

Effect of adhesion energy on the adsorption of CdTe modifiers

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The adsorption in high-dispersed CdTe systems containing medium-modifiers has been studied. As modifying substances, anionic phosphorous-containing organic compounds were selected. An analysis of the effect of the molecular structure of the disperse medium on the adhesion energy in disperse medium–CdTe systems was carried out. Introduction of phosphorus-containing modifiers into high-dispersed aqueous– and alcohol–CdTe systems produces a change of their characteristics, due to the formation of a monomolecular adsorption layer on the surface of particles of the disperse phase. By selecting appropriate compositions of the disperse medium modifier one can produce a purposeful effect on the stability of high-dispersed CdTe systems.

Modifying substances / High-dispersed system / CdTe nanoparticles / Adhesion / Adsorption / Surface

Introduction

The unique properties of high-dispersed and nano-sized systems have motivated their wide application in a number of science and technology fields. As one goes to nano-sized particles, quantum-sized effects become apparent that are not typical of the bulk samples [1,2]. The development of methods for manufacturing monodispersed systems that remain stable during operation of devices constructed on their basis is still the main problem of nanochemistry. The nanoparticles and the molecules of the dispersed medium are of approximately the same order of magnitude, which predetermines the specific features of their chemical interaction kinetics. The high particle density of the dispersed phase of nano-sized semiconductor systems leads to aggregation and loss of sedimentation stability. For the stabilization of semiconductor nanosystems, thiols and phosphonic acids are widely used as stabilizers during the synthesis [3]. The role of these substances and the mechanism of modification of the adsorption on the particle surface during the synthesis of high-dispersed systems are not yet completely understood [4].

It has been established that the adsorption of substances and the structure of the adsorption layer are determined not only by the character of the adsorbate-adsorbent interaction, but also by the adhesion energy in the solvent-adsorbent system [5]. There is a possibility to increase the monodispersity of cadmium

telluride colloidal solutions by using selective deposition stimulated by electrolytes [6].

Experimental procedure

For the investigations we used high-dispersed CdTe prepared by grinding single-crystalline blocks grown by the Bridgman method. Cadmium telluride was prepared from a charge obtained from samples of original components of semiconductor purity (class N6) taken in stoichiometric ratios. The granulometric composition of the samples is shown in Fig. 1.

The particle sizes were in the range from 40 to 450 nm (maximum 120÷150 nm). The selection of fractions of high-dispersed CdTe was done by fractionating the resulting powder. Particles of sizes in the range from 40 to 150 nm were selected for the studies.

As modifying substances (MS), anionic phosphorous-containing organic compounds that are widely used in the synthesis of cadmium chalcogenide nanoparticles were selected, in particular:

- tetradecylphosphonic acid $C_{14}H_{29}-PO(OH)_2$: MS-1;
- carboxyethylphosphonic acid $CO(OH)-CH_2-CH_2-PO(OH)_2$: MS-2;
- trioctylphosphine oxide $[CH_3(CH_2)_7]_3PO$: MS-3;
- hydroxyethylidenediphosphonic acid $C_2H_8O_7P_2$: MS-4;

• mono potassium salt of hydroxyethylenediphosphonic acid $C_2H_7O_7KP_2$: MS-5.

The work of adhesion was determined using a standard procedure [7]. The adsorption of additives on the surface of the particles was determined by means of an LIR-2 interferometer according to the change between the interference factor prior to and after contact between the adsorbent and the modifier solution. The value of the adsorption was calculated by the formula:

$$A = \Delta CV/m,$$

where ΔC is the change of the concentration of additive in the solution prior to and after adsorption, kg/m^3 ; V is the volume of the solution from which adsorption takes place, m^3 ; m is the mass of the adsorbent, kg .

