcohol (fig.1.a) and acetone (fig.1.b) is shown on the fig.1. As it is seen from the dependence the resistance increases with further saturation at the lap of gas or steams.

The influence of nano-composite content and composition on gas sensitivity kinetics is also studied, i.e. the nano-composite resistance change with different content of Cu₂S and CdS nano-particles with time in ethyl alcohol steam medium is studied. It is seen, that stabilization of resistance volume for samples gelatin/15 cycles Cu₂S takes place quicker, than for samples gelatin/30 cycles Cu₂S (~3 min. and ~20 min., correspondingly). This is said about the fact, that particles at 15 formation cycles have the relatively small dimensions, the distances between them is enough for free adsorption of gas or steam, and at 30 formation cycles the increase of concentration and nano-particle dimensions makes difficult the gas penetration and the velocity of resistance change decreases correspondingly.

The time dependence of nano-composite change gelatin/15 cycles Cu_2S , gelatin/15 cycles CdS and gelatin/30 cycles CdS in the air at normal pressure latm (760 torr) (region 1), after evacuation up to 10^{-1} atm (76 torr), after air lap (region 3), after repeated evacuation up to 10^{-1} atm (region 4) and after the lap of ethyl alcohol steams (region 5), when the pressure in the cell changes from 76 torr up to 117 torr.

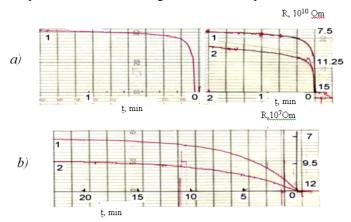


Fig.1. The resistance change of the film gel./Cu₂S at the lap of ethyl alcohol (1) and acetone (2) steams; a) gel./Cu₂S – 15 cycles; b) gel/.Cu₂S – 30 cycles.

It is seen, that values of initial resistance and resistance, corresponding to the pressure 10^{-1} atm (760 torr) with time don't change, i.e. they are relatively stable. But resistance change at the ethanol lap after evacuation up to 10^{-1} atm has the different values for different compositions. The best gas sensitivity at the lap of ethyl alcohol steams is observed for nano-composites gelatin/15 cycles CdS (9,5x10¹⁰Om/torr).

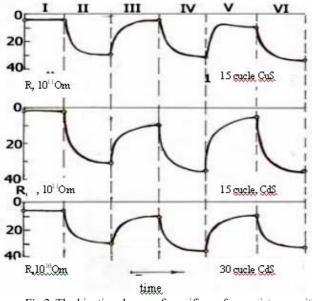


Fig.2. The kinetics change of specific surface resistance with time for nano-composites ge./15c. Cu₂S, gel./15c. CdS and gel./30c. Cds.

The second method is used for the definition of gas sensitivity of samples gelatin/15 cycles Cds.

On the fig.3 it is seen, that the samples resistance gelatin/15 cycles Cds changes with pressure value change of ethyl alcohol steams. The measurements are carried out at vessel heating with different velocity; steams of warm water, steams of hot water and the vessel are put in the warm water.

The same dependence, is shown on the fig. 4, but heating rate is changed: the vessel is heated independently at room temperature (c.1), by warm water with temperature 36 0 C (c.2), with water temperature 47 0 C (c.3) and with water temperature 60-65 0 C (c.4).

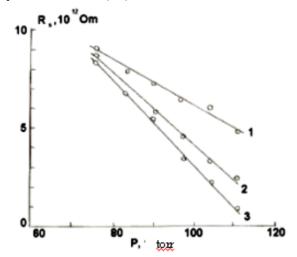


Fig.3. The resistance dependence on the change of ethyl alcohol steam pressure for the samples gel./15c. CdS at heating: 1 – warm water steams; 2 – hot water steams; 3 – the vessel in the warm water.

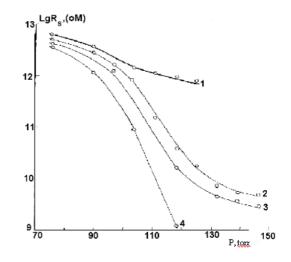


Fig.4. The resistance dependence with change of alcohol steam pressure for the samples gel./15c. CdS at the heating: 1- at room temperature; 2 – with water temperature 36° C; $3 - 47^{\circ}$ C; $4 - 60-65^{\circ}$ C.

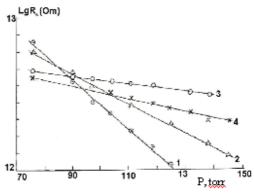


Fig.5. The resistance dependence with change of alcohol steam pressure for the samples gel./15c. CdS: 1 – alcohol;
2 - acetone; 3 – dichloroethane; 4 – methyl ethyl ketone.

From the fig.4 it is seen that the curve inclination angle, which says about the increase of steam saturation velocity changes with heating rate increase. This is equivalent to increase of alcohol molecule energy. The molecule energy increase leads to the increase of sample sensitivity in the result of more deep steam adsorption. CdS on saturated steam pressure of ethyl alcohol (c.1), acetone (c.2), dichlorethane (c.3) and methyl ethyl ketone (c.4) is shown on the fig.5. On the dependence inclination it is possible to say that the best gas sensitivity is observed at the lap of ethyl alcohol steams. Such changes of sensitivity will be understandable, if the chemical data of these solvents are compared.

