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# Growth kinetics of PbS nanocrystals in organo-metallic Langmuir-Blodgett films studied by optical absorption spectroscopy

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**Abstract.** Formation and growth of lead sulfide nanocrystals in lead stearate Langmuir-Blodgett (LB) films are investigated using the optical absorption spectroscopy method. The kinetics of changes in the concentration of lead ions in different states formed during the growth process, as well as the evolution of the nanocrystal average size versus growth time, are studied. Irrespective of the primary  $Pb^{2+}$  ion concentration in films, found was a nonlinear dependence of the nanoparticle growth rate vs time: at the initial stage the growth rate is higher than at the final one. The idea of diffusive decomposition of solid solution is used to analyze the experimental results. It is shown that high concentrations of metal ions at the interfaces of LB-film monolayers as well as diffusion restrictions of mass-transfer process play a decisive role in the formation and growth of nanocrystals in ordered organic matrixes.

**Keywords:** lead sulfide nanoparticles, Langmuir-Blodgett films, growth process, optical absorption.

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## 1. Introduction

Nowadays, investigation of semiconductor and metal nanoparticles in dielectric matrixes has evoked keen interest. This is caused, first of all, by the effects of size quantization of energy spectra as well as by considerable influence of nanocrystals surface on their properties [1]. Physico-chemical aspects of nanocrystal states are interesting too [2]. The processes of nanocrystal formation and growth are studied to a far lesser extent. One of the ways to control their size and shape is the growth of such structures *in-situ* in organic matrixes: polymers, self-organized molecular ensembles, Langmuir-Blodgett (LB) films, *etc* [3]. It should be expected that the nucleation efficiency, growth rate, initial and final sizes and shape of the nanostructures to be formed depend on the matrix morphology as well as on the type, concentration, distribution and precursor intercalation method. In the majority of inorganic matrixes the concentration of precursors is usually lower than 1% and mass transfer is realized by means of the bulk diffusion mechanism. However, in quasi-two-dimensional molecular structures such as metal-containing LB films, the morphological peculiarities, in particular, high metal ion concentration in

space-restricted matrix volume at the polar plane interfaces, mosaic block film texture nucleation of seeds and growth kinetics may significantly differ from those described in the frame of the classical conceptions [4].

There exist many works devoted to studying the methods of synthesis and physico-chemical properties of semiconductor nanocrystals. However, their formation and growth in organic matrixes, in particular, in multilayer high-ordered structures, have not been investigated so far. In this connection, it seems expedient to study the main stage of matrix-controlled growth of inorganic nanocrystals in organic matrixes. In the present paper the processes of nucleation and growth of PbS nanocrystals in LB films of lead stearate are studied. The conception of diffusive decomposition of solid solutions is used to analyse the experimental results.

## 2. Experimental

PbS nanocrystals in LB matrixes were grown by the methods described in detail in our paper [5]. Stearic acid (HSt) monolayers were formed at the surface of water subphase containing  $Pb(NO_3)_2$  salt with concentrations from  $2 \cdot 10^{-4} M$  up to  $5 \cdot 10^{-6}$ . Absorption of lead ions in the monolayer

was controlled by pH of the subphase (pH = 5.3). 30-bilayer Pb(St)<sub>2</sub> LB films (with a total thickness of about 150 nm) were formed on hydrofobized quartz substrate by the vertical lifting method at the surface pressure  $\pi = 30$  mN/m. The lead ion concentrations in the polar planes of LB film determined by X-ray photoelectron spectroscopy method (XPS "Kratos") were  $c_1 = 0.9$  at.% (corresponding to the stoichiometric composition of lead stearate LB film),  $c_2 = 0.41$  at.% (corresponding to 29% volume concentration of Pb(St)<sub>2</sub> in the mixed system Pb(St)<sub>2</sub>/HSt) and  $c_3 = 0.11$  at.% (corresponding to 9% of the volume concentration). To bring about the onset of the growth process the LB films were treated in sodium sulfide water solution with the concentration  $2 \cdot 10^{-3}$  M at 293 and 315 K.