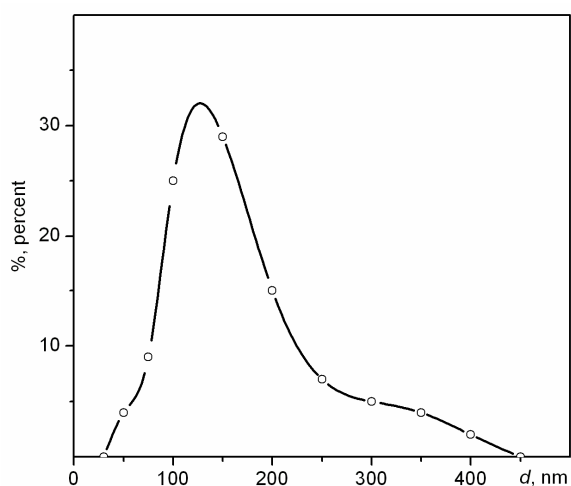


Fig. 1 Granulometric composition of dispersed CdTe.

Results and discussion

For high-dispersed systems the most widespread method of stability control is the modification of the adsorption at the particle surface that changes its physico-chemical characteristics. Adsorption of modifiers, as a rule, reduces the surface energy, which contributes to the destruction of aggregates in dispersed systems, and prevents the creation of coagulation contacts between particles during precipitation [7].

The value of the adsorption, as well as the character of the interaction in the adsorbate–adsorbent system, is determined by the chemical nature of the surface of the particles of the dispersed phase, as well as by the physico-chemical nature of the modifier [7]. At the same time, adsorption of substances on the surface of disperse phase particles of two- (and more)

component system can be considered as a competing process of fixation on the phase boundary surface of solvent and modifier molecules. The interaction energy in the solid surface–disperse medium system can be characterized by determining the work of adhesion.

The analysis of the effect of the molecular structure of the disperse medium on the adhesion energy of disperse medium–crystalline CdTe systems has shown that maximum values of the work of adhesion are peculiar to water–CdTe systems. Note that such a behavior was observed for CdTe samples immediately after etching of the crystal surface, as well as for samples that had been stored in air for four weeks. It must be emphasized that the adhesion energy in the water–cadmium telluride system changes considerably depending on the sample storage time. For the as-etched samples the work of adhesion is less than for the samples that are stored in the open air. In our opinion, this is due to gradual oxidation of the sample surface. Introduction of oxygen atoms into the structure of the surface layer results in formation of additional hydrogen bonds and increases the energy of interaction between the disperse medium (water) and the solid surface (Table 1). Despite the large adhesion energy in the water–CdTe system, there is no drop spread across the crystal surface, which is due to high surface tension of water.

In the ethanol–CdTe and isopropanol–CdTe systems the values of the adhesion energy are considerably reduced. Investigations show that the above disperse mediums are characterized by minimum values of the work of adhesion. In this case the work of adhesion is practically independent of the time passed after etching of the surface of the samples. Probably, the area of hydrophobic portions at the oxidation of surface is not reduced significantly, and introduction of new oxygen atoms into the structure of the surface layer does not affect the energy of interaction between the disperse medium and the CdTe surface.

Table 1 Work of adhesion in the disperse medium–crystalline CdTe system^a.

Disperse medium	$\cos\theta$	Surface tension, mJ/m^2	Work of adhesion, MJ
Water	0.814	72.75	131.98
	0.424		103.56
Ethanol	0.976	22.03	43.52
	0.950		42.96
Isopropanol	0.997	21.7	43.34
	0.995		43.30

^a The first value is for an oxidized cadmium telluride surface; the second value is for samples immediately after etching of the crystal surface.

Alcohol drops spread across the surface of the CdTe samples, and the larger the number of hydrophobic radicals in the alcohol molecule, the larger the drop spread. In this case, considerable spread (compared to water) can also be caused by the low values of surface tension in alcohols.

This behavior is observed both on the as-etched samples and after their storage in open air. It must be emphasized that the interaction between the disperse medium and the CdTe surface is limited to dispersion, as shown by experiments to determine the heat of wetting the surface. The introduction of dispersed CdTe, preliminarily dried at 353 K, into a disperse medium did in no case entail any thermal effect. That is, it can be asserted that no chemical interaction takes place in such systems.

