Semiconductor Nanoclusters in the Matrix of Langmuir − Blodgett Films

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Abstract

The formation of semiconductor nanoclusters during sulphidation of Langmuir − Blodgett layers of cadmium, lead and zinc behenates is described on the basis of thermodynamic analysis. It is shown by means of UV, IR, Raman spectroscopy, HREM and electron diffraction that the size of sulphide nanoclusters is 3−6 nm. The presence of localized surface modes characteristic of semiconductor quantum points is stated.

INTRODUCTION

In the recent decade, an increased interest arouse to low-dimensional semiconductor structures, *i. e.* quantum wells, quantum wire and quantum points, due to their electron and optical properties which differ from those of the crystal volume [1, 2]. Though optical properties of crystals and thin films have already been well studied, the investigation of optical phenomena in structures with nanoclusters requires substantial experimental and theoretical effort [3−5]. An example of these systems is cadmium and lead sulphides in silicate glass or in the matrix of Langmuir − Blodgett (LB) layers based on fatty acids [6, 7]. In the latter case, the material is prepared as follows. First, the film of fatty acid salts is grown (cations being, for example, lead, cadmium, zinc), then these layers are exposed to hydrogen sulphide atmosphere. Chemical reaction results in the formation of metal sulphides as nano-sized clusters in the matrix of fatty acids.

The present paper describes the preparation of cadmium, lead and zinc sulphides in LB films of the behenates of these metals. Their structure and optical properties are studied by means of IR, UV and Raman spectroscopy, electron diffraction and high-resolution electron microscopy (HREM)[a].

EXPERIMENTAL

Behenate films were prepared according to the Langmuir − Blodgett procedure. In order to create a monolayer on the surface of the liquid sub-phase, we used the solution of behenic acid in hexane (concentration was 0.1−0.2 mg/ml). The solutions of $CdCl_2 \cdot 2.5H_2O$, $3 \cdot 10^{-4}$ M, pH 6.0; $Zn(CH_3COO)_2 \cdot 2H_2O$, $(3-5) \cdot 10^{-4}$ M, pH 7.0; $Pb(NO_3)_2$, $1 \cdot 10^{-4}$ M, pH 5.0 salts were used as sub-phase. Monolayers were transferred under the surface pressure 30−35 mN/m and a temperature of 22−23 °C. Polished plates made of silicon, monocristalline one and covered with aluminium for IR measurements, were used as substrates. Sulphidation was carried out within the H_2S pressure range of 1−120 Torr.

IR spectra were recorded with a Bruker IFS-113v Furier-transform IR spectrometer within the frequency range of 100−4000 cm^{-1}, UV spectra were recorded with a Specord M-40

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[a] IR and Raman spectra were recorded at the Institute of Physics of Technical University in Hemnitz (Germany).

within the wavelength range of 250−800 nm. Micromorphology and structure of nanoclusters were studied by means of HREM, microdiffraction in a transmitting electron microscope of usual resolution and electron diffraction in the EF-Z4 electron optical set-up at 50−65 keV for reflection and transmittance. The studies were carried out using JEM-400EX (JEOL) electron microscope with accelerating voltage of 400 keV and resolution 0.165 nm with respect to points.

RESULTS AND DISCUSSION

Sulphidation of multimolecular behenate layers is based on the heterogeneous chemical reaction which can be written for cadmium behenate as

$$Cd[OOC(CH_2)_{20}CH_3]_{2(s)} + H_2S_{(g)}$$
$$= CdS_{(s)} + 2HOOC(CH_2)_{20}CH_{3(s)}, \Delta H_r \quad (1)$$
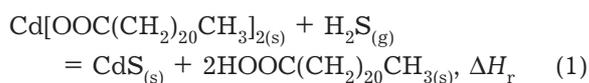
Sulphidation kinetics was studied by means of IR spectroscopy. Absorption spectra of cadmium and zinc behenate films deposited onto Ge prisms were recorded before and after sulphidation within a definite time interval under the given pressure. Figure 1 shows the changes in the intensity of absorption bands at 1540 and 1700 cm^{-1} which are characteristic of the vibrations of COO$^-$ and C=O in COOH group of cadmium and zinc behenates and in behenic acid during sulphidation for different time intervals. A decrease in the intensity of absorption band at 1540 cm^{-1} and increase at 1700 cm^{-1} are the evidence of behenate trans-