The resistance variation of samples gelatin/15 cycles

Tabl	e

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Steams	Ethyl alcohol	Acetone	Methyl ethyl ketone	Dichlorethane
Structure	C ₂ H ₆ O	C ₃ H ₆ O	C ₄ H ₈ O	$Cl_2C_2H_4$
Molecular weight	46	58	72	99
Boiling point, °C	78	56	83	79.6
P ₀ , torr	76	76	76	76
P ₁ , torr	125	146	146	139
$R_0, 10^{12} \text{ Om}$	1	2	3.5	5.3
R_1 , 10^{12} Om	8,5	8	6.5	6.8
ΔR , 10^{12} Om	7.5	6	3	1.5
ΔP , 10^{12} Om	49	70	70	63
γ , 10^{10} Om	15,3	8.6	4.3	2.38

The chemical structure, the boiling point and molecular weight of used solvents and gas sensitivity for the sample gelatin/15 cycles CdS, calculated on the formula (1) from the dependence, presented on the fig.5 is shown in the table. From the comparison it is seen, that the ethyl alcohol molecules have the least molecular weight among these materials and the best gas sensitivity is observed at the influence of its steams. The gas sensitivity consistency of the samples to the steams of these solvents should coincide with consistency of their molecular weight decrease. It is possible to say that the best adsorption and correspondingly, the best gas sensitivity is observed in the steams and gases with

- [1] *T. Moriizum*. Thin Solid Films, 1988. № 160. p. 413.
- [2] *T.A. Temofonte,K.E. Schoch.* J.Appl. Phys., 1989, v.65. № 3, p, 1350.
- [3] L.I.Traxtenberg, G.N. Gerasimov, I.K. Potapov, T.N. Rostovshikova, V.V. Smirnova, V.Yu. Zufman. Vesti.Mosk. Un-ta, ser. 2. Khimiya, 2001, t. 42, № 5, s. 325. (In Russian).
- [4] Ye.I. Grigoryev, P.S. Zavyalov, S.N. Chvalun. «Pisma v Jetf», 2003, t. 28, № 20, s.15. (In Russian).
- [5] P.S. Voroncov, G.N. Gerasimov, Ye.N. Golubeva, Ye.I. Grigoyev, S.A. Zavyalov, L.M.Zavyalova, L.I. Traxten-

relatively less molecular weight at the sample contact with the steams of these solvents. This is proved by the obtained results. Thus, the carried out investigations show that composites on the basis of polymer with cuprum sulfide and cadmium sulfide nano-particles are the sensitive ones on the steams of different solvents. The nano-composite gas sensitivity depends on the matrix population and on the chemical data of tested gas. These materials can be applied in the capacity of sensitive element of different gas sensors and sensing elements.

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berg. J. Phys. Khimiya. 1998. t. 2, № 10.s.1912. (In Russian).

- [6] A.V. Udaratin, M.I. Fedorov. Sensor, 2003, \mathbb{N}_{2} 1, s. 50. (In Russian).
- [7] O.V. Anisimov,N.K. Maksimova,N.G. Filonov, L.S. Khludkova,Ye.V. Chernikov. Sensor, 2003, № 1,s. 40. (In Russian).
- [8] V.V. Klechkovskaya, V.S. Maslov, M.B. Muradov. Kristallografiya, 34, №1,1989,182. (In Russian).

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POLİMER VƏ Cu₂S, CdS NANOZƏRRƏCİKLƏRİ ƏSASINDA OLAN KOMPOZİTLƏRİN QAZA HƏSSASLIĞI

Jelatin/Cu₂S və jelatin/CdS nümunələrinin etil spirti və müxtəlif həlledicilərin buxarlarında qaza həssaslığı tədqiq edilmişdir. Müəyyən edilmişdir ki, polimer və Cu₂S, CdS nanozərrəcikləri əsasında olan kompozitlər müxtəlif həlledicilərin buxarlarına həssasdırlar. Nanokompozitlərin qaza həssaslığı matrisin dolma dərəcəsindən və test olunan qazın kimyəvi göstəricilərindən asılıdır. Bu materiallardan müxtəlif qaz sensorlarında həssas element kimi istifadə etmək olar.

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ГАЗОЧУВСТВИТЕЛЬНОСТЬ КОМПОЗИТОВ НА ОСНОВЕ ПОЛИМЕРОВ И НАНОЧАСТИЦ Сu₂S и CdS

Исследована газочувствительность образцов желатин/Cu₂S и желатин/CdS при воздействие паров различных растворителей и этилового спирта. Показано, что композиты на основе полимера с наночастицами Cu₂S и CdS являются чувствительными на пары различных растворителей. Газочувствительность нанокомпозитов зависит от степени заполнения матрицы и от химических данных тестируемого газа. Эти материалы могут быть применены в качестве чувствительного элемента различных газовых сенсоров и датчиков.

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