Phase transformations and nanocrystal growth in LB films were studied by the method of optical absorption spectroscopy ("Specord" M40). Unlike known structural techniques, the method of optical absorption allows to analyse different states of precursors, in particular, to observe evolution of Pb<sup>2+</sup> ion concentration connected with both the carboxylic group of matrix molecules and sulfur ions in PbS nanocrystals. Moreover, this method permits to determine (more or less exactly) the nanocrystal size changing during the growth process. Simultaneously, by means of the X-ray photoelectron spectroscopy ("Kratos" XPS) and small-angle X-ray diffraction methods (DRON-4, Cu Ka -radiation) the element composition was analysed, and the regularity as well as roughness of interlayer boundaries in LB films were controlled.

### 3. Results and discussion

XPS analysis shows that at room temperature lead sulfide compounds are formed in LB films treated for several minutes in Na<sub>2</sub>S solution. At the same time, the optical absorption spectra are characterized by the decrease of

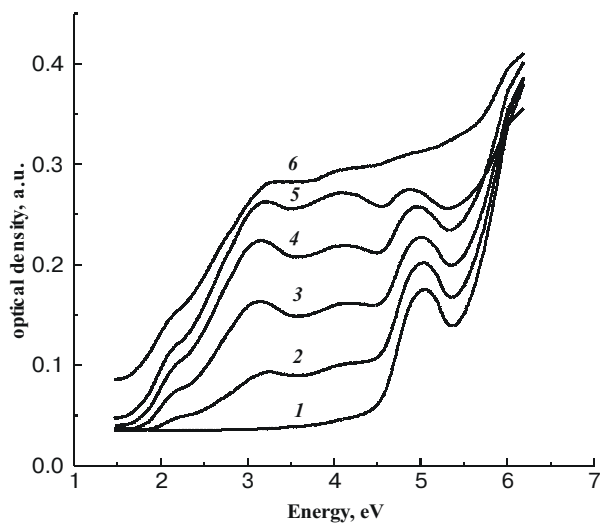


Fig. 1. Optical absorption spectra of Pb(St)<sub>2</sub> LB film before (1) and after (2)–(6) treatment in Na<sub>2</sub>S water solution: 2 – 2, 3 – 4, 4 – 10, 5 – 25, 6 – 40 min.

the intensity of the band corresponding to optical transitions in the charge transfer complexes  $(-\text{COO})_2\text{Pb}$  of matrix molecules [6], whereas the intensity of the band corresponding to the  $1s_h-1s_e$  optical transitions of  $e-h$  pair in nanocrystals [7], rises (Fig. 1). This "exciton" band is shifted towards the long-wavelength range when the film treatment duration is increased. The differential spectra (i.e. the absorption spectra of LB films measured before and after treatment) in the region of absorption edge, were compared with the fundamental absorption threshold in bulk PbS crystals and in molecular PbS [8]. As shown by the comparison (Fig. 2), PbS solid phase structures formed in LB matrix are in the quantum confinement state ( $Q$ -state). The average nanoparticle size is determined from the equation [9]

$$E_{ed} = E_g + \hbar^2 \pi^2 / 2\mu^* r^2 \quad (1)$$

where  $E_{ed}$  is the position of the absorption of  $1s_h-1s_e$  "exciton" peak,  $E_g$  and  $\mu^*$  are the band gap and the effective exciton mass for bulk PbS crystals, respectively,  $\hbar$  is the Planck constant,  $r$  is the average nanocrystal radius. Fig. 3 presents the dependences of absorption intensities  $I_{st}(t)$  and  $I_s(t)$  that correspond to the nanocrystals (curve 1) and the matrix (curve 2) optical absorption, respectively, on the treatment time  $t$ .

It can be seen that there is a correlation between the change of these intensities and the chemical transformations in LB matrix, i.e. the reduction of metal-containing molecules as a result of the ion-exchange reactions as well as the growth of PbS phase.