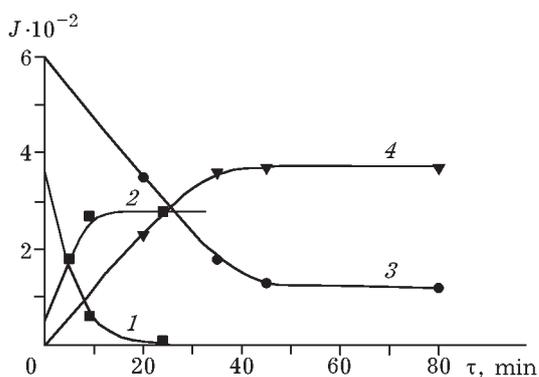Fig. 1. Change of band intensities of COO$^-$ and C=O (*2, 4*) with time during the interaction of CdBh$_2$ and ZnBh$_2$ with H$_2$S (*t* = 20 °C, P_{H_2S} = 1 atm, 20 monolayers).

formation into behenic acid, *i. e.* of the reaction to proceed according to (1).

Sulphidation is accompanied by volume change which can be estimated as the difference between molar volumes of cadmium behenate and reaction products − cadmium sulphide and doubled molecular volume of behenic acid. Using the data on the density and X-ray structural data [8] we obtain the change in molecular volume by 8.1·10^{-23} cm^3. Now we shall assume that the area per behenate molecule in the film corresponds to twice the area occupied by behenic acid molecule on the surface of liquid subphase, *i. e.* 40.0·10^{-16} cm^2. This means that one can expect an increase in monolayer thickness by 2.0 Å as a mean during sulphidation. Though thermodynamic data for polyatomic fatty acids are scarce, the properties of this reaction can be described as a first approximation using the additivity rule to estimate the heats of formation for the salts and behenic acid [9]. Let us take the data for acetic acid and the corresponding acetates as the basis. Having designated the enthalpies of formation (at 298 K) of acetate and acetic acid as ΔH^{Ac} and ΔH^{HAc} we can express the corresponding ΔH^{Bh} and ΔH^{HBh} for behenate and behenic acid at 298 K as $\Delta H^{Bh} = \Delta H^{Ac} + 40I_{CH}$, $\Delta H^{HBh} = \Delta H^{HAc} + 20I_{CH}$. Here I_{CH} is the increment of enthalpy increase per one CH$_2$ group. Then the heat effect of the reaction under consideration ΔH_r can be estimated as follows: $\Delta H_r = \Delta H^{Bh} + \Delta H^{H_2S} - \Delta H^{CdS} - \Delta H^{HBh} = = \Delta H^{Ac} + \Delta H^{H_2S} - \Delta H^{CdS} - 2\Delta H^{HAc}$. This equation contains only available reference data. Using [10], for example, we obtain the enthalpies of formation for cadmium sulphide 138.5 kJ/mol, lead sulphide 87.8 kJ/mol and zinc sulphide 76.9 kJ/mol. It is clear that these reactions are exothermal easily proceeding under usual conditions but it is important to stress that the heat effect decreases in the row Cd > Pb > Zn. Due to the linearity of activation energies and heat effects, the rate of cadmium sulphide formation will be the highest in this row. The rate of cadmium behenate sulphidation will be

$$w = k_0 p_{H_2S} \exp(- E_A/(RT))$$

where k_0 is rate constant. The calculated activation energy of the process E_A is 46.4 kJ/mol.

