Photoluminescence of the PbS quantum dots fabricated by the Langmuir-Blodgett technique

To cite this article: D.V. Gulyaev et al 2017 J. Phys.: Conf. Ser. 864 012074

View the article online for updates and enhancements.
Photoluminescence of the PbS quantum dots fabricated by the Langmuir-Blodgett technique

D.V. Gulyaev¹, L.L. Sveshnikova¹, S.A. Bacanov ¹, A.K. Gutakovskii¹,² and K.S. Zhuravlev¹,²

¹ Rzhanov Institute of Semiconductor Physics, Siberian Branch of Russian Academy of Sciences, 13, Lavrentiev avenue, Novosibirsk, 630090, Russia,
² Novosibirsk State University, 2, Pirogov Street, Novosibirsk, 630090, Russia

E-mail: gulyaev@isp.nsc.ru

Abstract. The optical and structure properties of the PbS nanoclusters in the Langmuir-Blodgett matrix as well as their properties after the matrix removal in the ammonium atmospheres have been studied. According to the electron microscopy data, it has been established that there are PbS nanoclusters formed on the surface of the samples. It has been found that the matrix removal results in a significant enlargement of the PbS nanocrystals accompanied by the shift of the luminescence into the infra-red range. It has been shown that the PL intensity of PbS quantum dots (QDs) in the matrix decreases with the temperature decrease due to the carrier transfer into defect QDs whereas the luminescence intensity of the PbS nanocrystals without a matrix grows at the temperature increase.

1. Introduction
Today PbS is the one of the most common narrow band gap semiconductor used in infra-red detectors, solar cell sensors and other elements in the semiconductor industry. Therefore, there are numerous methods described on the preparation of PbS itself and low-dimensional structures on its basis in an attempt to reduce the price of PbS preparation and/or improvement of its properties [1-5]. One of the lowest-cost technologies of the preparation of PbS quantum dots is the Langmuir-Blodgett (LB) technique which does not require the expensive equipment. However, the presence of a solid matrix in this method means the presence of surface defects in PbS nanostructures that can significantly influence its optical properties. But the recombination properties of PbS nanocrystals (NCs) synthesized by the LB method have been poorly studied so far [3]. Consequently, this research has been focused on the temperature and power dependences of the photoluminescence (PL) of PbS NCs formed by the LB method before and after the matrix removal.

2. Experimental methods
The structure under study was obtained by the Langmuir-Blodgett technique on the sapphire and porous carbon substrates. Initially, the lead behenate was grown by the substrate with thickness from 4 to 100 monolayes (ML’s) for different samples. Then a behenic acid – matrix (C_{21}H_{43}COOH) and lead sulfide particles were formed as a result of sulfidizing. Finally, to remove the LB matrix several samples were annealed in the ammonia atmosphere NH3 at the temperature of 125 °C.

The investigation of the sample structures was made by the high-resolution transmission electron microscopy (HRTEM). The studies were carried out by the electron microscope of high resolution -
JEM-4000EX (JEOL) equipped with the ultra-high-resolution pole piece UHP-40H with the high resolution of 0.16 nm.

The optical measurements were carried out by the photoluminescence method. To excite the PL, the HeCd laser with the wavelength/maximum power of 325 nm/10 mW or the YAG with the wavelength/maximum power of 512 nm/140 mW were used, respectively. The registration of the PL was conducted by the double diffraction monochromator equipped with different photodetectors to register visible and infra-red (IR) photons. The luminescence in a visible range was measured by the Si CCD matrix, whereas the luminescence in a near IR range ((0.8-1.7 μm)) was measured by the Ge detector.

3. Results and discussion

The typical HRTEM image of the LB film of the lead behenate after sulfiding is shown in figure 1. As one can see, the nanoparticles visualized on this image as brighter areas in comparison with the background demonstrate the crystallinity properties. According to the analysis of the interplanar spacing, the PbS nanoparticles have a cubic crystal structure with the Fm3m space group with the cell parameter a = 0.59 nm. Therefore, we can conclude that the nanocrystals of the lead sulfide with the average size of 2-3 nm and surface density of \(10^{12}\) cm\(^{-2}\) are formed as the result of the sulfiding of the lead begenate films.

The optical measurements were carried out to confirm the quantization of the PbS nanocrystals. The typical PL spectra of the samples under study at the room temperature are shown in figure 2. As one can see, the band with the maximum radiation of around 1.82 eV and a half width at the half-maximum (HWHM) of 110 meV dominates in the photoluminescence (PL) spectra of the non-annealed samples, whereas the band with the maximum radiation of around 0.8 eV and HWHM of 70 meV dominates in the PL spectra of the annealed samples. As these bands are absent in the PL spectra of the reference sample consisting of a single matrix, this allows us to refer them to the recombination of carriers in the PbS crystals. The shift of the PL band into a higher energy side can be explained only by the quantization effect as the band gap of the bulk PbS is equal to 0.43 eV [6]. According to the literature data [7], the energy of 1.8 eV corresponds to the QD of 2 nm thickness, whereas the energy of 0.8 eV corresponds to the PbS QDs of 5-6 nm diameter, which is in accordance with the microscopy data.
Figure 2. The PL spectra of the (1) LB matrix (2) sample with the PbS nanocrystals in the matrix and (3) the sample with the PbS nanocrystals after annealing. The measurement temperature is 300 K. The power of the HeCd laser is 10 mW.