The studies show that the isotherms of adsorption of the investigated substances from water, ethanol and isopropanol on CdTe particles are well described by the Langmuir equation (Figs. 2,3). This confirms the fact that formation of an adsorption layer on the adsorbent surface occurs due to adsorption of individual molecules of the investigated substances. The process of fixation of adsorbate molecules on the adsorbent surface occurs due to Van-der-Waals forces (that is, physical adsorption takes place). The adsorption is reversible, as confirmed by experiments on desorption of modifier substances by a pure solvent. The isotherm behavior indicates monomolecular character of the adsorption. It can be concluded that the values of substance adsorption and the structure of the adsorption layer are determined not only by the character of the adsorbate-adsorbent interaction, but also by the adhesion energy of the solvent-adsorbent system. The adsorption ability of the investigated substances on CdTe from different solvents is different. As can be seen from the referred data, the adsorption ability of the substances is arranged in the following series:

$$A_{(\text{ethanol})} > A_{(\text{water})} > A_{(\text{isopropanol})}$$

The adsorption of the substances under study takes maximum values when the process is conducted from ethyl alcohol. The large values of limiting adsorption in this case are due to the high wettability of the CdTe surface with ethanol, which facilitates the contact between modifier molecules and the adsorbent surface. Formation of a saturated adsorption layer from ethanol takes place at lower concentrations than from water or isopropanol (Figs. 2,3). At the same time, the relatively small dimensions of the ethanol molecules and their high mobility practically keep them from competing with the modifier molecules during the formation of the adsorption layer. On reaching the dynamic equilibrium, an exchange process occurs in the system: adsorbed modifier molecule-modifier molecule in solution.

The value of the limiting adsorption on conducting the process from water is much lower, which is due to the hydrophobic surface of the CdTe particles. The poor contact between the disperse medium and the

adsorbent surface creates additional difficulties for the fixation of modifier molecules. At the same time, water molecules do not form intermolecular associates with the modifier molecules and do not compete with them at the formation of an adsorption layer. Under these conditions, formation of an adsorption layer takes place in the low concentration region, and on reaching the dynamic equilibrium, as in the case of using ethanol as a solvent, an exchange of modifier molecules takes place. That is, the formation of the adsorption layer, its density and other characteristics are determined by the energy of dispersion interaction between the modifier molecules in it.

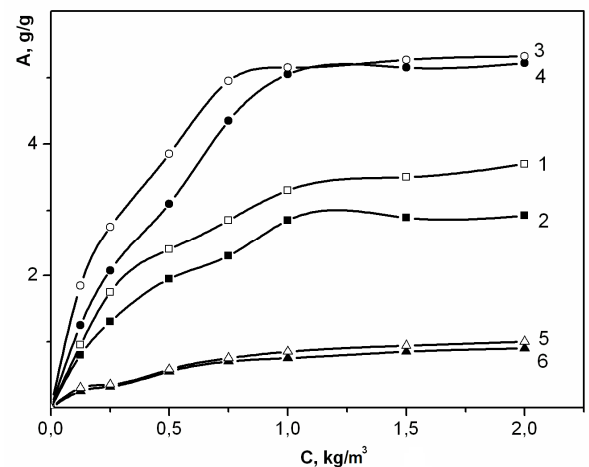


Fig. 2 Adsorption isotherms on a CdTe surface. Modifying substance MS-2: 1 – in water, 3 – in ethanol, 5 – in isopropanol; MS-5: 2 – in water, 4 – in ethanol, 6 – in isopropanol.