This energy is much less than the energy of one H—S bond rupture in hydrogen sulphide which is 92.0 kJ/mol [11]. Because of this, it is natural that the activation barrier of the limiting stage of the reaction is connected not with H_2S adsorption process but with the chemical transformation of adsorbed H_2S molecule in cadmium behenate monolayer. In [12] temperature dependence of the equilibrium constant of cadmium behenate sulphidation was studied and the heat effect of the reaction was estimated to be 4.6 kJ/mol. This value corresponds to weak endothermic effect of the reaction and is substantially different from the value calculated by us which is 138.5 kJ/mol. Here we approach the discussion of the major feature of sulphidation process, *i. e.* the formation of reaction product (metal sulphide) as disperse nanocrystal phase. This means that we are to subtract the work consumed for the formation of the surface of new phase from the estimates made earlier. The value to be subtracted is surface energy σ multiplied by the surface of disperse phase A. It is important to note that surface energy is proportional to the lattice energy (cohesion energy) [13], and cohesion energy increase in the sulphide row under consideration Cd < Pb < Zn [10]. This circumstance explains once more relatively easy reaction occurrence of cadmium behenate sulphidation compared to zinc behenate.

To determine the dispersity degree of the formed sulphide, we shall use the known characteristics. Specific surface energy of cadmium sulphide, according to Ormont's estimate [14], is 750 erg/cm^2. Complete sulphidation of monolayer results in the formation of $4 \cdot 10^{-10}$ mol of cadmium sulphide which corresponds to the volume of $1.2 \cdot 10^{-8}$ cm^3. Using surface energy determined by us we obtain the ratio of surface to volume $1.2 \cdot 10^{-8}$ cm^{-1} for the disperse phase. It is known that this value is connected with characteristic size of the disperse phase (d) by the relation $6d^{-1}$. It follows that the linear size of sulphide clusters is about 10 Å.

HREM studies showed that behenate films, judging from diffraction patterns, possess an ordered structure with 6th-order symmetry axis in the film plane. LB films exhibit poor stability towards high-energy electrons since irradiation with electrons causes amorphization. Point reflections in diffraction patterns disappear under electron beam after 1 s. Decrease of electron energy to 200 keV does not stabilize the patterns.

HREM reveals in the films the regions with crystal structure against the background of amorphous structure (Fig. 2). Mean size of the crystal regions is 4 nm for lead behenate films (size scattering from 2 to 6 nm) and 3 nm for cadmium behenate films (size scattering from 1.5 to 5 nm). The density of crystal regions distribution over the film area is $2 \cdot 10^{12}$ cm^{-2} and $1 \cdot 10^{11}$ cm^{-2}, respectively. The planes of lattice seen in Fig. 2 have interplanar distance of 0.3 nm and correspond to the crystallographic planes {200}PbS having cubic structure of the NaCl type (space group being *Fm3m*). The analysis of interplanar distances determined from the diffraction patterns of films with lead sulphide confirms the presence of the cubic modification of PbS. The absence of ring corresponding to diffraction from {111} planes allows us to conclude that the set of crystallographic orientations of lead sulphide corresponds to the texture with either (111) or (100)

80 Å

Fig. 2. HREM image of PbS nanoclusters in the matrix of behenic acid.

axis. In favour of the texture with (100) axis is the fact that {200} crystallographic planes are visualized in HREM images. For the texture with (111) axis, their observation would be impossible.

The lattice planes of cadmium behenate films after sulphidation are characterized by the distance of 0.33 nm which can correspond either to {111} planes of CdS possessing cubic structure of sphalerite type ($F43m$ space group) or to {111} planes of CdS possessing hexagonal structure of wurtzite type (space group $C6mc$). Microdiffraction studies of lead and cadmium behenate films after sulphidation allowed to reveal polycrystal phase with crystallite size less than 10 nm. Rather strong blur of rings in microdiffraction patterns is the evidence of this fact. Experimental interplanar distances are in sufficiently good agreement with the reference data for cubic PbS modification and for hexagonal CdS [15].