The temperature dependencies of the PL intensity of the PbS QDs in the matrix and after the matrix removal are shown in figure 3. As one can see, the luminescence intensity of the PbS QDs in the matrix decreases at the temperature increase. The temperature dependence of the PL intensity of the PbS QDs in the matrix is well described by the following equation:

\[
I(T) = \frac{I(0)}{1 + A \cdot \exp\left(-\frac{E_A}{kT}\right) + B \cdot \exp\left(-\frac{E_B}{kT}\right)}
\]

(1),

where the activation energy of the PL quenching is \(E_A=100\pm20\) and \(E_B=14\pm3\) meV. As the dependence of the PL intensity upon the excitation power remains linear at the temperature change (see figure 4) we suppose that the PL intensity decrease is caused by the transfer of the carriers from the bright non-defect QDs to the dark defect ones. In this case the number of the bright QDs and, consequently, the PL intensity decrease but the mechanisms of the carrier recombination in a QD do not change. Thus, the obtained energy can correspond to the average energy of the carrier delocalization from the QDs and the exciton binding energy, respectively.

Figure 3. The temperature dependencies of the PL intensity of the PbS QDs in the matrix (1, ■) and without the matrix (2, □). The solid lines show the curves approximated by the equations (1) and (2). The excitation power of the YAG laser is 100 mW.

Figure 4. The dependence of the PL intensity of the PbS QDs without a LB matrix on the excitation power (the PL band maximum is 0.8 eV) at the (1) 5 and (2) 300 K. \(T=300\) K. The PL was excited by the YAG laser.
The removal of the matrix in the ammonia atmosphere leads to the cardinal change in the temperature dependence of the PbS QDs, namely, the PL intensity starts increasing at the temperature increase. Therefore, we can conclude that the non-radiative recombination in the QDs is caused by the defects on the matrix/nanocrystal boundary. The temperature dependence of the PL intensity of the PbS QDs without a matrix is well described by the following equation:

\[
I(T) = I(0) \cdot (1 + \exp(-\frac{E_C}{kT}))
\]  

(2)

The activation energy of the PL enlargement is equal to \(E_C = 40 \pm 5\) meV that is close to the levels of the Pb vacancy in PbS [8]. It should be noted that the intensity of the PL of the PbS QDs without a matrix keeps increasing at the delay increase after the sample annealing, which can be explained as by the self-purification in semiconductor nanocrystals [9] as by the passivation of residual surface states by the oxygen.

4. Conclusion
The optical and structure properties of the PbS nanoclusters in the Langmuir-Blodgett matrix as well as their properties after the matrix removal in the ammonia atmosphere have been studied. The analysis of the obtained results has confirmed the formation of PbS QDs of 2-3 nm size in the LB matrix. The temperature and power dependences of QD PL indicate the possibility of the carrier transfer between the non-defect QDs and QDs with the surface states on the matrix boundary. The matrix removal in the ammonia atmosphere results in the enlargement of PbS QDs up to 5-6 nm accompanied by the passivation of surface defect states.

References
[1] H. Zhao, Z. Fan, H. Liang, G. S. Selopal, B. A. Gonfa, L. Jin, A. Soudi, D. Cui, F. Enrichi, M. M. Natile, I. Concina, D. Ma, A. O. Govorov, F. Rosei and A. Vomiero 2014 Nanoscale 6 7004.
[2] Y. Yang, T. Lian 2014 Coordination Chemistry Reviews 263–264 229.
[3] Zdenek Remes, Tomas Novak, Jiri Stuchlik, The-ha Stuchlikova,Vladislav Drinek, Radek Fajgar, Konstantin Zhuravlev 2014 Acta Polytechnica 54 426.
[4] Zhen Fang, Xiu Lin, Yueting Fan, Yufeng Liu, Yonghong Ni, Xianwen Wei 2010 Journal of Alloys and Compounds 493 L25.
[5] Liangfeng Sun, Lei Bao, Byung-Ryool Hyun, Adam C. Bartnik, Yu-Wu Zhong, Jason C Reed, Dai-Wen Pang, Hector D. Abrun’a, George G. Malliaras, and Frank W. Wise 2009 Nanoletters 9 789.
[6] J.N. Zemmel, J.D. Jensen, R.B. Schoolar 1965 Phys. Rev. A 140 330.
[7] Giovanni Pellegrini, Giovanni Mattei, and Paolo Mazzoldi 2005 J. Appl. Phys. 97 073706.
[8] Danylo Zherebetskyy, Yingjie Zhang, Miquel Salmeron, and Lin-Wang Wang 2015 J. Phys. Chem. Lett. 6 4711.
[9] Gustavo M. Dalpian and James R. Chelikowsky 2006 PRL 96 226802.