Assuming that some Pb<sup>2+</sup> ions are in  $(-\text{COO})_2\text{Pb}$  or in PbS states, and the total lead ion quantity remains unchanged in the growth process, the conservation mass equation is to be as follows:  $c_{St}(0) = c_{St}(t) + c_S(t)$ , for  $c_{St}(0) = c_S(t_{\max})$ , where  $c_{St}(0)$ ,  $c_{St}(t)$  are Pb<sup>2+</sup> ion concentrations in  $(-\text{COO})_2\text{Pb}$  state before the treatment and in arbitrary time of the growth process, respectively,  $c_S(t)$  and  $c_S(t_{\max})$

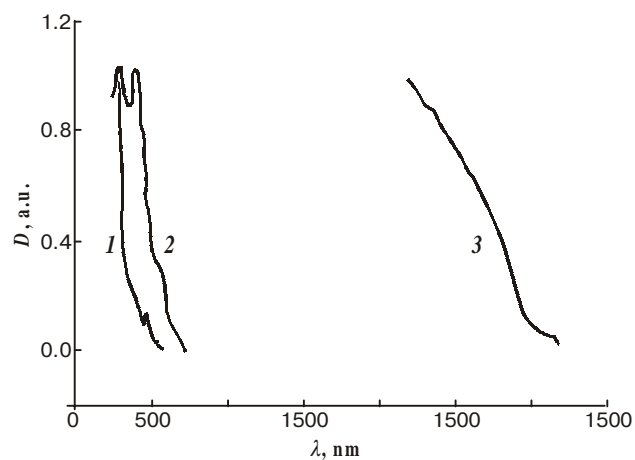
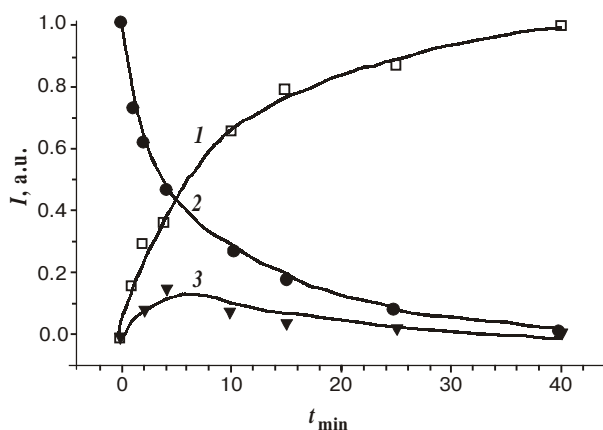


Fig. 2. Optical absorption spectra of: 1 – molecular PbS [8], 2 – PbS nanocrystals, 3 – bulk PbS crystals.



**Fig. 3.** Dependences of spectral band intensities corresponding to the optical transitions:  $1s_h-1s_e$  of the electron-hole pair in PbS nanocrystals (1), charge-transfer transition in  $(-\text{COO})_2\text{Pb}$  fragments of the matrix molecules (2), molecular-like structures PbS (3) on treatment time of the studied LB films.

are  $\text{Pb}^{2+}$  ion concentrations in PbS nanocrystal state. The corresponding equations for normalized intensities of absorption bands can be written as  $I_{S_i}(t)/I_{S_i}(0) + I_S(t)/I_S(t_{\text{max}}) = 1$ . But as it follows from Fig. 3,  $I_{S_i}(t)/I_{S_i}(0) + I_S(t)/I_S(t_{\text{max}}) < 1$  for the growth period. Therefore, we suppose that in LB matrix, besides  $(-\text{COO})_2\text{Pb}$  and PbS (condensed) states of lead ions, in the process of treatment there arise some intermediate molecular-like states: monomers, dimers, trimers, etc. (we shall further denote them as PbS m.u.).

