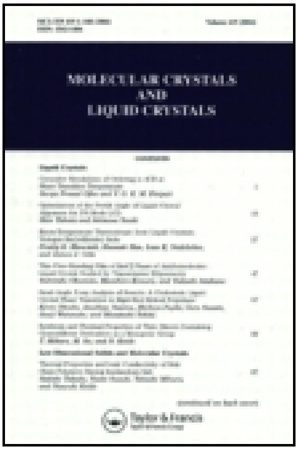

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The Formation and Growth Kinetics of PbS Nanoparticles in Lead Stearate Langmuir-Blodgett Films

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The Formation and Growth Kinetics of PbS Nanoparticles in Lead Stearate Langmuir-Blodgett Films

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The nucleation and growth processes of PbS nanoparticles in lead stearate Langmuir-Blodgett films depending on Pb content and the treatment duration in aqueous solution are presented. It is shown that nanoparticle growth kinetics is different due to different initial Pb concentration in LB films and otwo structure types-flat isolated nanoparticles and domains can be formed.

Keywords: Langmuir-Blodgett films; nanoparticles; lead sulfide; optical absorption spectra; growth kinetics

INTRODUCTION

At present, the formation and growth processes of semiconductor nanoparticles in organic substances, in particularly, Langmuir-Blodgett (LB) films, draw a great interest [1,2]. These ordered periodic structures are often used as model 2D objects to study the cooperative phenomena, transfer and other processes, since the active functional groups of amphiphilic molecules in LB films are arranged in the parallel planes separated by a distance of approximately 2-5 nm (that answers roughly to the length of amphiphilic molecule). In such structures, the diffusive mass transfer takes place mainly in the lateral direction and this may influence the kinetics of nanoparticle formation and growth. Moreover, the stoichiometric composition, nanoparticle dimensions and size distribution may depend on many factors, such as packing density of molecules in a monolayer, concentration of active functional groups, etc. [3-5]. The influence of these factors were studied not fully.

In this work, the optical research results are presented concerning the formation and growth of lead sulfide nanostructures in LB films depending on the lead ion initial concentration as well as on the duration and of LB films exposure in the sodium sulfide aqueous solution.

EXPERIMENTAL AND DISCUSSION

LB films containing lead sulfide nanoparticles were prepared in two stages. At the first one, lead stearate monomolecular films were formed on the surface of aqueous subphase containing lead ions at 10^{-4} M concenration. Then, LB films were transferred onto the quartz or silicon substrates at the surface pressure 28 mN/m by horizontal lifting method. The concentration of lead ions absorbed on the Langmuir monolayer was controlled by varying the subphase pH. The total number of layers at the substrate was 50. At the second stage, the samples were treated in sodium sulfide aqueous solution with sulfur concentration $2\bullet10^{-3}$ M. The optical absorption spectra were measured by SPECORD M-40 instrument at room temperature. PbS optical density was obtained as the difference between optical densities of treated and untreated LB films for every treatment duration. The direct band gap values for PbS nanostructures depending on the treatment duration and temperature were determined from the absorption edges of the difference spectra.

Figure 1 demonstrates optical absorption spectra of LB films before (a) and after (b)-(g) treatment at duration t_{exp}. A new absorption band with a maximum near 4 eV is seen to appear due to the treatment. This band intensity rises when treatment duration is increased. At the same time, the absorption band with a maximum near 5 eV which is due to optical transitions in the carboxyl groups of lead stearate molecules is decreased. The optical absorption edge of LB films is shifted towards the long-wave spectral range as the treatment duration increases.

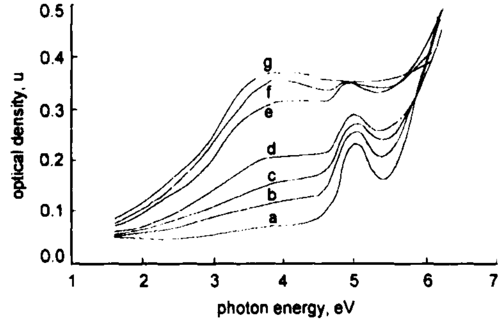

FIGURE 1. The optical absorption spectra before (a) and after (b)-(g) treatment of lead stearate LB films in Na_2S solution: (b)-3 min, (c)-7 min., (d)-15 min., (e)-30 min.,(f)-60 min., (g)-90 min.

The analysis of elemental compositions of untreated and treated LB films carried out using X-ray photoelectron spectroscopy has shown that the treatment results in PbS formation. The optical absorption edge of PbS in the molecular state lies at approximately 2.37 eV while in crystal semiconductors, 0,41 eV at room temperature. Therefore, an optical band with a maximum near 4 eV is due to the PbS nanostructures in the quantum-confined state.

The experimental dependences of band gap E_g values (Figure 2) show that the minimum and maximum band gap as well as the growth kinetics, are distinct for the different relative lead content. n_{Pb}/n_C (n_C is carbon content) in LB films of lead stearate. For the n_{Pb}/n_C=2.7%. , the band gap is approximately 2.24 eV at the t_{exp}= 1 min while being 1.71 eV when the treatment duration is 60 min. Over this time, the band gap is changed only slightly. The calculation of the nanoparticle average size under the hyperbolic band model approximation [6] yields the following nanoparticle radii, R: for concentration 1% at t_{exp}=1 min., R=1.2 nm, and at t_{exp}=60 min., R=1.6 nm. For concentration 2.7% at t=1 min., R=1.55 nm while at t=60 min., R=1.7 nm.