Thus, as a result of these studies, it is stated that hexagonal clusters of cadmium sulphide and cubic clusters of lead sulphide are formed during the sulphidation of cadmium and lead behenates in films. Mean cluster size is 3 nm for CdS and 4 nm for PbS.

Vibration spectrum of CdS nanoclusters in LB film matrix was studied by means of IR and UV spectroscopy. Measurements of IR reflection spectra with the structures containing CdS nanoclusters in LB film matrix were carried out at small inclination angles p of polarized radiation. This provided larger surface signal
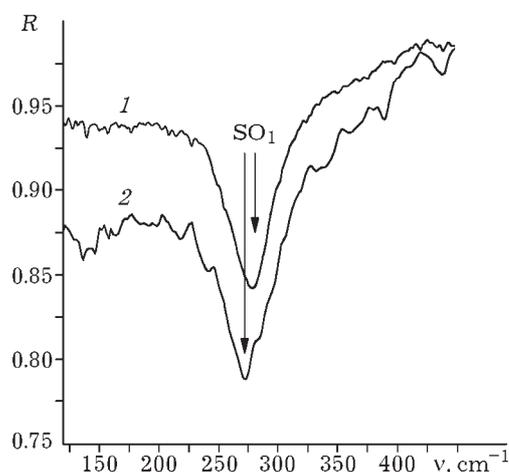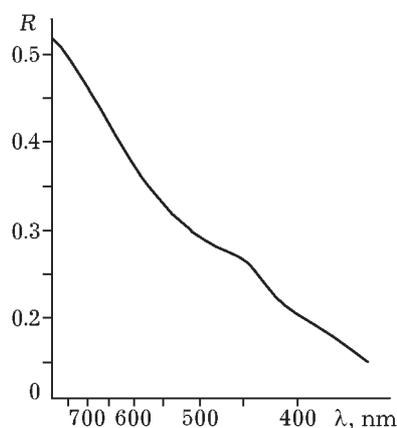

Fig. 4. UV absorption spectrum of the structure with CdS clusters after treatment with hexane.

from the normal component of electric field in the vicinity of crystal surface covered with film. Figure 3 shows the reflection spectrum of the structures with CdS clusters before and after the treatment of film in hexane. The spectrum of the initial film has one broad minimum located between the LO and TO phonons of the voluminous CdS crystal at a frequency of (273 ± 1) cm^{-1}. When the film is treated with the solvent removing behenic acid, the minimum shifts to (280 ± 1) cm^{-1}. Vibration modes attributed to this minimum correspond to surface optical modes SO in CdS clusters, the frequencies of which are dependent on the dielectric properties of the matrix. Larger half-width of this band can be determined by the statistical character of nanocluster size.

In order to estimate cluster size, we recorded UV absorption spectrum shown in Fig. 4. The edge of absorption is at 325–450 nm, shifted in comparison with voluminous samples (490 nm) which is explained by the presence of CdS nanoclusters. Estimates show that mean cluster size is 3–6.4 nm which is in good agreement with the results obtained by means of HREM. It is important to note that small cluster size does not allow to observe localized optical phonons.

The influence of quantum dimension effect on vibration modes was studied by means of Raman spectroscopy at excitation wavelengths varied within the range of 514.5–457.9 nm provided by a 40 mW Ar$^+$ laser. Figure 5 shows Raman spectrum of the structure with CdS clusters excited at 488 nm after the treatment of the film in hexane. A strong peak near
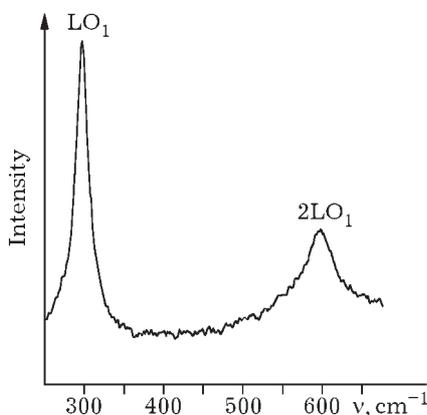

Fig. 3. IR reflection spectrum of the structure with CdS clusters ($\theta = 75°$): *1* − initial film, *2* − the same film after treatment with hexane.