The kinetics of  $I_{S_i}(t)$  reduction at different growth temperatures allows a possibility to evaluate the activation energy  $Q_a$  and the diffusion constant  $D_0$  for  $\text{S}^{2-}$  ions diffusing along the polar matrix planes, proceeding from the expressions  $I_{S_i}(t)/I_{S_i}(0) = \exp(-D_s t/L^2)$  and  $D_s/D_0 = \exp(-Q_0/kT)$ . Since real LB films have the mosaic block structure with an average block size of the order of  $L \sim 60-80$  nm [10], one can obtain  $Q_0 \approx 0.25$  eV,  $D_0 \approx 1.3 \cdot 10^{-16}$   $\text{m}^2/\text{s}$  suggesting that  $\text{S}^{2-}$  ions diffusion takes place along (001) planes simultaneously and identically in all the blocks of LB matrix.

The key experiments to determine the mechanism of nucleation and growth of the new phase inclusions in the solid solution is the study of the dependences of the inclusion size and concentration versus the growth time. As follows from Fig. 4, the nature of the dependences of the nanoparticle radius  $r$  vs the treatment time is similar for all the starting  $\text{Pb}^{2+}$  ion concentrations: at the initial stage the growth rate  $dr/dt$  is essentially higher than that of the final stage of the growth process.

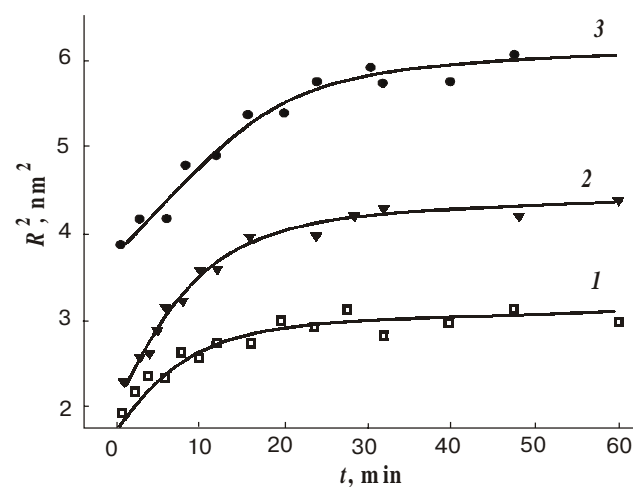
The dependences shown in Figs 3 and 4 allow to assume that the transition of  $\text{Pb}^{2+}$  ions from the initial to the final state is a result of at least three processes: (i) formation of supersaturated solid solution of molecular-like compositions of lead sulfide (PbS m.u.), (ii) their aggregation and formation of overcritical nuclei, (iii) the diffusive mass-transfer (PbS m.u.) to the seeds. One can

suppose that  $\text{S}^{2-}$  ion diffusion and ion-exchange reaction at the polar planes interface of LB matrix cause fast regeneration (owing to the high value of the PbS formation rate) to non-metallic state (stearic acid), simultaneously with the formation of molecular structure PbS m.u. Due to the high PbS m.u. concentration as well as small dimensional discrepancy between the  $\text{Pb}^{2+}-\text{Pb}^{2+}$  distance in (001) planes of  $\text{Pb}(\text{St})_2$  and the corresponding distance in (111) plane of PbS crystal lattice, the state which corresponds to individual PbS m.u. (solid solution PbS m.u. in HSt matrix) is metastable. As a result, its aggregation into overcritical nuclei takes place in each LB film mosaic block. The initial inclusion size determined by fitting the experimental dependences  $r(t)$  to  $r(0)$  at  $t = 0$  for various initial  $\text{Pb}^{2+}$  concentrations gives close values:  $r(0) \approx 1.3-1.6$  nm. The final nanocrystal sizes ( $t = 60$  min,  $T = 393$  K) are of the order of  $2.7-3.3$  nm, depending on the initial  $\text{Pb}^{2+}$  ion concentration. In the approximation of statistically homogeneous distribution of PbS nanocrystal nuclei, one can obtain the approximate value of the average distance between nanocrystal seeds,  $d \approx 6$  nm.