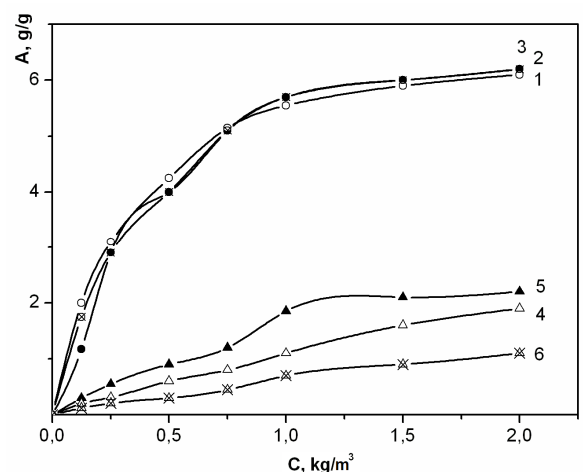


Fig. 3 Adsorption isotherms on a CdTe surface. Modifying substance MS-3: 1 – in ethanol, 4 – in isopropanol; MS-1: 2 – in ethanol, 5 – in isopropanol; MS-4: 3 – in ethanol, 6 – in isopropanol.

When using isopropyl alcohol as disperse medium, the values obtained for the limiting adsorption are much lower than from ethanol and water. At the same time, the work of adhesion in the isopropanol–CdTe system does not differ significantly from the ethanol–CdTe system. Apparently, during the formation of an adsorption layer from a given solvent, the solvent molecules compete with the molecules of the dissolved substance, which complicates the formation of a saturated adsorption layer of modifier molecules. On reaching the dynamic equilibrium, the adsorbed modifier molecules can be replaced by solvent molecules, and *vice versa*, which changes considerably the structure of the layer. Owing to this, in the area of investigated concentrations, no formation of a saturated layer occurred. Besides, one must take into account the possibility of formation of molecular associates between molecules of dissolved substance and solvent molecules, which also affects the adsorption of the substances under investigation.

Investigations have shown that at modification of CdTe particle surface, the nature and properties of the solvent are of great importance. Solvents with a diphilic molecular structure (ethyl and isopropyl alcohols), wet the surface of the CdTe particles better, which facilitates fixation of stabilizer molecules. At the same time, as a result of the increase of the molecular mass of the solvent molecules and the number of functional groups in the molecule, the molecules can successfully compete with the modifier at the formation of an adsorption layer on the adsorbent surface. At the phase boundary, during the formation of the adsorption layer a complicated dynamic equilibrium is created. A layer structure is formed with active participation of solvent molecules that are also adsorbed on the surface of the particles.

Conclusions

Introduction of phosphorous-containing modifiers to high-dispersed aqueous– and alcohol–CdTe systems brings about a change in their characteristics due to the formation of a monomolecular adsorption layer on the surface of the disperse phase particles. An increase of the molecular mass of the disperse medium results in a change of the structure of the adsorption layer due to a stable fixation of solvent molecules on the surface of the particles. By selecting the composition of the disperse medium-modifier one can produce a purposeful effect on the stability of high-dispersed CdTe systems.

Reference

- [1] G.B. Sergeev, *Russ. Khim. Zh.* 66(5) (2002) 22-29.
- [2] H.S. Nalwa (Ed.), *Handbook of Nanostructured Materials and Nanotechnology*, Vols. 1-5, Academic Press, New York, 1994, 222 p.
- [3] A.L. Rogach, T. Franzl, T.A. Klar, J. Feldmann, N. Gaponik, V. Lesnyak, A. Shavel, A. Eychmller, Y.P. Rakovich, J.F. Donegan, *J. Phys. Chem. C* 111(40) (2007) 14628-14637.
- [4] R.F. Khairutdinov, *Usp. Khim.* 67(2) (1998) 125-139.
- [5] D. Boruk, S.G. Dremlyuzhenko, I.M. Yuriychuk, Yu.M. Davydyuk, O.A. Savchuk, *Novi Tekhnol.* 2(20) (2008) 222-225.
- [6] Yu.B. Khalavka, P.I. Feichuk, L.P. Shcherbak, *Nauk. Visn. Chernivtsi Univ.* 270 (2005) 18-24.
- [7] A.P. Shpak, Z.P. Ulberg (Eds.), *Colloidal Chemical Fundamentals of Nanoscience* Akadempriodyka, Kyiv, 2005, 466 p. (*in Ukrainian*).