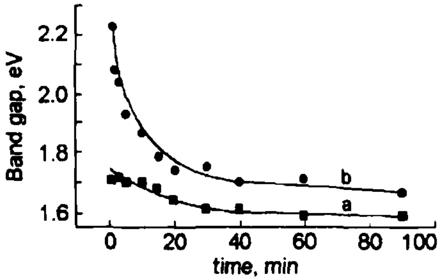

FIGURE 2. Band gap of PbS nanostructures in the lead stearate LB films depending on the treatment duration (a)-n_{Pb}/n_C=2.7%., (b)- n_{Pb}/n_C=1% .

Since optical density D is proportional to a number of PbS molecular units and the nanoparticle volume is proportional to R^3, the nanoparticle number N_R is proportional to (D/R^3). Figure 3 presents N_R/N_{R0} dependences (N_{R0} is the normalized constant-the greatest number nanoparticles in LB films at t_{exp}=90 min.) on the treatment time for two lead ion concentrations.

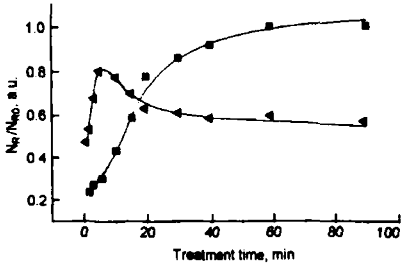

FIGURE 3. The dependences of ratio N_R/N_{R0} on the treatment duration (a)-n_{Pb}/n_C=2.7%., (b)- n_{Pb}/n_C=1%.

The N_R/N_{R0} ratio is observed to increase monotonously when the lead concentration is 2.7%. For the low lead concentration, the N_R/N_{R0} dependence has an extremum value at t_{exp} about 5 min. The significant differences are observed for the extremely short (1min.) and maximum (90 min.) treatment duration.

The dependences in Figures 2 and 3 show that several stages of the nanoparticle growth take place during the LB film treatment. At the first stage (time is <10 min. for LB film with the lead concentration 1% and <20 min. for LB film with lead concentration 2.7% a relatively fast increase of band gap is observed as well as N_R/N_{R0}. The experimental dependences in Fig.2 can be approximated by parabolic ones. At the second stage (>10 min. treatment for the lead concentration 1 % and >20 min. for concentration 2.7% at.), the nanoparticle radii are changed relatively slowly, approximately as $R^3 \sim t$ for low lead concentration and as R~constant for LB films with a high Pb content. Besides, the nanoparticle number is reduced for LB films with the lead concentration 1% at. while it continues to increase for LB films with lead concentration 2.7%.

It can be supposed that the growth of semiconductor nanoparticles in LB matrixes, similar to that in glasses, is due to diffusive decomposition of the solid solution. In our case, the matrix molecules and the lead sulphide ones can be considered as solid solution components. Then, the size increasing can be compared with the nucleation, normal and competitive growth stages in the growth theory of semiconductor phase from supersaturated solid solutions in dielectric inorganic matrices. Our experimental data together with the results of other work [2] show that in organic LB films, being two-dimensional structures, the nanoparticle growth behaviour is similar to that in three-dimensional structures [7,8].

Figure 3 shows that for the low lead concentration, the N_R/N_{R0} dependence on the t_{exp} has a maximum while for the high one, it increases monotonously. This reflects the distinction in processes of nanoparticles formation. For the low Pb concentration at large treatment time, big nanoparticles grow at the expense of small ones due to diffusive mass transfer. In this case, the total number of particles is decreased. For the high Pb concentration, a relatively narrow band gap even at t_{exp}=1 min and its slight changing with treatment time mean probably the low diffusive transfer extent of lead sulfide molecules. And since N_R/N_{R0} ratio increases monotonously as the treatment time is increased, it means that there is no competitive growth. It can be supposed that in LB films on the monolayer interfaces at high Pb concentrations, two-dimensional structures of flat domain type are formed, instead of isolated nanoparticles forming at low initial lead concentrations. And as the transverse domain size cannot be changed significantly, due to the restricted interlayer space, the band gap of such nanostructures is not altered significantly at the treatment, too.

Thus the nanostructure growth kinetics depends on the initial lead concentration: for the low one, the kinetics of lead sulfide nanoparticles growth is similar to that in isotropic substances, while for high Pb content, the diffusive mass transfer of lead sulfide molecules is probably absent.

References

[1] C. Zylberajch, A. Ruadel-Teixier, A. Barraud, *Synth. Met.*, **27,** B609, (1988).
[2] I. Moriguchi, F. Shibata, Y. Teraoka and S. Kagawa, *Chem. Lett,* 761, (1995).
[3] R.S. Urquhart, D.N. Furlong, T. Gengenbach, N.J. Geddes, F. Grieser, *Langmuir,* **11,** 1127, (1995).
[4] Yu.N. Savin, *Functional Materials,* **4,** 515, (1997).
[5] A.G. Fedorov, Yu. N. Savin, A.V. Tolmachev, I.A. Shneiderman, *Functional Materials,* **6,** 556, (1999).
[6] Y. Wang. A. Suna, W. Mahler and R. Kasowski, *J. Chem. Phys.*, **87,** 7315, (1987).
[7] L.C. Liu, S.H. Risbud, *J. Appl. Phys.*, **68,** 28, (1990).
[8] I.M. Lifshiz, W.W. Slyosov, *JETP,* **35,** 479 (1958). (Russ. ed.).