Based on the diffusion mechanism of the formation and growth of nanocrystals in the organo-metallic matrices, the evolution of nanocrystal sizes  $r(t)$  in quasi-stationary approach (the rate of change of PbS m.u. flow is much less than that of the inclusion size increase) can be expressed as [12]

$$dr/dt = D_n a^{n-3} (\Delta - \alpha r) / r^{n-2} \quad (n \geq 2), \quad (2)$$

where  $D_n$  is the PbS m.u. diffusion constant,  $\Delta$  – is the supersaturation parameter,  $\alpha = 2\sigma V_m c_\infty / kT$ ,  $\sigma$  is the interphase surface energy,  $V_m$  and  $c_\infty$  are the volume and equilibrium PbS m.u. concentration,  $n$  and  $a^n$  are the parameters depending on the mass transfer mechanism. The solution of Eq. (2) in the general form can be approximated as



**Fig. 4.** Dependences of the average radius of PbS nanocrystals grown in LB films at  $T = 393$  K for the initial  $\text{Pb}^{2+}$  – ion concentrations: 1 – 0.9, 2 – 0.41, 3 – 0.11 at. %.

$$r^k = f(D_k, \Delta) t, \quad (3)$$

where  $k = n - 1$  for initial growth stage and  $k = n$  for final stage.

It should be noted that the quasistationary approach is usually carried out when  $\Delta \ll 1$ , i.e. at the final growth stage. At arbitrary  $\Delta$  it is necessary to modify Eq. (2) taking into consideration the non-stationary of diffusive flow [13]. Thereat, the solution of the modified equation can be approximated by the function of the type (3), however, the parameter  $f$  is a complex function of  $D_k$  and  $\Delta$ . From the slopes of the experimental curves  $r(t)$  in the double-logarithmic coordinates  $\lg r - \lg t$ , the values  $1/n_1$  and  $1/n_2$ , were determined for all  $\text{Pb}^{2+}$  ion concentrations. As found: (i)  $r(t)$  dependences describe two different growth process stages: the initial ( $1/n_1 \approx 0.1 \div 0.2$ ), responsible for comparatively fast increase of the nanocrystals size, and the final stage ( $1/n_2 \approx 0.06 \div 0.09$ ), which correspond to the moderated growth, and (ii)  $n_1$  and  $n_2$  do not depend on the initial  $\text{Pb}^{2+}$  ion concentration in LB films, (iii) both  $1/n_1$  and  $1/n_2$  are essentially smaller than the analogic parameters describing the inclusion growth as a result of the volume diffusion mechanism (for  $1/n_1 = 1/2$ ,  $1/n_2 = 1/3$ ) [4].

The most significant result which follows from Fig. 4 is comparatively small values of  $1/n$ . To comment this, it is necessary to understand that the density of precursor diffusive flow and, consequently, the rate of the inclusion growth depend on the specific mechanism of the mass transfer in the matrix. For example, at the volume precursor diffusion at the stage of "normal" growth  $n_1 = 1/2$ , at the mass-transfer along the grain boundary  $n_1 = 1/3$ , and along the dislocation line  $n_1 = 1/4$  [4]. Thus, one can assume that the found small values  $1/n$  are due to a strong effect of spatial (dimensional) restriction on diffusion processes in LB films. In our experiments the influence of the initial  $\text{Pb}^{2+}$  ion concentration on the value of the exponents  $1/n_i$  was not observed in spite of different average distances between lead ions in the polar planes of LB films. Therefore, the nucleation of seeds and nanocrystal growth in non-stoichiometric LB films (i.e., containing both  $\text{Pb}(\text{St})_2$  and  $(\text{HSt})$  molecules) takes place in the regions (domains) of closely packed  $\text{Pb}(\text{St})_2$  molecules irrespective of the initial  $\text{Pb}^{2+}$  ion concentration. The domain sizes determine the seed and final nanocrystal sizes.