Fig. 5. Raman spectrum of the structure with CdS clusters after treatment with hexane ($\lambda_{exc} = 488$ nm).

300 cm^{-1} and a weak one with double frequency at 600 cm^{-1} are observed in the spectrum. The former corresponds to LO phonons while the latter refers to 2LO overtones in CdS clusters. Depending on excitation frequency, LO phonons are in the region of 297.1–301.5 cm^{-1} which is lower than the corresponding values for volume phonons by 5 cm^{-1}. This is due to the localization of optical phonons in nanoclusters.

CONCLUSION

Sulphidation kinetics of multimolecular layers of cadmium, lead and zinc behenates has been studied by means of IR spectroscopy. Thermodynamic analysis of the formation of CdS, PbS and ZnS nanoclusters has been carried out. The formation of hexagonal CdS and cubic PbS nanoclusters has been stated. Mean cluster size is 36 nm. Vibration spectrum of CdS nanoclusters in the matrix of LB films has been studied by means of IR and Raman spectroscopy. IR spectra of the structures with CdS nanoclusters exhibit surface optical modes, their frequencies depending on the dielectric properties of the matrix. Raman spectra exhibit a low-frequency shift of LO phonon of CdS with respect to its volume value, due to the localization of optical phonons in nanoclusters.

REFERENCES

1 G. Bastard, Wave Mechanics Applied to Semiconductor Heterostructures, Halsted Press, New York, 1988.
2 S. P. Beaumont and C. N. Sotomayor-Torres (Eds.), Science and Engineering of One- and Zero-Dimensional Semiconductors, vol. 214, Plenum Press, New York, 1990.
3 R. Rossetti, S. Nakahara and L. E. Brus, *J. Chem. Phys.*, 79 (1983) 1086.
4 T. D. Krauss and F. W. Wise, *Phys. Rev. Lett.*, 79 (1997) 5102.
5 H. Yukselici, P. D. Persans and T. M. Hayes, *Phys. Rev. B*, 52 (1995) 11763.
6 C. Zylberajch , A. Ruaudel-Teixier and A. Barraud, *Synthetic Metals*, 27 (1988) B609.
7 P. Facci, V. Erokhin, A. Tronin and C. Nicolini, *J. Phys. Chem.*, 98 (1994) 13323.
8 A. S. Akhmatov, Molekulyarnaya fizika granichnogo treniya, Gos. izd-vo fiz.-mat. lit-ry, Moscow, 1963, p. 105.
9 V. A. Kireev, Metody prakticheskikh raschetov v termodinamike khimicheskikh reaktsiy, Khimiya, Moscow, 1975, p. 216.
10 V. P. Glushko (Ed.), Termicheskiye konstanty veshchestv, Izd-vo AN SSSR, Moscow, 1972.
11 V. I. Vedeneev, L. V. Gurevich, V. N. Kondratyev *et al.*, Energiya razryva khimicheskikh svyazey: Spravochnik, Izd-vo AN SSSR, Moscow, 1974.
12 S. M. Repinsky, L. L. Sveshnikova and Yu. I. Khapov, *ZhFKh*, 72 (1988) 825.
13 A. I. Rusanov and V. A. Prokhorov, Mezhfaznaya tenzometriya, Khimiya, St. Petersburg, 1994, p. 16.
14 B. F. Ormont, Vvedenye v fizicheskuyu khimiyu i kristallokhimiyu poluprovodnikov, Vysshaya shk., Moscow, 1968, p. 369.
15 A. K. Gutakovsky, L. D. Pokrovsky, S. M. Repinsky and L. L. Sveshnikova, *ZhSKh*, 40 (1999) 589.