X-ray diffraction study of LB films at various growth stages shows that the structural period of  $\text{Pb}(\text{St})_2$  LB films remains unchanged during the growth process. Thereat, the root mean square roughness of interlayer boundaries increases with the treatment time of LB films and reaches the highest value  $\langle U^2 \rangle^{1/2} \approx 0.3 \text{ nm}$   $t = 60 \text{ min}$  (at  $T = 293 \text{ K}$ ). A small rise of the structural period of the matrix in the direction normal to the polar planes of LB film testifies to the primary nanocrystal growth along the polar planes. Therefore, PbS nanocrystals grown in LB films are quasi-two-dimension structures, like disks or plates.

In accordance with [4], at the normal growth stage the raise of the total mass of the new phase inclusions takes place owing to the predominant growth of the aver-

age size of the nanocrystals with respect to the formation of seeds. At the final growth stage (the competitive growth stage) the inclusion quantity must be reduced at the expense of the dissolution of small particles and increase of the sizes of large particles. However, as shown in Fig. 5, during the whole period of treatment a monotonic increase of the concentration  $N_{nc}$  of the average radius nanocrystals is observed, i.e.  $dN_{nc}/dt > 0$ . Inasmuch  $N_{nc} = c_m v_m / v_{nc}$ , where  $c_m$  and  $v_m$  are the concentration and volume of PbS molecular-like structures,  $v_{nc} = \pi r^2 h$  is the volume of cylindrical nanocrystal, and therefore  $dc_{nc}/c_{nc} > 2d\langle r \rangle / \langle r \rangle$ , so both the initial and the final growth stages in organic matrix are accompanied with the generation of a large quantity of seeds and comparatively slow increase of the average sizes of nanocrystals. The absence of the observed decrease of  $N_{nc}$  may signify the ineffectiveness of the competitive growth stage in LB films bound up with high diffusion barriers in the structures with dimensional restriction of the diffusion processes.

#### 4. Conclusions

In summary, we would like to point to the basic peculiarities of the formation and growth processes of PbS nanocrystals in LB films of lead stearate. (i) The primary stage of non-organic phase is the formation of molecular-like structures of lead sulfide at the polar planes of organo-metallic LB films. This stage is induced by the diffusion of sulphur ions caused by the treatment in  $\text{Na}_2\text{S}$  solution. (ii) Due to a small dimensional disparity between the lattice parameters of the growing PbS nanocrystals and the organic matrix in the conjugated planes, PbS molecular-like structures are rapidly aggregated and form crystal seeds of lead sulfide nanocrystals. (iii) Owing to the domain structure of monolayers of LB films, the formation and growth of the nanocrystals takes place in the domain consisting of the lead stearate molecules only. The interlayer space in LB films and the domain

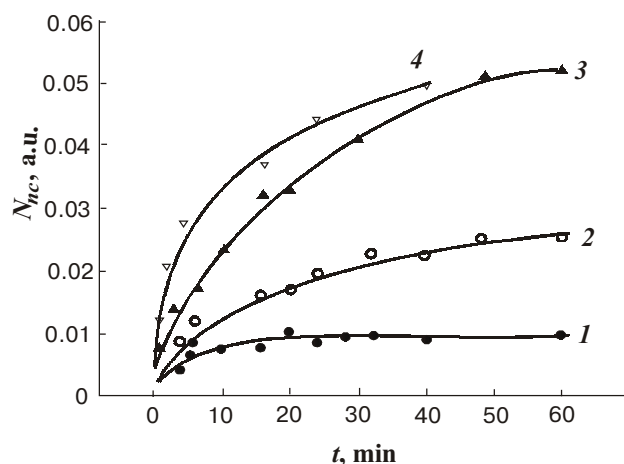


Fig. 5. Relative concentrations of PbS nanocrystals of the average radius versus the treatment time of LB films in  $\text{Na}_2\text{S}$  water solution at  $T = 393 \text{ K}$ : 1 – 0.9, 2 – 0.4, 3 – 0.1 at %, 4 –  $c_1 = 0.9$  at % at 313 K.

sizes determine the radius of seeds and the greatest nanocrystal sizes. (iv) The main role in the nanocrystal growth process belongs to the high local concentration of  $Pb^{2+}$  ions as well as to the dimensional restrictions of the respective diffusion mass transfer.

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